PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM FINAL REPORT - ADDENDUM

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FINAL REPORT

PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM

ADDENDUM

Contract No. NAS9-13387

March, 1975

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

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PRELIMINARY FLIGHT PROTOTYPE SILVER ION MONITORING SYSTEM

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

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1.0 SUMMARY

This report covers final effort on Contract NAS9-13387 and is an addendum to Beckman FR-2656-101 (NASA CR134361).

One of the problems observed in the earlier phases of this program was the relative instability of the silver ion sensing electrode, leading to unpredictable manufacturing yield, performance, and life. The primary goal of the current effort was to define and produce an electrode meeting Shuttle mission requirements for functional life and stability as well as accuracy and precision of measurement. A number of electrode fabrication techniques were investigated to achieve these goals and they have been met.

A second consideration in this program was the investigation of the apparent instability of a silver bromide column when employed in a closed loop calibration scheme. The mechanism for the observed deterioration has been elucidated and a solution for the correction of the observed problem suggested.

2.0 ELECTRODE FABRICATION AND TEST

It appeared that most of the failures that were observed with the previous silver ion electrodes could be explained by migration of fluid through the interstices of the membrane material, causing interferences at the junction between the pellet and silver conductor of the electrode. Initial attempts at resolving this issue were directed toward the fabrication of electrode configurations which would slow this transmigration, eliminate it, or avoid its effects. Four different types of electrodes were fabricated. The first configuration was fabricated, as were the previous electrodes, to serve as a control and baseline

A 0.012-inch (0.3 mm) diameter 99.99% pure silver wire was cleaned in a 10% nitric acid solution, then washed with distilled water and dried. A ball of

approximately 0.060 inch (1.5 mm) was formed on the end of the silver wire in a gas flame and the wire cut to a length of approximately 0.5 inch (13 mm). The silver wire contacts were then annealed in nitrogen atmosphere furnace. The silver contact wire was placed in the mold and 200 ±5 mg of silver sulfide powder was formed into a pellet around the ball on the silver wire at a pressure of 4200 pounds per square inch (2900 N/cm^2). The center conductor of a shielded cable was soldered to the silver contact wire on the silver sulfide pellet. The silver sulfide membrane was held in place in a plastic holder with black wax.

Early performance of other configurations would be compared to the performance of this electrode (illustrated in Figure 1).

A second series of electrodes was fabricated employing the same silver sulfide membrane as in the control group. The silver wire, rather than being molded in place, was attached with silver-conductive epoxy. At the suggestion of Mr. J.L. Day, NASA-JSC, the back surface of the pellet was coated with the same epoxy per a print provided by NASA. The effect of this coating was to preclude fluid migration through the pellet. This electrode is shown in Figure 2, and was constructed as follows: Eccobond Silver Epoxy #57C

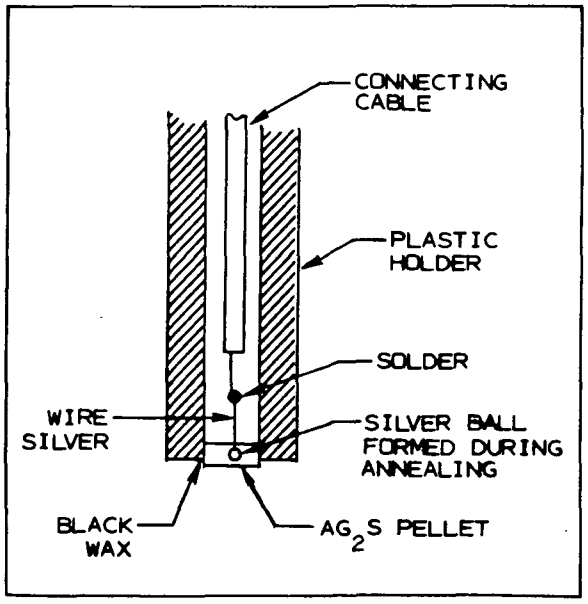

Figure 1. Molded Silver Wire

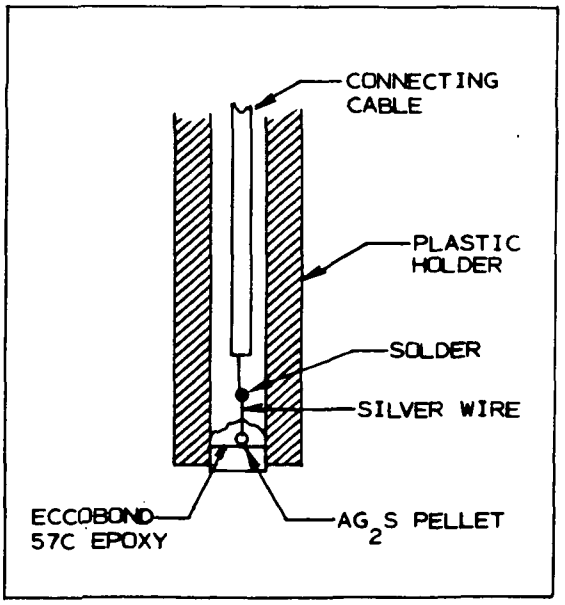

Figure 2. Eccobond Attachment

(Emerson and Coming) was thinned with toluene and two coats were applied to a pressed pellet. Each coat was allowed to cure at 100°C (373 K) for one-half hour. Unthinned Eccobond epoxy was then used to hold the silver wire to the pellet.

A third configuration again employed the same silver sulfide membrane as used in the first two, but electrical contact between the pellet and the conductor was established through an electrolyte solution maintained in place by glass wool. In this case, migration of fluid through the pellet would have minimum effect because of dilution into the conducting electrolyte. This configuration is shown in Figure 3.

A fourth series of electrodes was fabricated employing a different material--in this case, silver. A silver billet was machined from a bar of 99.999% pure silver. The billet was cleaned, etched, and annealed, and then installed into a plastic holder as were the other electrode pellets. The connection was made by the Eccobond epoxy technique. This electrode is shown in Figure 4.

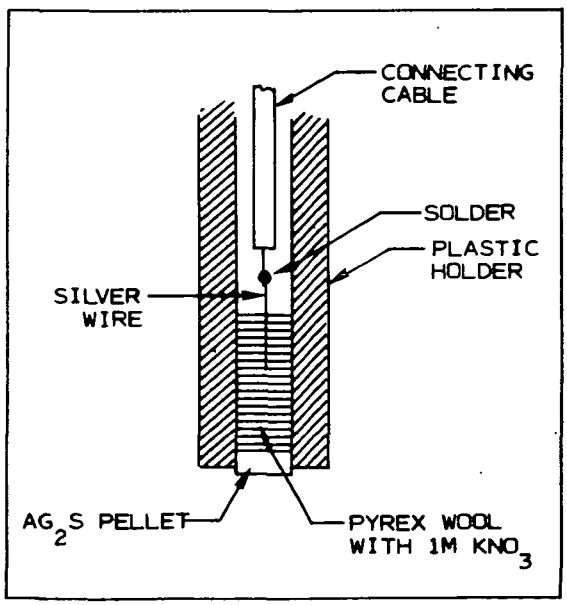

Figure 3. Liquid Junction

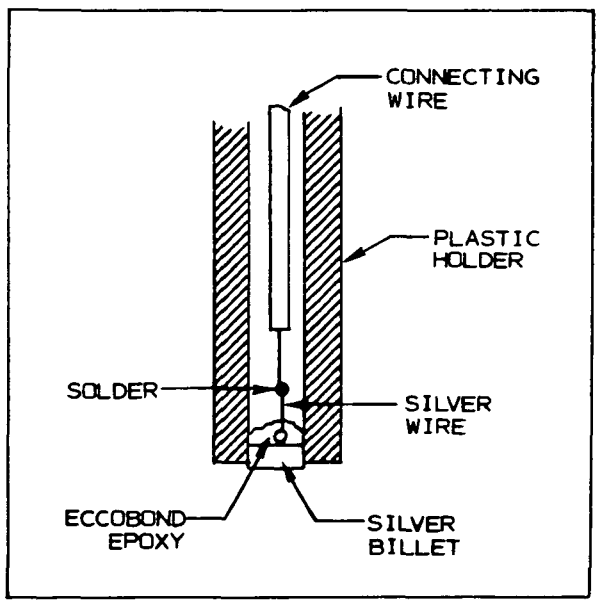

Figure 4. Silver Billet Electrodes

3.0 ELECTRODE TESTS

The objectives of the electrode tests were to establish the manufacturing yield of electrodes and to investigate the relative long-term stability of each of the configurations. Initial studies were conducted in beaker test setups, illustrated in Figure 5. Each working day, one electrode of each group of electrodes was measured in 50 ppb and 500 ppb silver ion solutions (silver nitrate). A second group of electrodes compatible with the flow-through cell was fabricated in four configurations. These electrodes were also beaker tested. The groups of electrodes were identified as follows:

B-3 Series, Eccobond attachment, beaker test type
B-4 Series, Molded wire, beaker test type
B-5 Series, Liquid junction, beaker test type
B-6 Series, Molded wire, test stand type
P-7 Series, Liquid junction, test stand type
B-8 Series, Eccobond attachment, test stand type
B-9 Series, Silver billet, test stand type

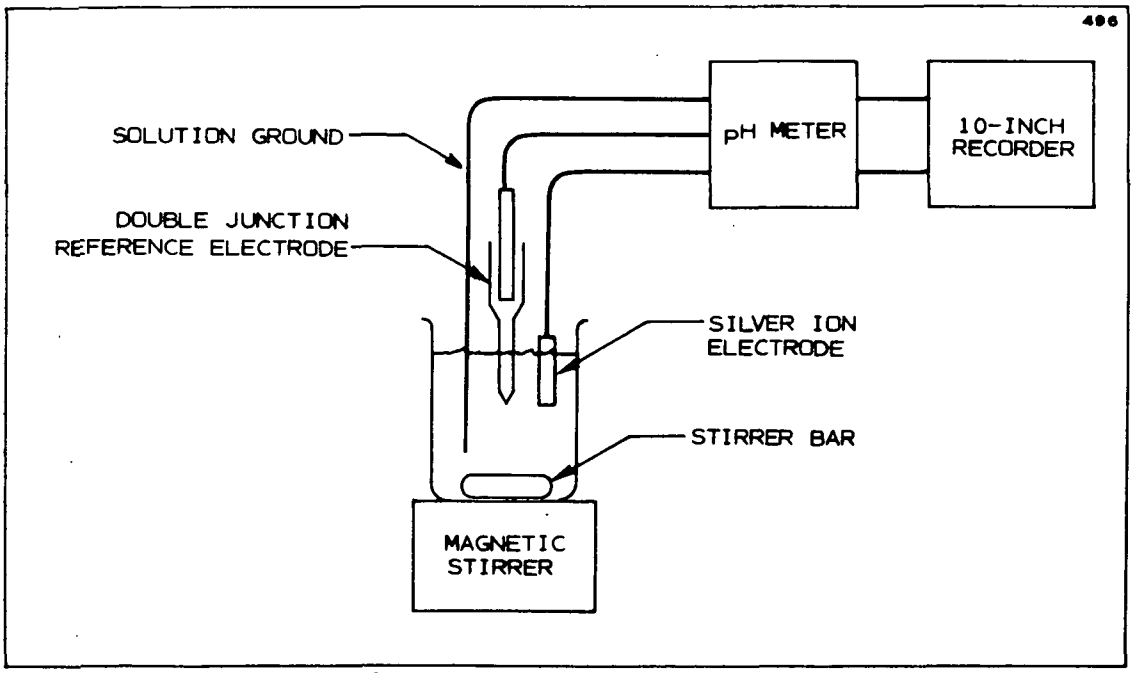

Figure 5. Beaker Test Setup

3.1 Results of Beaker Tests

3.1.1 Series B-3, Eccobond Attachment, Beaker Test Type

Three of the six electrodes fabricated were good on initial testing. These were B-3-B, B-3-C, and B-3-D. Beaker tests on these electrodes continued from 98 to 102 days. The spans over this interval on each electrode appeared to be normally distributed with the following results:

	B-3-B	B-3-C	B-3-D
N	24	21	21
Standard Deviation	4	4	2
$\bar{X}$	58	57	59

Offset potentials also appeared to be normally distributed. Although the electrodes were used with different meters about halfway through the study, examination of the offset data since the 40th day shows very little spread and no apparent trend.

	B-3-B		B-3-C		B-3-D	
	50 ppb	500 ppb	50 ppb	500 ppb	50 ppb	500 ppb
N	13	13	12	12	12	12
Standard Deviation	12	12	7	7	5	5
$\bar{X}$	185	244	182	240	200	260

These electrodes have far exceeded the design goal of 720 hours, and even after 100 days of testing no apparent deterioration, defined in terms of drift or noise, is apparent.

3.1.2 Series B-4, Molded Wire, Beaker Test Type

This electrode design was the same as employed in earlier programs. A greater yield upon fabrication was observed. Only one electrode was found to be

nonfunctional. Five electrodes have survived almost three months of beaker testing. This is surprising in light of the relatively poor history observed in earlier models of this configuration. The data from these electrodes, however, does not appear to be nearly so consistent as that observed with the Eccobond-type electrode. The standard deviation of the span is generally broader as illustrated below:

	B-4-A	B-4-B	B-4-C	B-4-E	B-4-F
N	17	10	9	17	10
Standard Deviation	8	6	12	5	6
$\bar{X}$	58	57	55	56	57

In several of the electrodes, the offset potentials do not appear to be normally distributed, as may be observed from the data sheets. This appears to be especially the case in electrodes B-4-A and to a lesser extent with B-4-C. Since they are not normally distributed, standard deviation data is not presented on these electrodes. However, for electrodes B-4-B, B-4-E, and B-4-F, the offset data are presented below. Again, the instrumentation was changed about halfway through the program and so the offset statistics were calculated on approximately the final 60 days of the test period.

	B-4-B		B-4-E		B-4-F	
	50 ppb	500 ppb	50 ppb	500 ppb	50 ppb	500 ppb
N	8	8	7	7	7	7
Standard Deviation	11	15	13	14	4	4
$\bar{X}$	68	124	70	127	66	128

Thus, although the span data for these electrodes appear to be reasonable, the data are less internally consistent than the data of the B-3 series. That is, the range of the span data is broader for the B-4 Series showing an average range of 24 mV compared to 14 mV for the B-3 Series. In addition, the span

range of the B-3 Series became much narrower with continued exposure. During the final 30 days of tests on each series, the maximum range of the B-3 Series was only 2 mV while the B-4 Series showed a range of up to 20 mV. Further testing of the B-4 Series for a total time equivalent to the B-3 Series might have reduced the B-4 range further since the B-3 Series showed essentially the same range as the B-4 Series at equivalent intervals in time (45-75 days).

The relatively better performance of these B-4 electrodes as compared to the electrodes fabricated during earlier portions of the program is as yet unexplained. Certainly, the electrodes in the B-4 Series have exhibited a longer life than any of the earlier electrodes.

3.1.3 Series B-5, Liquid Junction, Beaker Test Type

All of the B-5 Series electrodes exhibited reasonably stable response upon original testing. Although several exhibited short spans, it was decided to continue testing them for a short time to see if they became conditioned to provide the proper response. Generally speaking, however, the response of these electrodes never equaled that of either the B-3 or B-4 Series exhibiting only periodic theoretical response and at other times wide excursions from expected span values. The span data from these electrodes are shown below:

	B-5-A	B-5-B	B-5-C	B-5-D	B-5-E	B-5-F
N	8	8	4	7	7	5
Standard Deviation	6	19	27	4	10	10
$\overline{X}$	47	47	49	55	51	51

These electrodes were relatively short-lived, lasting a maximum of 38 days before drifting and erratic response made further testing useless. The offset potentials do not appear to be normally distributed for the most part and were not statistically reduced.

3.1.4 Series B-6, Molded Wire, Prototype Test Stand Type

Five of the six electrodes fabricated in this series were placed on test. The performance of these electrodes generally was much poorer than the performance of the B-4 Series showing a much broader scatter of span values--so broad, in fact, as to negate their use in the potable water supply system. This is essentially the same type of failure mode as observed with earlier electrodes. The electrodes were continued in test, however, to see if they became conditioned after repeated exposure to silver ion solutions and if their outputs would stabilize. These data can be observed from the data sheet. Because the performance was so poor, statistical reduction was not attempted.

3.1.5 Series B-7, Liquid Junction, Prototype Test Stand Type

Like the B-5 Series, all electrodes in the B-7 Series were available for test. Three of the electrodes, however, later exhibited a cable short which was repaired and the electrodes were placed back into test. Generally, the span data from these electrodes looked acceptable. However, the life of the electrode was never longer than 30 days, making them unsuitable for the proposed application. Statistical reduction of these data was not attempted because of the small number of data points.

3.1.6 Series B-8, Eccobond Attachment, Test Stand Type

Four of the six prototype electrodes were placed into test. Examination of the early span data showed erratic results, but the electrodes stabilized after a period of time (approximately 12-13 days) and showed quite consistent data during the later period of the test. The four electrodes that originally made it into the test survived the test for a total test life ranging from 50 to 55 days. Three of these electrodes were tested in beakers. The fourth was used for system level tests. The span data from the beaker-tested electrodes are shown following:

	B-8-B	B-8-C	B-8-D
N	13	12	11
Standard Deviation	5	3	4
$\bar{X}$	58	58	56

The offset potential range for these electrodes also falls within the capability of electronic compensation although the coefficient of variation is somewhat wider than that observed in the B-3 Series. No trends are observed in the offset data of B-8-B or B-8-C. A trend is observed, however, in B-8-D which is much steeper at the initial phases of the study than during the latter phase. Because of this trending, no statistical data reduction was attempted for this electrode. The offset potential data for electrodes B-8-B and B-8-C are shown below:

	B-8-B		B-8-C	
	50 ppb	500 ppb	50 ppb	500 ppb
N	12	12	12	12
Standard Deviation	25	24	52	54
$\bar{X}$	347	402	401	459

Electrode B-8-A of this series has been exposed to continuously flowing silver ion solutions for 72 days with quite uniform results.

3.1.7 Series B-9, Silver Billet, Test Stand Type

The silver billet electrodes did not exhibit theoretical response despite extended testing. It appeared that the electrodes became coated in use which may have contributed to their poor response characteristics. Because of the irreproducible and non-Gaussian distribution, statistical reduction of these data was not attempted.

From the above data, it was apparent that the Eccobond epoxy electrodes offer greatest promise for meeting program objectives. The next portion of the program involved a total sensor subsystem integration.

4.0 SYSTEM INTEGRATION

System integration proceeded in a logical series of stages in order to verify the performance of each subsystem, isolated from variables that might have been introduced by other subsystems. The performance element considered of major importance was the stability and life of the sensing electrode during exposure to flowing solutions, since previous electrodes had shown degraded performance under this test condition. If the test electrode showed adequate performance when exposed to flowing solutions of differing concentrations of silver ion, the major problems related to the reliability of the basic technology previously observed would have been overcome.

4.1 Flow-Through Studies

4.1.1 Sensor Performance Verification

The objective of this effort was the verification that the electrode configuration selected for use in the system--Eccobond attachment, B-8 Series--would provide an accurate and precise response to different levels of silver ion in a flowing stream and that the life of the electrodes would be adequate for Shuttle requirements, i.e., 720 hours. The single most important parameter was the capability of the sensor to respond to change in silver ion concentration in an accurate and predictable manner over extended intervals of time. Although it is possible to perform this study using reservoirs of solutions with differing concentrations, earlier experience has shown that this approach was not desirable for two reasons. First, at reasonable flow rates, e.g., 100 ml/min (1.7×10^{-5} m^3/s), large reservoir volumes are required for an extended test interval. In addition, multiple reservoirs are required to provide a number of concentration intervals. To overcome these objections, a means to provide a variable concentration of silver ion in a manner to eliminate the requirement for numerous reservoirs of different concentrations is desirable.

To meet this need, the test system illustrated in Figure 6 was designed. Deionized water from reservoir #1 entered reservoir #2 at a constant flow rate regulated by a constant hydrostatic head and a restrictor on the interconnecting line. The water from reservoir #2 passed through the prototype flow cell at a constant rate, also regulated by a hydrostatic head and a line restrictor. The volume of water within reservoir #2 was maintained constant by an overflow line.

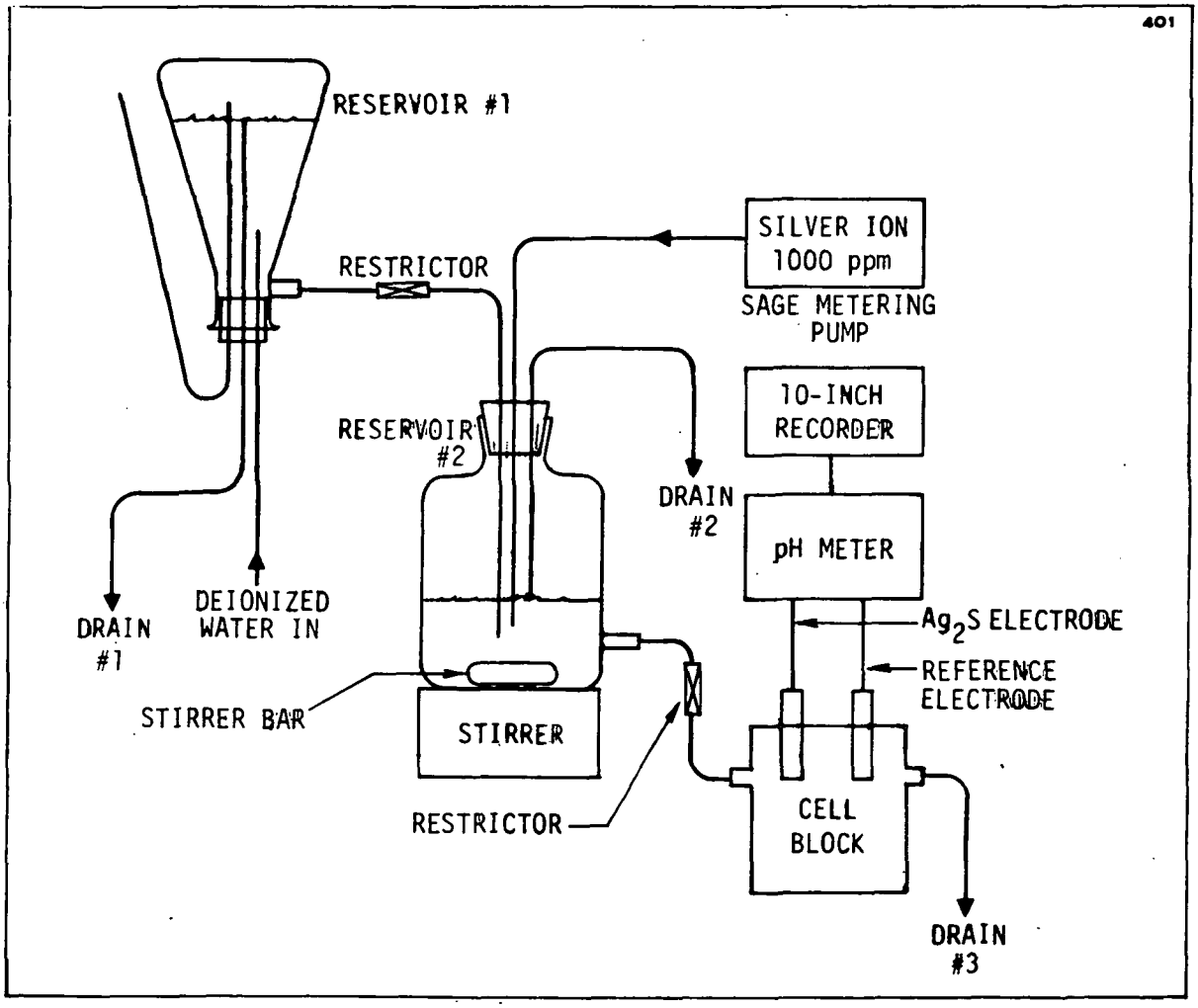

Figure 6. Flow System

Silver ion was added to reservoir #2 as a concentrated solution of silver nitrate (1000 ppm). This solution was contained in a syringe mounted in a variable speed

syringe metering pump. The concentration of silver ion in reservoir #2 was increased or decreased by altering the rate at which the concentrated solution was added to the reservoir. Rapid mixing of the solution was accomplished with a Teflon-coated magnetic stirring bar placed in the reservoir. Electrode B-8-A was inserted into the prototype flow cell for performance evaluation. Read-out was provided by a pH meter and the analog data was recorded on a Beckman 10-inch (25.4 cm) recorder.

The accuracy of electrode B-8-A would be evaluated by comparing the recorded output of the flow system electrode against the reading obtained in a reference measurement system. The test solution would be collected periodically at the outlet of the flow cell and analyzed in a beaker test with a second electrode pair. Electrode B-3-D was employed as the referee electrode in these tests. The reference system was calibrated with standard silver-nitrate solutions prior to the comparison measurements to provide an accurate estimate of actual silver ion concentration.

4.1.1.1 Initial Performance Characteristics of the Test System

As was anticipated, some difficulties were observed in the start-up and operation of the test system. These problems included irregular operation of the syringe metering pump, bubble interference caused by degassing of the test solutions, and interference due to static charges on the interconnecting tubing. The following reproductions of actual recorder tracings illustrate the problems observed. In all illustrations, the recorder speed is 0.1 in./m (2.5 mm/m). Each division is 5 mV.

Figure 7 shows what appears to be a static charge on the tubing connections of the system. Figure 8 shows irregular silver ion addition by the syringe pump in combination with the static charge. Figure 9 shows the interference produced by bubbles in the outlet of reservoir #2.

These problems were largely corrected through repair of the metering pump, the use of all glass and plastic tubings and connections, etc. The stability of the output following the corrections is shown in Figure 10. It will be noted

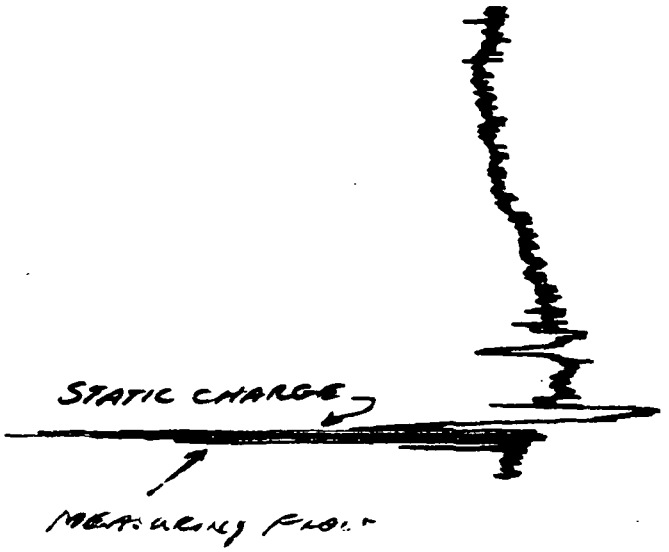

Figure 7. Static Charge on Tubing Connections

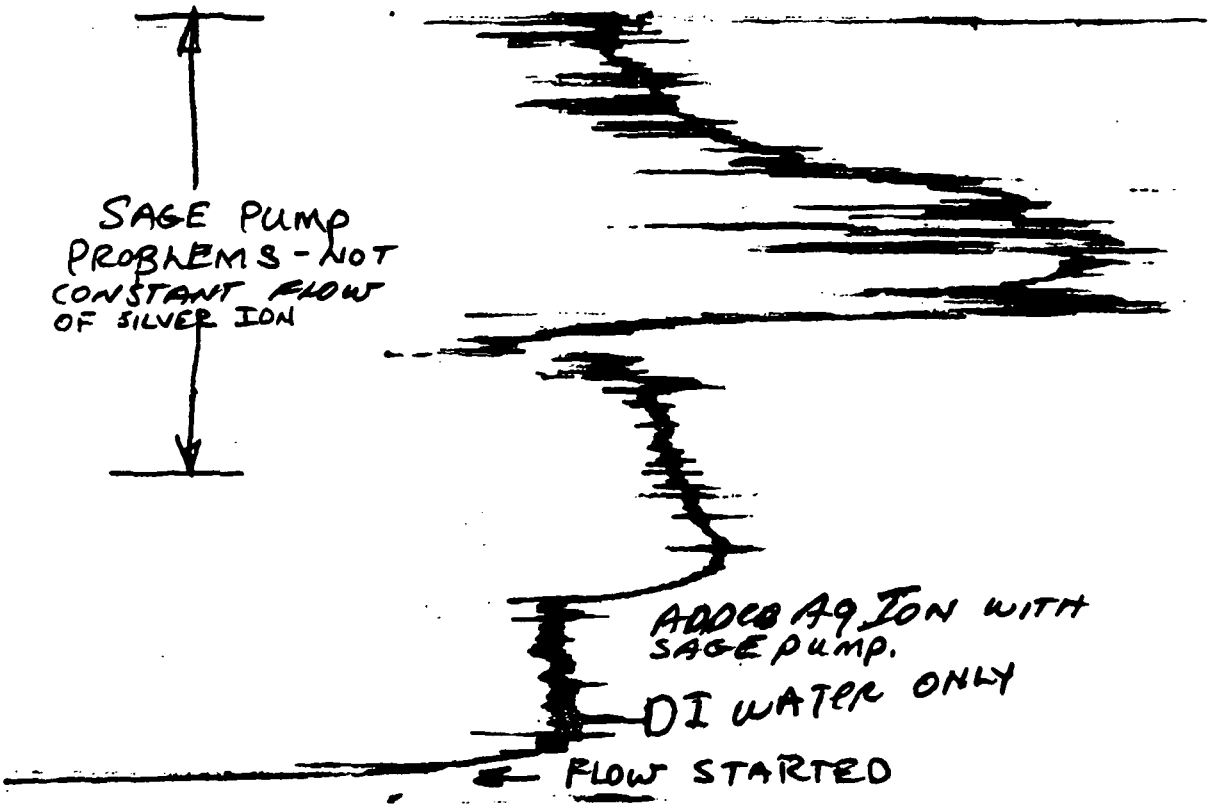

Figure 8. Noise and Ag Pump

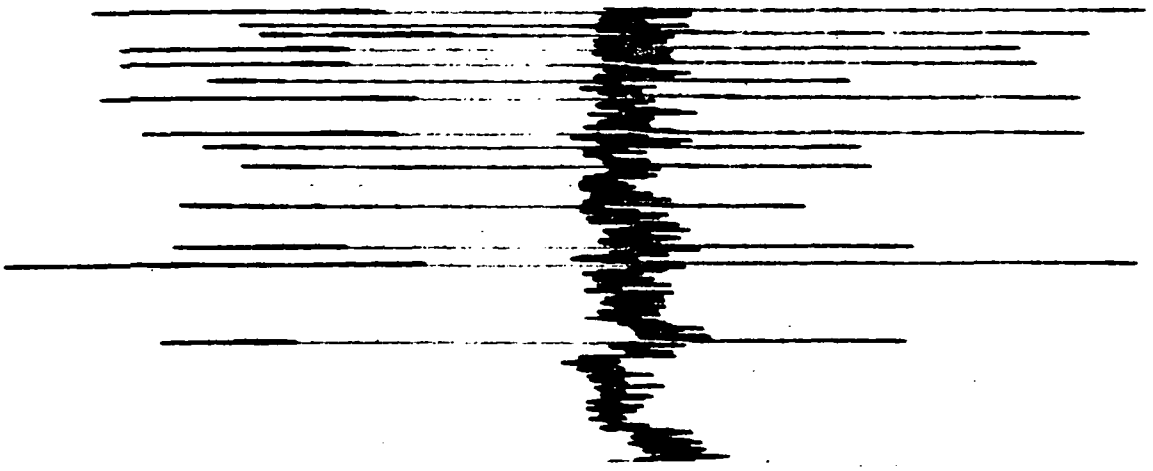

Figure 9. Air Bubbles in the Sample Line Outlet

Figure 10. Output Noise After Corrections

that reasonably stable tracings are produced although these are occasional high-frequency spikes. These spikes were later attributed to the use of high purity deionized water (18 megohm) for the solutions, thus limiting the electrical conductivity. After recognizing this, solutions were made with distilled water (1.2 megohm) and stable readings with no noise were obtained. This is illustrated in Figure 11. This figure also illustrates freedom from flow artifact.

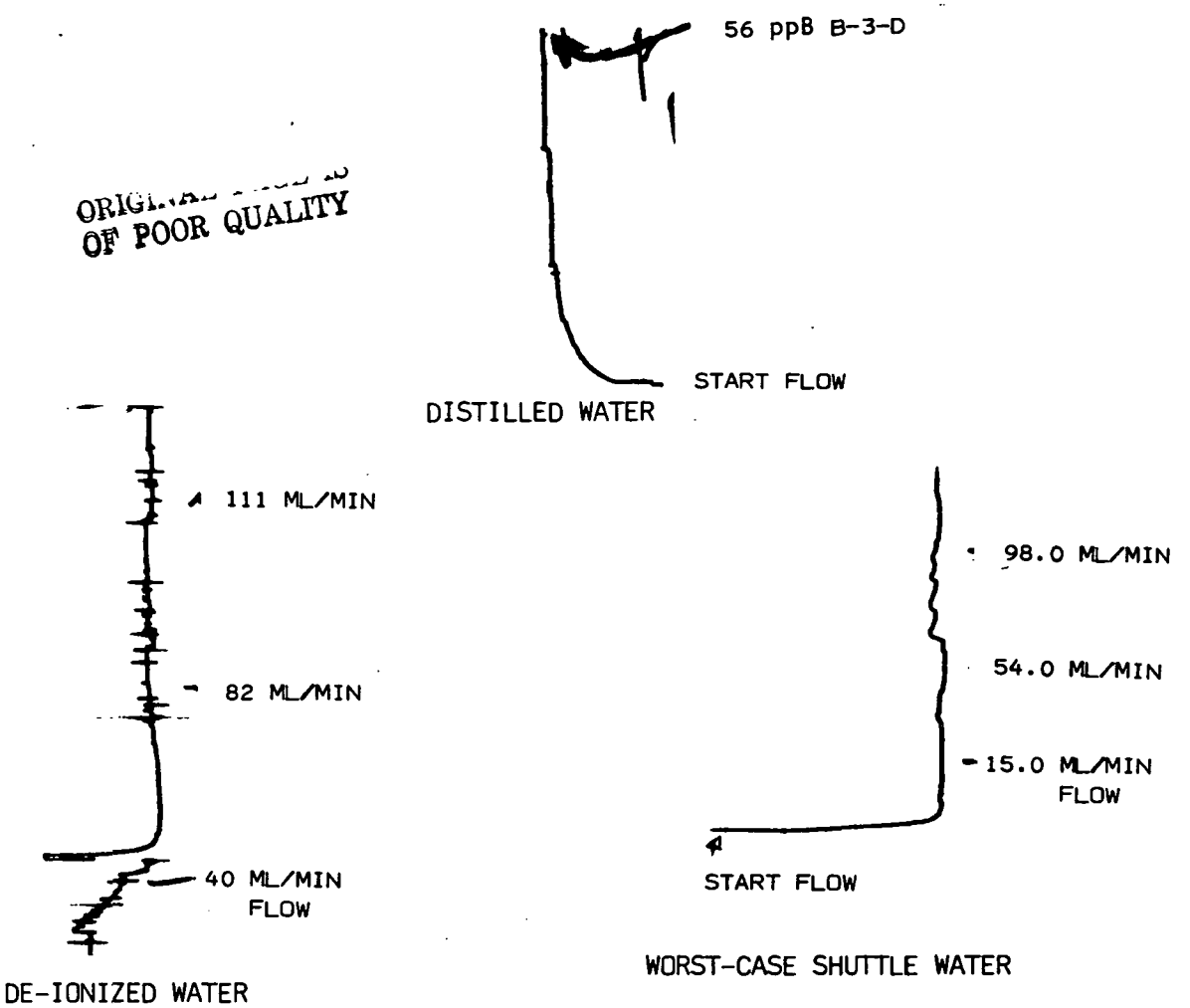

Figure 11. Relative Noise and Stability with De-Ionized Water, Worst-Case Shuttle Water, and Distilled Water in Flow Cell--B-8-A Output

4.1.1.2 Test System Performance

Continuing problems were experienced with the various elements of the test system, especially with the syringe metering pump. Occasionally, accurate metering of the concentrated silver ion solution was observed, as illustrated in Figure 12. In this experiment, replicate experimental runs were made at three different switch positions on the syringe metering pump. The diluted solutions were passed through the flow cell and aliquots collected at the flow cell outlet for beaker-type measurements. The replicate measurements fell in the Nernstian line and within the circles representing the data points.

Series like this were rare, however, and a reliably operating system was never achieved. A typical example of test system performance is shown in Figure 13, reproduced from the tracings recording B-8-A system electrode output. The noise initially observed is attributed to static charges which rendered the system electrode readings meaningless. Shielding between the #2 reservoir and the flow cell decreased noise substantially. Several samples were obtained for beaker testing, as indicated on the tracing to determine actual silver ion concentration. The first of these was obtained when concentrated silver ion solution was being added to reservoir #2 at Switch Position 4. The response of the system electrode at the time of sample collection was 370 mV and the concentration of the solution as measured in a beaker was 40 ppb. The syringe metering pump speed was changed to Switch Position 2 and a period of stabilization was awaited (it is necessary to equilibrate all the solution in reservoir #2 before the concentration will stabilize). This stabilization was never achieved, as indicated by the continuous downward drift indicated by the system electrode. This drift could have been due either to a bad electrode response or improper functioning of the syringe metering pump. To check electrode performance, a sample was taken as indicated and the concentration was determined to be 8 ppb by beaker testing. The system electrode response at the time of sample collection was 327 mV. The syringe metering pump speed was changed to Switch Position 6 and electrode response is observed. At this position, reasonable stabilization was observed. To verify that the system electrode was operating properly during the run, the two data points were plotted, as shown in Figure 14. It will be seen that the span of the electrode

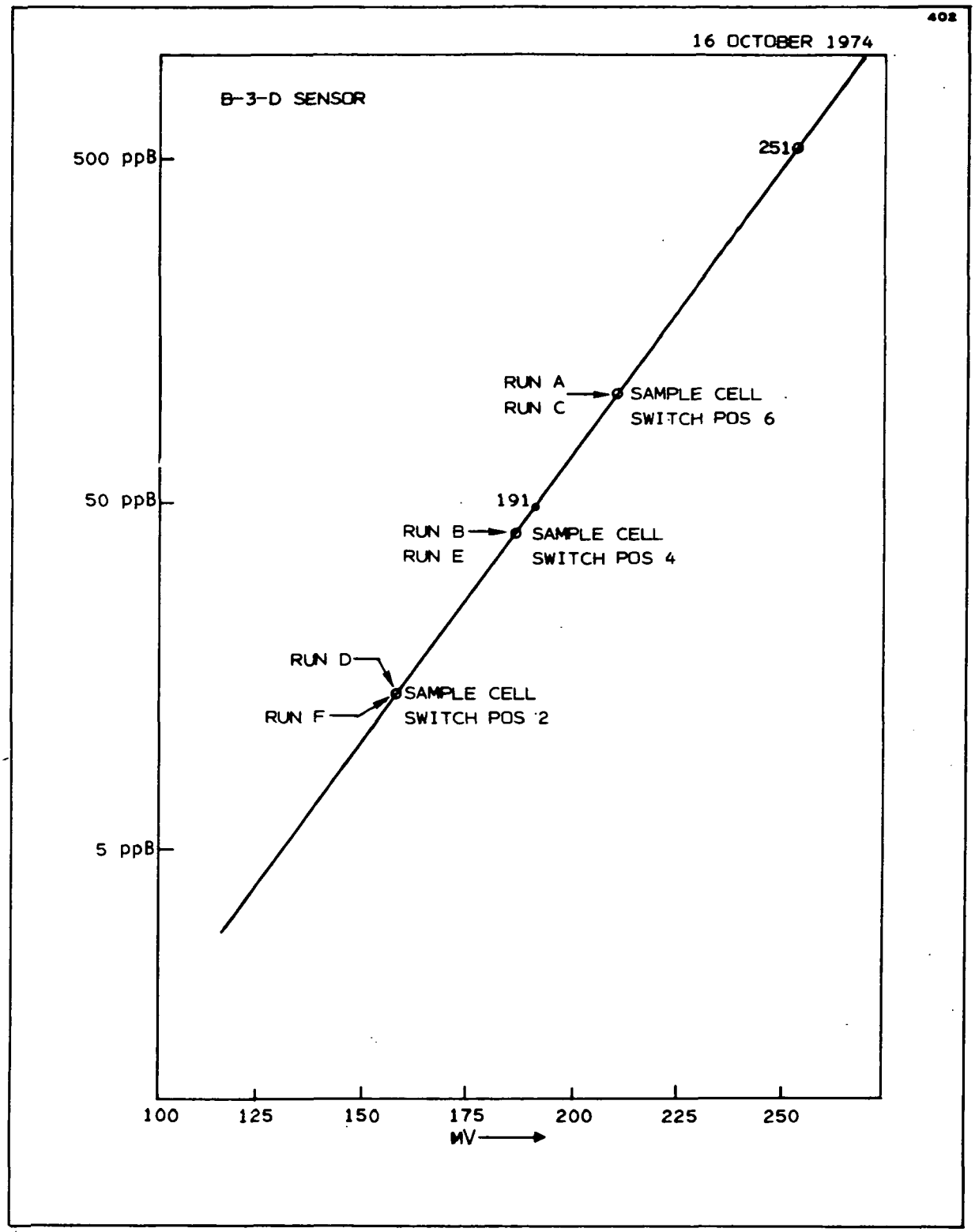

Figure 12. Electrode Response

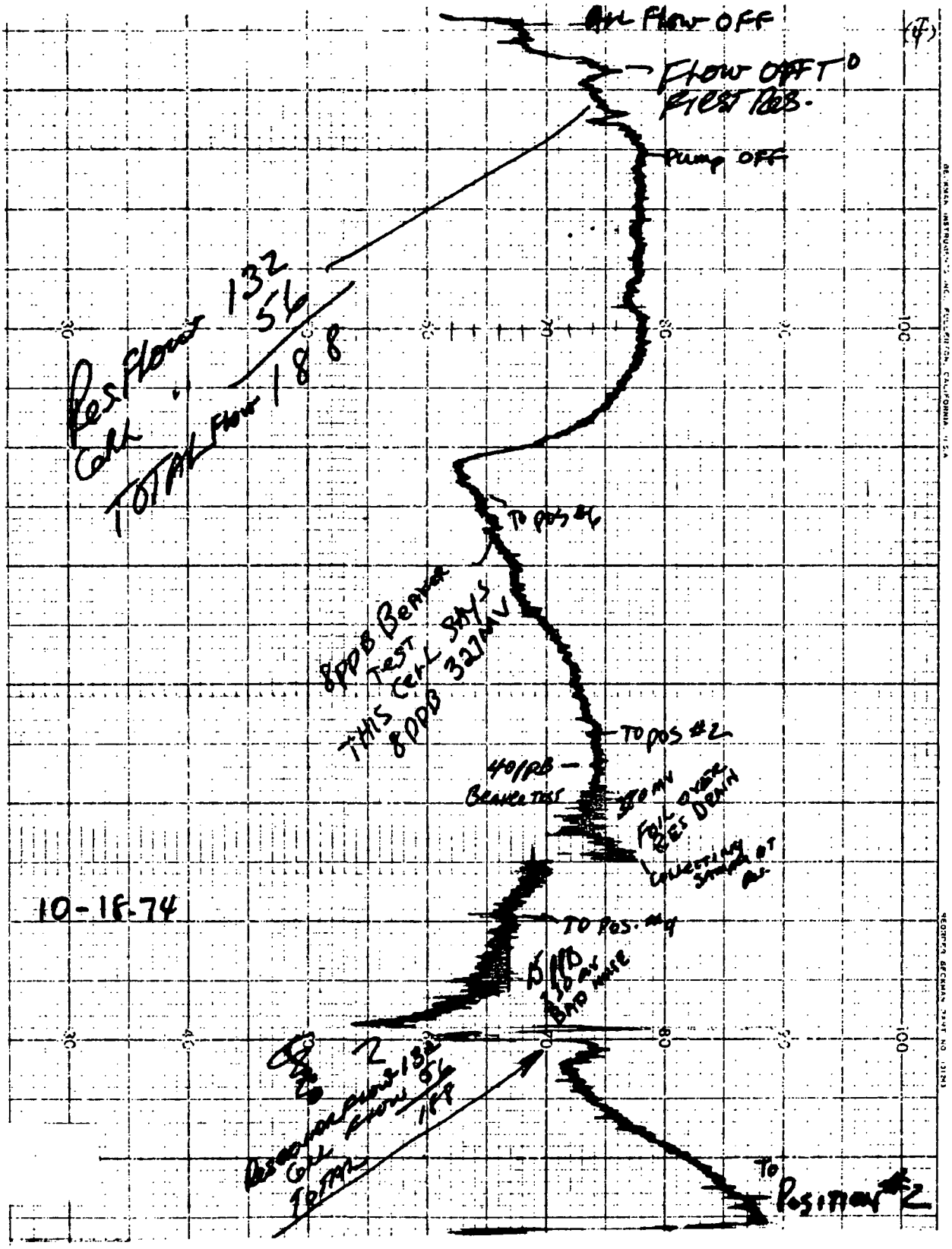

Figure 13. Test System Performance Characteristics

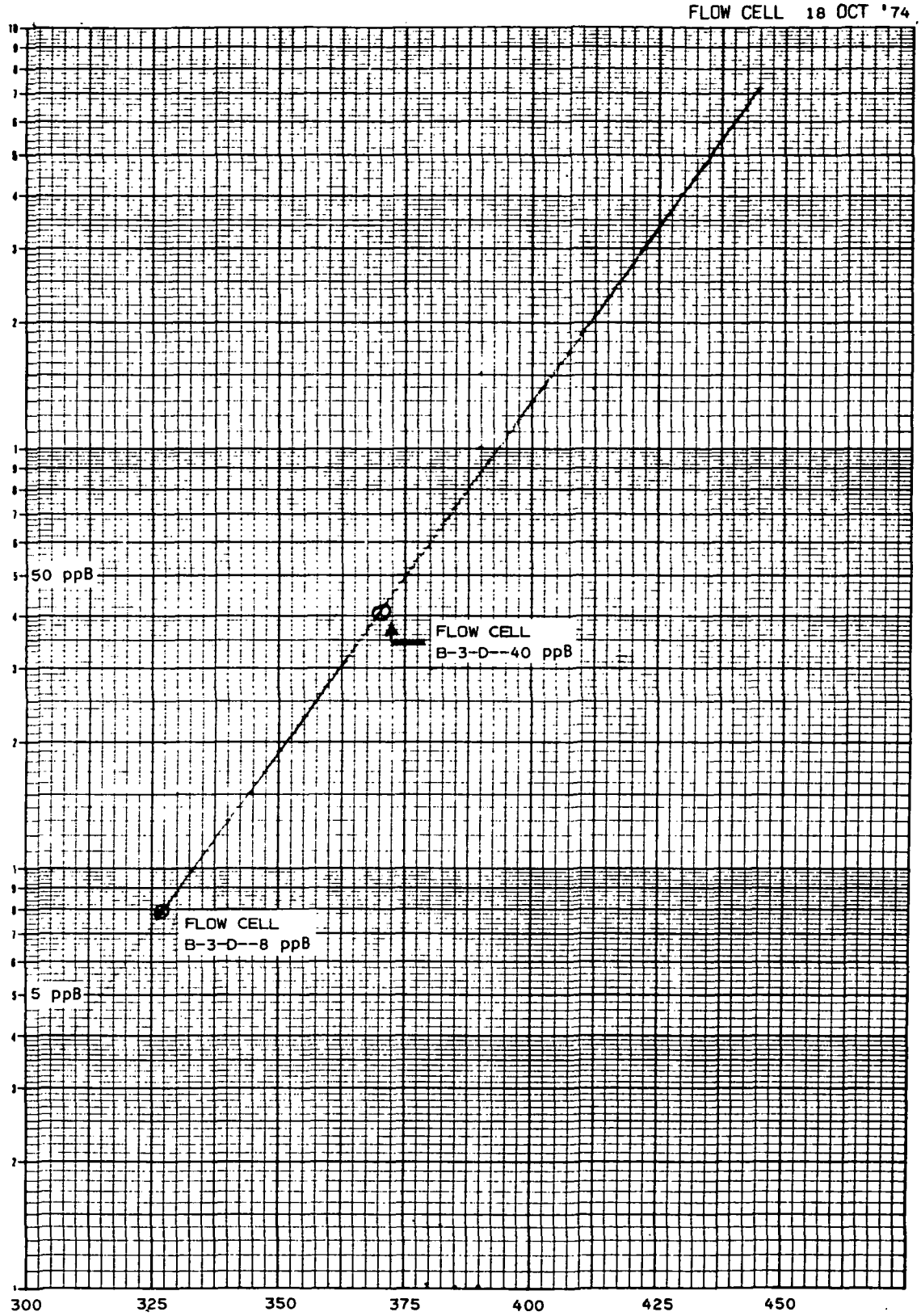

Figure 14. mV Flow Cell

is Nernstian and therefore the electrode was functioning properly but the test system was not.

It was decided that further effort expended in this direction would not be cost-effective, especially since the problems revealed during these tests were only peripherally related to the performance of the silver ion monitoring system, with a single exception. This exception was the tendency of the current flow-through cell to entrap air bubbles generated by degassing of the test solutions. These bubbles will collect in the reference electrode pressure equalizing system to the point where the reference junction can be affected. Although this phenomenon may be an artifact of the test system employed, i.e., the potable water supply system of the Shuttle will have a low dissolved gas content, use of the cell over several days will result in a significant entrainment of gas. Redesign of the test cell is indicated to minimize this occurrence.

The conclusions derived from these flow-through studies were that no deterioration was observed in the performance of the sensing electrode during the duration of the study. When problems raising a question about sensor performance arose, a span check of the electrode always showed that the sensor was performing properly. On the occasion when the test system could be made to function, the response of the sensors could be demonstrated. Such a tracing is shown in Figure 15. Although the span shown is short, the sensitivity of the response is evident. The electrode showed Nernstian response in a beaker check before and after the flow test.

Another tracing is illustrated in Figure 16, showing sensitivity over the range of 21 to 90 ppb. A plot of the data points showing Nernstian response is shown in Figure 17.

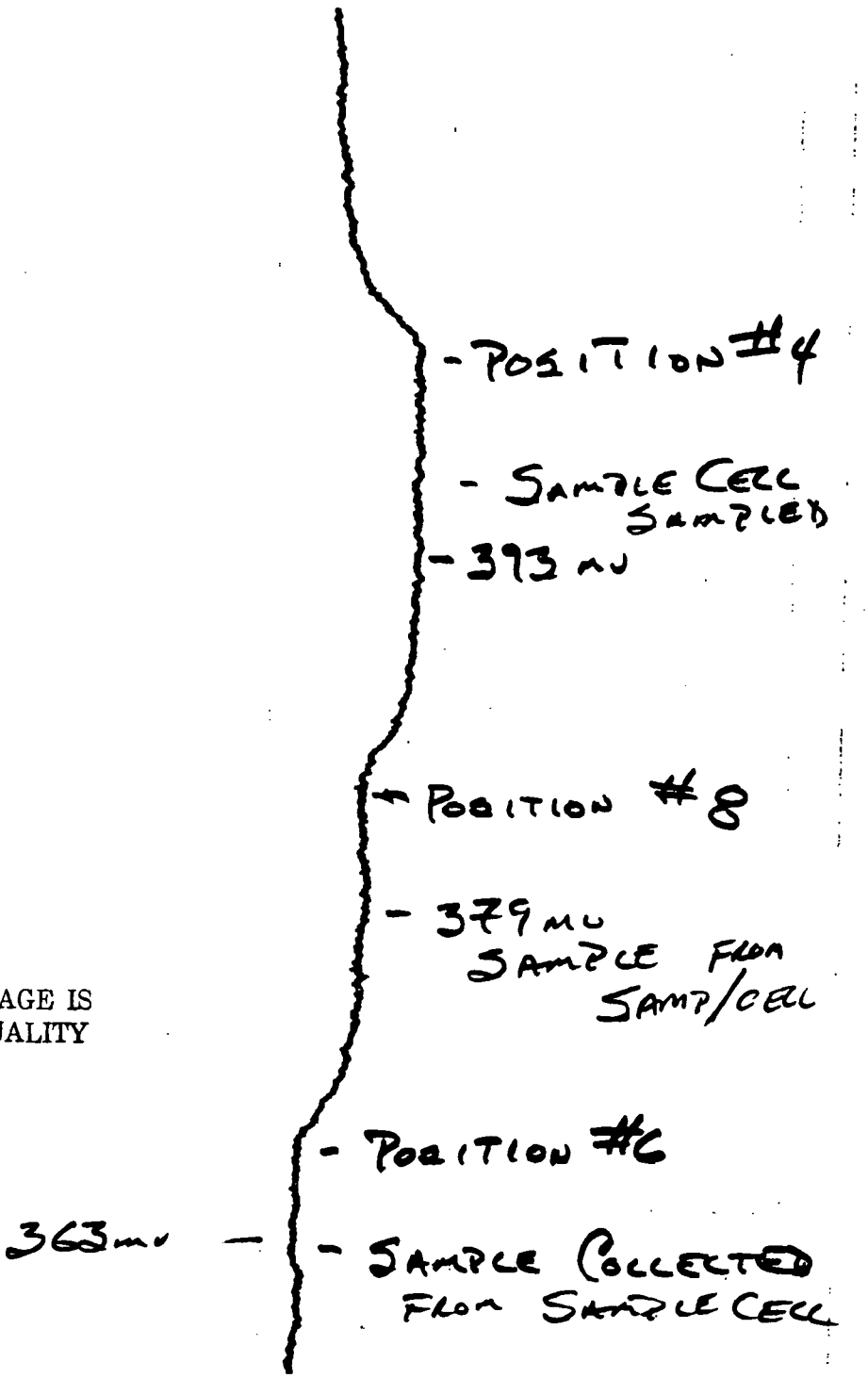

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Figure 15. Flow System Response to Silver Ion

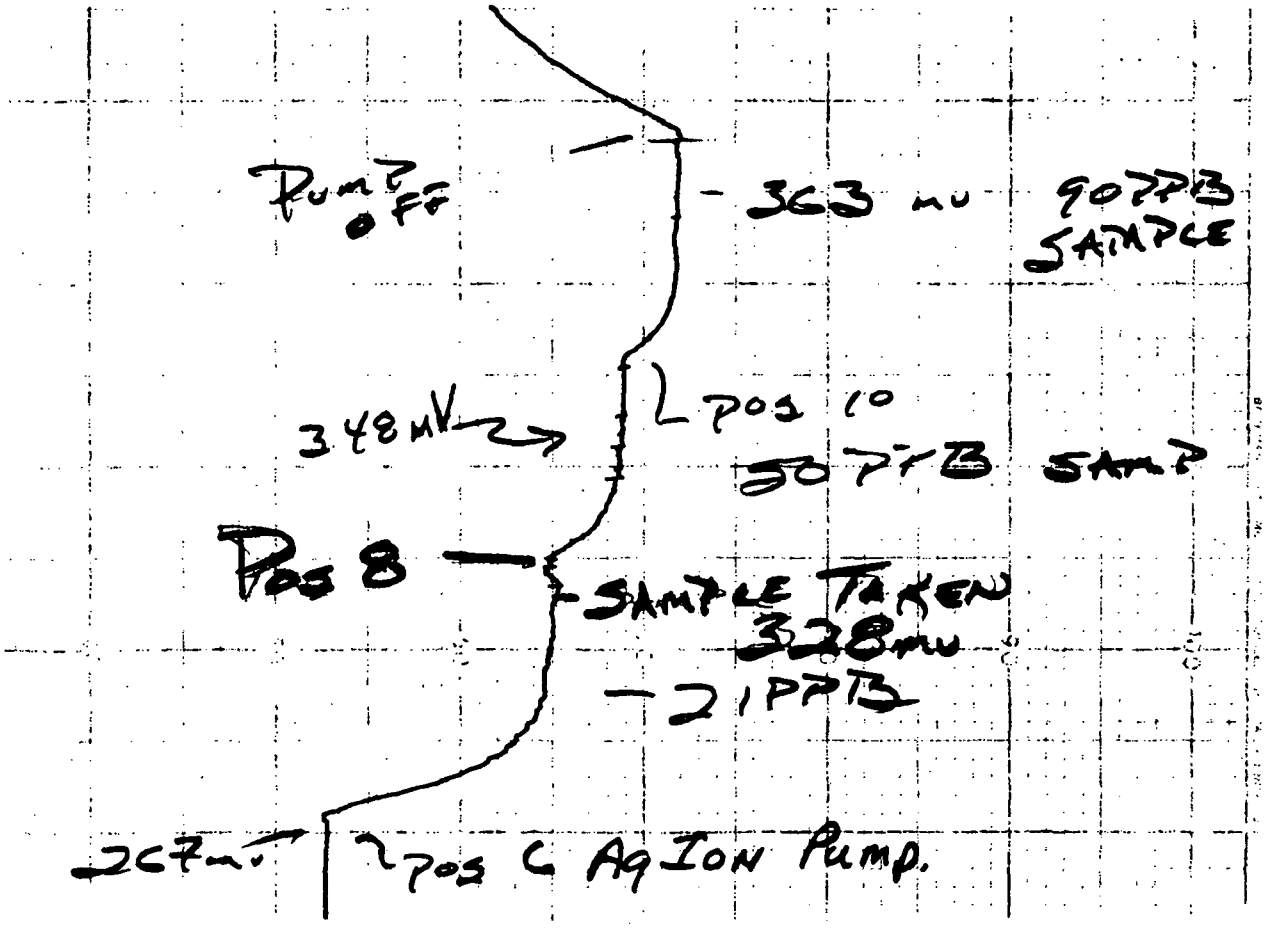

Figure 16. Flow Cell Response to Silver Ion

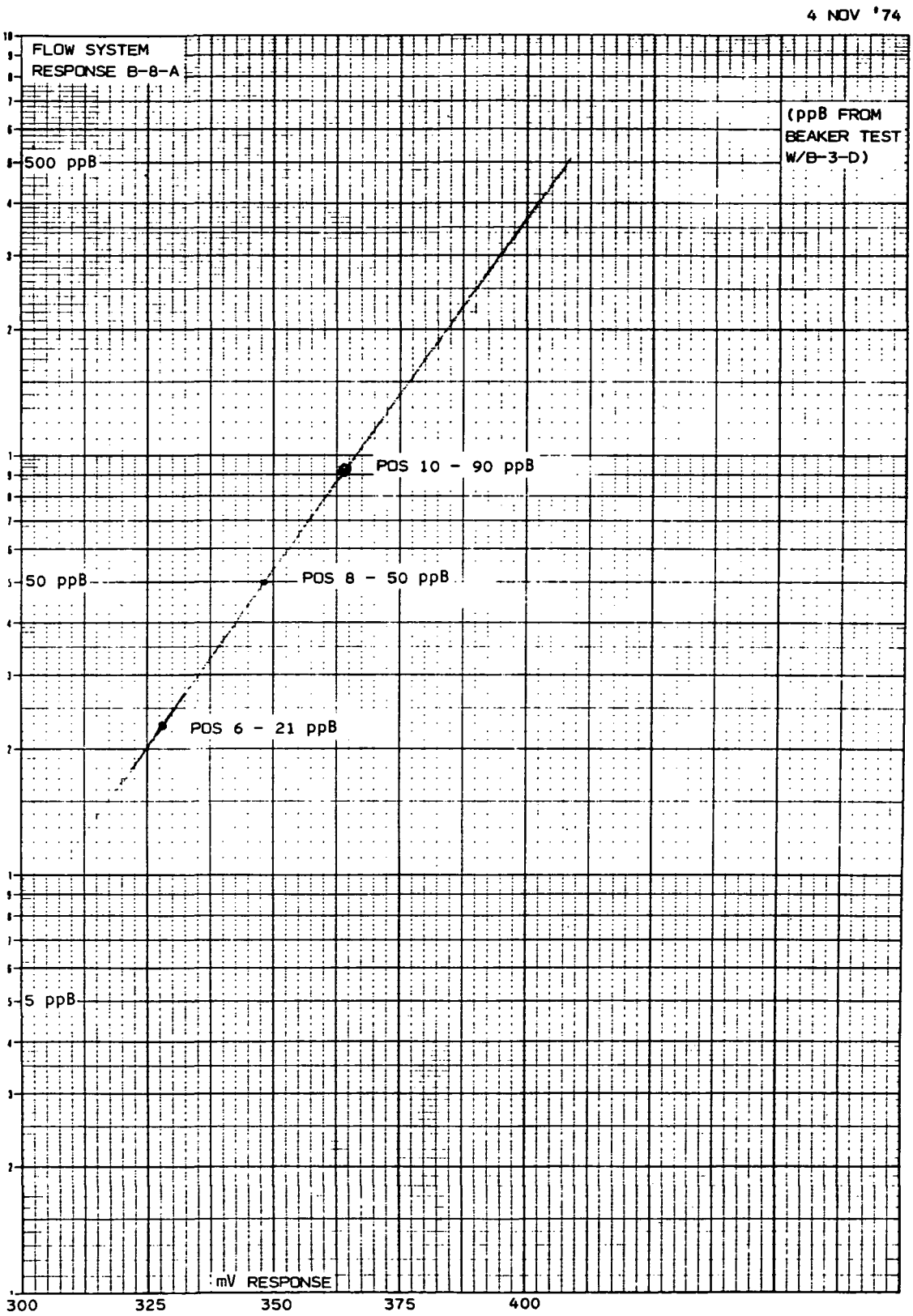

Figure 17. Flow System Response (Nernstian)

5.0 SYSTEM INTEGRATION-CALIBRATION LOOP

Having demonstrated the stability of the sensor, the next most significant problem area was the achievement of theoretical output of the silver bromide calibration column. One of the initial concerns in earlier tests was that the dwell time of the water within the silver bromide column was inadequate to yield theoretical concentrations of silver bromide in the calibration solution. To investigate this parameter, a test system was fabricated as shown in Figure 18. The flask was pressurized with nitrogen to force water through the AgBr column. Three different types of water were investigated--de-ionized water, spring water that was inadvertently delivered in place of distilled water, and Shuttle worst-case water provided to Beckman by Life Systems, Inc. The data from this experiment are reproduced below:

DE-IONIZED WATER

m^3/s (x 10-6)	Flow ml/m	Water Temp. °C	Water Temp. K	Theory ppb	Flow Cell mV	Cal Electrode B-3-D, mV	B-3-D ppb
.17	10	21.8	294.9	63.5	319	210	63
.67	40	21.8	294.9	63.5	314	210	63
.67	40	21.8	294.9	63.5	315	211	64
.67	40	21.8	294.9	63.5	328	211	64
1.38	83	21.75	294.9	63.0	326	210	63
1.85	111	21.8	294.9	63.5	326	211	64

SPRING WATER

.88	53	21.3	294.5	61.0	244	170	17
1.38	83	21.3	294.5	61.0	247	170	17
1.37	82	21.3	294.5	61.0	256	170	17

SHUTTLE WORST-CASE WATER

.25	15	21.8	294.9	63.5	297	200	57
.90	54	21.8	294.9	63.5	299	199	56
1.63	98	21.8	294.9	63.5	299	199	56

It is apparent that the flow rate plays a relatively minor role achieving theoretical output from the column. Looking at the millivolt outputs from

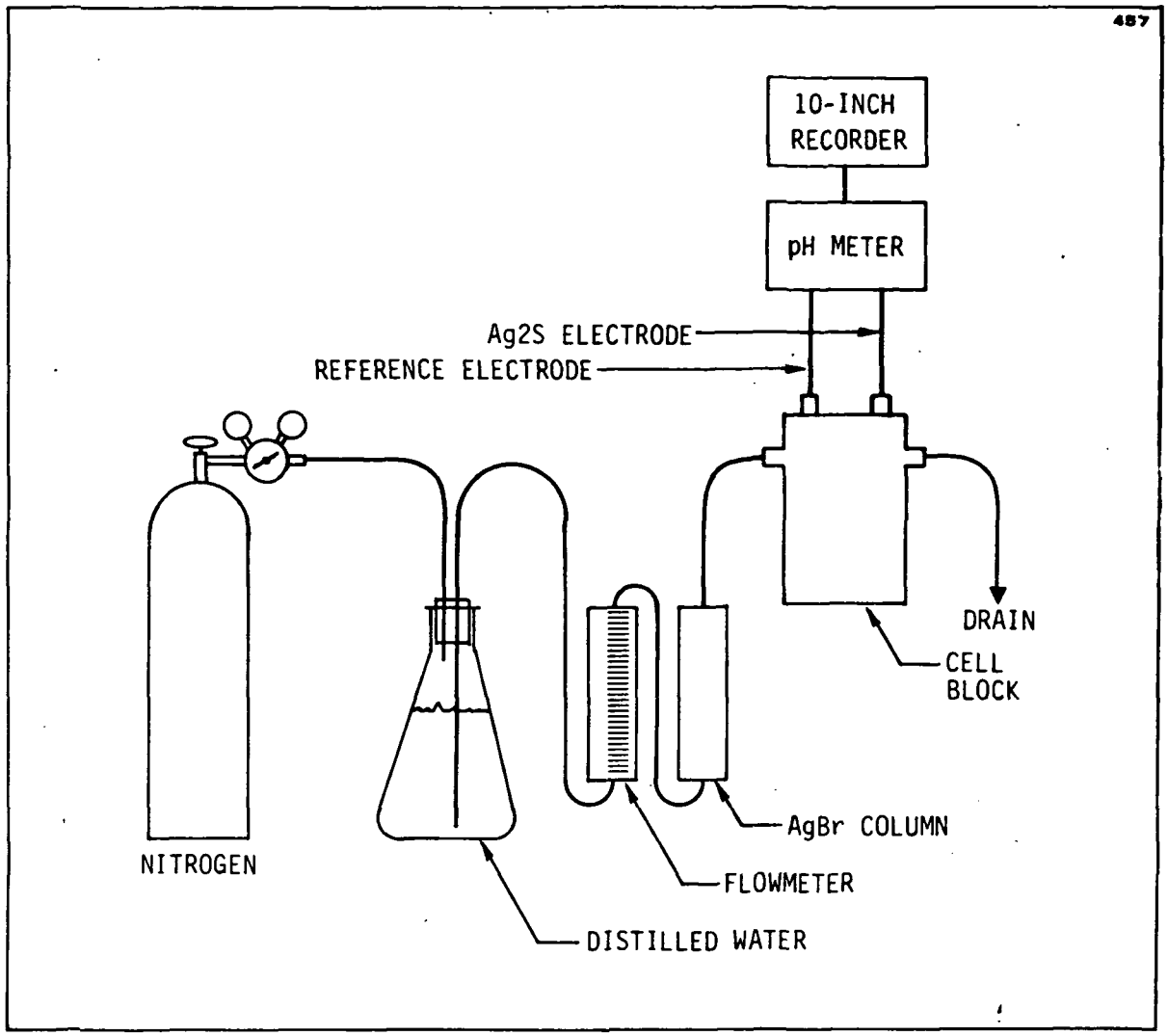

Figure 18. Test System

the flow cell, it appears that variability is unrelated to flow over a broad flow range. The cell fluid output that was collected and analyzed in a beaker test using B-3-D electrode shows good agreement with theoretical output over the flow range. Some decrease is observed with Shuttle worst-case water, but this can be anticipated because of the chemical impurity of the water which would be expected to complex some of the silver. Indeed, it is surprising that a larger decrease from theory was not observed. It is interesting to note the decrease in span when using the spring water. The apparent complexing of silver is worse than in the worst-case Shuttle water, possibly due to high chloride levels.

The next stage in the integration procedure was to calibrate the B-8-A flow system electrode so that absolute, rather than relative readings could be obtained. This was accomplished by calibrating the flow cell electrodes with silver nitrate solution added to the reservoir with a Sage metering pump. Distilled water was used as the carrier. The calibration column was placed in line and the system was run "open loop." The following readings were obtained:

First Reading:	Theory - 66 ppb B-3-D - 60 ppb Flow Cell - 50 ppb
Second Reading:	Theory - 66 ppb B-3-D - 67 ppb Flow Cell - 70 ppb
Third Reading:	Theory - 56 ppb B-3-D - 56 ppb Flow Cell - 50 ppb

Thus, except for the first reading, good reproducibility and reasonable agreement with B-3-D obtains.

The next phase in the integration procedure was to close the calibration loop, employing a sample pump, the AgBr column, and the electrode block to determine column output stability under closed-loop conditions, again using distilled water. Under these conditions, the output of the sensing electrode showed a slow decrease in silver ion concentration. The loop was again opened and in approximately 20 minutes the silver in solution as measured by the B-3-D

electrode had recovered to theoretical. The loop was again closed, recirculating the same water back through the silver bromide column and once again the silver ion concentration decreased.

To investigate this phenomenon further, the calibrating column was removed from the system and mounted on the bench. A liter of distilled water was repeatedly passed through the column and the solution checked with electrode B-3-D after each pass. The data from this experiment are shown below:

First time through:	77 ppb
Second time through:	60 ppb
Third time through:	77 ppb
Fourth time through:	35 ppb
Fifth time through:	18 ppb

Fresh distilled water was then passed through the column and the column output recovered to theoretical. Some variability is observed in the number of cycles required to demonstrate this silver depletion effect, which is somewhat puzzling since at relatively constant flow rates, uniform behavior should be expected. Cycle variability was also observed between columns, but the end result was always the same--repeated cycling of the same water resulted in silver depletion.

These results could be explained by ionic competition, perhaps made worse by the removal of silver through adsorption leaving relatively high concentrations of bromide ion in solution. To verify this theory, an anion exchange column was fabricated using Amberlite IR-45 (Rohm and Hass Co.). The results of this experiment are shown below:

Without Anion Exchange Column:

First time through:	62 ppb
Second time through:	50 ppb
Third time through:	40 ppb
Fourth time through:	40 ppb
Fifth time through:	30 ppb

Anion Exchange Column was installed between Reservoir and the AgBr Column and the same water passed through twice more:

Sixth time through:	62 ppb
Seventh time through:	62 ppb

This experiment implies that a closed loop calibration system could be employed for the monitoring system, but an anion column will be required immediately in front of the silver bromide column.

6.0 ELECTRONIC INTEGRATION

Following the definition of the problems previously experienced with the integration of the silver bromide column into the monitoring loop, integration of the silver system with the read-out and calibration electronics proceeded.

Due to the fact that the AgBr column does not perform as expected in a closed loop, it was decided not to use the AgBr column as a calibration tool in this prototype system; instead, the system can be calibrated with a known concentration of silver ion passing through the cell block and manually adjusting a calibration control mounted on the front panel. Removing the AgBr column calibration mode necessitated the dismantling, but not removing, of the sample and hold circuit and the repeat calibration circuit.

Turning the monitor on or operating the manual calibration button initiates a calibration cycle. During the first six minutes of the 12-minute cycle, the panel meter pegs below zero and the calibration control has no effect. During the last six minutes of the calibration cycle, the calibration control is active and at this time with a known concentration of silver ion in the solution passing through the cell block, the calibration of the monitor should be performed. After the 12-minute calibration cycle, the calibration control becomes inactive and remains this way until the calibration cycle is started again. The frequency of calibration required will depend on the system accuracy desired, but it is reasonable to consider 12- to 24-hour intervals between calibration cycles. The integrated electronic-sensing system appears quite stable. Long-term testing with a stable source of silver ion, e.g., Shuttle generators and tanks, are required before system performance verification can be completely demonstrated.

Thus, the prototype system is operational except for the automatic calibration feature and may be used for monitoring of silver ions in a flowing stream.

7.0 CONCLUSIONS

The major objectives of this effort have been achieved. That is, solid-state electrodes capable of sensing silver ion concentrations of less than 20 ppb, and for longer than any presently conceived Shuttle mission, can be reliably manufactured with acceptable yields.

The use of these electrodes in a flow-through system has permitted the isolation of system level problems that could not previously be identified due to unreliable sensor performance. With the identification of these problem areas, it will be possible to proceed expeditiously in the development program, if and when this is indicated. It is emphasized, however, that long-term testing of the present system, modified only to the extent required to achieve functional performance goals, should be performed before any additional development effort is considered. This is required to ensure that all system level problems are uncovered in a cost-effective manner. It is felt that the hardware and sensor systems are at a stage of development to permit this testing with the exception of the flow cell. As previously mentioned, the present configuration permits the entrainment of air bubbles and this design deficiency should be corrected.

System flow, pressure, and temperature stability tests were conducted as previously reported (NASA CR134361). Verification of flow stability was repeated during this study and while the pressure and stability tests were not repeated, it is not felt that, within the nominal Shuttle ranges specified for these parameters, any significant design disturbances would obtain.

Type: Ag_2S Silver Epoxy (Eccobond)

Series: B-3 Electrodes

Configuration: Beaker Test

B-3-B

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1			51
19	166	227	61
20	175	228	53
21	163	220	57
25	116	182	66
28	176	230	54
29	167	225	58
30	176	230	54
34	177	240	63
39	186	242	56
40	189	242	53
46*	190	242	52
49	190	255	65
54	176	233	58
61	156	216	62
64	171	232	61
69	182	242	60
74	183	242	59
77	187	246	59
82	190	249	59
85	202	263	61
90	187	246	59
97	190	250	60
102	198	259	61
	N=13	N=13	N=24
	SD=11.9	SD=12.4	SD=4
	$\bar{X}$=184.8	$\bar{X}$=244	$\bar{X}$=58.4

B-3-C

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1			51
19	400	450	50
20	385	440	55
21	382	435	53
25	360	420	60
28	390	442	52
29	389	442	53
30	383	440	57
34	380	440	60
47*	184	231	47
50	168	232	64
55	177	232	55
62	180	239	59
67	179	238	59
70	184	243	59
75	178	237	59
78	178	238	60
83	183	243	60
88	193	252	59
95	182	243	61
98	194	254	60
	N=12	N=12	N=21
	SD=7	SD=7.4	SD=4.3
	$\bar{X}$=182	$\bar{X}$=240	$\bar{X}$=56.8

B-3-D

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1			51
19	186	244	60
20	189	245	56
21	183	244	61
25	165	224	59
28	185	245	60
29	182	241	59
30	188	248	60
34	192	252	60
48*	191	250	60
51	193	253	60
56	195	255	60
63	202	262	60
68	198	257	59
71	201	260	59
76	204	264	60
81	201	261	60
84	205	265	60
89	204	264	60
96	203	263	60
99	202	262	60
	N=12	N=12	N=21
	SD=4.6	SD=4.8	SD=2.1
	$\bar{X}$=199.9	$\bar{X}$=259.6	$\bar{X}$=59.2

*Change of test setup.
**Offset potential.

Type: Ag_2S Molded Wire

Series: B-4 Electrodes (Page 1 of 2)

Configuration: Beaker Test

B-4-A			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	301	362	61
4	323	386	63
5	333	394	61
6	330	386	56
12	514	574	60
13	581	644	63
14	602	648	46
15	682	718	36
20	587	637	50
25	651	718	67
32*	147	212	65
38	133	200	67
43	163	223	60
53	65	126	61
61	90	150	60
68	70	131	61
75	97	151	54
			N=17
			SD=8
			$\bar{X}$=58.3

B-4-E			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	115	212	61
4	266	316	50
5	373	327	54
6	270	328	58
12	236	296	60
13	253	312	59
14	250	300	50
15	243	299	56
20	244	302	58
25	278	330	52
35*	74	117	43
42	58	114	56
51	61	121	60
58	70	131	61
66	66	124	58
73	64	125	61
82	98	157	59
	N=7	N=7	N=17
	SD=13	SD=14	SD=5
	$\bar{X}$=70	$\bar{X}$=127	$\bar{X}$=56.2

B-4-B			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	385	439	54
25	85	143	58
33*	70	128	58
40	65	126	61
44	53	110	57
54	88	149	61
62	59	120	61
69	79	141	62
80	63	104	41
86	59	114	55
	N=8	N=8	N=10
	SD=10.8	SD=15.3	SD=6
	$\bar{X}$=67.6	$\bar{X}$=124	$\bar{X}$=56.8

*Change of test setup.
**Offset potential.

Type: Ag_2S Molded Wire

Series: B-4 Electrodes (Page 2 of 2)

Configuration: Beaker Test

B-4-C

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	-30	38	68
20	98	41	57
34*	142	166	24
41	71	129	58
48	53	109	56
55	59	117	58
63	102	160	58
70	76	136	60
81	79	138	59
			N=9
			SD=12
			$\bar{X}$=55

B-4-D

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	383	425	42

B-4-F

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	268	313	45
20	332	390	58
26	331	379	48
36*	63	127	64
47	69	126	57
52	67	123	56
59	72	133	61
67	60	120	60
74	63	124	61
83	70	129	59
	N=7	N=7	N=10
	SD=4.4	SD=4.2	SD=5.9
	$\bar{X}$= 66.3	$\bar{X}$=128	$\bar{X}$=56.9

*Change of test setup.
**Offset potential.

Type: Ag_2S Liquid Junction

Series: B-5 Electrodes (Page 1 of 2)

Configuration: Beaker Test

B-5-A

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	487	535	48
2	500	537	37
3	602	648	46
4	489	536	47
8	487	540	53
13	492	542	50
20*	4	60	56
25	Drift		
35	32	9	41

Drifting and erratic--discontinued

B-5-B

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	252	301	49
2	216	275	59
3	241	269	28
4	230	293	63
13	-218	-157	61
21*	-162	-104	58
28	-234	-224	10
36	-259	-209	50

Drifting and erratic--discontinued

B-5-C

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1			64
22*	-60	2	62
29	-110	-100	10
35	-462	-401	61

Drifting and erratic--discontinued

*Change of test setup.
**Offset potential.

Type: Ag_2S Liquid Junction

Series: B-5 Electrodes (Page 2 of 2

Configuration: Beaker Test

B-5-D

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	230	281	51
2	230	287	57
3	225	280	55
4	230	283	53
13	215	279	64
23*	2	57	55
38	-296	-243	53

Drifting and erratic--discontinued

B-5-E

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	-8	49	57
2	-2	54	56
3	23	55	32
4	1	57	56
13	6	60	54
24*	2	59	57
34	-15	-15	43

Drifting and erratic--discontinued

B-5-F

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	190	251	61
2	196	252	56
3	218	252	34
4	201	254	53
8	201	254	53

Cable Connector Broken

*Change of test setup.
**Offset potential.

Type: Ag_2S Molded Wire

Series: B-6 Electrodes (Page 1 of 2)

Configuration: Test Stand

B-6-B			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	312	365	53
5	317	381	64
12*	101	170	69
17	101	163	62
23	56	108	52
35	63	103	40
42	149	178	28
49	122	178	56
56	95	134	39
65	102	133	31

B-6-C			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	542	609	67
5	543	609	66
13*	90	126	36
21	81	101	30
29	71	115	44
36	76	109	33
43	113	163	50
50	116	176	60
61	81	115	34
68	158	212	54

B-6-D			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	285	342	57
5	295	349	54
14*	114	175	61
21	116	150	34
30	69	139	70
37	38	109	71
44	102	133	31
51	37	68	31
62	60	104	44

*Change of test setup.
**Offset potential.

Type: Ag_2S Molded Wire

Series: B-6 Electrodes (Page 2 of 2

Configuration: Test Stand

B-6-E				B-6-F			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv	Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	235	300	65	1	520	582	62
5	263	321	58	5	538	591	53
15*	110	157	47	16*	63	114	51
22	43	60	27	28	20	54	34
33	-91	-71	20	34	15	55	40
40	Drift			41	Drift		
47	22	58	36	48	76	116	50
54	46	90	44	55	69	117	48
63	70	132	62	64	20	60	40

*Change of test setup.
**Offset potential.

Type: Ag_2S Liquid Junction

Series: B-7 Electrodes (Page 1 of 2)

Configuration: Test Stand

B-7-A

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	101	144	43
5	-5	54	59
12*	237	291	54
20	231	291	60

Drifting and erratic--discontinued

B-7-B

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	82	122	40
5	Cable Short		
13*	234	289	55
21	50	111	61

Drifting and erratic--discontinued

B-7-C

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	Cable Short		
5	-5	21	26
14	230	291	61
22	230	290	60

Drifting and erratic--discontinued

*Change of test setup.
**Offset potential.

Type: Ag_2S Liquid Junction

Series: B-7 Electrodes (Page 2 of 2)

Configuration: Test Stand

B-7-D

Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	7	63	56
5	-3	53	56
15*	238	298	60
27	200	249	49

Drifting and erratic--discontinued

B-7-E

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	39	102	63
5	-13	56	69
16*	239	302	63
28	-112	55	57

Drifting and erratic--discontinued

B-7-F

Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	Cable Short		
5	138	210	72
17*	250	315	65
29	350	405	55

Drifting and erratic--discontinued

*Change of test setup.
**Offset potential.

Type: Ag_2S Silver Epoxy (Eccobond)

Series: B-8 Electrodes

Configuration: Test Stand

B-8-B			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1*	370	440	70
2	378	442	49
8	352	410	58
15	350	410	60
18	345	398	53
23	341	400	59
30	340	398	58
35	302	352	50
38	331	391	60
43	335	394	59
50	330	390	60
53	395	396	61
	N=12	N=12	N=12
	SD=24.6	SD=23.5	SD=5.53
	$\bar{X}$=347	$\bar{X}$=402	$\bar{X}$=58.08

B-8-C			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1*	237	289	52
3	421	472	51
8	420	478	58
15	421	478	57
20	410	470	60
23	413	473	60
30	412	470	58
35	408	470	62
38	412	470	58
43	418	476	58
50	416	478	62
55	422	480	58
	N=12	N=12	N=12
	SD=51.8	SD=53.5	SD=3.4
	$\bar{X}$=401	$\bar{X}$=459	$\bar{X}$=57.8

B-8-D			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1*	421	471	50
3	411	462	51
8	387	442	55
15	346	398	52
20	337	398	61
24	340	398	58
30	305	363	58
35	302	361	59
40	301	357	56
47	292	350	58
50	296	356	60

*Change of test setup.
**Offset potential.

Type: Ag Silver Epoxy (Eccobond)

Series: B-9 Electrodes (Page 1 of 2)

Configuration: Test Stand

B-9-A			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	477	533	56
4	475	536	61
10	510	538	28
18	502	538	36
24	496	536	40
30	485	540	55
36	492	543	49
42	494	542	46

B-9-B			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	505	518	13
4	515	542	27
14	470	510	40
20	470	501	31
24	485	528	43
30	526	538	12
36	528	542	14
42	524	538	14

B-9-C			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	517	546	29
	Connector Broke		

**Offset potential.

Type: Ag Silver Epoxy (Eccobond)

Series: B-9 Electrodes (Page 2 of 2)

Configuration: Test Stand

B-9-D			
Day	**O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	494	537	43
5	511	550	39
13	520	547	27
19	515	535	20
25	510	542	32
29	514	546	32
35	514	550	36
41	515	552	37

B-9-E			
Day	O.P. Mv 50 ppb	O.P. Mv 500 ppb	Span Mv
1	498	539	41
8	502	539	37
14	501	540	39
20	496	538	42
26	492	541	49
30	489	539	50
40	541	587	46

**Offset potential.