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25 July 1962

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Dear Sir:

Enclosed are six (6) copies of the Final Report for the Elfin I Project. This completes the work on the contract and it would be appreciated if you would notify the contracting officer of this completion.

Very truly yours,

Project Manager

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ELFIN I
FINAL REPORT
C25-7

July 25, 1962

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I. INTRODUCTION

The purpose of the present study has been to develop electroplating cell of sufficient sensitivity to integrate extremely small electrical signals. The quantity of charge specified as the sensitivity level was one-tenth micro coulomb. This charge is to be integrated by passing a small current through the cell in one direction and read-out by passing a known current through the cell in the reverse direction, noting when the potential across the cell rises as the result of removal of all the material plated onto one of the electrodes by the initial current.

The cell is to be used as an integrator of currents from such sources as antenna-diode combinations, transducers, and recording instruments. Applications to timers, radiation monitors, and computers have been investigated on other projects.

This report summarizes the final four months of a seven month study of electroplating cell development. A previous report was issued at the end of the third month.

The results of the study have exceeded the initial goals for cell sensitivity. Electroplating cells can be produced which will integrate quantities of charge as small as a millimicro coulomb, two orders of magnitude smaller than the original goal. This quantity of charge corresponds to one micro-microgram of silver plated onto an electrode. The sensitivity of the technique can be increased even further. Lack of available time is responsible for the present limit.

The techniques which have contributed most to the improvement of sensitivity are the elaborate cell cleaning procedures and electrode construction methods. Removal of platinum oxides from the electrodes has yielded consistently cells of high sensitivity.

The organization of the report is apparent from the Table of Contents. Section 3.1 is a particularly detailed chronological discussion of the cell development program during the past four months. Section 3.2 is a report of results of some preliminary work done with determining

cell resistance and other characteristics as a function of current level. Although the discussion of this section is somewhat tentative, the results are now thoroughly understood and presented in Section 3.3. The Appendix provides a detailed look at some of the theoretical techniques for calculating cell potentials under various conditions which depart from the standard cases. In particular, the effect of an electrode only partially covered with the ionizing metal is considered.

The cell work is continuing with applications being investigated and a field test program planned.

2. EXPERIMENTAL PROCEDURES

2.1 ELECTRODE PREPARATION AND TESTING

Early in the study electrolytic experiments were performed by using electrodes made of 20 mil platinum (Pt) wire sealed into soft glass or pyrex tubing, cut and ground flush with the glass so that only the cross-sectional area of the wire was exposed. The glass tubing was either dipped into the electrolyte or sealed into cell walls of glass. This technique did not result in adequate sensitivity because of the fracturing of glass around the Pt causing diffusion of the electrolyte into the seal.

Progressive losses of silver from cycling current between electrodes were thought to be due to diffusion into the electrode material. Tungsten electrodes were tried because its crystal structure is different from that of silver and some improvement was noticed.

By a chance experiment very fine (3 mil) Pt wire was sealed into a small soft glass tube and clipped short rather than ground flush. The result was a considerable improvement in sensitivity, allowing plating currents as small as 0.01 microamperes to be used.

Numerous electrodes were made of three mil Pt wire sealed in soft glass tubing with data taken by holding two electrodes in a rubber stopper inserted in a small medicine bottle. Later cells were made by sealing the soft glass electrodes into opposing ends of glass "T"'s, the stem of the "T" used for filling and closing the cell. Pyrex tubes were tried and found unsatisfactory because the expansion coefficient did not match that of Pt.

2.1.1 Cleaning of Glass Tubes and Pt Wire

There were three procedures for preparing Pt electrodes and in the later experiments the Pt wire and the tubing were first cleaned before fusing the wire into the ends of the glass tubes. The wire and glass tubing were first cut into suitable lengths using a good grade of alloy scissors for the wire and a steel file for the tubing. The lengths of tubing used varied from about one inch to 2-1/2 inches and the wire

about one inch longer than the tubing in which it was later fused. The wire was immersed in a beaker containing dilute nitric acid for about three minutes. The acid was then poured off and distilled water added until the wire was covered. The water was then poured off in such a way that the entire inner walls of the beaker were washed. This rinsing with distilled water was then repeated six times. The wire and beaker were then rinsed with reagent acetone three times using the same techniques as when rinsing with water. Nitrogen was then blown into the beaker to dry the wire.

The glass tubing was immersed in cleaning solution ($K_2Cr_2O_7$ dissolved in concentrated sulfuric acid) for about ten minutes and then well rinsed with Braun distilled water. The tubes were then shaken to remove most of the water and placed in a beaker containing reagent acetone. The tubes were then removed from the acetone and blown dry with nitrogen. The object of using acetone in the final rinsing of the wire and tubes is to remove the water which is soluble in all proportions in acetone. The wire and tubes were then placed in clean, dry, covered glass dishes. Most of the glass tubing used was soda lime glass; however, in a few experiments pyrex tubing was used in preparing the Pt electrodes. The glass tubes, whether previously cleaned or not, were fire polished at each end before fusing the Pt wire into one of the ends. One of the following procedures was then used in preparing the electrodes.

2.1.2 Preparation of "Wire" Pt Electrodes

The Pt wire is threaded through the tube until it extends a little further out from the end of the tube than its final planned length. The wire is then rapidly fused into the end of the tube while rotating the latter. The tube is then quickly removed to a point just beyond the tip of the outer gas flame and held there a short time to anneal the glass. A gas-air torch is used for soda lime glass and a gas-oxygen torch for pyrex. The wire is then cut off with a good grade of alloy scissors to the correct length.

2.1.3 Preparation of "Sphere Type" Pt Electrodes

After threading the Pt wire into the tube as described under Section 2.1.2 until the wire extends about half an inch out, the tip of the wire is held in the flame of the gas-oxygen torch at a point about half an inch beyond the inner cone until the wire scintillates and a sphere is formed on the end of the wire by the melting of the platinum. The wire is retracted into the tube until the sphere is just flush with the end of the tube. It is easiest to determine if the sphere is flush by viewing the sphere and tube under the microscope. The Pt wire and its sphere is then fused into the end of the tube as described under Section 2.1.2. The electrode is then examined under the microscope and if the sphere extends out too far, or not far enough, the procedure is repeated using another piece of tubing. In some cases when the sphere does not extend out far enough, it may actually be covered with a thin film of glass. The preparation of this type of electrode is difficult because often a fair number of trials are necessary before a satisfactory electrode can be made. Another difficulty that presents itself in some cases is that there is apparently formed on the surface of the sphere a film of an oxide of Pt which is sufficiently thick or of such a nature that the electrode will not conduct current. If, upon examination under the microscope, there appear bubbles or other defects in the Pt to glass interface the electrode is to be rejected.

2.1.4 Preparation of "Broken Wire" Type Pt Electrodes

The Pt wire is threaded into the tube until it extends about half an inch out from the end and is then fused into the tube as described in 2.1.2. After the tube has cooled to room temperature the wire is grasped with a forceps from about 1/2" to 3/4" from the end of the tube and, keeping the wire slightly taut, it is carefully bent back and forth until it breaks off approximately flush with the end of the tube. The end of the tube and wire are then examined under the microscope and if there are any bubbles, splintering (due to the bending of the wire), or other defects in the Pt to glass seal the electrode is rejected.

2.1.5 Testing Procedure

The numbers of the Pt electrodes, recorded in the "Pt Electrode Log," are to be noted on the chart; the one with the lowest number being "L", the other "R".

The materials used in this test consist of (besides the two Pt electrodes) two medicine bottles, cylindrical in shape, I.D. = 18 mm, height = 50 mm; silver wire 0.020" in diameter; a neoprene stopper having three holes drilled in it, one for the silver wire and the other two for the Pt electrodes; vaseline; distilled water (Puritas and Braun); conc. HNO_3 C.P. and cleaning solution ($K_2 Cr_2 0_7$ dissolved in conc. H_2SO_4 C.P.).

The two Pt electrodes are to be placed in the two larger holes of the stopper by first threading the Pt wire leads into the two holes, then pushing the electrodes through the holes so that the ends extend a predetermined distance "ℓ" below the bottom side of the stopper. A No. 1 stopper is used, the three holes having been previously greased with a little vaseline by running a nail through them before placing the electrodes in.

The Pt electrodes (assembled in the stopper) are next dipped in hot cleaning solution and well rinsed in Puritas water followed by Braun water.

A short length of the silver wire is dipped in conc. HNO_3, heated in the gas flame and dipped, while hot, in the acid a second time, then heated carefully in the gas flame until all black $Ag_2 0$ is reduced to Ag. Using a small pliers or forceps, the silver wire is then forced through the smaller hole on the bottom side of the stopper until its end is in a plane slightly above the lower ends of the Pt electrodes.

In assembling the three electrodes into the stopper, they are not to be touched or to be in contact with any material except clean forceps (after being cleaned) on any part which is to be in contact with the water or water solution of $Ag NO_3$ in which they are later tested.

The electrode assembly, consisting of the two Pt electrodes, the Ag electrode and stopper, are then placed in a medicine bottle containing

5.0 ml Braun water and checked for conductivity using a scale of 0.03 or 0.01 μa. Depending on the residual currents obtained, the electrodes may be tested again in 5.0 ml fresh Braun water after first rinsing them and the bottle in this water.

The electrode assembly is next removed and, after shaking off excess water, placed in a second bottle containing 5.0 ml of the appropriate $AgNO_3$ solution and tested. The medicine bottles are to be first cleaned in cleaning solution and well rinsed in Puritas and Braun water.

2.2 CELL CONSTRUCTION AND CLEANING

The principle problem of cell construction is the necessity of using soft glass. It was discussed in Section 2.1 (see also p. 3.23 ff) that pyrex cannot be used to seal the Pt electrodes because of the poor match in thermal expansion coefficients. The entire cell body must therefore be made of soft glass which is more difficult to work with than pyrex. One particular problem is the sealing of a second electrode into the cell body can cause the first seal to crack from the heat radiation of the torch. This problem is ameliorated by using the "T" shaped cell with the electrode seals placed far apart.

2.2.1 Cell Construction Procedures

Two kinds of electrolytic cells have been standardized. The series "A" cell has three electrodes of relatively large surface area to operate in the 10-100 microampere region. The series "B" cells are the high sensitivity cells made in the inverted "T" shape. They are designed to operate in the 10-100 millimicro ampere region. The procedures for making these cells is as follows:

Series "A" Cell

Three twenty thousandths platinum leads are cut approximately one inch long. Hold the three leads, properly spaced, and imbed in the end of a glass rod. Using the rod as a holder, wind hot glass around the three leads approximately in the center of the leads. Heat the bead just formed and flatten into a round button using tweezers. The platinum is then cut off approximately 1/4 inch above the button.

The seal is made into a tube end with a small gas-oxygen flame and annealed in a soft gas-air bunsen flame. The leads are then cut off above the glass rod.

Series "B" Cell

Cut a piece of 2 1/2 mm O.D. lime glass tubing approximately 6 inches long. Two "marias" are then formed about 1/2 inch either side of the center of the tube. The so-called "maria" is formed by slowly rotating the tube in a pin-point flame and pushing the two ends toward each other. Next, two small holes are blown approximately 1/2 inch from each maria on the outer sides. The tube is then cut in two, either in the flame or with a file. Gas-oxygen is used for these steps.

A piece of three thousandths platinum, three inches long is inserted into one of the above tubes and sealed at the end with the maria, leaving about 1/2 inch extending past the seal. After the seal is cooled the wire is broken off as close as possible by bending back and forth with a pair of tweezers. The glass tubing is then cut about one inch from the maria on the side of the small hole. Next cut a piece of twenty thousandths platinum wire about 3/4 inch long. The fine wire is wrapped around one end of the larger wire about six or eight times the excess wire clipped off. This coil is then inserted into the end of the tube and the glass is sealed around it, imbedding the coil and the larger platinum in the seal. Gas-air is used for this step.

The cell envelope is a "T" tube made of eight mm tubing with a constriction in the center tube. Gas-oxygen is used.

The electrodes are sealed in one at a time using gas-oxygen and annealing well with a gas-air bunsen burner flame.

Once the cells have been cleaned, filled with electrolyte, plated with silver on one electrode, and tested, the cell is sealed at the tube constriction by applying a hot flame and pulling or pinching the constriction. If this is done quickly and the electrolyte level is below the constriction, the liquid will not rise to its boiling point.

2.2.2 Cell Cleaning Procedures

In general the cells were cleaned by an application of cleaning solution (sulfuric acid and potassium dichromate), nitric acid, and liberal rinsing with distilled water. Later it was found that substitution of the nitric acid with aqua regia removed and Pt oxide layer, giving excellent reproducibility. The details of cleansing some of the B-series cells which were used as examples in Section 3 are listed below.

Pt Cell B1 - Exp. D, III, 6-4-62

Prior to above cell was dumped from Parts I - II of Exp. D, 6-4-62, rinsed and cleaned as follows: Warm 1: 1 HNO_3, H_2O, hot cleaning solution, H_2O, H_2O (stand).

Pt Cell B1 - Exp. A, 6-5-62

Cell tested directly without any cleaning since Exp. D, III, 6-4-62.

Pt Cell B1 - Exp. C, I, 6-8-62

Cell tested directly without any cleaning since Exp. D, III, 6-4-62.

Pt Cell B10 - Exp. D, I - III, 6-11-62

Cleaning solution, H_2O (stand), H_2O.

Pt Cell B16 - Exp. C, 6-13-62

Cleaning solution (~1 - 1/4 hrs), H_2O, H_2O (stand ~ 45 minutes), H_2O.

Pt Cell B11 - Exp. E, I - III, 6-11-62

Cleaning solution, H_2O, H_2O stand, H_2O.

Pt Cell B19 - Exp. B, III, 6-14-62

Cleaning solution (~ 1 hr), H_2O, H_2O (stand~2 hrs), H_2O.

Preliminary Testing of Electrodes (later Sealed into Pt Cell B5) Exp. D, II, 6-5-62

Hot cleaning solution (electrode dipped in), H_2O (stand), H_2O.

Pt Cell B5 - Exp. F, I, 6-6-62

Hot 1: 1 HNO_3, H_2O, hot cleaning solution, H_2O, H_2O (stand), H_2O.

Pt Cell B6 - Special Exp., 6-11-62

Cleaning solution (~ 2 hrs), H_2O, H_2O (stand ~ 15 minutes), H_2O prior to running. Prior to running $Ag NO_3$ solution used, dumped and cell rinsed with H_2O first, then reagent acetone and dried with a stream of N_2. Cell then constricted and filled with fresh 0.10 N $Ag NO_3$ and run with right electrode charged with Ag about five minuates at 1.03 μa. Next, cell was sealed and used.

Pt Cell B10 - Exp. B, II, 6-12-62

See P 3.42. No cleaning since.

Pt Cell B24 - Exp. I, 6-15-62

Cleaning solution (~ 1 hr), H_2O, H_2O(stand ~ 2-1.2 hrs), H_2O.

Pt Cell B24 - Exp. 3, 6-18-62

0.10 N $Ag NO_3$ solution dumped from the cell rinsed and cleaned as follows: 1: 1 HNO_3 - HCl (~ 1 min), H_2O (stand), H_2O.

2.3 ELECTROLYTES AND MATERIALS

In general the electrolytes were made using analytical reagent grade Ag NO_3 and KNO_3 packaged by Mallinckrodt Chemical Corp. The chemicals were mixed the distilled, deionized water packaged in polyethylene containers by Braun Chemical Company. Weighings were done with an analytical balance and solutions mixed in volumetric flasks. The electrolytes were generally prepared fresh for each experiment. However when fresh mixture were not used, no degradation in performance was noted.

The silver wire used as the initial anode was specified as 99.999% pure by the supplier, The Wilkinson Co. of Santa Monica. The wire was cleaned thoroughly in hot, concentrated HNO_3 to remove any contaminants from the drawing process.

The platinum wire was also supplied by the Wilkinson Company with no quantitative specification of its purity. The B series cells were made using thermocouple grade Pt drawn to .003 inches.

2.4 CIRCUITRY AND DATA TAKING

The circuitry and data taking procedures are very similar to those described in the previous summary report. The circuit used is somewhat simpler than that used before and is shown in Figure 3.32 of this report.

Current is controlled through the electroplating cell by means of a large resistor in series with a potentiometer across an ordinary dry cell. The potentiometer insures that the voltage across the electroplating cell does not exceed a specified value when the cell is in the open circuit condition. The current through the cell is measured by a Hewlett-Packard Microvolt-ammeter, the output of which is displayed on a Varian Chart recorder with a tape speed of one inch per minute.

Once the maximum open circuit voltage across the cell had been set and the cell connected in place, the shorting switch across the cell was closed and the proper current setting made. A silver wire or silver rod which had been thoroughly cleaned in nitric acid, oxidized, and reduced in a hot flame is then inserted into the cell and connected to the positive side of the cell terminals in order to serve as an anode. The series switch in the circuit is opened and the shorting bar across the cell is opened and the chart recorder operating with the Hewlett-Packard Microvolt-ammeter is started. At the appropriate time on the recorder the series switch is closed and current passes through the cell plating silver from the inserted anode onto the negative electrode.

At the end of a two or three minute plating period the series switch is opened and the silver rod is removed from the cell. The reversing switch is thrown causing the previous cathode to become an anode and the other electrode is connected into the circuit so that it may become a cathode. The series switch is then closed and the current causes the silver previously deposited to be plated from the anode to the cathode and be recorded by the chart recorder. At the end of this deplating period the potential across the cell rises and the current is reduced nearly to zero. When the current has become sufficiently small the reversing switch is thrown and the process

is repeated. This sequence continues several times depending on the character of the data and the purpose of the experiment.

No difficulty was experienced using this technique or circuitry except for occasional failure of the switches. The switches were replaced periodically if the data gave evidence of poor contact or corrosion effects.

3. EXPERIMENTAL RESULTS

3.1 DISCUSSION OF SIGNIFICANT EXPERIMENTS

The following set of figures are chosen from a large group of experiments to illustrate some of the typical problems and effects met in the electro-chemical work. The figures themselves are reproductions of part of the Varian chart recorder data showing the current versus time behavior of some of the cells. The experiments are arranged chronologically and are summarized in Table 3.1 with all the pertinent data. This section will be a discussion of the experiments individually to indicate their significance to the cell development program.

Much of the significant work during the past three months was accomplished using bottle cells described in Section 2.1. These cells are composed of a medicine bottle with a rubber stopper. Into two holes of the stopper are inserted glass covered electrodes. The electrolyte and the wire size used in the electrodes are indicated in Table 3.1. The maximum current indicated in the table is that current which passed through the cell during most of the time it was conducting. As the current dropped to zero, the back voltage across the cell increased until it reached a value opposing the driving voltage of the circuit. This maximum voltage which is equal to the circuit driving voltage is also listed in Table 3.1. Finally, it is important to keep in mind that the chart paper moves through the recorder from left to right in the orientation of the figures as given. This means that the direction of time on the charts is from right to left, in a sense opposite to what is usually encountered in graphical analysis. The time scale is one minute per inch.

Figure 3.1 indicates some rather good data taken with a carefully cleaned cell and cleaned electrodes. The electrode diameter was 20 thousandths of an inch; however, the left electrode was 32 millimeters in length, considerably longer than the 2 millimeter length of the right electrode. The effect of this longer electrode can be seen in the figure

TABLE 3.1 SIGNIFICANT EXPERIMENTS WITH PT BOTTLE CELLS

Example	Experiment	Cell Number	Electrolyte	Electrode	Maximum Current	Max. Volt.	Figure No.	Comments
1	A-II-3/6/62	Pt Bottle Cell No. 2	0.10 N $AgNO_3$	20 mil Pt Wire	1.6 μa	0.2	3.1	Effect of low current density L = 32 mm, R = 2 mm
2	A-III-3/13/62	Pt Bottle Cell No. 2	0.10 N $AgNO_3$	20 mil Pt Wire	0.16 μa and 0.10 μa	0.0777	3.2	Effect of low current density and low voltage
3	E-I-3/16/62	Pt Bottle Cell No. 4	0.10N $AgNO_3$	20 mil Pt Wire	1.38 ma	0.93	3.3	Effect of large driving voltage
4	A-II-4/10/62	Pt Bottle Cell No. 9	5.0 N $AgNO_3$	3 mil Pt Wire	.0179 μa	0.358	3.4	High sensitivity due to small electrode area
5	A-II-4/13/62	Pt Bottle Cell No. 16	1.0 N $AgNO_3$	3 mil Broken	0.0155 μa	0.358	3.5	Effect of "broken-wire" electrode construction
6	A-III-4/17/62	Pt Bottle Cell No. 18	0.10 N $AgNO_3$	3 mil sphere	0.0152 μa	0.358	3.6	Erratic current behavior
7	A-I-4/18/62	Pt Bottle Cell No. 19	1.0 N $AgNO_3$	3 mil sphere	0.0152 μa	0.358	3.7	Good behavior with sphere electrodes
8	A-II-5/1/62	Pt Bottle Cell No. 24	0.11 N $AgNO_3$ and 0.10N KNO_3	3 mil sphere	0.0145 μa	0.358	3.8	Effect of supporting electrolyte

TABLE 3.1 (cont.)

Example	Experiment	Cell Number	Electrolyte	Electrode	Maximum Current	Max. Volt.	Figure No.	Comments
9	A-I-5/2/62	Pt Bottle Cell No. 24	0.11 N $AgNO_3$ and 0.10N KNO_3	3 mil sphere	0.0141 μa	0.358	3.9	Effect of supporting electrolyte
10	A-IX-5/2/62	Pt Bottle Cell No. 24	0.11 N $AgNO_3$ and 0.10 N KNO_3	3 mil sphere	0.0128 μa	0.161	3.10	Lowered driving voltage with supporting electrolyte
11	A-V-5/2/62	Pt Bottle Cell No. 24	0.11 N $AgNO_3$ and 0.10 N KNO_3	3 mil sphere	0.00178 μa	0.229	3.11	Very low current data
12	A-VIII-5/2/62	Pt Bottle Cell No. 24	0.11 N $AgNO_3$ and 0.10 N KNO_3	3 mil sphere	0.00240 μa	0.161	3.12	Very low current data with low residual current
13	B-I-5/25/62	Pt Bottle Cell No. 28	0.10 N $AgNO_3$ and 0.10 N KNO_3	3 mil Broken	0.010 μa	0.161	3.13	Sensitive "broken-wire" electrodes
14	B-III-5/28/62	Pt Bottle Cell No. 28A	0.10 N $AgNO_3$ and 0.10N KNO_3	3 mil Pt. wire	0.0086 μa	0.161	3.14	Effect of pyrex

TABLE 3.1 (cont.)

Example	Experiment	Cell Number	Electrolyte	Electrode	Maximum Current	Max. Volt.	Figure No.	Comments
15	B-I-5/17/62	Pt Bottle Testing Cell	5.0 N $AgNO_3$	3 mil sphere	0.0083 μa for No. 2	0.13	3.15	Testing of electrodes for cell of Figure 3.17
16	B-IV-6/4/62	Pt Bottle Testing Cell	5.0 N $AgNO_3$	3 mil broken	0.0104 μa	0.161	3.16	Testing of electrodes for cell of Figure 3.18
17	A-III-5/18/62	Pt "S" Cell No. 2	5.0 N $AgNO_3$	3 mil sphere	.008 μa	0.13	3.17	Erratic performance after assembly of electrodes into cell
18	D-III-6/4/62	Pt Cell B1	5.0 N $AgNO_3$	3 mil broken	0.0103 μa	0.161	3.18	Better result with "broken-wire" electrodes
19	A-I-6/5/62	Pt Cell B1	5.0 N $AgNO_3$	3 mil broken	0.0108 μa	0.161	3.19	Accumulation of silver on standing overnight
20	C-I-6/8/62	Pt Cell B1	5.0 N $AgNO_3$	3 mil broken	0.010 μa (No. 2)	0.161	3.20	Accumulation of silver on standing three days
21	D-I, II, III-6/11/62	Pt Cell B10	0.10 N, 1.0 N and 5.0 N $AgNO_3$	3 mil broken	0.0094 0.0097 0.0100 μa	0.161	3.21 thru 3.23	Effect of changing electrolyte concentration
22	E-I, II, III 6/11/62	Pt Cell B11	0.10 N, 1.0 N 5.0 N $AgNO_3$	3 mil broken	0.0100 0.0102 0.0103 μa	0.161	3.24 thru 3.26	Effect of electrolyte concentration

TABLE 3.1 (cont.)

Example	Experiment	Cell Number	Electrolyte	Electrode	Maximum Current	Max. Volt.	Figure No.	Comments
23	C-I-6/13/62	Pt Cell B 16	0.10 N $AgNO_3$	3 mil broken	0.0101 μa	0.161	3.27	Large progressive losses
24	D-II 6/5/62	Pt Cell B 5	5.0 N $AgNO_3$	3 mil broken	0.0100 μa	0.161	3.28	Large loss with later recovery
25	F-I-6/6/62	Pt Cell B 5	5.0 N $AgNO_3$	3 mil broken	0.00995 μa	0.161	3.29	High sensitivity cell with capacitance surge
26	Special 6/11/62	Pt Cell B 6	0.10 N $AgNO_3$	3 mil broken	0.0090 μa	0.161	3.30	Progressive loss of silver
27	B-II-6/12/62	Pt Cell B 10	5.0 N $AgNO_3$	3 mil broken	0.00090 μa	0.161	3.31	Correction of cell behavior shown in Figure 3.30

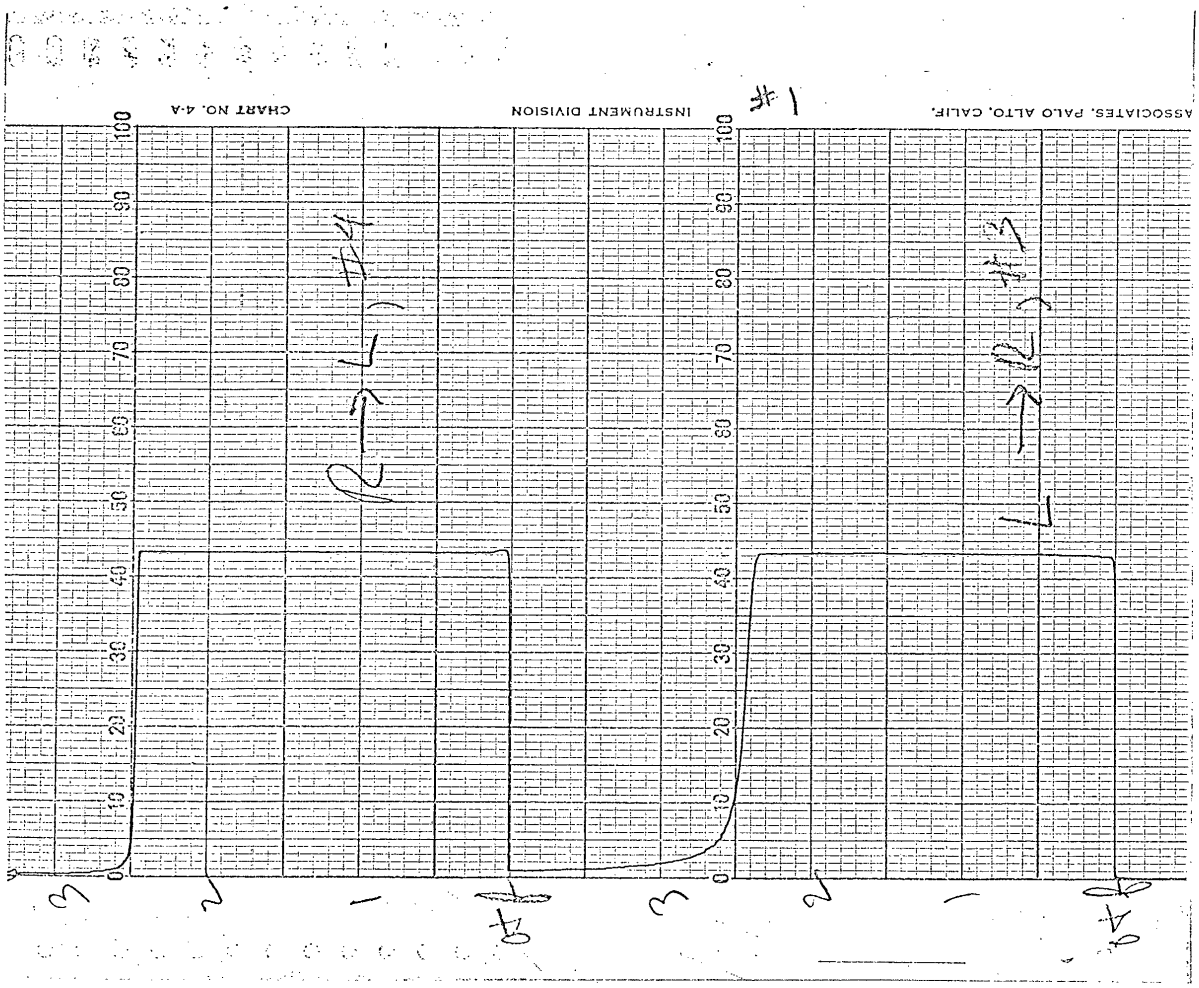


Figure 3.1

as a result of the increased length of the tail in the run from left to right* and the less-than-vertical slope of the trailing edge of that particular run. This effect was reproduced over and over again in succeeding runs of the data which, however, are not presented here for the sake of conciseness. The explanation for this length and tail of the curve as a result of the larger surface area and lower current density at this electrode is not entirely understood. One mechanism can be postulated, however. When the silver is initially deposited from the smaller electrode onto the larger electrode, some of the silver is deposited at distances along the large electrode considerably removed from the small electrode. When the current through the cell is reversed, that silver nearest the small electrode is removed from the large electrode first. As we approach the tail of the curve, it is necessary for silver to be plated off of the large electrode at the remote points. This would result in larger resistive drops through the electrolyte causing overvoltages to be required to remove this last bit of silver. The "effective" voltage across the cell would then be reduced and the rate at which this silver is removed would be considerably less than the rate of removal of silver from those points near to the cathode.

In Figure 3.1 the current density at the large electrode was a maximum of 3 micro amperes per square centimeter. In Figure 3.2, the ~~same cell~~ was used but with a lower current level overall so that the current density has become as small as two-or-three-tenths of a micro ampere per square centimeter. The difference, in effect, between the right electrode being the anode and the left electrode being the anode is still apparent. Another effect can also be observed in Figure 3.2. The series resistance of the circuit is sufficiently large and the sensitivity of the microvolt ammeter is sufficiently high so that one can see the effect of charging up of the capacitance layer at the electrodes. That is to say, the initial peak on each of the charging curves is due to a surge of current into the double layer at the interface between the electrodes and the electrolyte. Once this layer is

* Indicated on the chart by L → R.

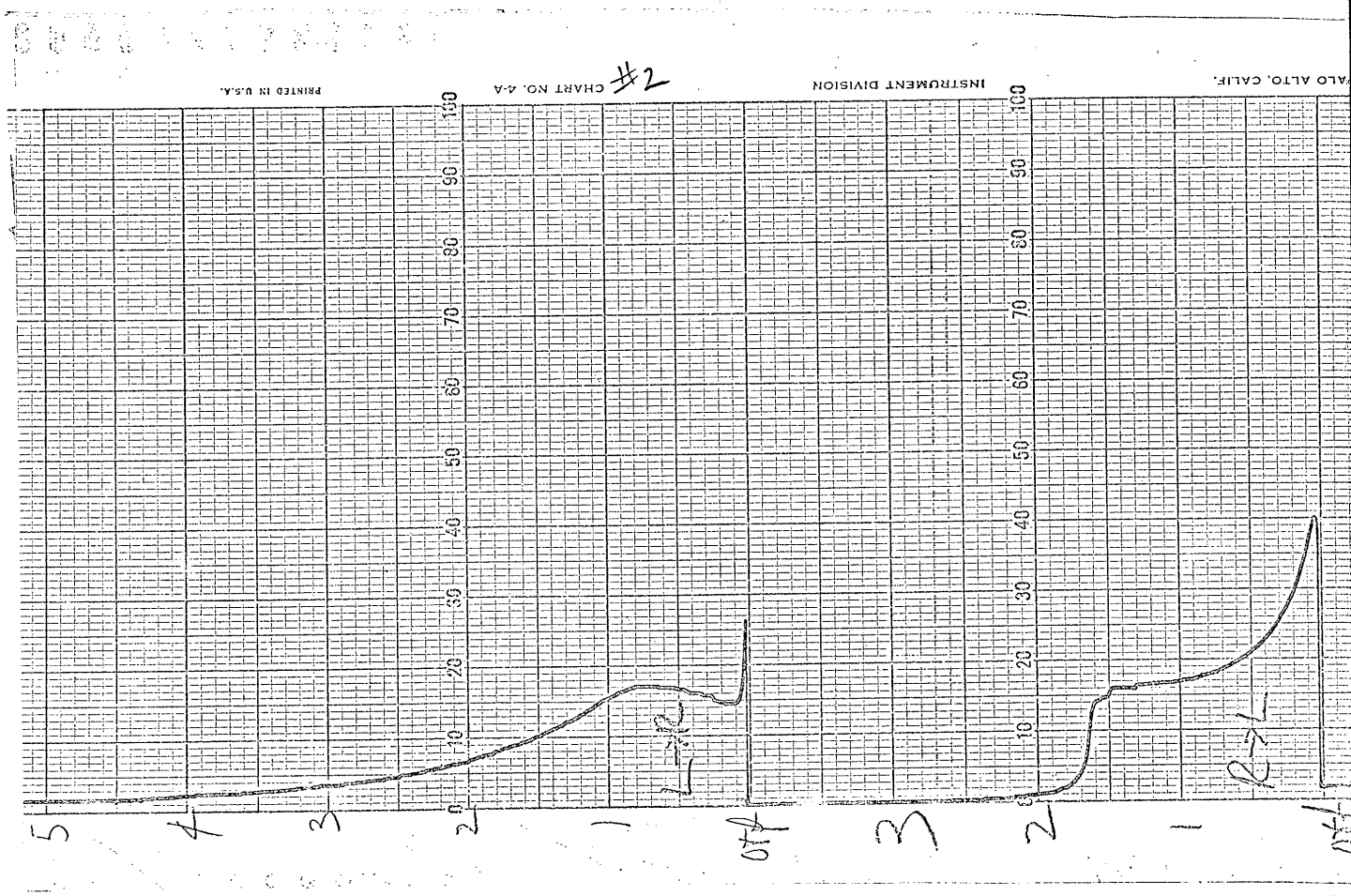


Figure 3.2

charged and current begins to flow at a rate determined by the cell resistance and back voltages, the current level drops down. The time constant for this drop of the capacitance charging current is consistent with a value of approximately 20 to 40 microfarads capacitance per square centimeter of electrode area.

Figure 3.3 illustrates an entirely different effect. In this experiment the current density was considerably higher than the previous one, the experiment here having a current density of approximately 2 milliamperes per square centimeter or four orders of magnitude higher than that of the previous experiment. A long tail, however, still appears on these data but has clearly a different characteristic. The trailing edge of the charging curves is still rather vertical in spite of the long tail. The long tail in this experiment can be explained by the high maximum voltage that was used across the cell being over 0.9 volt. The effect of this large voltage across the cell is to cause spurious reactions to take place in the cell so that silver can be deposited at the cathode as the result of other oxidation reactions taking place at the anode other than the removal of silver from the anode. It will be noticed as we proceed from right to left in Figure 3.3 that the area under the block type curves gradually increases due to the contribution of these spurious reactions.

The lessons learned from the previous experiments with various current densities suggest that if low current data were to be obtained, it would be necessary to use very small electrodes. Accordingly, an electrode was made of 3 mil platinum wire embedded in a soft glass rod and clipped short with a pair of scissors so that approximately only 1 millimeter length was exposed to the electrolyte. The electrodes were carefully cleaned in cleaning solution, nitric acid, and distilled water. The results are indicated in Figure 3.4 for one of the experiments with electrodes of this type. The current level, it will be noted, is less than 0.02 microamperes so that the integrated charge under the curves is of the order of 2 microcoulombs. The reproducibility of this data, however, appears to be approximately one percent of this, or 0.02 microcoulombs. This cell, then, will exceed the sensitivity of the initial goal of 1/10 of a microcoulomb. It was learned by experience, however, that electrodes of this sensitivity could not be made reproducibly and

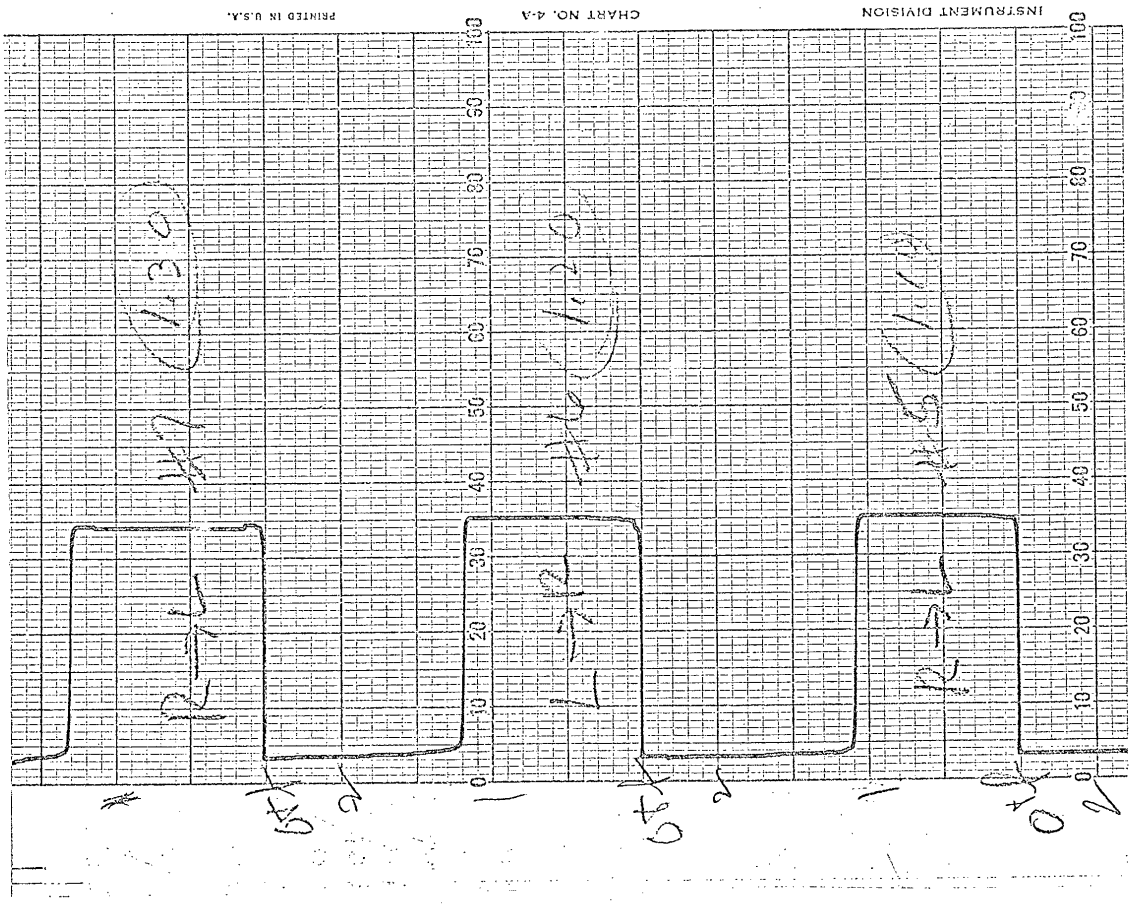


Figure 3.3

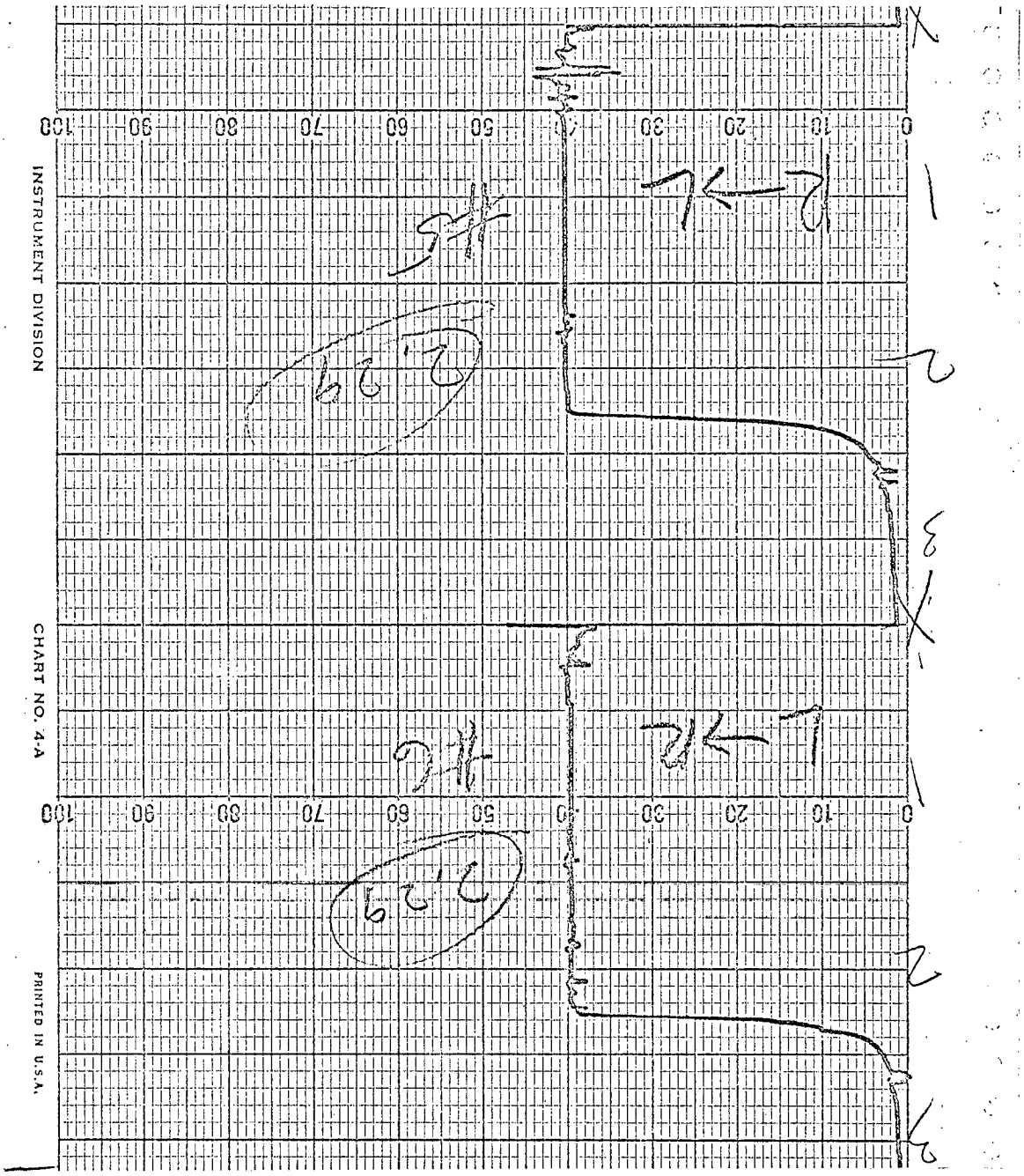


Figure 3.4

that a somewhat different procedure would have to be employed in order to accomplish this goal.

One technique that was followed to obtain reproducibility has its results indicated in Figure 3.5. Here the electrode was prepared by embedding the 3 mil platinum wire in soft glass allowing a centimeter or so of the wire to extend beyond the glass and then breaking the wire off at the base near the glass by fatigue; that is, bending the wire back and forth until it was broken at the glass metal interface. Almost all electrodes made in this manner seemed to yield fairly good results and the data indicated in Figure 3.5 shows a current level of 0.015 microamperes with a form to the curve nearly as good as that obtained in the previous example.

Not all our results at this time were entirely satisfactory, however, as is indicated in Figure 3.6. This shows what can happen during the run when the current level no longer maintains itself at a constant value until all the silver is removed from the electrode. The electrodes of this cell were fashioned by heating the 3 mil platinum wire in a very hot flame until a little sphere of molten platinum is formed at the end. This sphere is then mounted at the tip of the glass tube to serve as the electrode. This erratic effect was occasionally noticed with other electrodes made by different techniques, but not so frequently as it was with this technique. It was found that this erratic behavior of the current was not the result of any loss of silver during the plating process or any increase in the cell resistance but, rather, the effect of some kind of an erratic back voltage which opposed the driving voltage through the cell and lowered the current accordingly. Figure 3.7 indicates some good results obtained with sphere type electrodes. Here, the maximum current level is also about 15 millimicroamperes.

Figures 3.8 and 3.9 indicate the effect of adding a supporting electrolyte, in particular potassium nitrate, to the silver nitrate electrolyte, the idea being in principle that the supporting electrolyte will not be reactive in the electroplating process because of the voltage required to reduce potassium at the cathode. However, the addition of the supporting electrolyte should have an effect in lowering the over all cell resistance

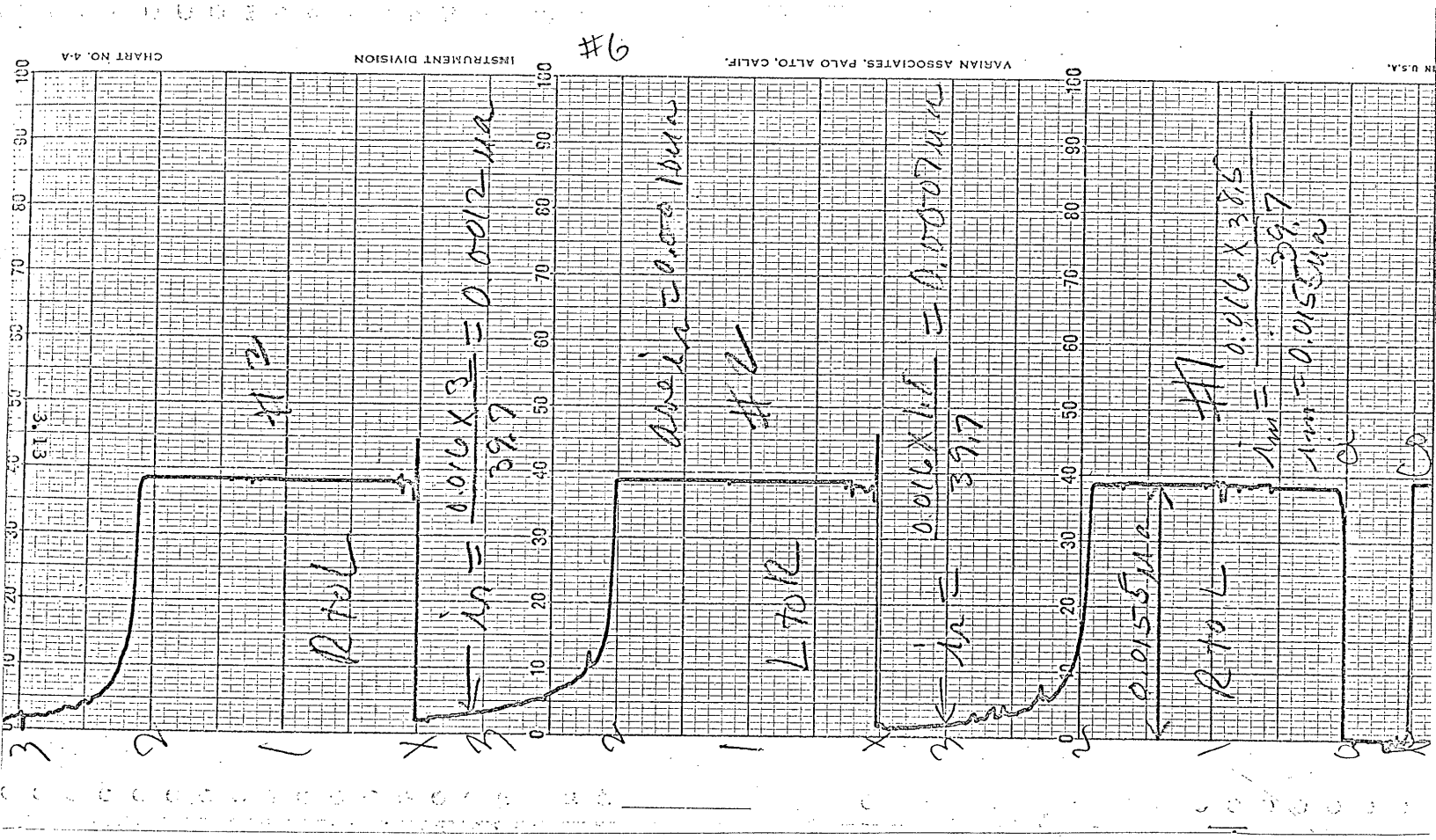


Figure 3.5

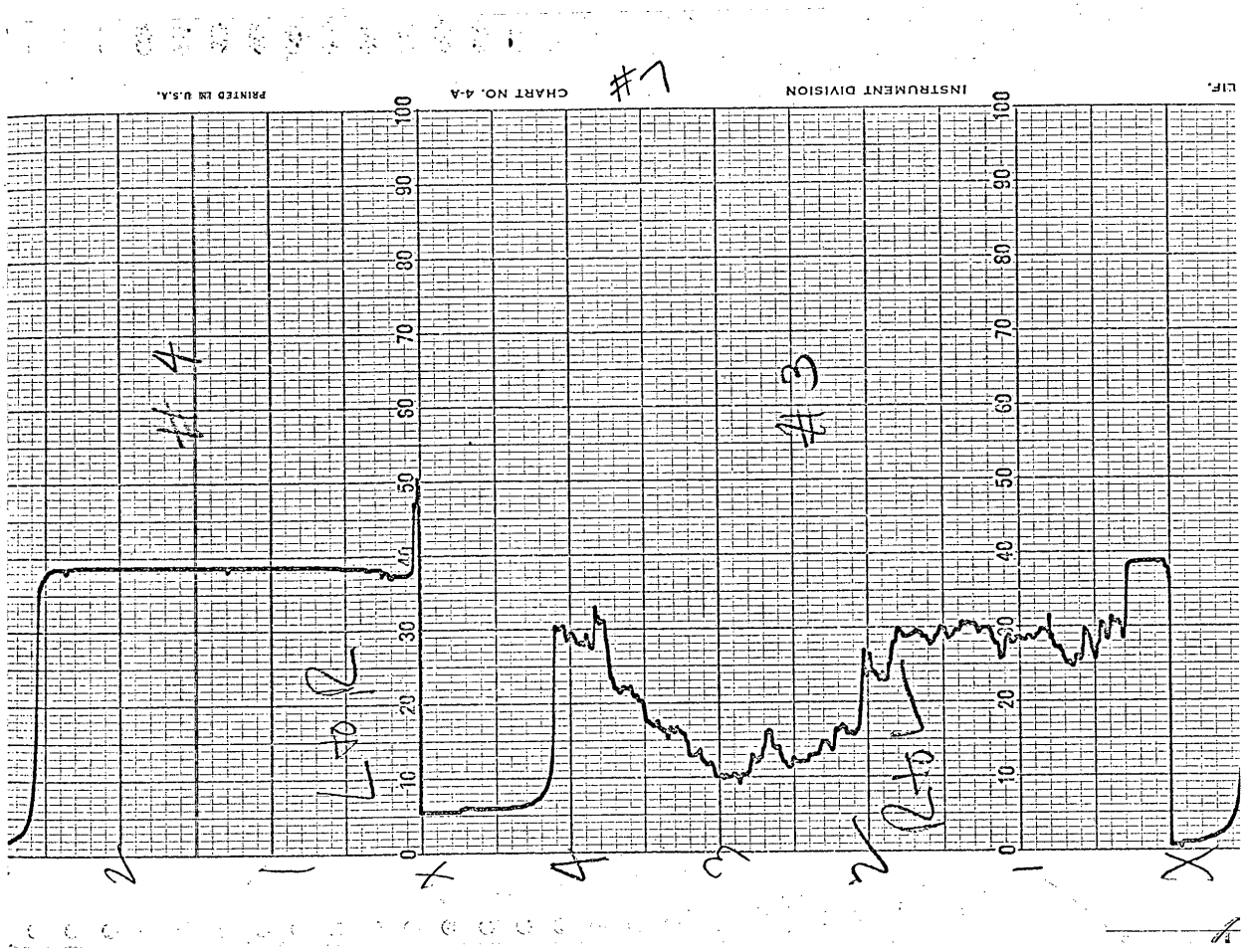


Figure 3.6

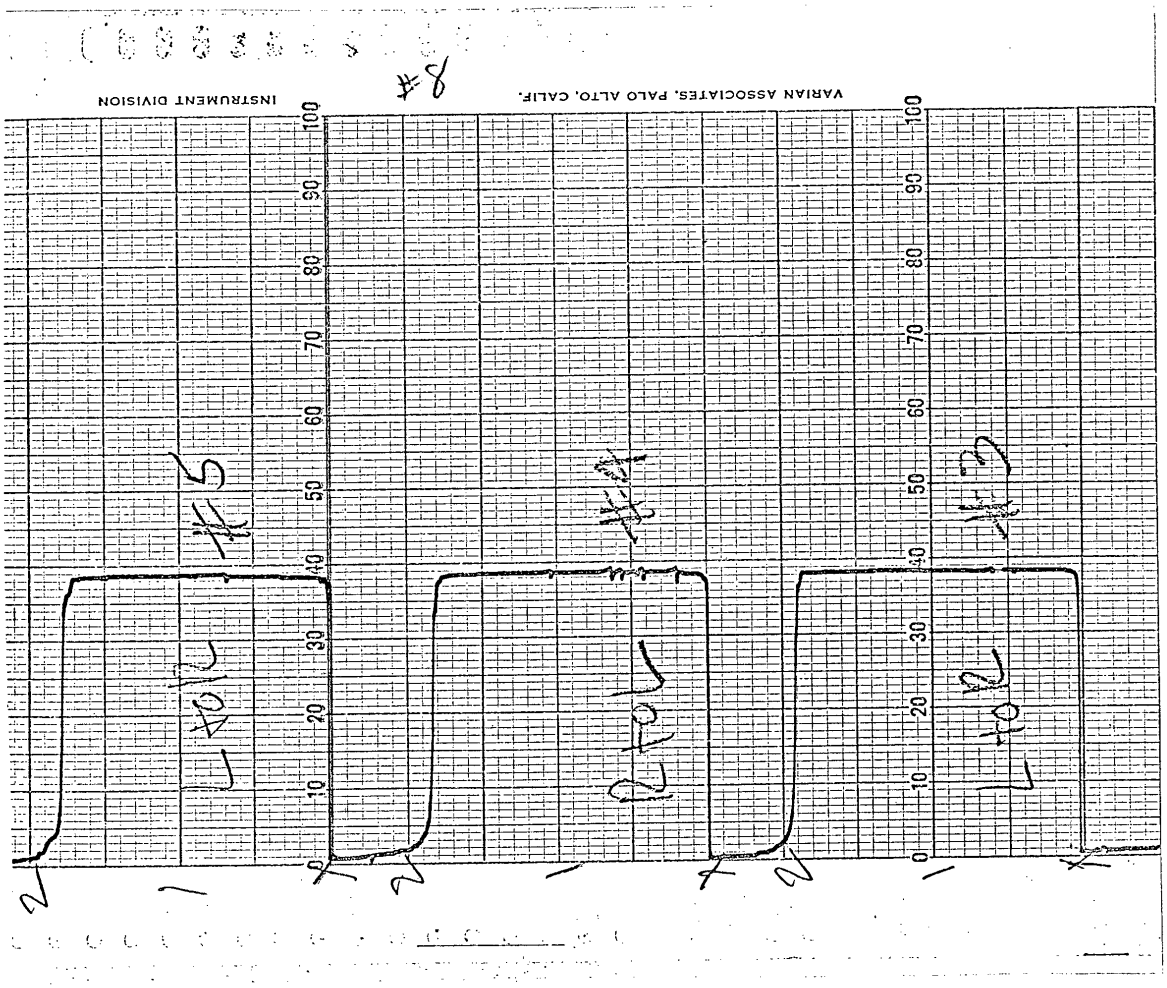


Figure 3.7

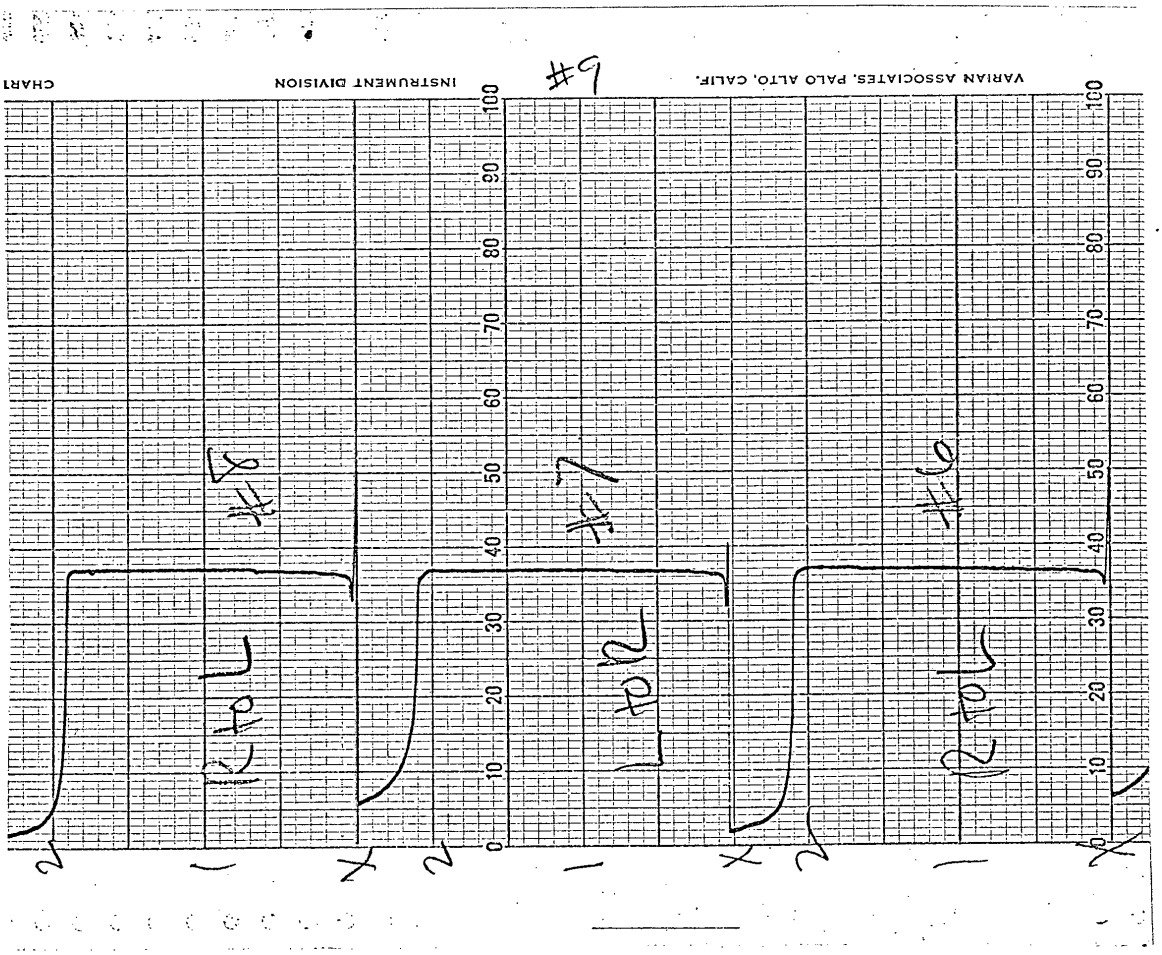


Figure 3.8

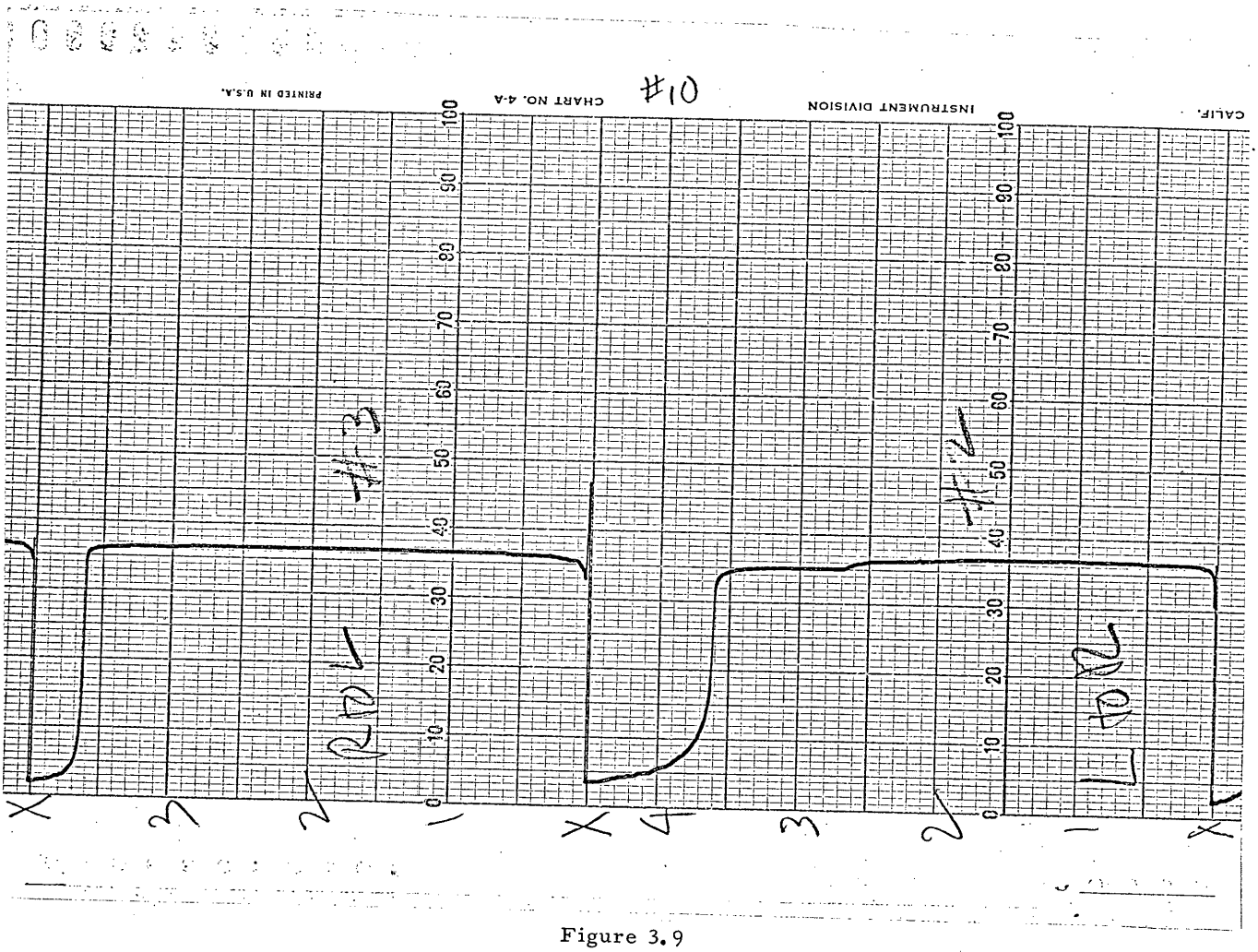


Figure 3.9

and may be of interest if the cell resistances obtained with the silver nitrate alone are too high. It can be seen from Figures 3.8 and 3.9 that one of the effects the supporting electrolyte has is to raise the residual current in the tail of the curves which is undesirable. This effect can be eliminated, however, by lowering the driving voltage through the cell which was done in Figure 3.10. The effect of lowering the residual current by reducing the driving voltage allowed us to improve our current sensitivity by an order of magnitude and data was taken as shown in Figure 3.11 and 3.12 at current levels of the order of a millimicroampere. Also in Figures 3.11 and 3.12 can be seen the effect at this level of sensitivity of lowering the driving voltage and reducing the residual currents. In Figure 3.11 the driving voltage was .229 volts whereas in 3.12 it was .161 volts. The residual current was reduced by approximately a factor of 2 accordingly. It will be observed that in Figure 3.12, the residual current is of the order of 5×10^{-11} amperes which correspond to 1/20 of a micro microgram of silver per second. This is an amazing sensitivity for the detection of silver itself and is several orders of magnitude better than anything reported in the literature with similar techniques.

It was found that it was not possible to make cells of the sensitivity of Figure 3.12 in a consistent and predictable manner. These cells had, as was described previously, electrodes of small spherical shape embedded in the tips of glass rods inserted into the cell. Many erratic results were obtained from these electrodes and it was found that more reproducibility, consistency, and the same level of sensitivity could be obtained by making the electrodes in the manner described in Section 2.1 with the broken wire technique. In these cells the electrodes were given a fresh surface by breaking the 3 mil wire through metal fatigue after the wire has been sealed into the glass. It was not understood at the time the reason for this improvement in results but later it was shown to be due to the formation of an oxide surface on the platinum if it is heated in the flame to seal the wire into the glass envelope. The breaking of the wire in this manner gave a surface more or less free of an oxide layer. Figure 3.13 illustrates the results of a cell made with broken wire electrodes. It can be seen to be of comparable sensitivity and reproducibility of those shown previously.

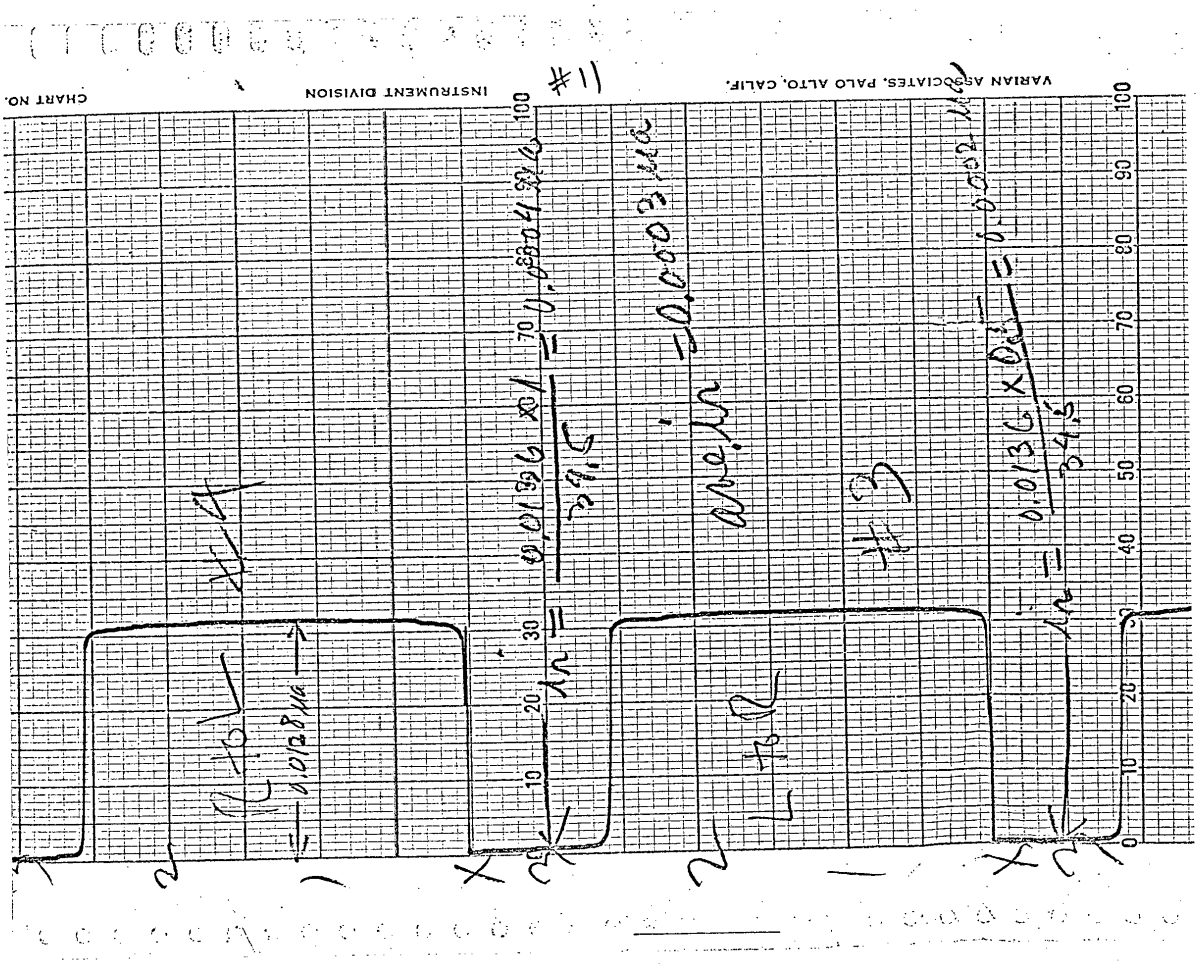


Figure 3.10

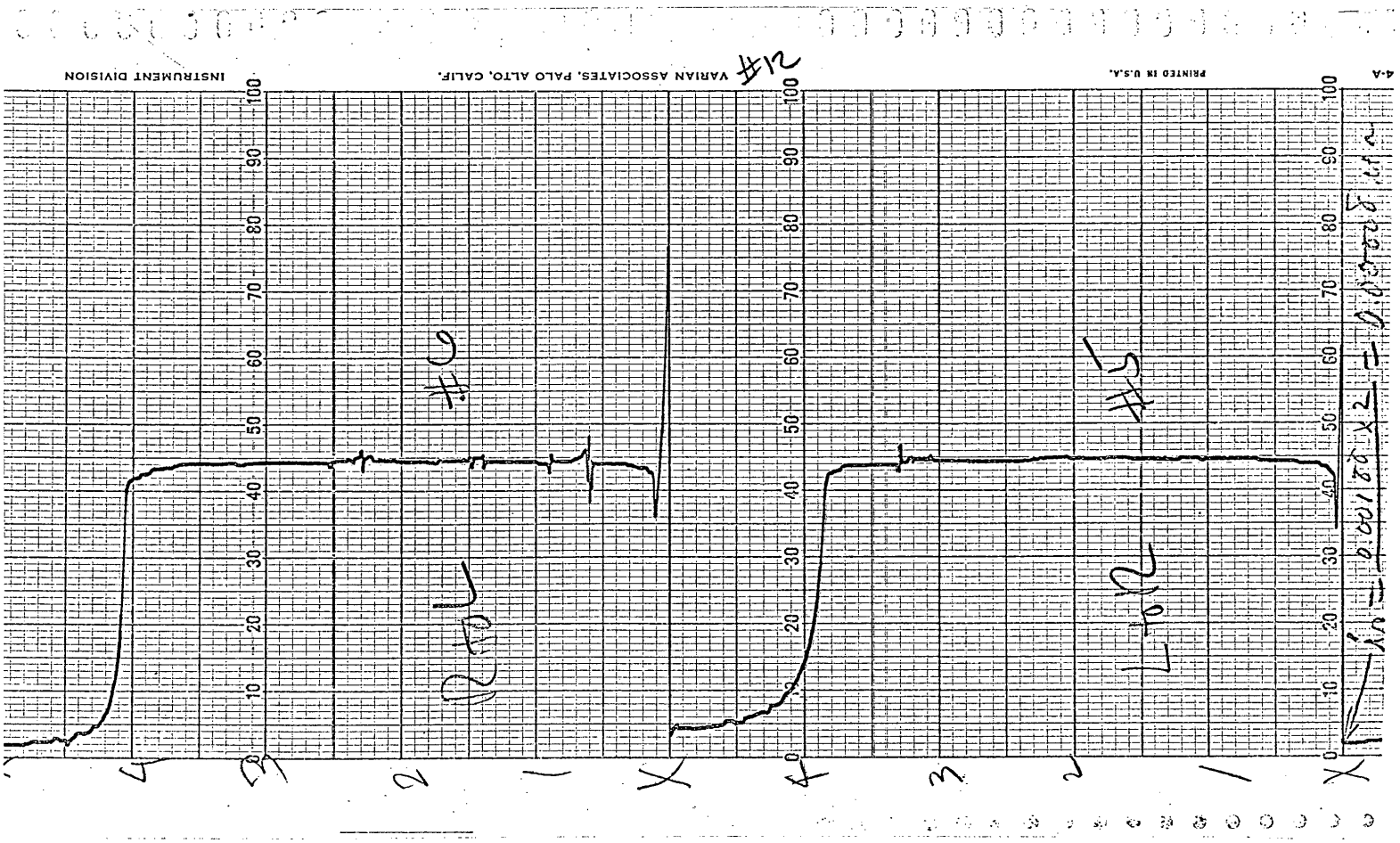


Figure 3.11

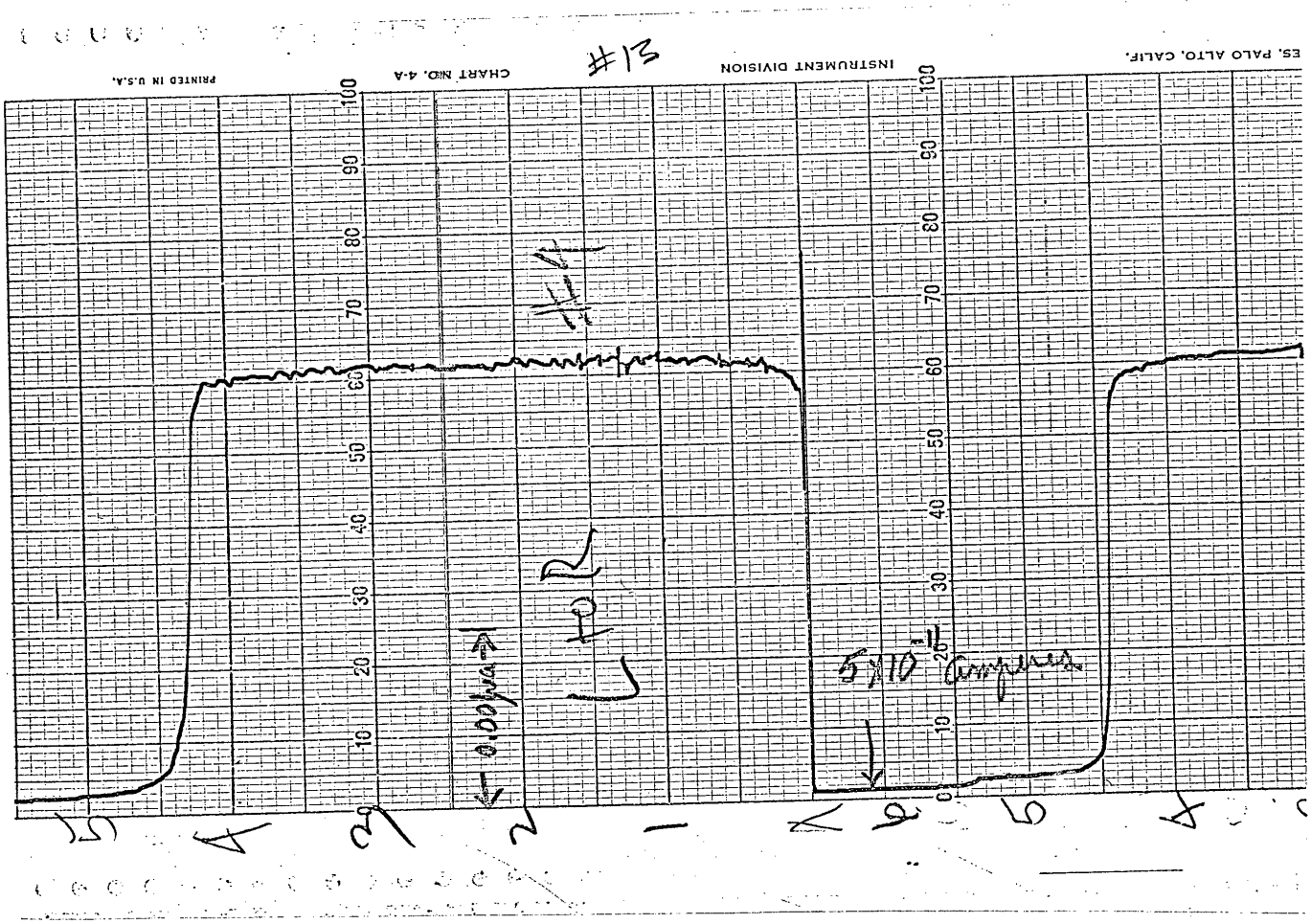


Figure 3.12

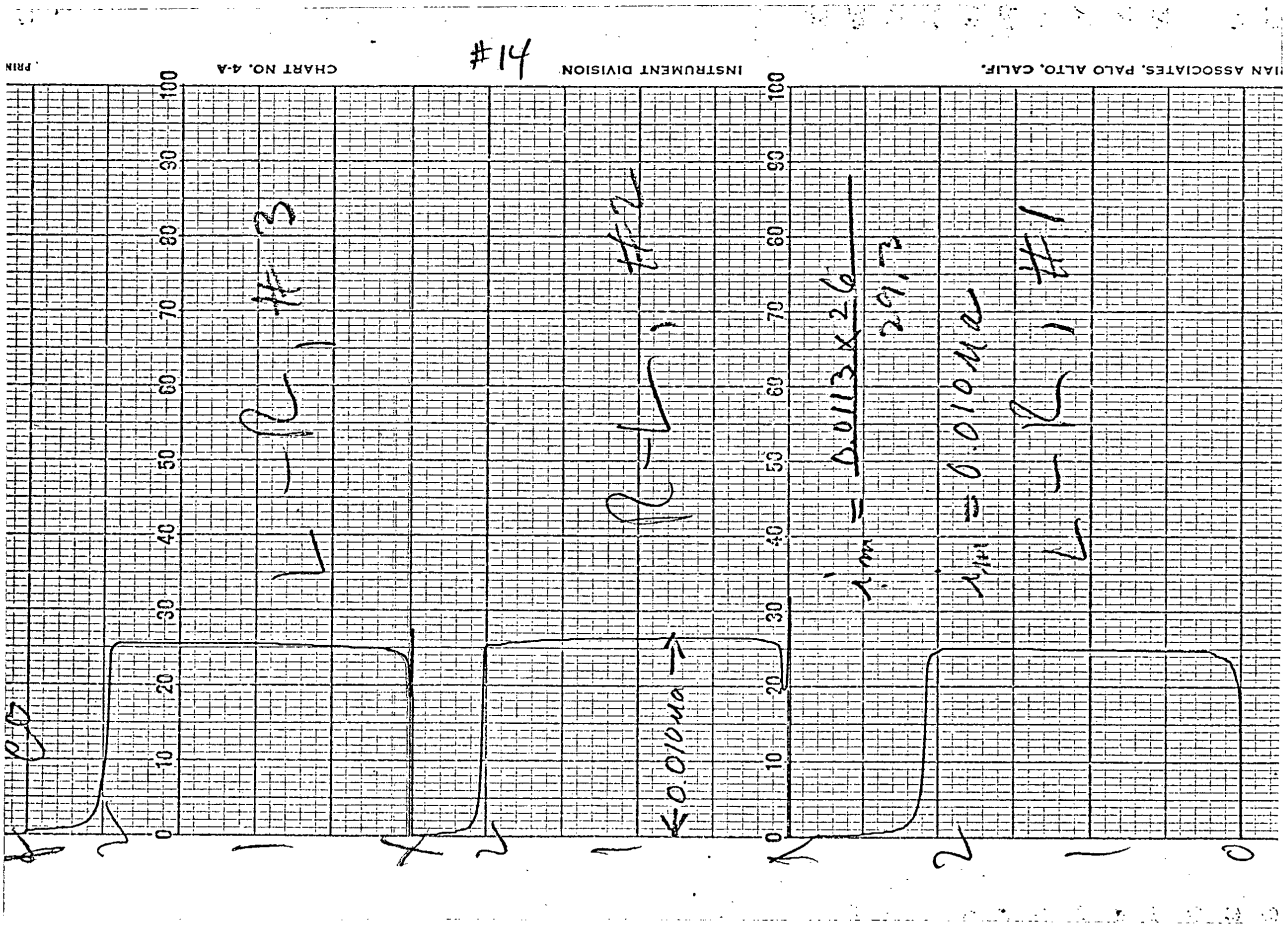


Figure 3.13

About this time in the development program, it was decided that sufficient sensitivity was obtained with the electrodes inserted in the bottle cells. It was decided that the next step should be to assemble these electrodes into sealed glass containers for operations use. Several electrodes were prepared in the usual way and assembled into T-shaped cells and filled with electrolyte to be tested before sealing. The results with these cells were completely inadequate. The cells performed many orders of magnitude less sensitivity than previous cells and in a manner which was completely new to us. Several days of experiementing did not reveal any insight into the problem, this experimenting including various cleaning procedures and techniques for removing any oxide layers that might have accumulated on the cells during assembly. The electrodes themselves were tested before assembly into the cells and, surprisingly enough, they were found also to behave rather poorly although not so badly as when assembled in the cells. It was realized at this time that the one factor which had changed from previous experiments was that the electrodes were being made out of platinum sealed into thin pyrex tubing where a soft tubing had been used before. In order to better understand the effect of pyrex and whether or not it was decisive in the inferior operation of the electrodes, a specially designed experiment was performed in which the conventional bottle cell was operated using three electrodes; two made of soft glass, one made of pyrex, and all prepared, cleaned, and treated in exactly the same manner. A partial result of this experiment is illustrated in Figure 3.14. Silver was plated onto one of the soft glass electrodes, then plated onto the other soft glass electrode, and then plated onto the pyrex electrode and cycled among the electrodes in that manner. The result of plating from the left electrode to the pyrex electrode was found to be a nice square-shaped curve of the type usually encountered with soft glass electrodes. However, when the silver was removed from the pyrex electrode and plated back onto the previous electrode, the curve had the unusually long tail shown in Figure 3.14. However, although not shown in this figure, there appeared to be no loss of silver since plating from the left electrode onto the right electrode gave an area comparable to the earlier amount. This is also confirmed by a planimeter measurement of the curve of which the silver was plated from pyrex to soft glass showing the total

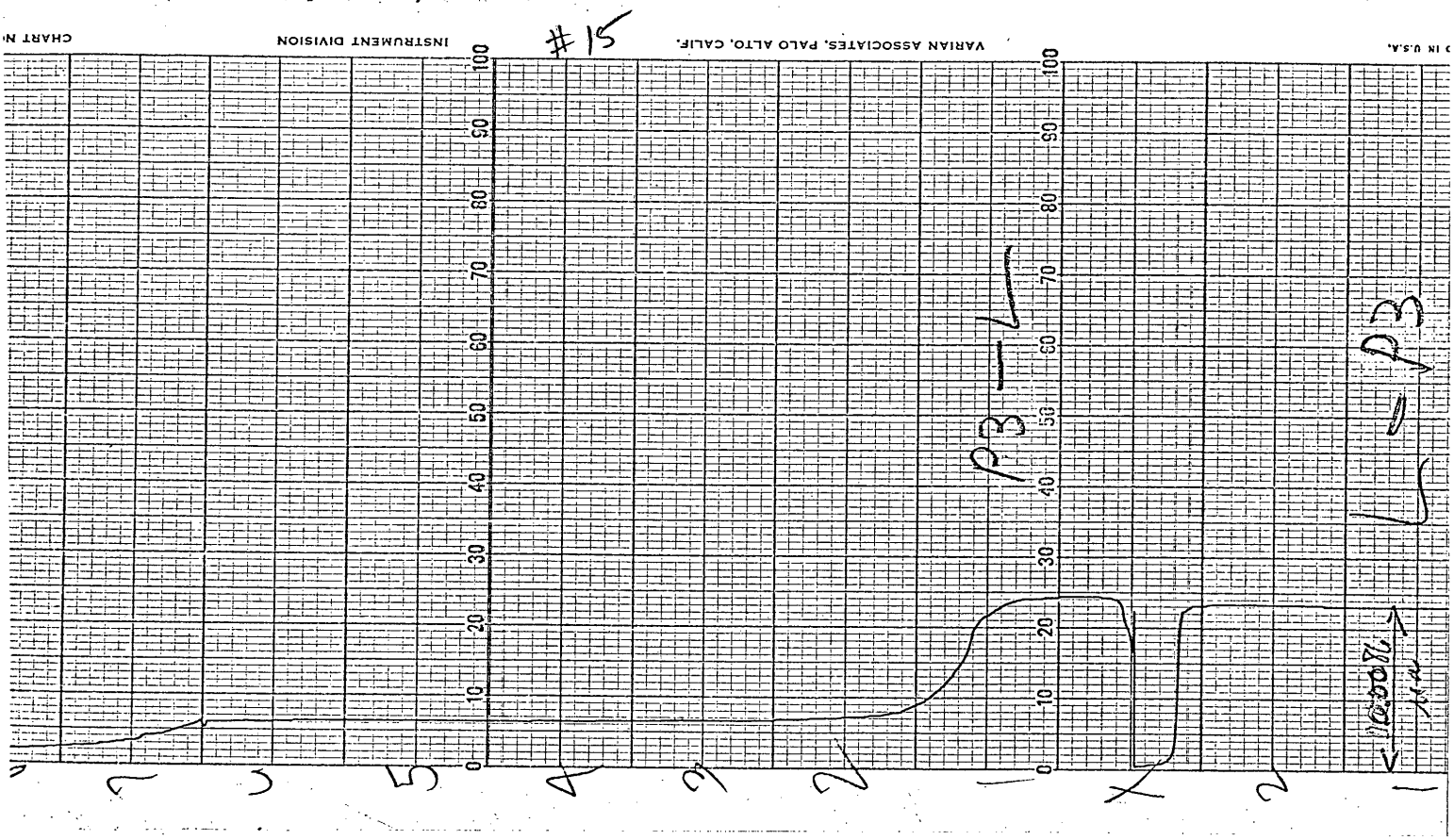


Figure 3.14

area under the curve and the tail to be approximately equal to the rectangular curves obtained previously. Since the problem of making the cells of soft glass was of sufficient difficulty that it was worthwhile investigating whether or not the problems with pyrex could be eliminated, a series of experiments were undertaken in order to determine what the source of the difficulty with pyrex was. These experiments indicated that the electrodes using pyrex exhibited a considerable back voltage which was somewhat erratic in nature and which opposed the driving voltage through the cell. Elimination of chemical sources for this back voltage left the only explanation that the voltage was the result of the difference in the expansion coefficient of pyrex and platinum. When the electrode is sealed into the pyrex tube, it contracts on cooling at a rate faster than pyrex, leaving a separation of perhaps only a few hundred angstroms between the platinum and the pyrex. This separation is sufficient, however, to allow electrolyte to diffuse between the platinum and the pyrex but at a sufficiently slow rate that the concentration of the electrolyte in this region would be expected to differ from that in the main solution. This concentration gradient sets up a concentration potential which it is theorized is responsible for the potential opposing the driving voltage through the cell. Since it was not known how to control the diffusion or the concentration potential that was set up, the use of pyrex for electrodes and consequently for the cell body had to be abandoned. Cells were manufactured of soft glass from this point onward.

It was the rule initially that before assembling the electrodes in the soft glass cells, that they be tested in bottle cells to see if their performance was adequate. Figure 3.15 and 3.16 illustrates the testing of such soft glass electrodes in bottle cells prior to assembly. In the case of Figure 3.15 the electrodes were made having small spheres of platinum extending just beyond the glass tubes which held the platinum wire. In Figure 3.16 the electrodes were made by the broken wire technique. The results of these experiments are illustrated typically in Figures 3.17 and 3.18. Figure 3.17, the spherical electrodes showed a considerable degradation in performance with various erratic backvoltages being generated, when the spherical electrodes were used as anodes. The broken wire electrodes, however, showed very little

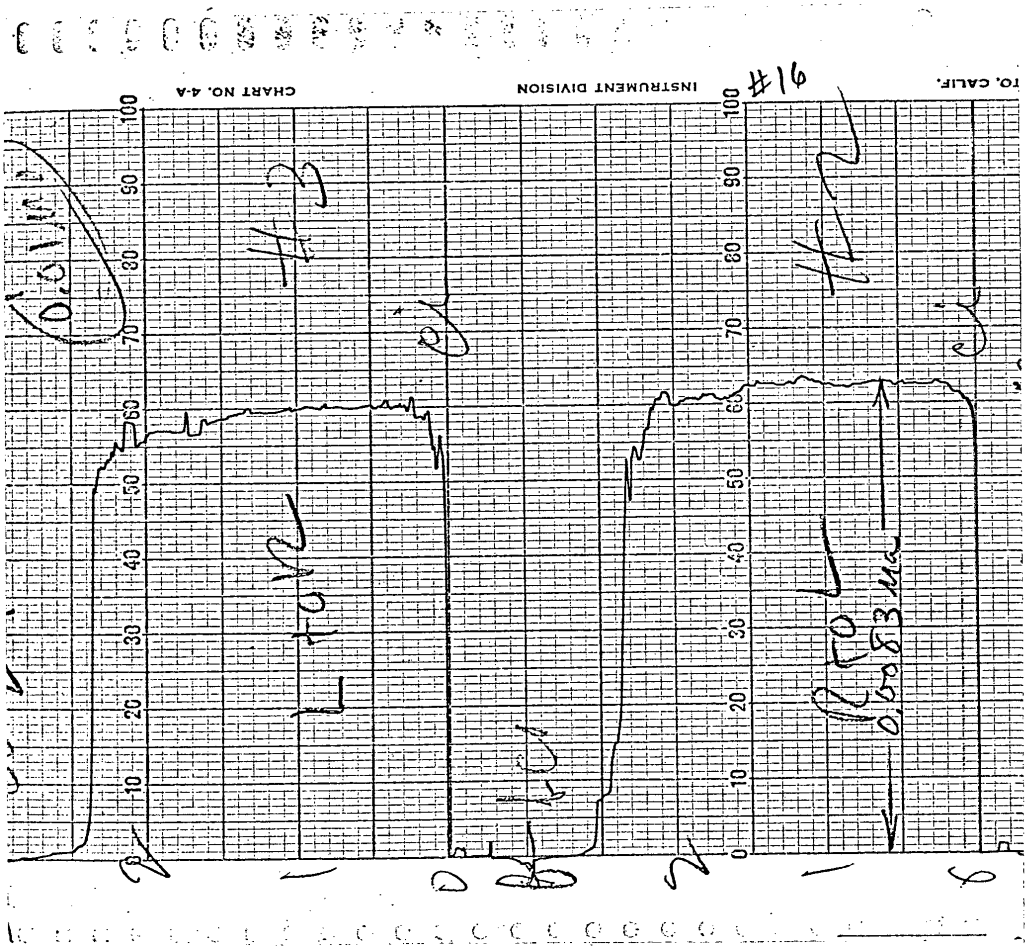


Figure 3.15

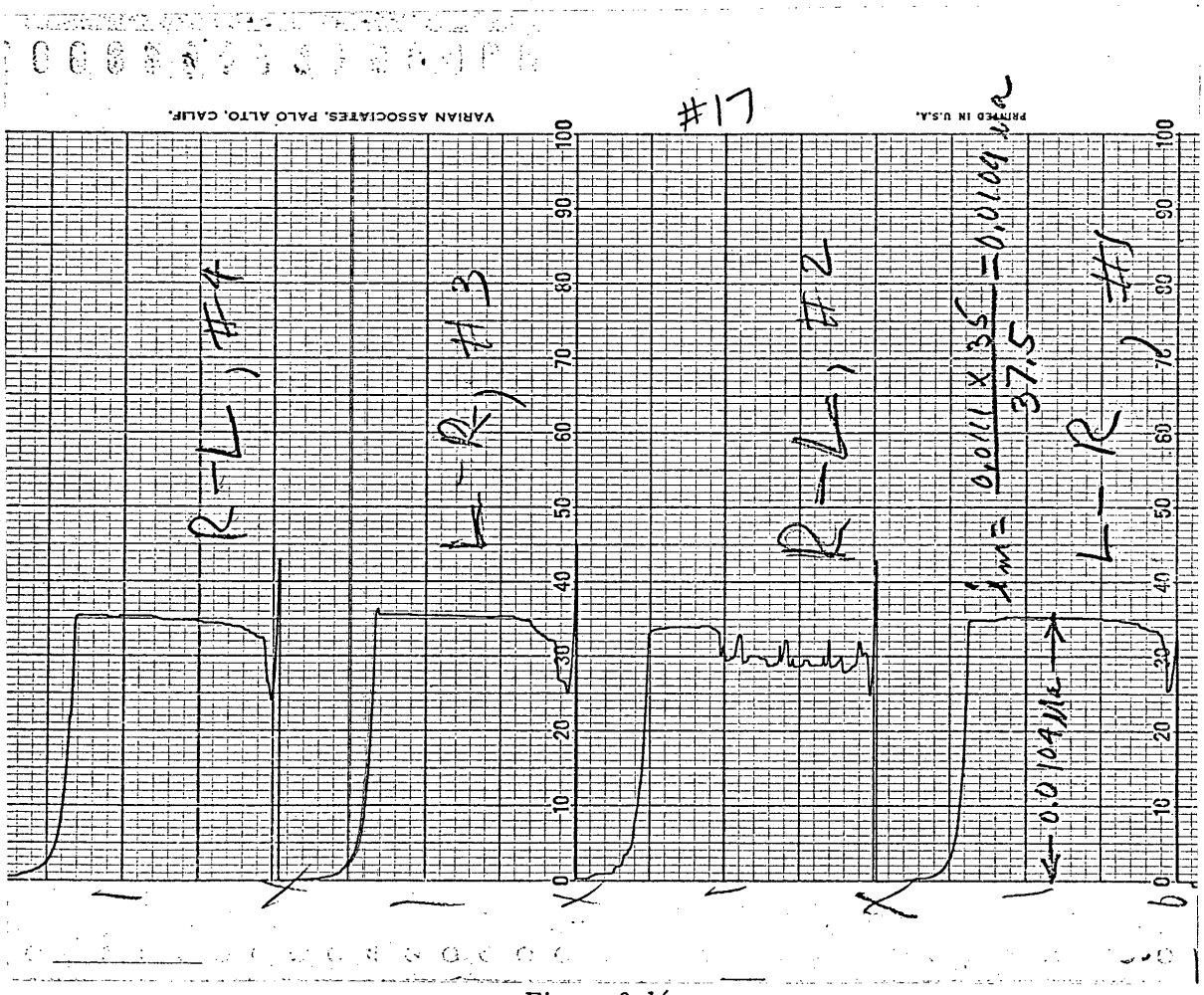


Figure 3.16

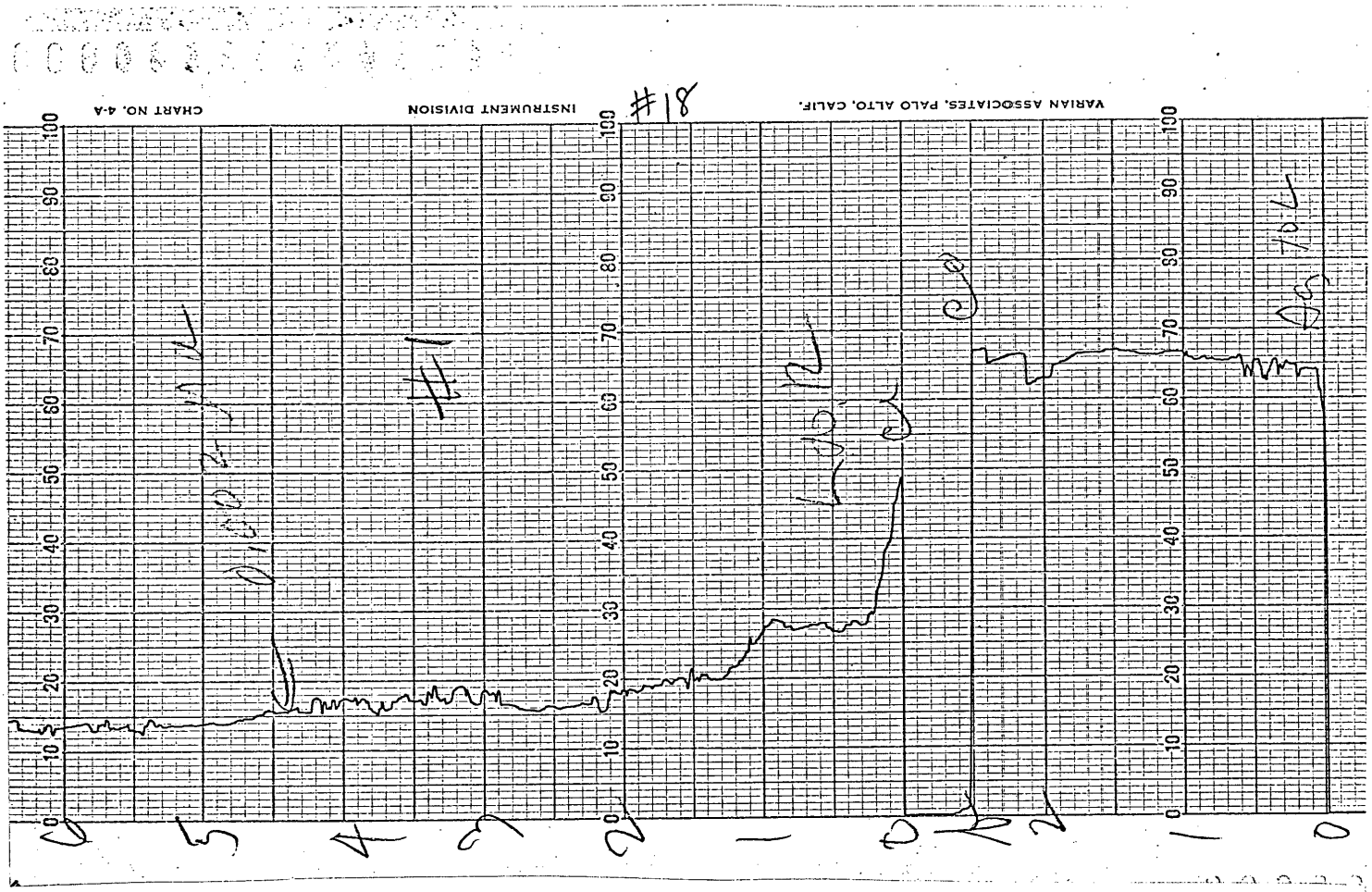


Figure 3.17

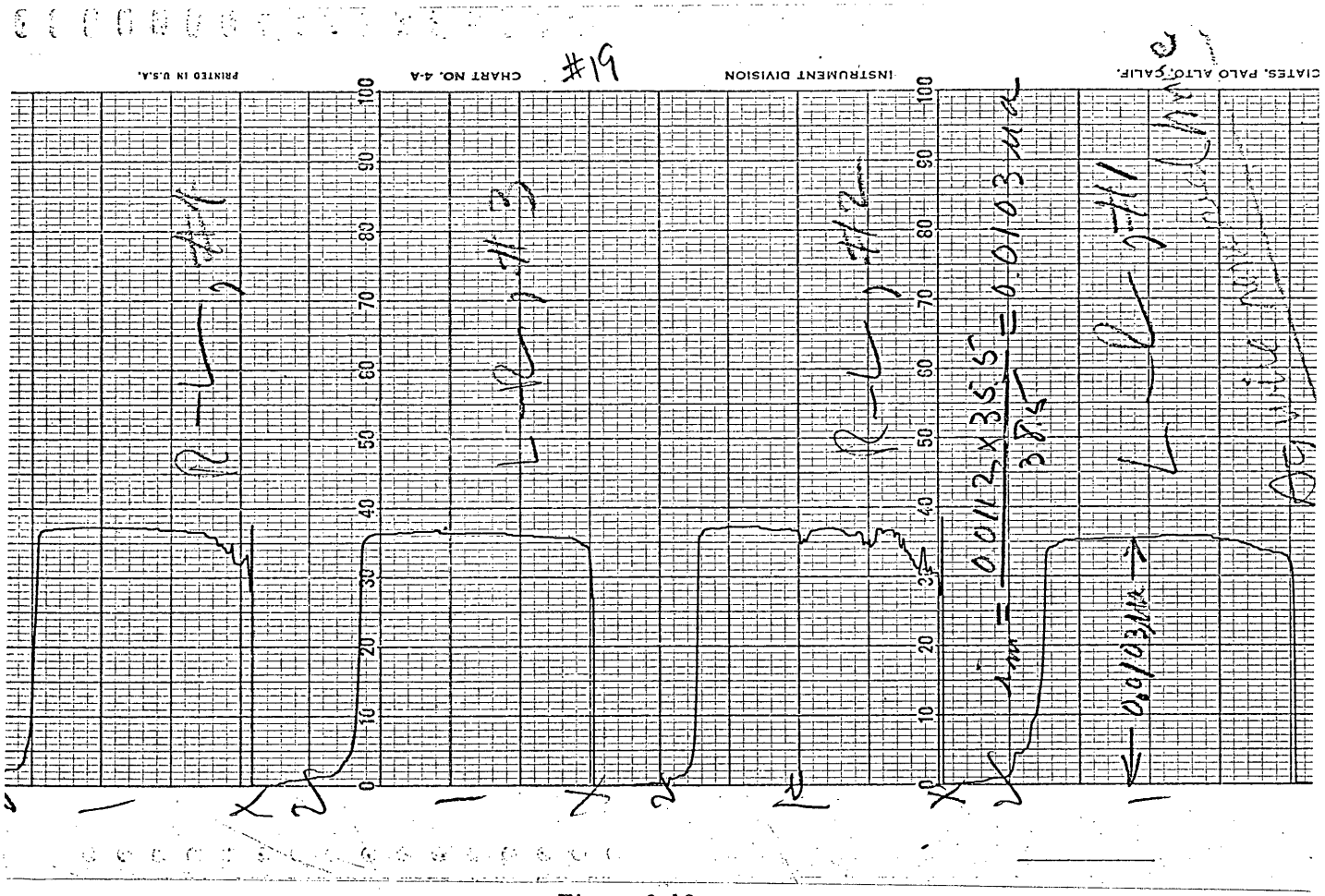


Figure 3.18

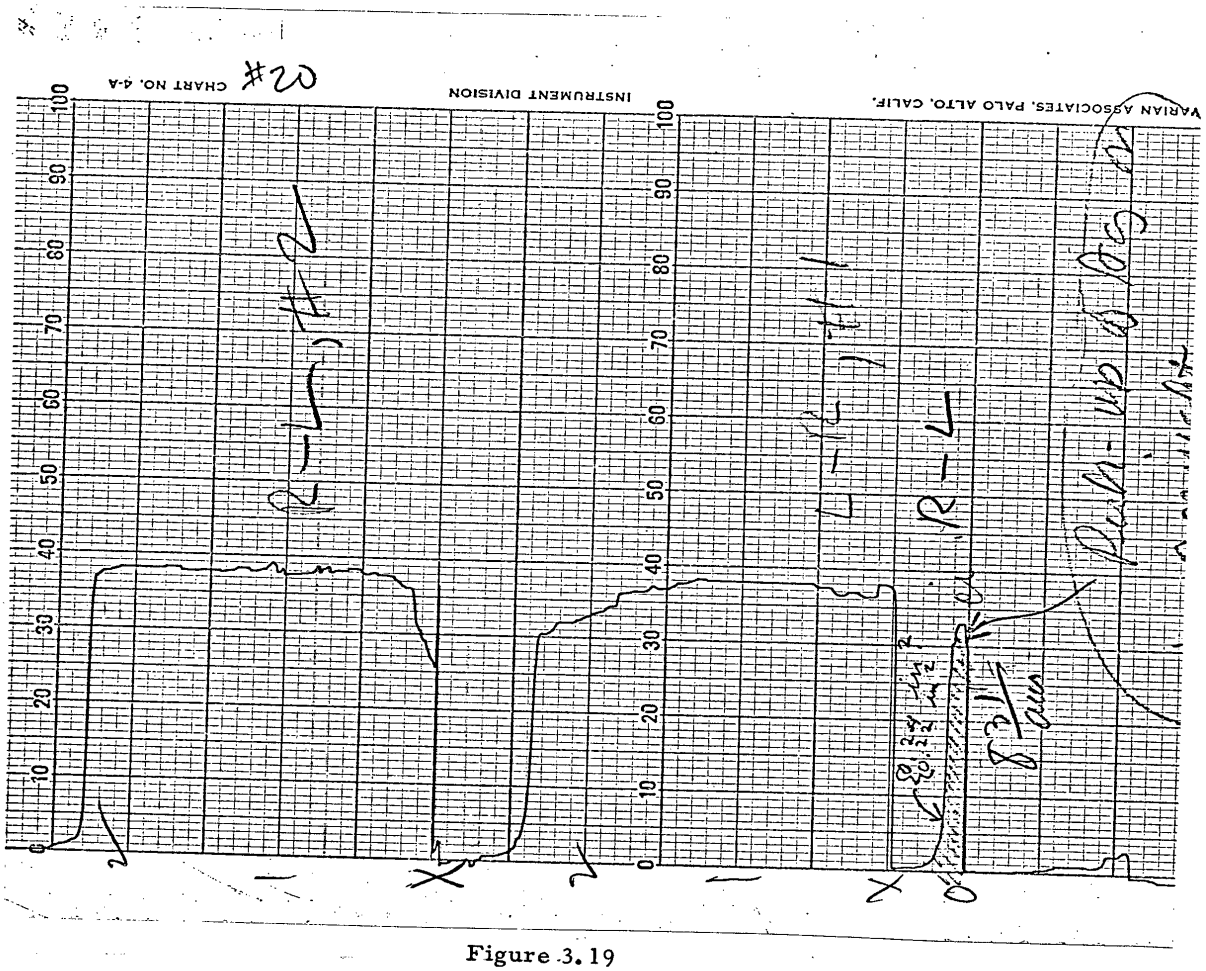


Figure 3.19

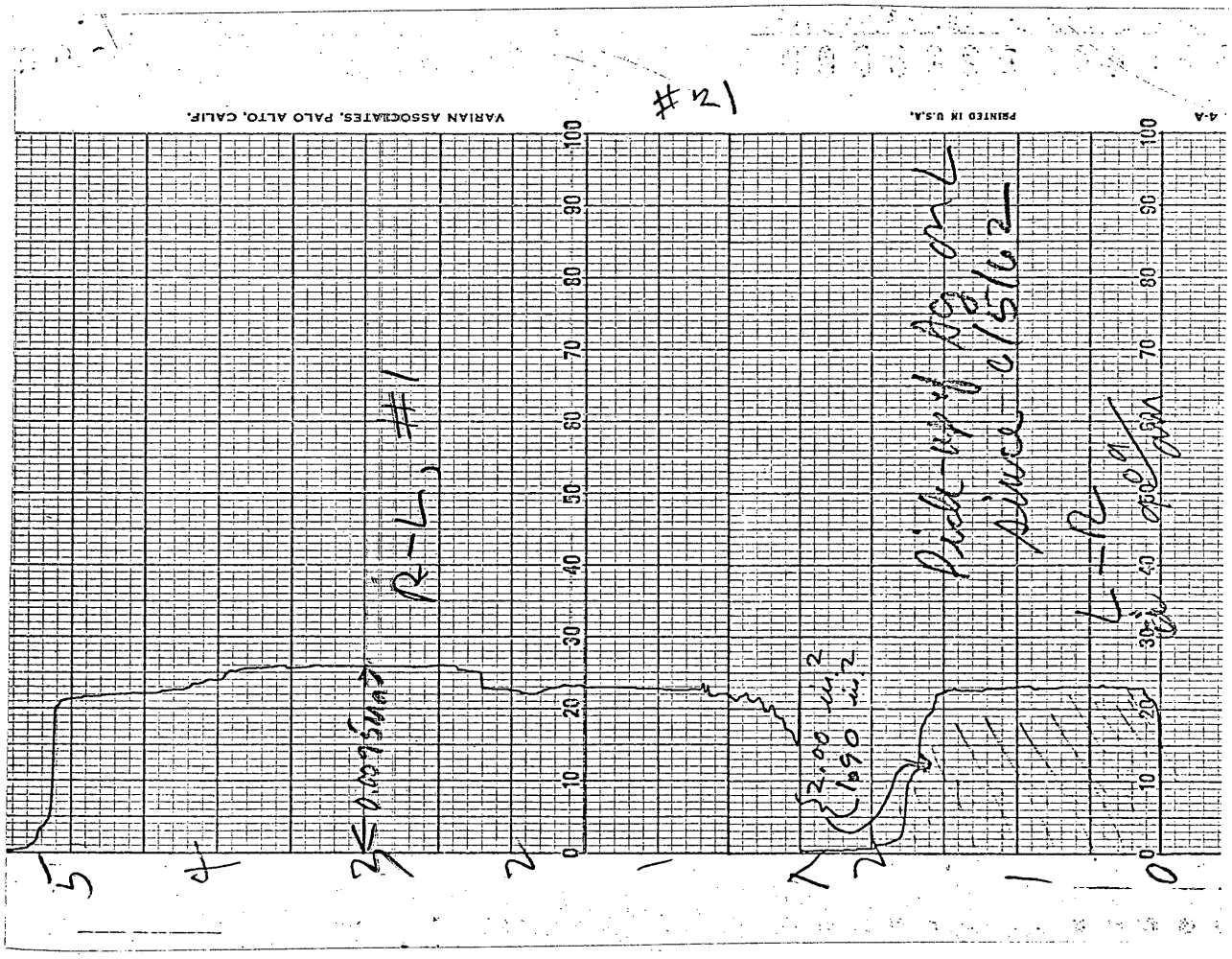


Figure 3.20

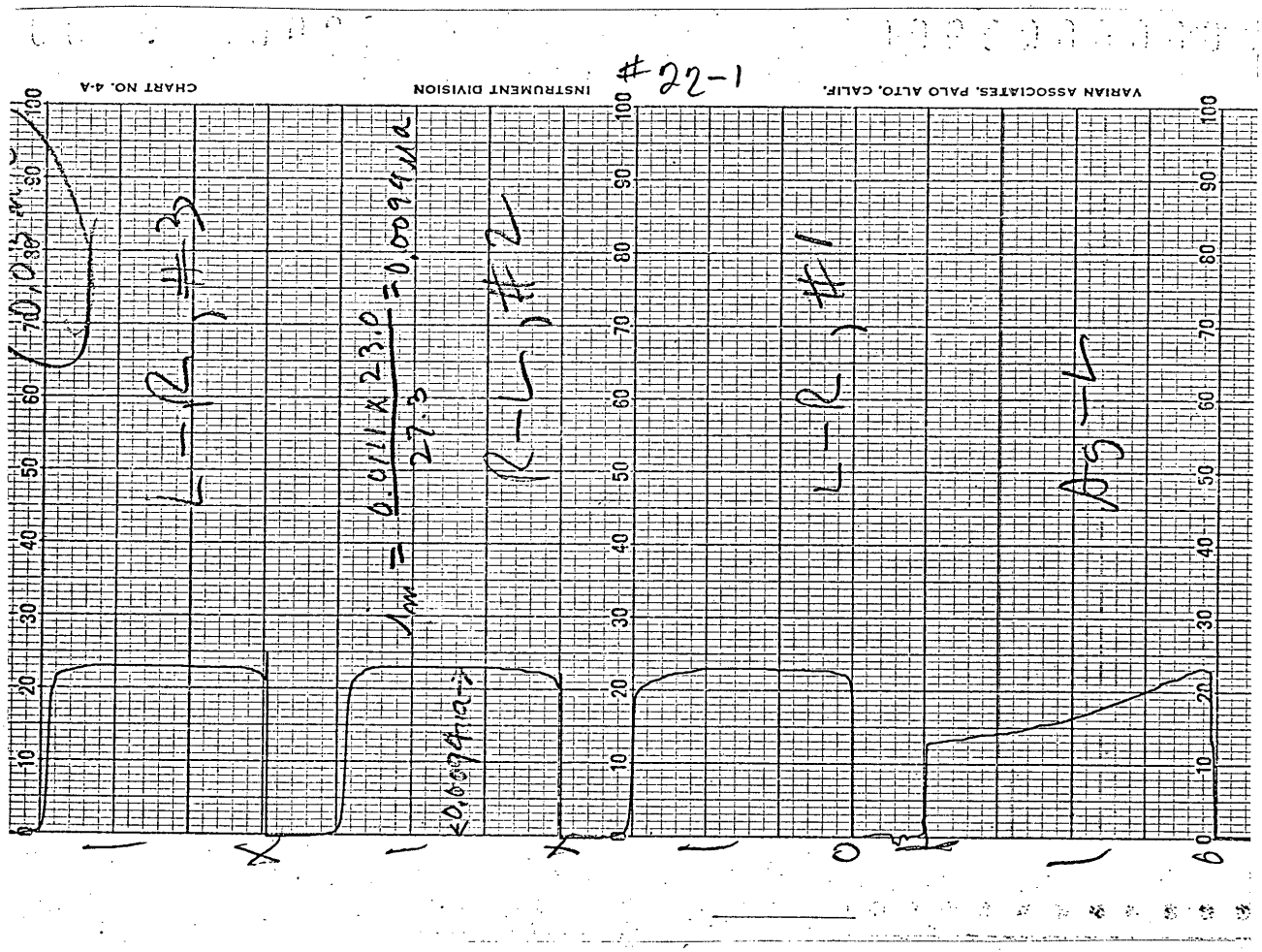


Figure 3.21

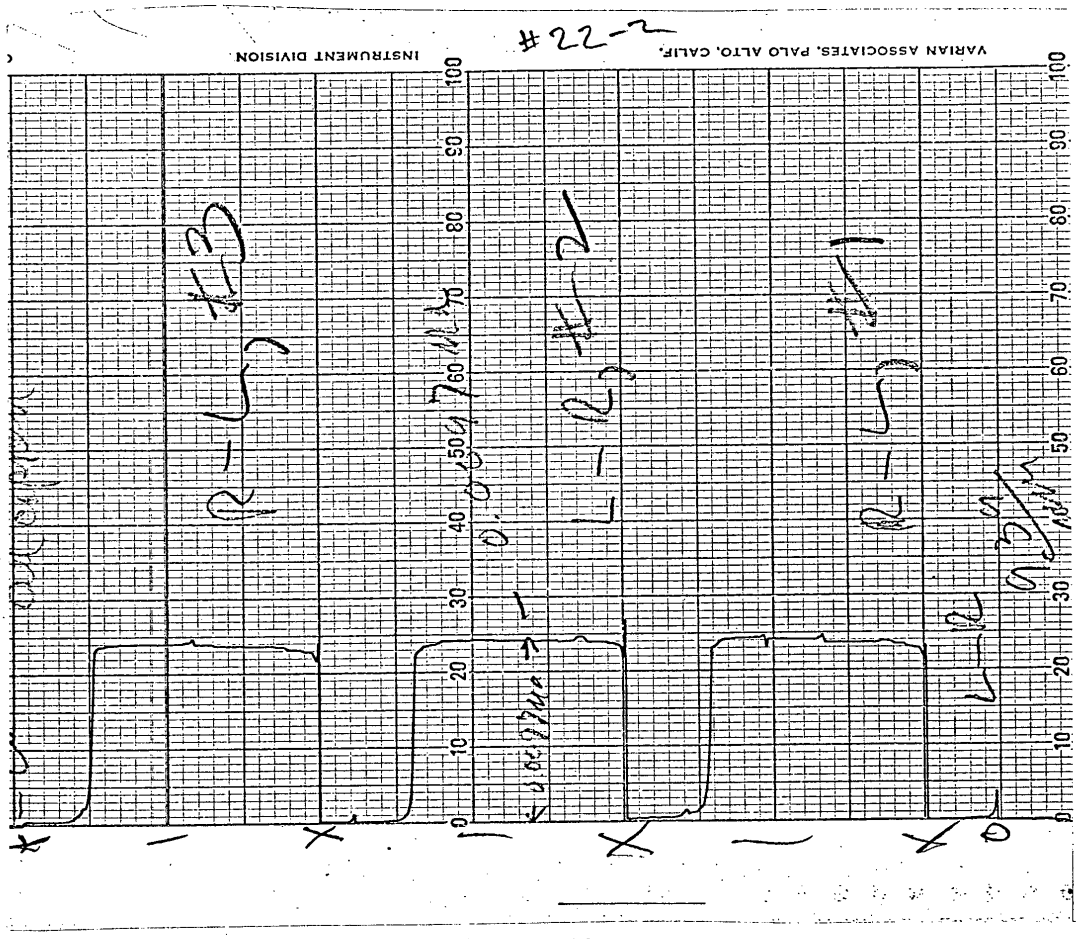


Figure 3.22

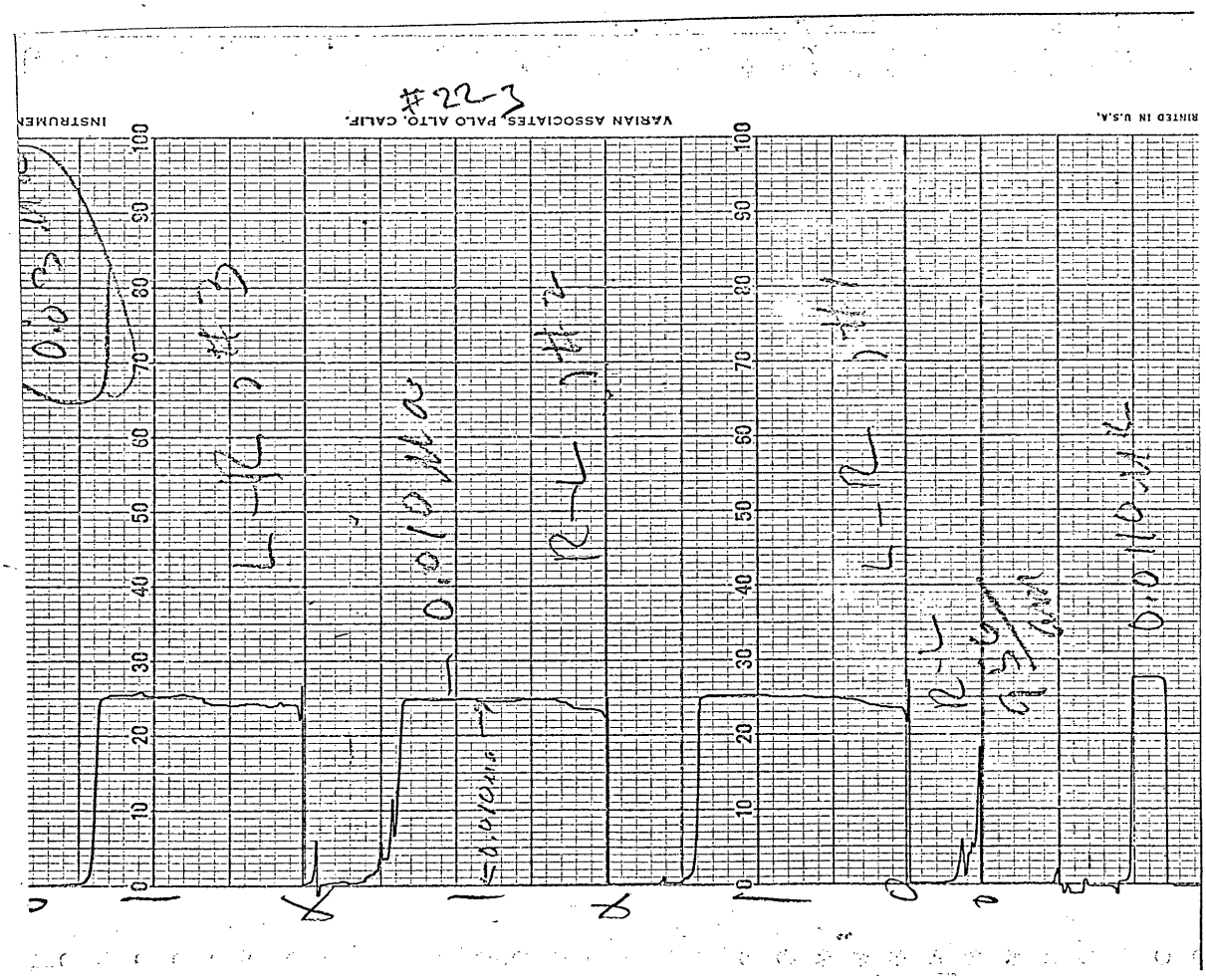


Figure 3.23

tendency to give this kind of erratic behavior. A typical result is illustrated for the electrodes of Figure 3.16 after they were sealed into cells and obtained the results of Figure 3.18. Even so, in Figure 3.18 it can be seen that when the right electrode is the anode, there is still some erratic behavior at the beginning of the plating process. Another problem with the electrodes when assembled into soft glass cells is illustrated in Figure 3.19 and Figure 3.20. This problem is the apparent accumulation of silver on an electrode as a result of standing overnight or for several days. The cell of Figure 3.19 had all the silver removed by plating from the right electrode onto the left electrode. The cell was then allowed to stand overnight and a current put through the cell to move material from the right electrode to the left electrode. It was found that the current was able to pass as a result of apparent accumulation of silver on the right electrode. However, this accumulation could have been the result of another chemical process which was reversed as the result of the applied voltage across the cell. This effect is even more pronounced in Figure 3.20 where the accumulation was quite significant in size as the result of standing over a three day period. The exact mechanism of this apparent silver accumulation is not yet understood, however it is believed to be related to the formation of oxides, or hydroxides on the electrode as a result of standing. The apparent accumulated current-time product then represents that charge which is necessary to decompose these oxides or other chemical products which were formed.

Among the experiments which were performed with the cells constructed for operational use are a set of experiments used to investigate the effect of changing concentration of the electrolyte on the performance of the cells at low current. An example of this kind of experiment is illustrated in Figures 3.21, 3.22 and 3.23. In these three figures the same cell was used and experiments were performed successfully by first electroplating silver with tenth normal silver nitrate concentration, removing the electrolyte, continuing the plating of silver from one electrode to the other with one normal silver nitrate, removing the electrolyte and finishing the experiment by plating the silver back and forth between electrodes with five normal silver nitrate. It will be noticed that not only

is there little change in the shape of curves, the effect of the residual current and the height of the curve, but there is also little loss in the amount of silver plated onto an electrode when the electrolyte was completely removed from the cell and replaced with new electrolyte. A careful examination will reveal however that as expected the higher concentration of electrolyte does increase the current through the cells somewhat due to its lower resistance in the circuit controlling the current level. Another set of experiments illustrating the effect of varying concentration is indicated in Figures 3.24, 3.25 and 3.26. With this cell it will be noticed however that increasing the concentration of the electrolyte does produce miscellaneous random variations in voltage, both while current is being conducted through the cell and after the apparent shut-down of the cell by the completion of the silver plating. These miscellaneous background variations are probably due to effects of oxides or other chemicals formed in minute quantities during the electroplating process. This formation of spurious compounds is evidently enhanced somewhat by the use of higher concentration of silver nitrate.

Occasionally some of the cells made by the broken-wire technique gave very poor results when subjected to tests. One such cell, indicated in Figure 3.27, shows very large progressive losses as the silver is plated from one electrode to the other. There appears to be no anomalous back voltages and the shape of the curves is very good. There is also no significant residual current after the cell has cut off.

Occasionally a catastrophic loss of silver from one of the electrodes will occur during the cycling process and then reappear at a later time when more silver is added to the cell. This is illustrated in Figure 3.28. In area 10 can be seen a reasonably good shaped square pulse as the silver was plated from left to right. However, when the right electrode was made an anode, the silver apparently disappeared and area 11 is almost nil. In area 12, the silver wire was inserted into the cell and a new current time product of silver was plated onto the left electrode. The silver was then cycled in area 13 from the left electrode to the right electrode and when the right electrode was made an anode and the silver plated onto the left electrode, not only was the current time product of

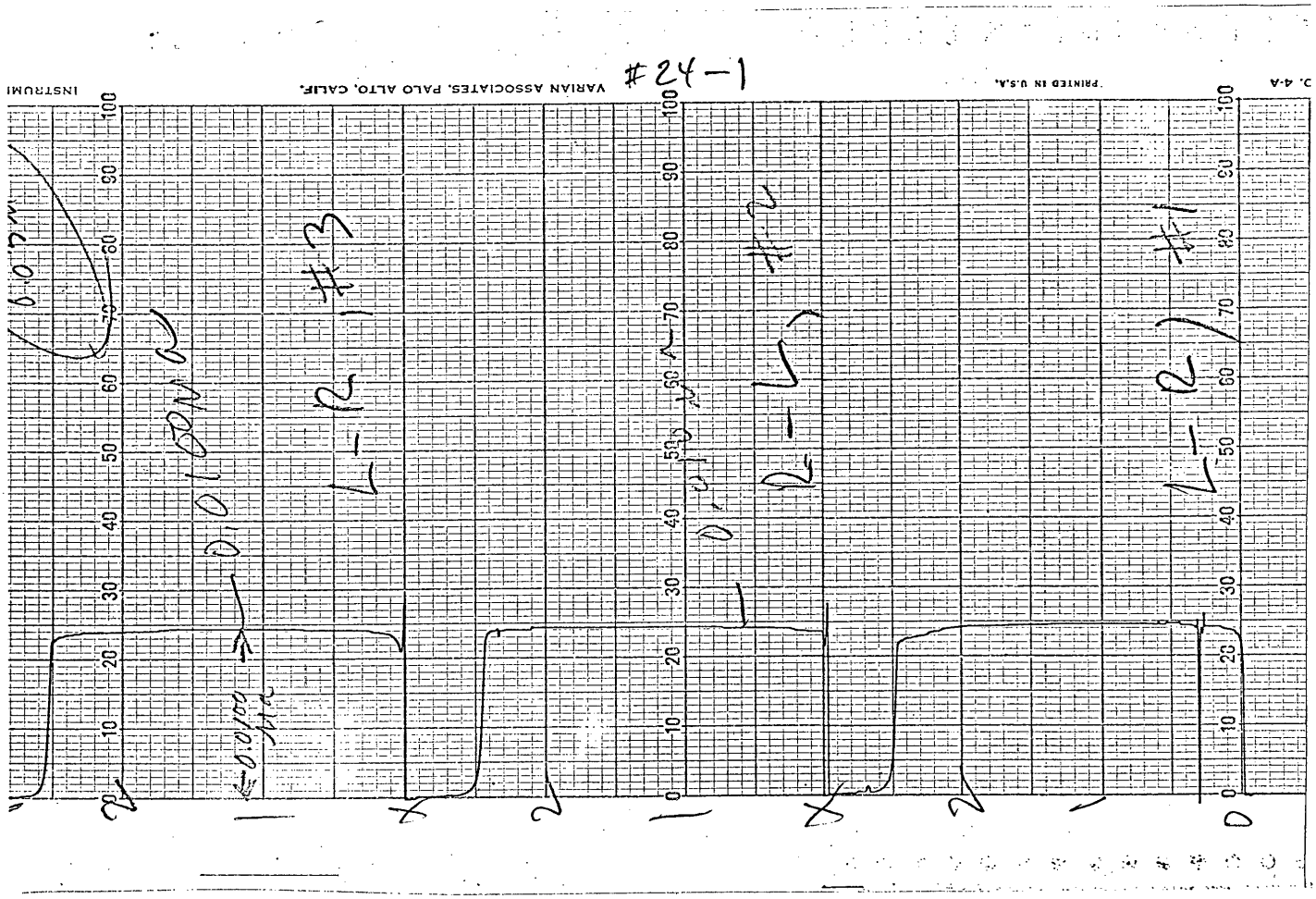
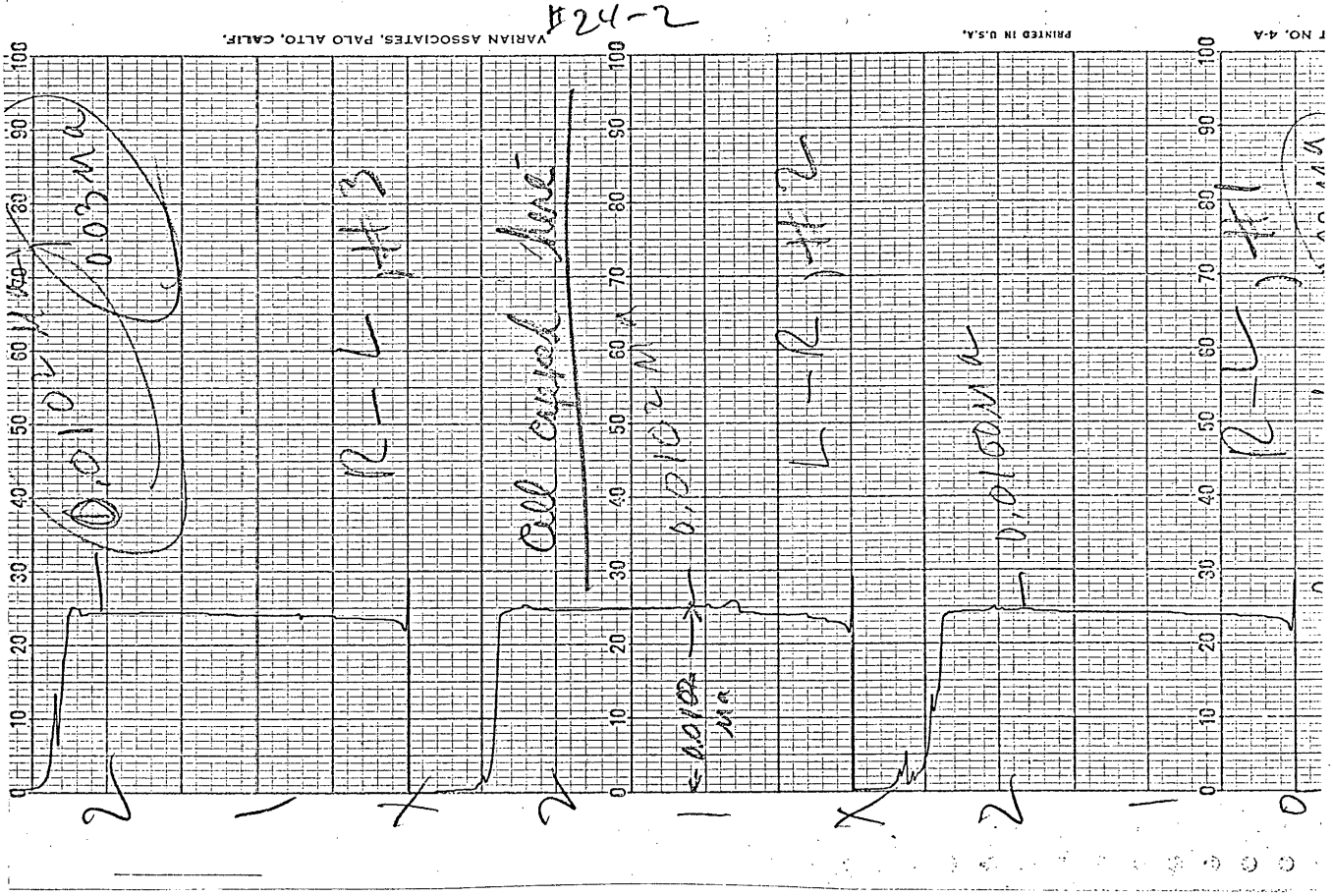


Figure 3.24



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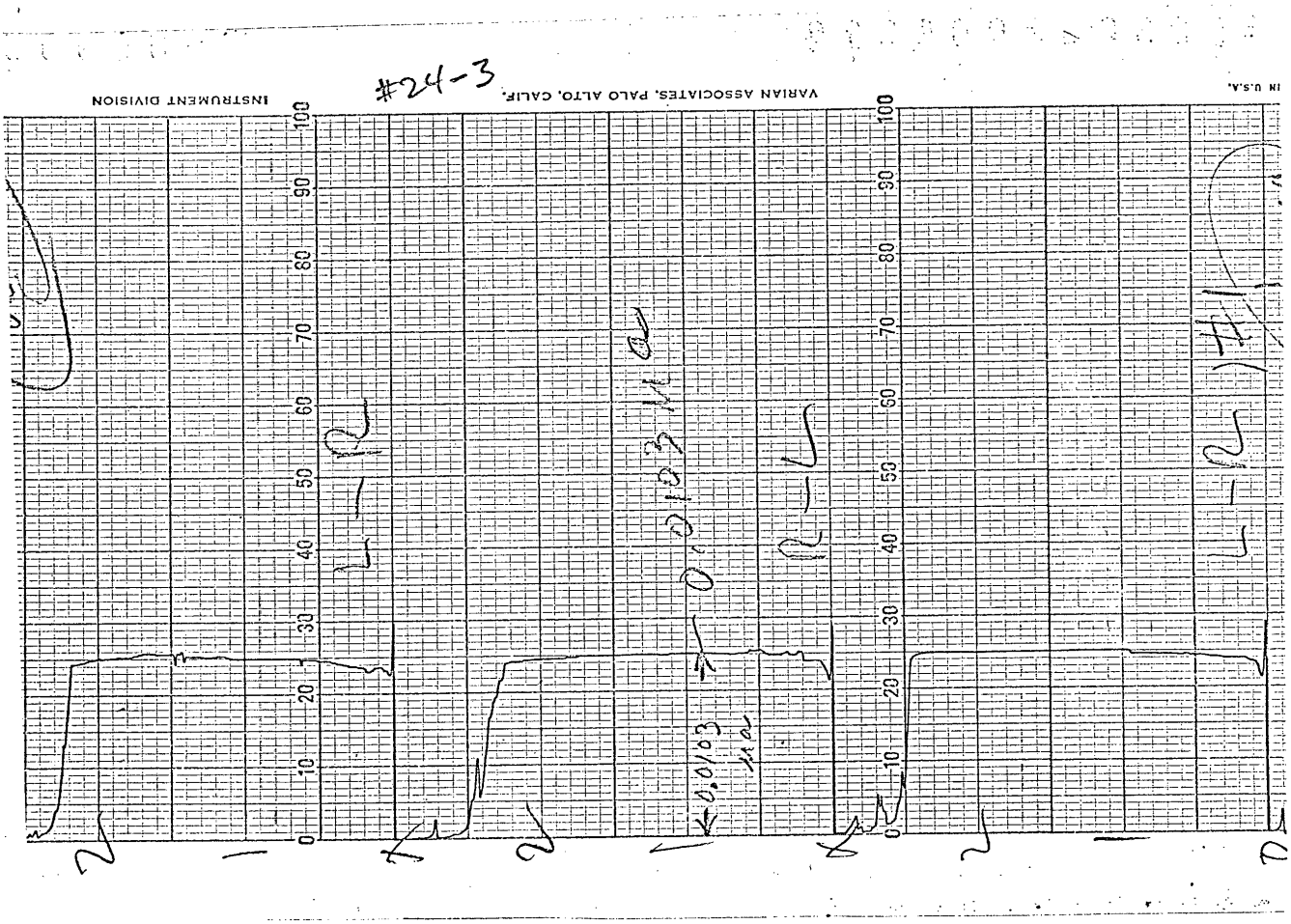

Figure 3.26

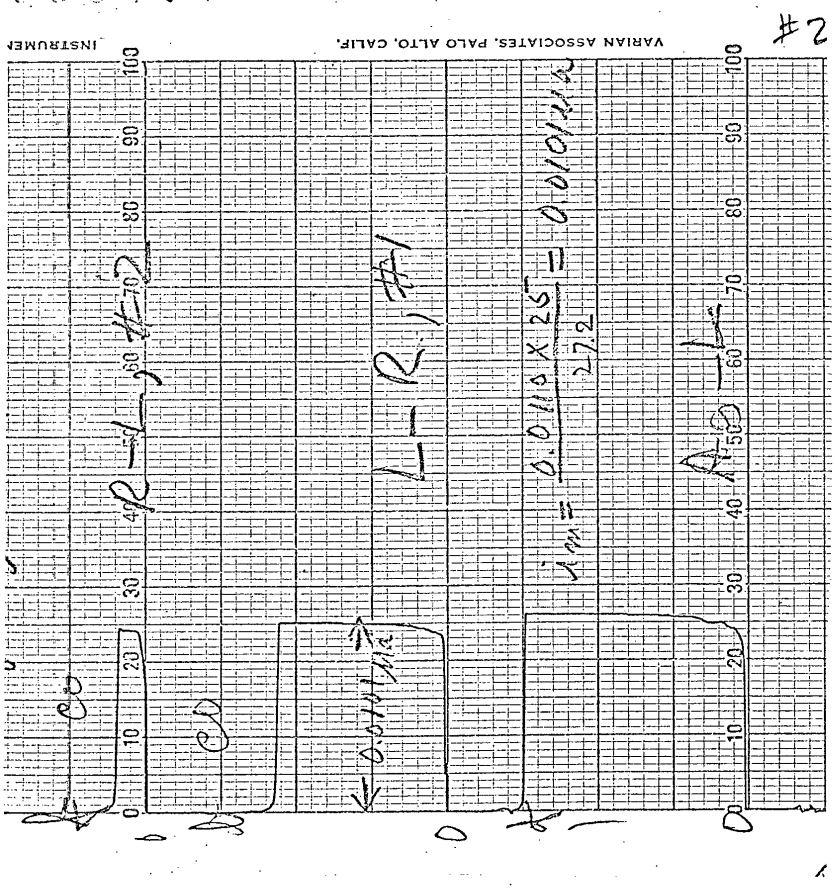

Figure 3.27

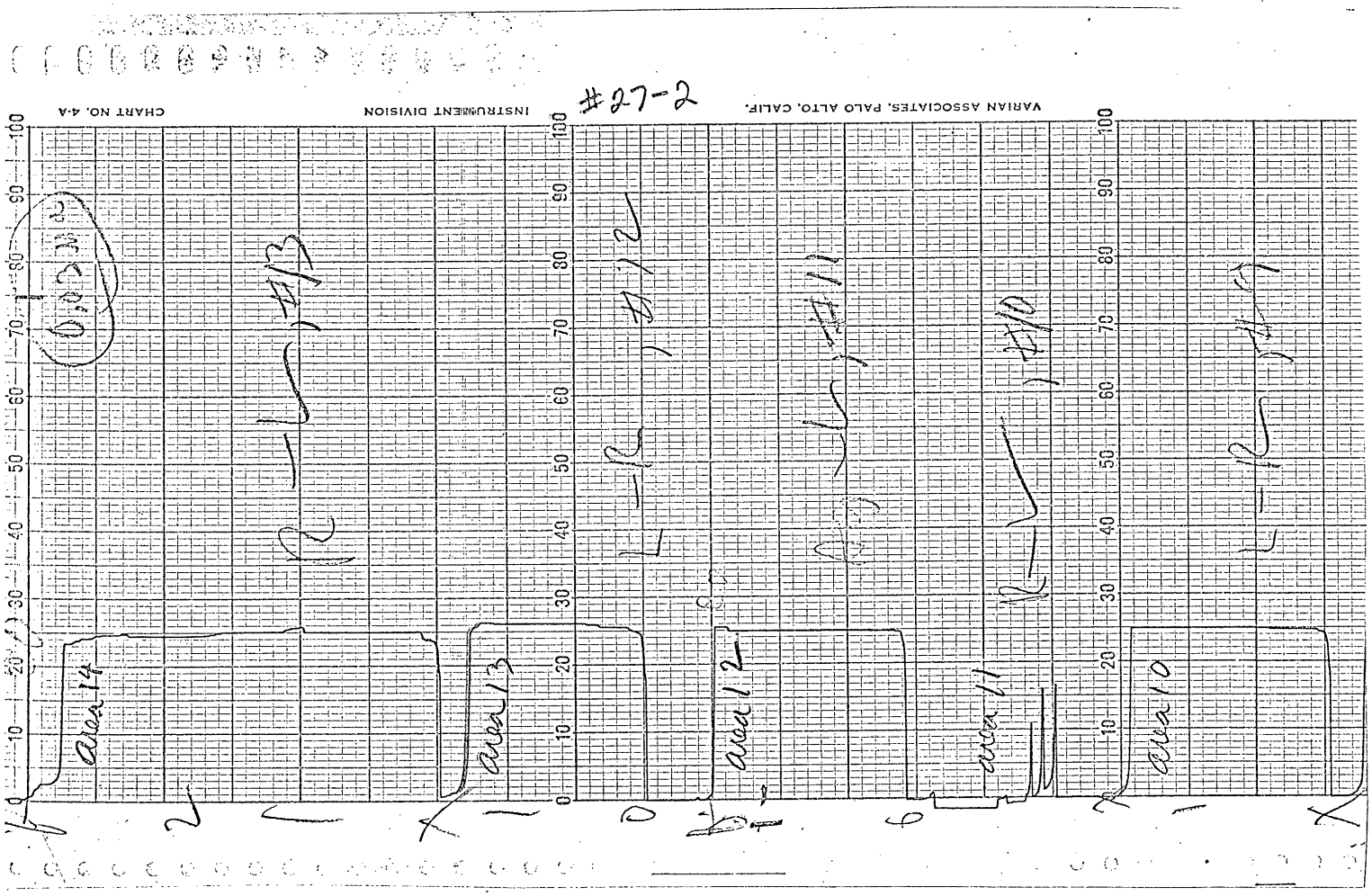

Figure 3.28

area 13 reproduced, but the area under the curve suggests that what appeared to be lost in area 11 was now reappearing and adding to the amount of silver in area 13 so that the silver was not lost at all, but merely made passive in some way. It is now understood that these various forms of losses of silver are due to the most part to chemical impurities in the cell which can be removed by more careful cleaning procedures or due to the formation of oxides on the electrode during the assembly process or on standing in an electrolyte which has been saturated with atmospheric oxygen.

Figure 3.29 indicates results from one of the more sensitive cells with a electrolyte concentration of five normal silver nitrate. This cell was made by the broken wire technique and performs reasonably well at a current level of less than one millimicro ampere. The large spike at the beginning of each curve is the result of the capacitance surge caused by the current charging up the electrode's face before silver ions begin to move through the solution. This spike is often noticed at these low current levels because the large series resistance in the circuit allows the RC time constant to be significantly greater than the microvolt ammeter time constant. The residual current in this figure appears to be very small. Indeed, there is some suggestion that it is actually negative as the result of miscellaneous potentials in the cell.

Figure 3.30 shows a progressive loss of silver in one of the sensitive cells when a current level of less than a millimicro ampere was used. However this loss can be rectified as is illustrated in Figure 3.31. The electrolyte was removed from this cell, the silver plated on the electrodes was dissolved with acid, the cell cleaned with acqua regia, and rinsed several times with distilled water. The aqua regia treatment produces exceptionally good results and it is now known that this is due in part to the removel of platinum oxides from the surface of the electrode. The residual current in Figure 3.31 appears to ~~be of the~~ order of 10^{-11} amperes corresponding to a flow of silver through the cell of 1/100 of a microgram per second. This is exceptionally good results for an electrolytic cell ~~and provides~~ a very sensitive means of measuring the quantity of silver and deposited onto the electrode.

? I get 1.16×10^{-14} g Ag/sec

$\mu\mu g$?

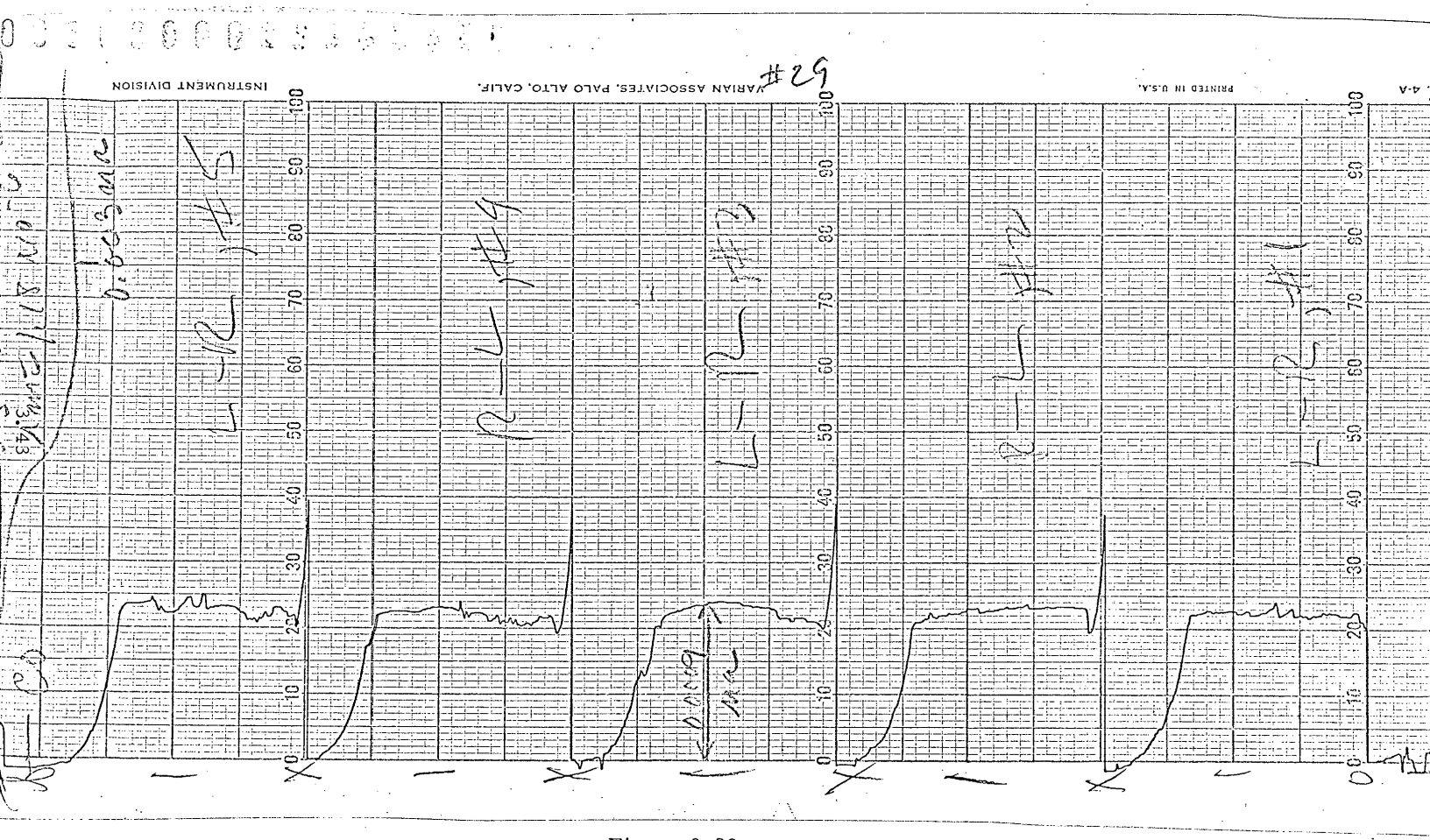

Figure 3.29

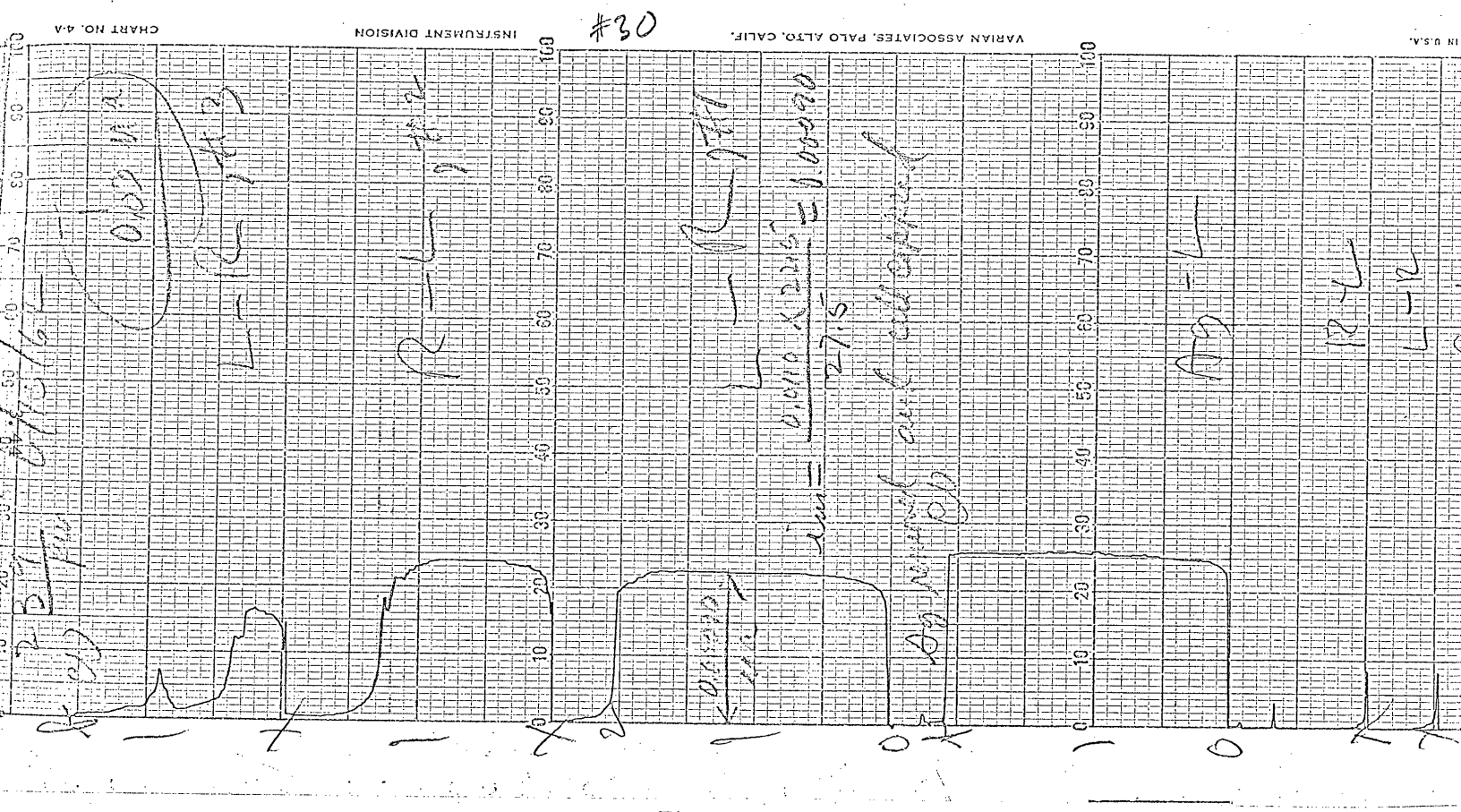

Figure 3.30

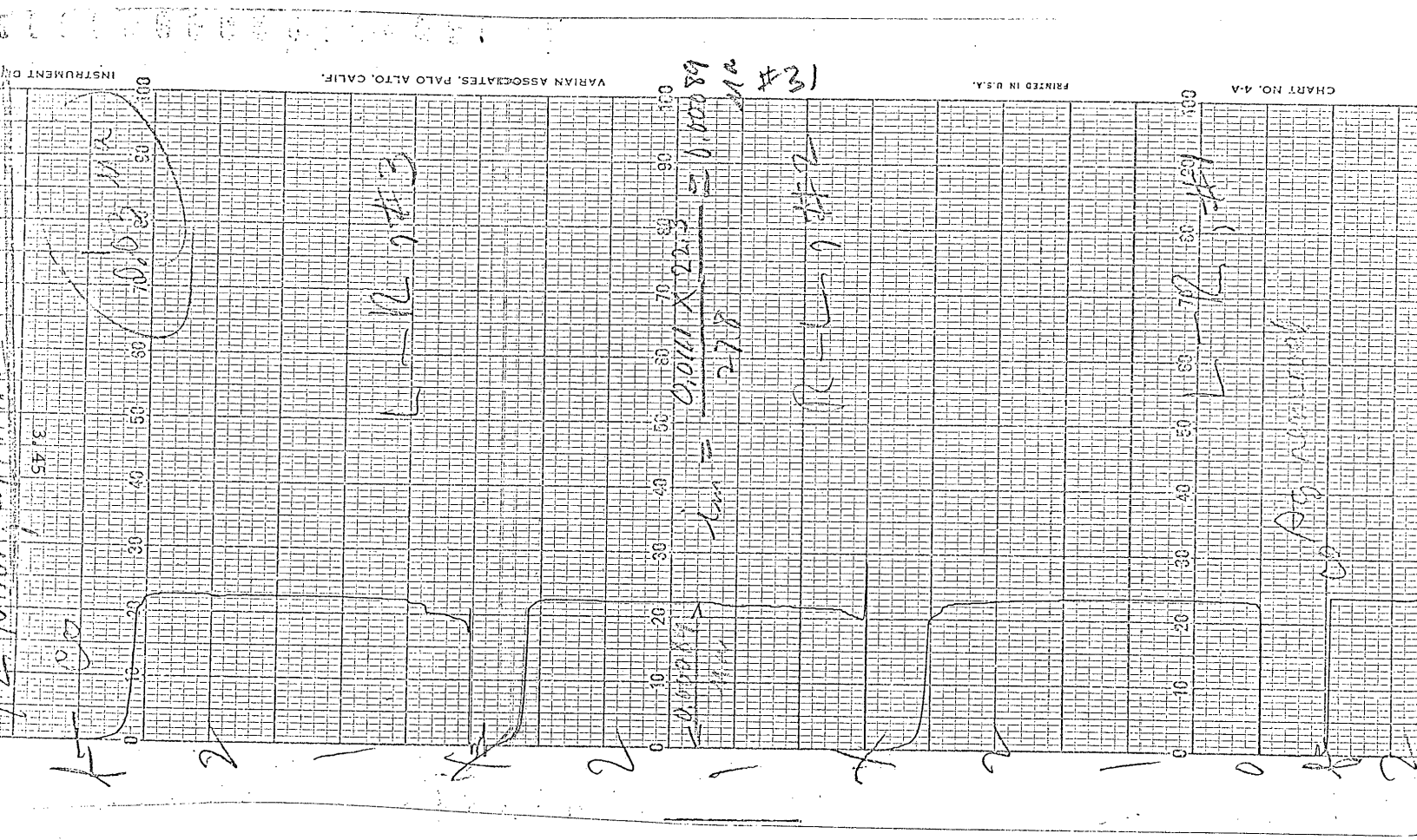

Figure 3.31

Recent results indicate that most of the problems encountered with cells and described in this section can be cured by the special aqua regia cleaning technique and careful rinsing with distilled water. These cells all perform with a sensitivity similar to that indicated in the figure just shown. Experiments are still continuing to investigate the long term stability of these cells and the effect of dissolved oxygen and other electrolytes than those used.

3.2 RESISTANCE MEASUREMENTS OF E-CELLS

Purpose of the Experiment

Preliminary measurements of the resistance of E-cells of the low current type (.01 to 1 μa) was undertaken to determine the individual cells resistance characteristic prior to utilizing such cells as integrators of DC current from a microwave detector. The ability to match the impedance of the cell to the source impedance of the detector is desirable to transfer the maximum energy to the cell and consequently accurately obtain a constant proportionality between field intensity, for a given antenna structure, and cell stored current-time integral. As a first step in achieving these ends, simple E-I characteristics of several cells have been determined.

Operation of the Experiment

Battery E and dividers R_1 and R_2 of Figure 3.32 provide a low voltage power source for the E-cell circuit. Switch S_1 is a simple on-off device for convenience. The source voltage which is approximately 0.16 volts is applied to R_3 in series with the E-cell under test. The voltage (V) and current (I) are read directly with a single instrument. Shorting switch S_2 is provided to bypass the ammeter when the instrument is being used as a voltmeter. Switch S_3 is provided to reverse the polarity imposed on the E-cell under test.

The first cell tested was Cell No. A1. The cell is of the three platinum electrode type. In this case the silver was initially all deposited on the center electrode and measurements were taken of V and I about 30 seconds after the cell was turned on. The silver was then returned to the electrode and the process repeated for a new current level. The data is shown in Figure 3.33 and Table 3.2 for this experiment.

Another experiment was performed, in a similar manner to the above, on two electrodes, low current type cell No. B-21. In this experiment data was obtained not only for the condition when the silver migrates from the silver plated electrode to the unplated electrode, but also for the reverse process. Results of this experiment are shown in Figure 3.34 and Table 3.3.

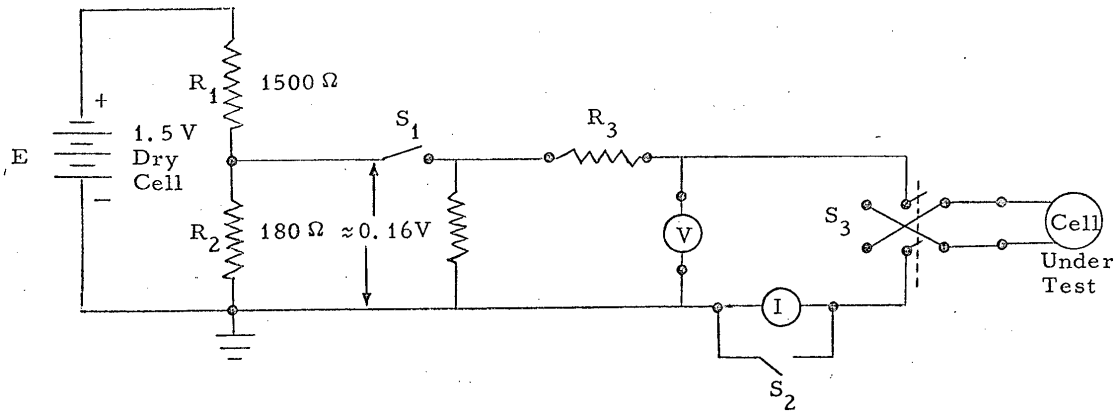

Figure 3.32 Test Circuit

Table 3.2

Electrolytic Cell A-1

R_3	I Through Cell	ΔI	E Across Cell	ΔE	R Cell = $\frac{\Delta E}{\Delta I}$ From Slope on Fig. 1
3.3 MΩ	.045 μA		3.2 mv		
		.108		2.2 mv	~20 KΩ
1.0 MΩ	.153 μA		5.4 mv		
		.042		.4 mv	~10 KΩ
0.82 MΩ	.195 μA		5.8 mv		
		.245		2.4 mv	~10 KΩ
0.33 MΩ	.44 μA		8.2 mv		
		.24		1.8 mv	~4.5 KΩ
0.22 MΩ	.68 μA		10.0 mv		

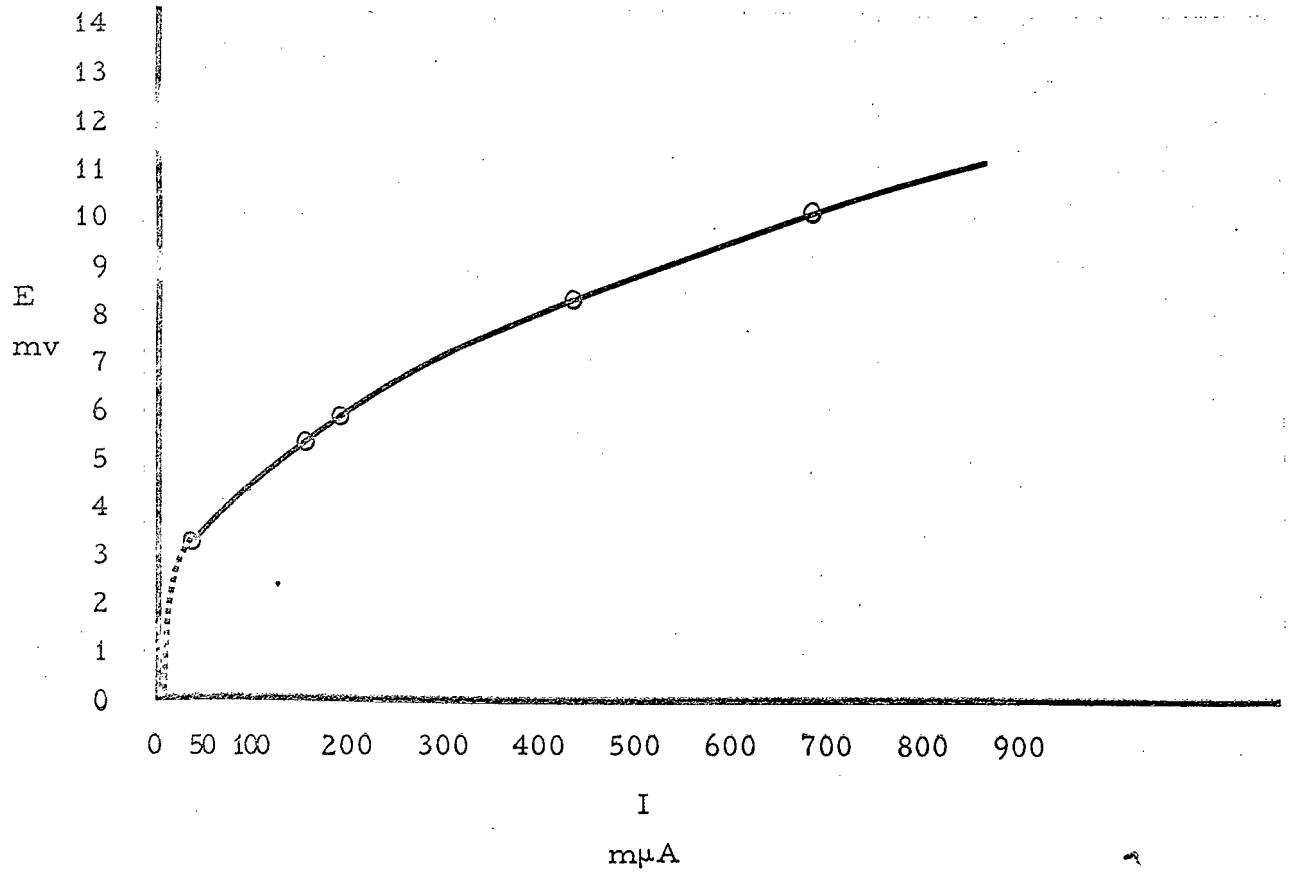

Figure 3.33

Table 3.3

Electrolytic Cell B-21

(a) Data taken with plating action taking silver from Ag plated platinum electrode to platinum electrode. Data is for period immediately after 30 seconds from start.

R_3	I Through Cell	ΔI	E Across Cell	ΔE	R Cell = $\frac{\Delta E}{\Delta I}$
2.2 MΩ	.054 μA		26 mv		
		.068		5	73 KΩ
1.0 MΩ	.122 μA		31 mv		
		.097		3	33 KΩ
.56 MΩ	.215 μA		34 mv		
		.255		4	15 KΩ
.270 MΩ	.470 μA		38 mv		
		.310		8	25 KΩ
.150 MΩ	.780 μA		46 mv.		
		1.01		10	10 KΩ
.056 MΩ	1.80 μA		56 mv		

(b) Data under same conditions as above except plating action in opposite direction.

2.2 MΩ	.056 μA		26 mv		
		.069		6	90 KΩ
1.0 MΩ	.125 μA		32 mv		
		.097		7	70 KΩ
.56 MΩ	.222 μA		39 mv		
		.248			
.27 MΩ	.470 μA		38 mv		
		.340			
.150 MΩ	.810 μA		50 mv		
		1.09		10 mv	10 KΩ
.056 MΩ	1.90 μA		60 mv		

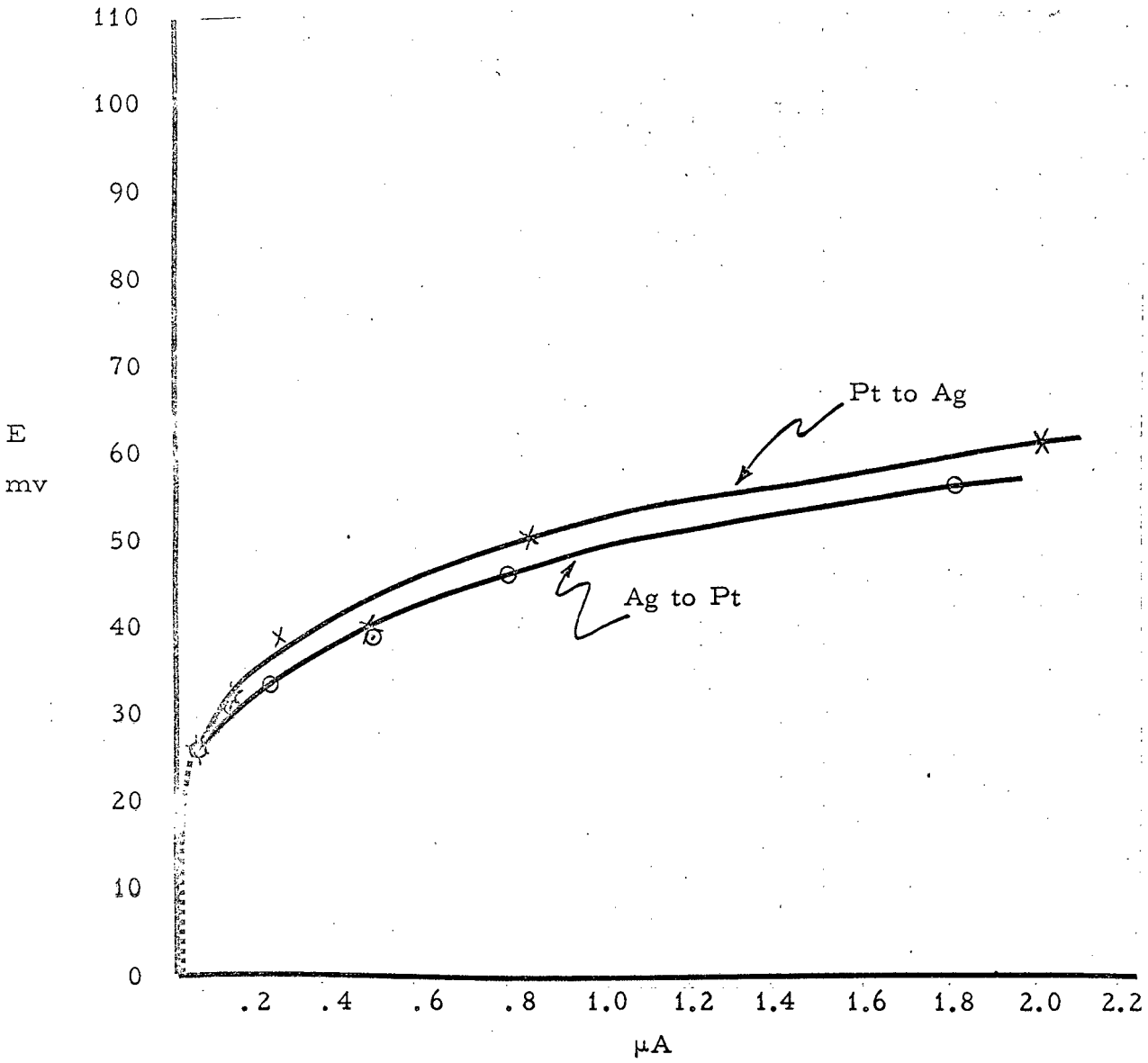

Figure 3.34

A third experiment was performed in an attempt to determine if the impedance of a low current cell was naturally different when approximately half the silver had been deposited from one electrode to the other platinum electrode than when operated as in the previous two experiments where the silver was primarily on one side. Cell No. 15 was used for this experiment. This cell had indicated erratic operation on earlier other tests; however, it appeared satisfactory on the morning of the test and was used for about four hours. In the afternoon the cell again displayed erratic behavior and the tests were discontinued. Data for this experiment are on Figure 3.35 and Table 3.4.

After the preceding experiments were concluded, an attempt was made to see if a typical cell could be used to collect the output of a microwave detector of a small antenna-detector scheme. Figure 3.36 shows the setup for this test. The X-band transmitter was operated at approximately 25 to 40 milliwatts output. The antenna was placed from 12 inches to 40 inches away to adjust the field intensity intercepted.

Initially a 10K Ω resistor was inserted in the circuit instead of the cell to adjust the apparatus. DC current was indicated on the DC galvonometer. After the DC circuit was adjusted by either adjusting the RF power level or the distance between horn and antenna, the cell was substituted. This test was prepared with Cell No. B-21 and Cell A-11 which is a three electrode heavier current type.

Conclusions

In all the resistance measurements, the cells displayed a threshold or back EMF property. In the case of the cell with the large electrode, this threshold appears to be about 3 mv and in the case of the cell with small electrode it is approximately 20 - 30 mv. Both cells displayed approximately 10 KΩ resistance while conducting in the region of 1 μamp. It should be noted that the three electrode cells were designed for much larger currents than used in these tests and hence the resistance measured is not indicative of its design region.

In addition to this threshold characteristic the cells displayed a changing value of impedance dependent upon the ratio of silver at the

Table 3.4

Electrolytic Cell No. B-1 (Low Current Cell)

Plating with Silver Initially on Both Electrodes

R_3	I	E
8.8 MΩ	.016 μA	11 mv
6.6 MΩ	.022	15 mv
4.4 MΩ	.033	12 mv
2.2 MΩ	.061	20 mv
1.0 MΩ	.145	13 mv

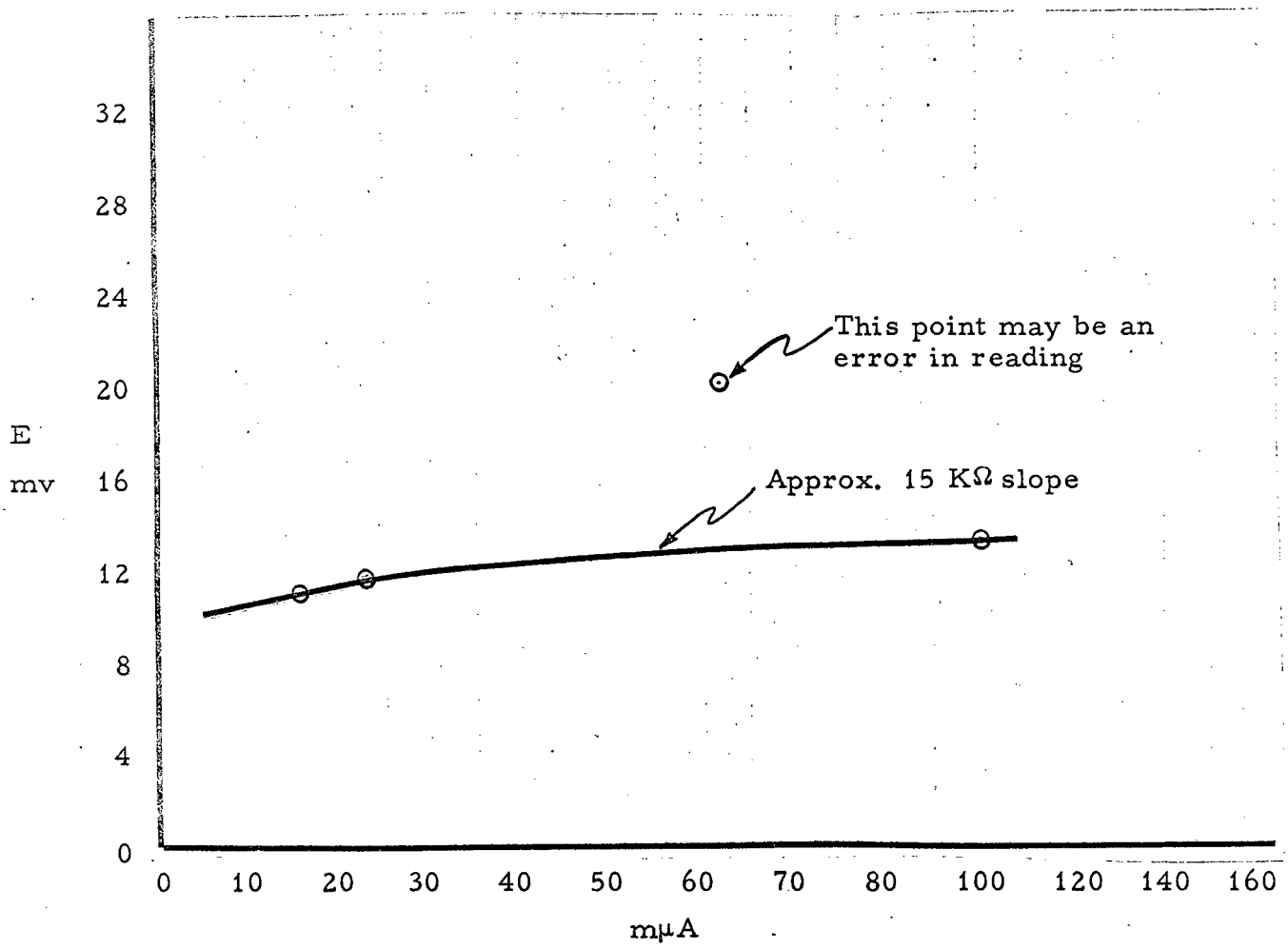

Figure 3.35

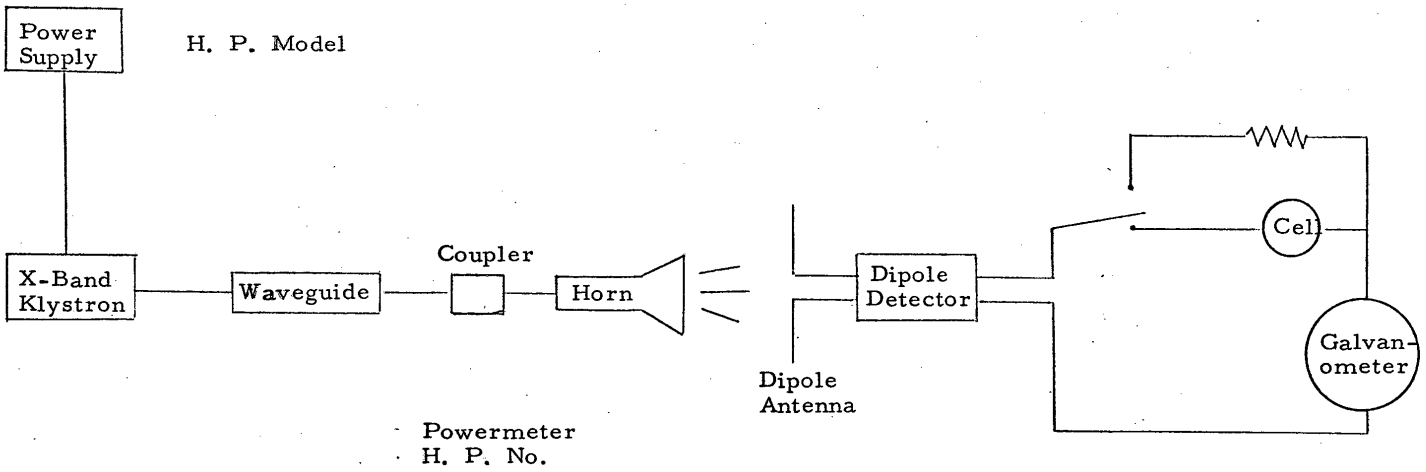

Figure 3.36

positive and negative electrodes. In the case where almost no silver is yet at the negative electrode, the impedance is higher than when an equal amount of silver is at both electrodes.

The importance of eliminating or reducing the threshold characteristic and the operating impedance of the cells was borne out by the qualitative tests employing RF microwave detection and accumulation of charge. Cell B-21 which had about 25 - 30 mv of threshold would not conduct current from the detector because the output potential of the detector was below the threshold. Even if the cell were precharged (i.e., some silver on both electrodes), it still could not overcome the threshold. Cell No. A-11 was then used which is similar to Cell A-1 which was not available. This cell also would not carry current when all the silver was only on one electrode because of the high initial impedance, but not because of the threshold. When Cell A-11 was precharged, it did carry current at a value indicating an impedance of slightly below 10 KΩ. (3 μA from the detector were run through the cell.) These measurements are only preliminary and do not represent adequately the capability of the cells. The bias voltages can be removed in principle once their origin is understood. This work is still continuing.

3.3 DISCUSSION OF RESULTS

Experiments to improve cell integration sensitivity were done without much consideration for cell resistance. Since at very low current levels the series resistor of Figure 3.32 was very large compared to the cell resistance, little consideration was given to cell resistance during the taking of data. It was intended that resistance could be controlled by electrode spacing and concentration of the electrolyte.

Proceeding in this manner, cells of extremely high sensitivity were obtained with noise levels (residual current) as low as 10^{-11} amperes (see for example Figure 3.31). This kind of cell allows reproducible integration of the order of 10^{-9} coulombs with a few percent error.

Experiments to determine cell resistance were at first misleading (see Figures 3.33, 3.34, and 3.35) because of the apparently high resistance at low current levels. Actually this can directly be explained in terms of the behavior of electrodes from a statistical mechanical point of view. The potential, E, across a cell is the sum of the resistive potential drop, i R, and the overpotentials, η_1 η_2 at the two electrodes. The form of these overpotentials can be understood from the following consideration. During equilibrium with no net current through the cell, silver ions move back and forth across the electrode-electrolyte boundary due to thermal motion with a mean current density in one direction j_o. The dependence of j_o on the height of the potential barrier at the boundary is exponential due to the Maxwellian distribution of energies of the ions. The application of overpotentials to the electrodes produces a net current density which is also exponentially related to the overpotential. In fact, the overpotential is of the form:

$$\eta = \alpha \frac{R\,T}{F} \log\,(1 + {}^{j}/_{j_o})$$

where α is a constant of order one, R the gas constant, T the absolute temperature, and F the Faraday. RT/F is about 25 millivolts at room temperature. The slope of the potential versus current at small currents

$$\frac{d\eta}{dj} = \frac{\alpha RT}{F} \frac{\left(\frac{1}{j_o}\right)}{\left(1 + \frac{j}{j_o}\right)} = \frac{\alpha RT}{F} \frac{1}{(j_o + j)}$$

$$R_o = \alpha \left(\frac{d\eta}{dj}\right)_{j=0}$$

is approximately:

$$R_o = \frac{\alpha}{A} \frac{RT}{F} \frac{1}{j_o}$$

where A is the effective electrode area. For small area cells R_o can be large compared to the cell ohmic resistance.

Consideration of the potential drop across the cell as $iR + \eta_1 + \eta_2$ where η has the form given above provides explanation of the Figures 3.33 to 3.35.

4. CONCLUSIONS AND FUTURE WORK

The high sensitivity cells which were obtained exhibited high resistance at low voltage levels. This hampered initial measurements of electromagnetic field strengths at low levels. However, now that the magnitude and origin of this apparent resistance is understood, two remedies are possible. The coupling of the antenna to the diode-cell combination can be designed so that low field strengths produce high voltages and lower currents through the cell. Secondly, the cells can be designed with somewhat larger area electrodes, lowering the resistance for small current levels. Weak electromagnetic fields have already been measured in this manner in a preliminary way.

The next logical step in the present program is to take operating cells and use them in a field test program. Such a program has already been planned.

Other areas of future research are:

1. Investigation of other electrolytes
2. Improve cell packaging techniques
3. Improve sensitivity
4. Investigate high frequency response
5. Expand the sophistication of systems using the cells

These and other areas of investigation are underway and will continue.

APPENDIX

SOURCES OF THE BACK E. M. F. OF THE CELL DURING THE FLOW OF MAXIMUM CURRENT AND AT ZERO CURRENT

I. Back EMF at Maximum Current with both Platinum Electrodes Completely Plated with Silver

It is proposed in this section to advance an explanation as to the probable cause of the back emf shown by the cell during the flow of current when both platinum electrodes are completely covered with silver (current = i_m and the portion of the curve considered being the middle part of AB, Figure 1).

During the flow of electrons through the platinum wire connecting the source of emf with the cathode and anode, from right to left as shown in Figure 2, the cathode becomes negatively charged and attracts the positively charged silver ions, Ag^+, which on contact with the cathode deposit becoming metallic silver, each ion having received an electron from the cathode. At the same time the anode, being positively charged because of the flow of electrons away from it to the cathode under the influence of the applied emf, repels the silver ions, Ag^+, in the silver plating on the platinum anode into the adjacent solution. It is believed from a study of metallurgy that crystalline metals contain their atoms in a charged state; e.g., as Ag^+ ions in the case of silver, and that the valance electrons are free to have a net motion under the influence of an applied emf. In the case of the anode this net motion is upward. It is known from the principles of electro-chemistry (Reference 1, page 438) that during the flow of current with the accompanying migration of silver ions from

the anode to the cathode that the concentration of the silver ions adjacent to the anode is greater than that in the main body of solution and adjacent to the cathode is less than in the main body of the solution. In electrochemistry the term "potential of an electrode" means the potential of the electrode minus the potential of the solution adjacent to the electrode. (Reference 2, page 600.), Although it is common practice in electrochemistry to use the terms potential and emf interchangeably, this practice will not be adopted in this report, the term E being reserved for emf and π for potential (see Reference 2, pages 575-624; and Reference 3, page 52). E and the corresponding value of π are numerically equal but opposite in sign. This distinction will tend to eliminate any confusion in the application of emf or potential values to considerations involving thermodynamics.

The equations giving the electro-chemical reaction and expressing the mathematical relation between the emf of an electrode immersed in a solution of its ions to the concentration of its ions (the Nernst equation) are as follows, respectively:

$$M = M^{+n} + ne \qquad (1)$$

and

$$E_M = E_M^o - \frac{RT}{nF_y} \ln\left[\frac{a_{M^{+n}}}{a_M} (a_{e^-})^n\right] \qquad (2)$$

where E_M = emf of the electrode

E_M^o = standard emf of the electro-chemical reaction $M = M^{+n} + ne$

R = the gas constant = 8.314 joules deg^{-1} $mole^{-1}$

F_y = the Faraday = 96,489 coulombs

T = the absolute temperature in degrees Kelvin

$a_{M^{+n}}$ = the activity of the metal ion M^{+n}

a_M = the activity of the free metal M

and n = number of electrons required to discharge one ion.

Substituting the above numerical values in Equation (2)

$$E_M = E^o_M - \frac{8.314 \times 298.18 \times 2.3026}{n\ 96489} \log \left[\frac{a_{M^{+n}}}{a_M} (a_{e^-}) \right]$$

$$E_M = E^o_M - 0.05916 \log \frac{a_{M^{+n}}}{a_M} \quad \text{at } 25^\circ \text{ C} \qquad (3)$$

where

$a_{M^{+n}} = (M^{+n})\, f_{M^{+n}}$

$f_{M^{+n}}$ = the activity coefficient of the ion M^{+n}

and a_M = unity in the case of a pure metal dipping into a solution of its ions or in the case of an inert electrode, as platinum, completely covered with the metal, M, dipping into a solution of the ions of the metal.

In the case of silver or a platinum electrode completely plated with silver, Equation (1) becomes

$$Ag = Ag^+ + e \qquad (4)$$

and Equation (3) becomes

$$E_{Ag} = E^o_{Ag} - 0.05916 \log (Ag^+)\, f_{Ag^+} (a_{e^-}) \quad \text{at } 25^\circ \text{ C} \qquad (5)$$

(See Reference 2, pages 597-603.) It is to be noted that in Equation (5) (Ag^+) signifies the concentration (in gram-moles per liter) of the silver ion, Ag^+, adjacent to the electrode and that when a current is flowing this concentration is not the same as that in the main body of the solution.

During the flow of the current through the cell, Figures 1 and 2, let

E_{ca} = emf of the cathode

E_{an} = emf of the anode

E = back emf of the cell

and E_c = emf applied across the cell.

$(Ag^+)_{ca}$ = concentration of Ag^+ adjacent to the cathode

$(Ag^+)_{an}$ = concentration of Ag^+ adjacent to the anode

and f_{ca} and f_{an} the respective activity coefficients. It is to be noted that E opposes E_c during the flow of a current and hence is a back emf.

The emf of the cell E is related to the cathode and anode emfs as follows:

$$E = E_{ca} - E_{an} \qquad (6)$$

as $$E_{ca} = E^o_{Ag} - 0.05916 \log (Ag^+)_{ca} f_{ca} \text{ at } 25^\circ \text{ C}$$

and $$E_{an} = E^o_{Ag} - 0.05916 \log (Ag^+)_{an} f_{an} \text{ at } 25^\circ \text{ C}$$

$$E = E^o_{Ag} - 0.05916 \log (Ag^+)_{ca} f_{ca} - \left[E^o_{Ag} - 0.05916 \log (Ag^+)_{an} f_{an}\right]$$ ✓

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a_{e^-} cancel out for whole cell (but not so for the cell reaction previously considered)

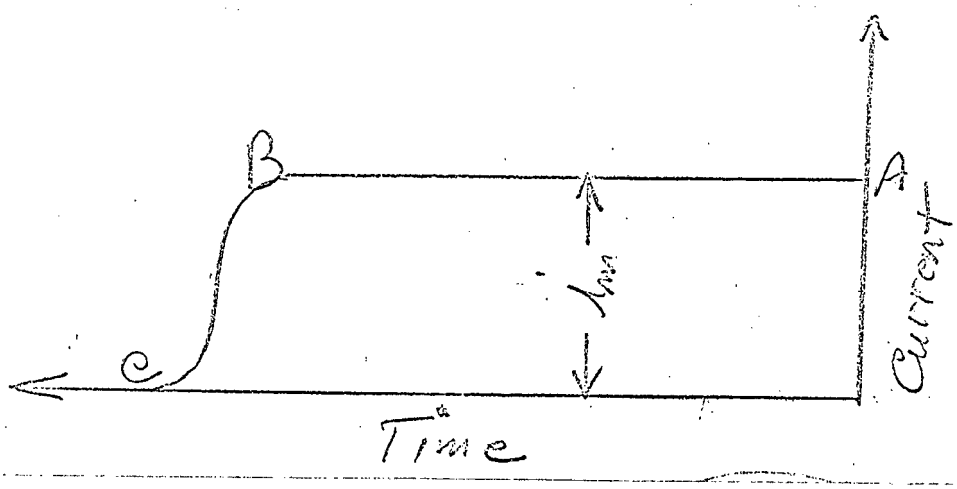


Figure 1. Current - Time Curve

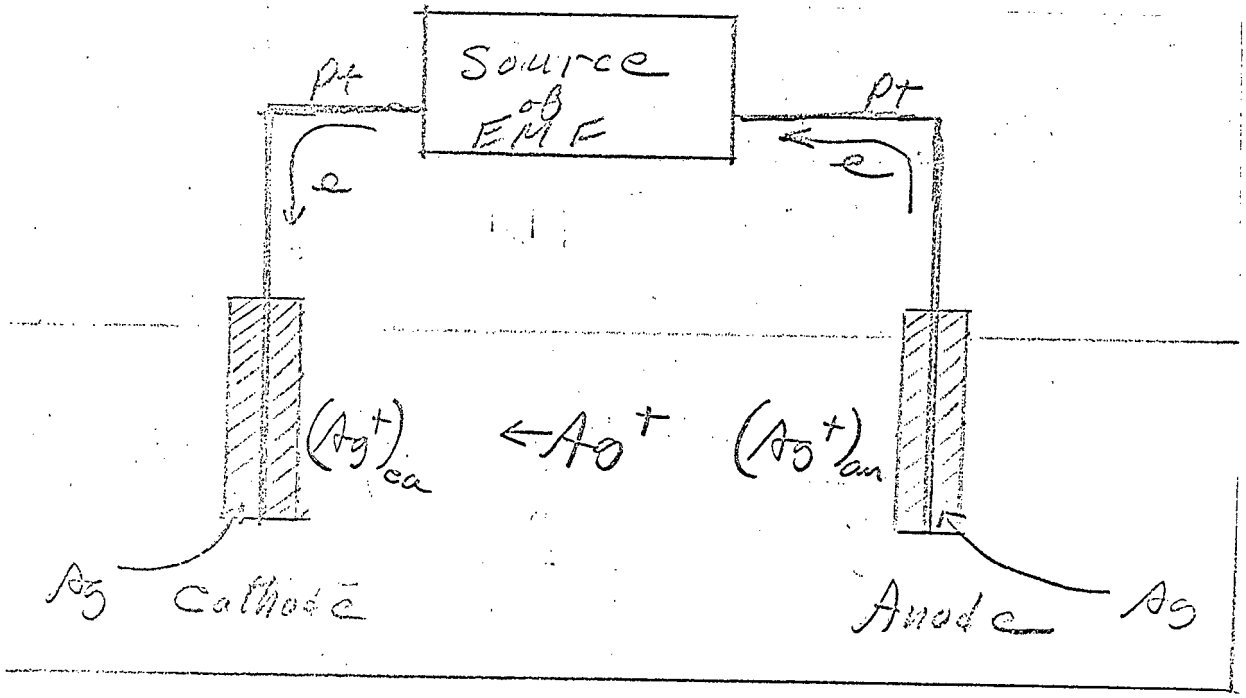


Figure 2. Schematic Diagram of Electrolytic Cell With Both Pt Electrodes Plated With Silver During Flow of Current

$$E = 0.05916 \log \frac{(Ag^+)_{an} f_{an}}{(Ag^+)_{ca} f_{ca}} \quad \text{at } 25^\circ \text{ C} \qquad (7)$$

The activity coefficient of an ion is not constant but varies with the concentration of the ion and with the concentration of other ions if these are present in the solution.

As $(Ag^+)_{an} > (Ag^+)_{ca}$ in Equation (7), f_{an} and f_{ca} are not strictly equal but as an approximation $f_{an} \cong f_{ca}$ and Equation (7) can be written

$$E \cong 0.05916 \log \frac{(Ag^+)_{an}}{(Ag^+)_{ca}} = \text{a positive number} \qquad (8)$$

It is known from the principles of electro-chemistry that, as the current increases for a given cell (due to an increase in the applied emf), $(Ag^+)_{an}$ increases, $(Ag^+)_{ca}$ decreases and as a result E increases (Reference 1, page 438). It is evident that, at the beginning and end of the period of time AB, Figure 1, Equation (8) does not strictly hold because the platinum electrodes are not completely covered with silver.

In two experiments with platinum bottle cell number 24, experiments A-IX and A-VIII of 5-2-62, an attempt was made to verify the above statement that E, the back emf, increases as i_m increases.

Shown in Table I are pertinent data obtained or calculated from these two experiments.

Table I

Experiment	A-IX of 5-2-62	A-VIII of 5-2-62
E (when i = 0)	0.161 V	0.161 V
i_m	0.0125×10^{-6} amp.	0.00240×10^{-6} amp.
R_{eff}	0.895×10^{6} ohms	5.21×10^{6} ohms

The term R_{eff} is the effective or apparent resistance of the cell and is calculated from the equation

$$R_{eff} = \frac{R_3 (i_s - i_m)}{i_m} = \frac{E}{i_m} + R_c \qquad (9)$$

where the terms are defined and equation derived in the section entitled "Derivation of Equations."

As R_c, the resistance of the solution between the two electrodes in the cell, is the same in both examples

$$R_c = R'_{eff} - \frac{E}{i'_m} = R''_{eff} - \frac{E''}{i''_m} \qquad (10)$$

where the primes refer to Experiments A-IX and A-VIII, respectively.

Substituting the values in Table I in Equation (10)

$$0.895 \times 10^{-6} - \frac{E'}{0.0125 \times 10^{-6}} = 5.21 \times 10^{6} - \frac{E''}{0.00240 \times 10^{-6}}$$

$$\frac{E'' \times 10^{6}}{0.00240} = (5.21 - 0.895)\, 10^{6} + \frac{E' \times 10^{6}}{0.0125}$$

and $$E'' = 0.0104 + 0.192\, E'.$$

It is seen, however, that it is impossible to determine that $E' > E''$ from the above relation.

In Table II are given values for E (the galvanic emf of the cell at the tail of the curve when i = 0), the short current i_s, the current through the cell i_m during the time interval AB in Figure 1, the reciprocal of i_m, R_{eff} and R_3 for a series of experiments with platinum bottle cell number 24

Table II

Platinum Bottle Cell No. 24 - 0.11 N $AgNO_3$ and 0.10 N KNO_3

$$R_{eff} = R_c + \frac{E}{i_m} = R_3 \frac{(i_s - i_m)}{i_m}$$

Exp. Desig.	Date Run	Blue No.	E (i=0)	$i_s \times 10^9$	$i_m \times 10^9$	$\frac{10^{-9}}{i_m}$	$R_{eff} \times 10^{-5}$	$R_3 \times 10^{-6}$
A-II	5-1-62	1a	0.358	15.2	14.2	0.0704	14.3	20.34
A-I	5-2-62	2	0.358	15.1	14.3	0.0699	11.4	20.34
A-II	5-2-62	3	0.310	12.5	12.03	0.0830	7.90	20.34
A-III	5-2-62	4	0.271	11.0	9.48	0.1054	32.6	20.34
A-IV	5-2-62	5	0.271	2.10	1.997	0.500	55.5	108.1
A-V	5-2-62	6	0.229	1.88	1.78	0.561	60.6	108.1
A-VI	5-2-62	7	0.192	1.40	1.30	0.768	83.0	108.1
A-VII	5-2-62	8	0.161	1.35	1.19	0.839	145.3	108.1
A-VIII	5-2-62	9	0.161	2.63	2.40	0.416	52.1	54.1
A-IX	5-2-62	10	0.161	13.6	12.5	0.080	8.95	10.21
A-	5-3-62	11	0.161	13.6	12.1	0.0826	12.64	10.21

containing 0.11 N $AgNO_3$ plus 0.10 N KNO_3. In the section entitled "Derivation of Equations" the equation

$$R_{eff} = R_c + \frac{E}{i_m} = R_3 \frac{(i_s - i_m)}{i_m} \qquad (11)$$

is derived.

If E, the galvanic emf of the cell (back emf opposing the applied emf), were the same in all the experiments, the plot of R_{eff} versus $\frac{1}{i_m}$ would be a straight line as seen from Equation (11), R_c being constant.

In Figure 3 the values of $R_{eff} \times 10^{-5}$ are plotted against the respective values of $\frac{1}{i_m} \times 10^{-9}$ and it is seen that a linear relation is not obtained, thus demonstrating that E varies with current.

As described in Reference 1, pages 29-42 and Reference 2, pages 495-505, R_c could be determined for a cell using an alternating current, a Wheatstone bridge, earphones, and a standard solution of K cℓ (1 N, 0.1 N or 0.01 N). The conductivities of the latter are known accurately. (See Table 89, page 499, Reference 2.) Once R_c were known the value of E for any given cell, electrolyte and current could be determined from Equation (11) and in any given cell the relative contribution of $\frac{E}{i_m}$ to the effective resistance could be found.

For platinum bottle cell number 24 an approximate calculation of R_c can be made from the following relation

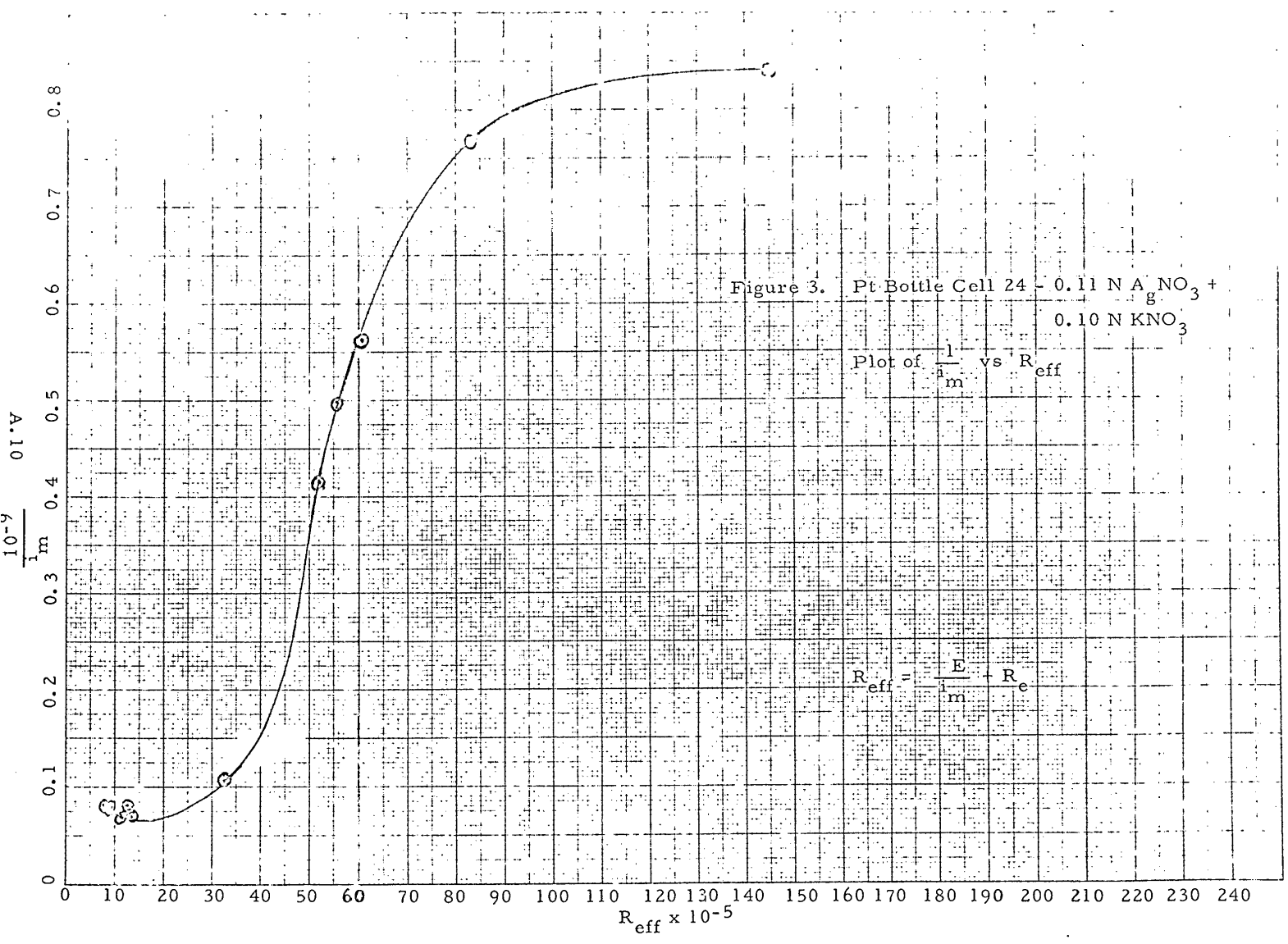
$$R_c = \frac{1000\, d}{NA\lambda} \qquad (12)$$

where d = distance separating the platinum electrodes in cm

N = normality of the solution

A = area of one electrode in cm^2

and λ = equivalent conductance of the solution



As the diameter of the "sphere" platinum electrodes is 0.006" or 0.015 cm

$$A \cong (0.015)^2 = 0.00023 \text{ cm}^2$$

d = 0.7 cm (from measurement)

λ' = 109.14 for 0.10 N $AgNO_3$, Table 91, page 504, Reference 2.

λ'' = 120.40 for 0.10 N KNO_3, Table 91, page 504, Reference 2.

$$\frac{1}{R_c} \cong \frac{1}{R_c'} + \frac{1}{R_c''}$$

where

R_c' = portion of the cell resistance contributed by the $AgNO_3$

and R_c'' = portion of the cell resistance contributed by the KNO_3

$$R_c' = \frac{1000\,d}{NA\lambda'} = \frac{1000 \times 0.7}{0.10 \times 0.00023 \times 109} = 0.28 \times 10^6 \text{ ohms}$$

$$R_c'' = \frac{1000\,d}{NA\lambda''} = \frac{1000 \times 0.7}{0.10 \times 0.00023 \times 120} = 0.25 \times 10^6 \text{ ohms}$$

As $$\frac{1}{R_c} \cong \frac{1}{R_c'} + \frac{1}{R_c''}$$

$$\frac{1}{R_c} \cong \frac{10^{-6}}{0.28} + \frac{10^{-6}}{0.25}$$

$$\frac{1}{R_c} \cong (3.57 + 4.00)\,10^{-6} = 7.57 \times 10^{-6}$$

$$R_c \cong 0.132 \times 10^6 \text{ ohms}$$

In Table III are shown values of i_m and calculated values of R_{eff}, E and $\frac{E}{i_m}$ for two experiments having a high and low value of R_{eff}, respectively, for platinum bottle cell number 24.

TABLE III

Exp.	A-I of 5-2-62	A-VII of 5-2-62
R_{eff}	1.14×10^{6} ohms	14.53×10^{6} ohms
i_m	0.0143×10^{-6} amp	0.00119×10^{-6} amp
E	0.0144 volts	0.0171 volts
$\frac{E}{i_m}$	1.01×10^{6} ohms	14.4×10^{6} ohms

The values of E in Table III are calculated from the relation

$$E = i_m(R_{eff} - R_c) \qquad (13)$$

where $R_c \cong 0.132 \times 10^{6}$

and are only approximate because the calculated value of R_c is, at best, only approximate. It is thus seen that in the case of Experiments A-I and A-VII of 5-2-62, $\frac{E}{i_m}$ seems to contribute a large proportion of the effective resistance.

If it can be concluded from Table III that E is larger when the current is smaller, it is seen that Equation (8) does not hold when considered in relation to statements made in Reference 1, page 438, regarding variations in $(Ag^{+})_{an}$ and in $(Ag^{+})_{ca}$ with increasing current. It might also be indirectly concluded that the platinum electrodes were not completely covered with silver in one of the experiments (Exp. A-VII of 5-2-62) and possibly not in the other experiment from the data of Table III.

II. Back EMF at Maximum Current with both Platinum Electrodes Partly Plated with Silver

According to Rogers and Stehney (Reference 4, pages 26-29), the Nernst equation can be modified to describe the relation of the emf of an inert electrode only partially plated with another metal to the concentration of the ions of the metal in a solution surrounding the electrode. This relationship can be expressed as follows:

$$E_M = E_n^o - \frac{RT}{n\,Fy}\,\ell n\,\frac{a_{M^{+n}}}{f_r\,a_M} \qquad (14)$$

where E_M^o = standard emf of the electro-chemical reaction

$M = M^{+n} + ne$

R = the gas constant = 8.314 joules deg^{-1} $mole^{-1}$

Fy = the Faraday = 96,484 coulombs

T = the absolute temperature in degrees Kelvin

$a_{M^{+n}}$ = the activity of the metal ion M^{+n}

a_M = the activity of the free metal M

n = the number of electrons required to discharge one ion

and f_r = fraction of the inert electrode plated with the metal M.

At 25° C Equation (14) reduces to

$$E_M = E_M^o - 0.05916 \log \frac{a_{M^{+n}}}{f_r\,a_M} \qquad (15)$$

Equation (15) in the case of a platinum electrode partly plated with silver becomes at 25° C

$$E_{Ag} = E^{o}_{Ag} - 0.05916 \log \frac{(Ag^{+})\, f_{Ag^{+}}}{f_r} \qquad (16)$$

where $f_{Ag^{+}}$ = activity coefficient of Ag^{+}

and f_r = fraction of the platinum electrode plated with Ag

It is to be noted that a_M = unity in Equation (15) because of the convention adopted in all electro-chemical equations derived from thermodynamics assigning to the activities of all pure elements, liquid and solid, the value of unity.

A relationship for the emf of a cell containing platinum electrodes partially plated with silver can be derived from Equation (16) as a similar relationship for a cell with platinum electrodes completely plated with silver was derived from Equation (5). Using the same notation as in the derivation from Equation (5) and designating $f_{r\ ca}$ and $f_{r\ an}$ as the fractions of the platinum cathodes and anodes covered with silver, respectively,

$$E_{ca} = E^{o}_{Ag} - 0.05916 \log \frac{(Ag^{+})_{ca}\, f_{ca}}{f_{r\ ca}} ,$$

$$E_{an} = E^{o}_{Ag} - 0.05916 \log \frac{(Ag^{+})_{an}\, f_{an}}{f_{r\ an}} ,$$

$$E = E_{ca} - E_{an} = \underline{\text{back}} \text{ emf of cell} \qquad (17)$$

$$E = E^{o}_{Ag} - 0.05916 \log \frac{(Ag^{+})_{ca}\, f_{ca}}{f_{r\ ca}} - \left[E^{o}_{Ag} - 0.05916 \log \frac{(Ag^{+})_{an}\, f_{an}}{f_{r\ an}} \right]$$

and

$$E = 0.05916 \log \frac{(Ag^+)_{an} f_{an} f_{r\,ca}}{(Ag^+)_{ca} f_{ca} f_{r\,an}} . \qquad (18)$$

Setting $f_{an} \cong f_{ca}$, as before, Equation (17) becomes

$$E \cong 0.05916 \log \frac{(Ag^+)_{an} f_{r\,ca}}{(Ag^+)_{ca} f_{r\,an}} \qquad (19)$$

If, in Equation (17) the anode is silver, it can be seen that $f_{r\,ca}$ increases from zero to one as charging progresses (while $f_{r\,an}$ remains at unity) and also that as a result E will increase until $f_{r\,ca} = 1$ when the cathode is covered completely with silver. These considerations are based, however, on the assumption that $\frac{(A^+g)_{an} f_{an}}{(Ag^+)_{ca} f_{ca}}$ remain constant. This term would not be constant during the initial part of the charging period but would become at least approximately constant as charging progressed. Starting at zero time $(A^+g)_{an}$ increases and $(Ag^+)_{ca}$ decreases while f_{an} and f_{ca} vary slightly and the direction of the variation depends on the values of $(Ag^+)_{an}$ and $(A^+g)_{ca}$ at the time.

It would seem from the above considerations that the average value of E during the charging of a platinum electrode would be less when the platinum anode is completely covered with silver during the entire charging period than when it is not. In addition, as it is known that an increase in the area of one or both electrodes will decrease the value of R_c, the ohmic resistance of the cell, it can be seen that an increase in the area of the anode will decrease the value of R_c. If the area of the cathode is increased, however,

it has been found by experiment that for a given current a limiting area will be reached above which a block-type curve can no longer be obtained. It is thus seen from the equation

$$R_{eff} = \frac{E}{i_m} + R_c$$

that, for a given value of i_m, R_{eff} could probably be reduced in any given cell whose cathode area did not exceed the above mentioned limiting value when a platinum anode of large relative area and completely covered with silver during the entire charging period is used rather than a small anode initially only partly plated with silver.

In Experiment A-II of 5-1-62 (platinum bottle cell number 24) the calculated values of R_{eff} for Run No. 3 (R - L) was 1.43×10^6 ohms while the value of R'_{eff} for Ag - L, the initial charging, was 0.83×10^6 ohms. In this case, the area of the silver wire in contact with the solution was, of course, much greater than that of the left platinum electrode.

III. Back EMF at Zero Current with the Platinum Cathode Completely Plated with Silver

It is proposed in this section to advance an explanation for the emf of the cell at the tail end of the current-time curve when the current is zero (C in Figure 1).

As only a limited number of reactions can occur at the electrodes under these conditions, two probable ones will be considered here.

In Figure 4 is shown a schematic diagram of the cell under these conditions including the electrode reactions.

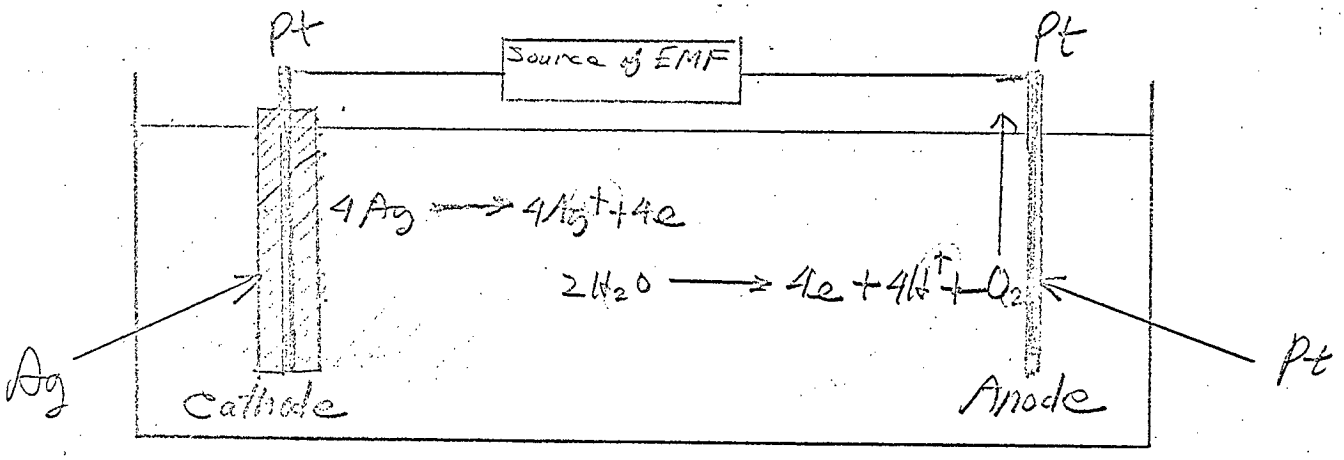


Figure 4. Schematic Diagram of Electrolytic Cell with Platinum Cathode Plated with Silver and Platinum Anode Deplated at Zero Current

Following is a derivation of the equations involved and a calculation of the emf of the cell when the current is zero. This cell emf, being a back emf, is equal and opposed to the emf, E_c, applied across the cell at this point.

$$4Ag = 4Ag^{+} + 4e \quad , \qquad E_{Ag} \tag{20}$$

$$4e + O_2 + 4H^{+} = 2\,H_2O \quad , \qquad -E_{O_2} \tag{21}$$

$$4Ag + O_2 + 4H^{+} = 4Ag^{+} + 2\,H_2O, \qquad E_{Ag} - E_{O_2} \tag{22}$$

Equation (22) is the sum of the two electrode reactions, Equations (20) and (21). It will be noted that as Equation (21) is written with the symbol for the electrons on the left side of the equal sign, its emf, $-E_{O_2}$, must have the opposite sign to the emf E_{O_2} which by convention expresses the emf of that electrode reaction which involves the oxidation of one or more of the reactants (symbols for electrons on right side of equality sign)

$$E = E_{Ag} - (E_{O_2} + w) \tag{23}$$

$$E_{Ag} = E^{o}_{Ag} - \frac{RT}{4Fy}\, \ell n\, (Ag^{+})^{4} f_1^4$$

$$E_{O_2} = E^{o}_{O_2} - \frac{RT}{4Fy}\, \ell n \left[P_{O_2} (H^{+})^{4} f_2^4\right]$$

$$E = E^{o}_{Ag} - \frac{RT}{4Fy}\, \ell n\, (Ag^{+})^{4} f_1^4 - \left(E^{o}_{O_2} - \frac{RT}{4Fy}\, \ell n \left[P_{O_2} (H^{+})^{4} f_2^4\right] + w\right) \tag{24}$$

where f_1 = activity coefficient of Ag^{+},

f_2 = activity coefficient of H^{+},

P = partial pressure of O_2 dissolved in the electrolyte,

E^{o}_{Ag} = standard emf for Equation (20),

$E^{o}_{O_2}$ = standard emf for Equation (21),

w = overvoltage of O_2 on platinum,

and E = emf of cell when $i = 0$.

When $(Ag^+) = 0.10$ (0.10 N $AgNO_3$ solution)

$f_2(H^+) = 10^{-6.7}$ (P H of solution assumed as 6.7)

$f_1 = 0.723$, Table 109, Page 627, Reference 2.

$P = 1/5$ atmosphere

$E^\circ_{Ag} = -0.799$, Table 106, Page 610, Reference 2

$E^\circ_{O_2} = -1.2256$, Table 106, Page 610, Reference 2

$$E = -0.799 - 0.05916 \log (0.10 \times 0.723) + 1.2256 + 0.05916 \log 10^{-6.7}$$

$$+ \frac{0.05916}{4} \log 0.20 - w \text{ at } 25^\circ \text{ C}$$

$$E = -0.799 - 0.05916 (8.8591 - 10) + 1.2256 - 6.7 \times 0.05916$$

$$+ \frac{0.05916}{4} (9.301 - 10) - w$$

$$E = -0.799 - 0.05916 \times 8.8591 + 0.5916 + 1.2256 - 6.7 \times 0.05916$$

$$+ \frac{0.05916 \times 9.301}{4} - \frac{0.5916}{4} - w$$

$$E = -0.799 - 0.5245 + 0.5916 + 1.2256 - 0.3690$$

$$+ 0.1376 - 0.1478 - w$$

$$E = (+0.0875 - w) \text{ volt at } 25^\circ \text{ C} \qquad (25)$$

According to Reference 2, pp. 659-660, w = -0.45 volt when there is a visible evolution of O_2 at the platinum anode and, as the current density decreases, w becomes less negative. Considering that the current is zero in the above derivation, w lies somewhere between zero and about - 0.45 volt.

IV. Back EMF at Zero Current with the Platinum Cathode Partly Plated with Silver

The Nernst equation (Reference 4, Pages 26-29) can also be modified to describe the emf relations existing under these conditions when the platinum cathode is partly plated with silver.

It is assumed that the following cell reactions occur as in Section III.

$$4Ag = 4Ag^{+} + 4e \quad , \quad 4e \, , \quad E_{Ag}$$

$$4e + 0_2 + 4H^{+} = 2\,H_2O \quad , \quad , \quad -E_{o_2}$$

$$4Ag + 0_2 + 4H^{+} = 4Ag^{+} + 2H_2O \, , \quad E_{Ag} - E_{o_2}$$

The equation relating the cell emf E to the silver ion concentration, pH of the solution and partial pressure of 0_2 dissolved in the electrolyte is derived in a manner similar to the derivation in Section III, excepting that the value of E_{Ag}, however, is expressed as in Section II.

Following is the derivation allowing for the fact that the platinum cathode is only partly plated with silver:

$$E = E_{Ag} - (E_{o_2} + w) \tag{26}$$

$$E = E^{o}_{Ag} - \frac{RT}{4Fy} \ln \frac{(Ag^{+})^{4}_{ca} f_1}{f_r} - \left[E^{o}_{o_2} - \frac{RT}{4Fy} \ln (H^{+})^{4} f_2^{4} P + w \right]$$

$$E = E^{o}_{Ag} - \frac{RT}{Fy} \ln \frac{(Ag^{+})_{ca} f_1}{f_r} - \left[E^{o}_{o_2} - \frac{RT}{4Fy} \ln (H^{+})^{4} f_2^{4} P + w \right]$$

$$E = (-E^{o}_{o_2} + E^{o}_{Ag} - w) + \frac{RT}{Fy} \ln \frac{(H^{+}) f_2 P^{1/4} f_r}{(Ag^{+})_{ca} f_1} \tag{27}$$

where f_r = fraction of platinum cathode covered with silver with the other symbols having the same meaning as in Section III.

Using the same values for (H^+) $f_2 P_3$ $(Ag^+)_{ca}$ and f_1 as in Section III Equation (23) becomes at 25° C

$$E = (+ 0.0875 - w + 0.05916 \log f_r) \text{ volt at } 25^\circ \text{ C} \qquad (28)$$

V. Modification of Equations for Back EMF by the Introduction of the Term E_a

This term E_a, according to Rogers and Stehney (Reference 4, Page 30), when included in the Nernst equation will allow for any difference in free energy between the deposition of an atom on a surface of similar atoms and on a surface of dissimilar atoms. In the case of the equations derived in Sections I and II from Equations (6) and (17), $E = E_{ca} - E_{an}$, for the back emf of the cell, the terms E_a cancel out in the expression for E and it is thus seen that any differences in free energy as noted above will not alter the back emf.

In the expressions for E when i = 0 derived in Section III, Equation (23) becomes

$$E = E_{Ag} - E_a - (E_{o_2} + w) \tag{29}$$

Equation (24) becomes

$$E = E^o_{Ag} - E_a - \frac{RT}{4Fy} \ell n \, (Ag^+)^4 \, f_1^4 - \left[E^o_{o_2} - \frac{RT}{4Fy} \ell n \left(P(H^+)^4 \, f_2^4 \right) + w \right] \tag{30}$$

and Equation (25) becomes

$$E = (+ 0.0875 - w - E_a) \text{ volts at } 25^\circ \text{ C} \tag{31}$$

In the equations for E when i = 0 derived in Section IV, Equation (26) becomes

$$E = E_{Ag} - E_a - (E_{o_2} + w) \tag{32}$$

Equation (27) becomes

$$E = \left(- E^{o}_{o_2} + E^{o}_{Ag} - w - E_a \right) + \frac{RT}{Fy} \ell n \frac{(H^+) f_2 P^{1/4} f_r}{(Ag^+)_{ca} f_1} \qquad (33)$$

and Equation (28) becomes

$$E = (+ 0.0875 - w + 0.05916 \log f_r - E_a) \text{ at } 25^{\circ} C \qquad (34)$$

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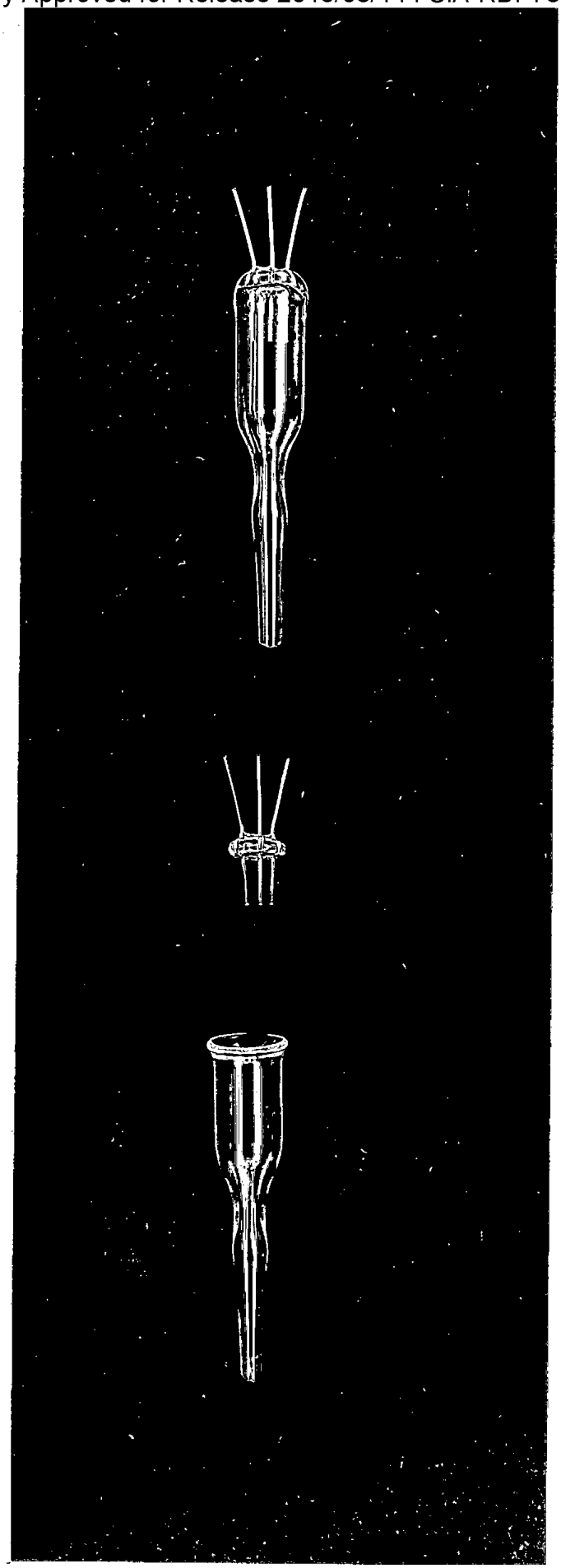

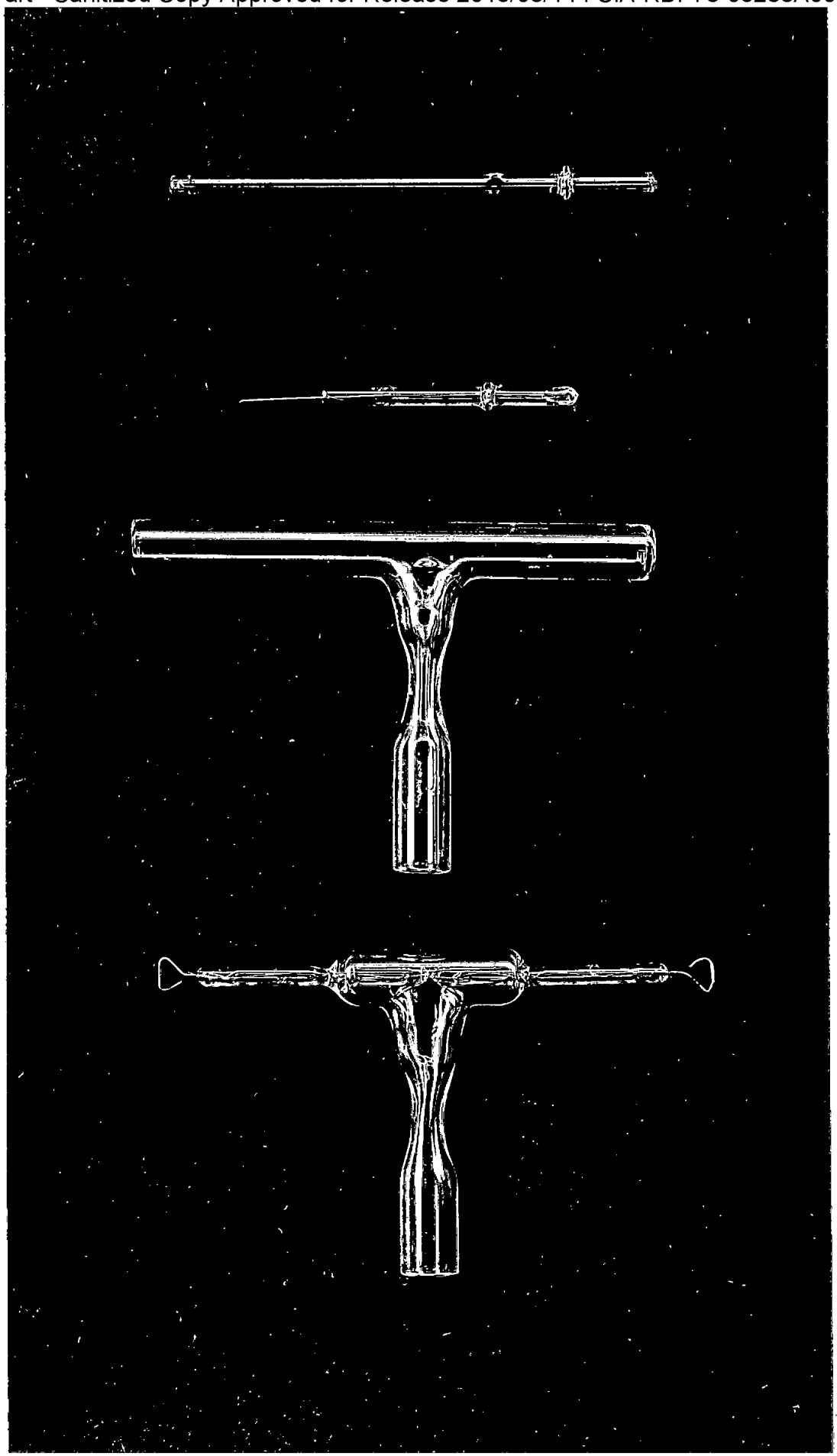

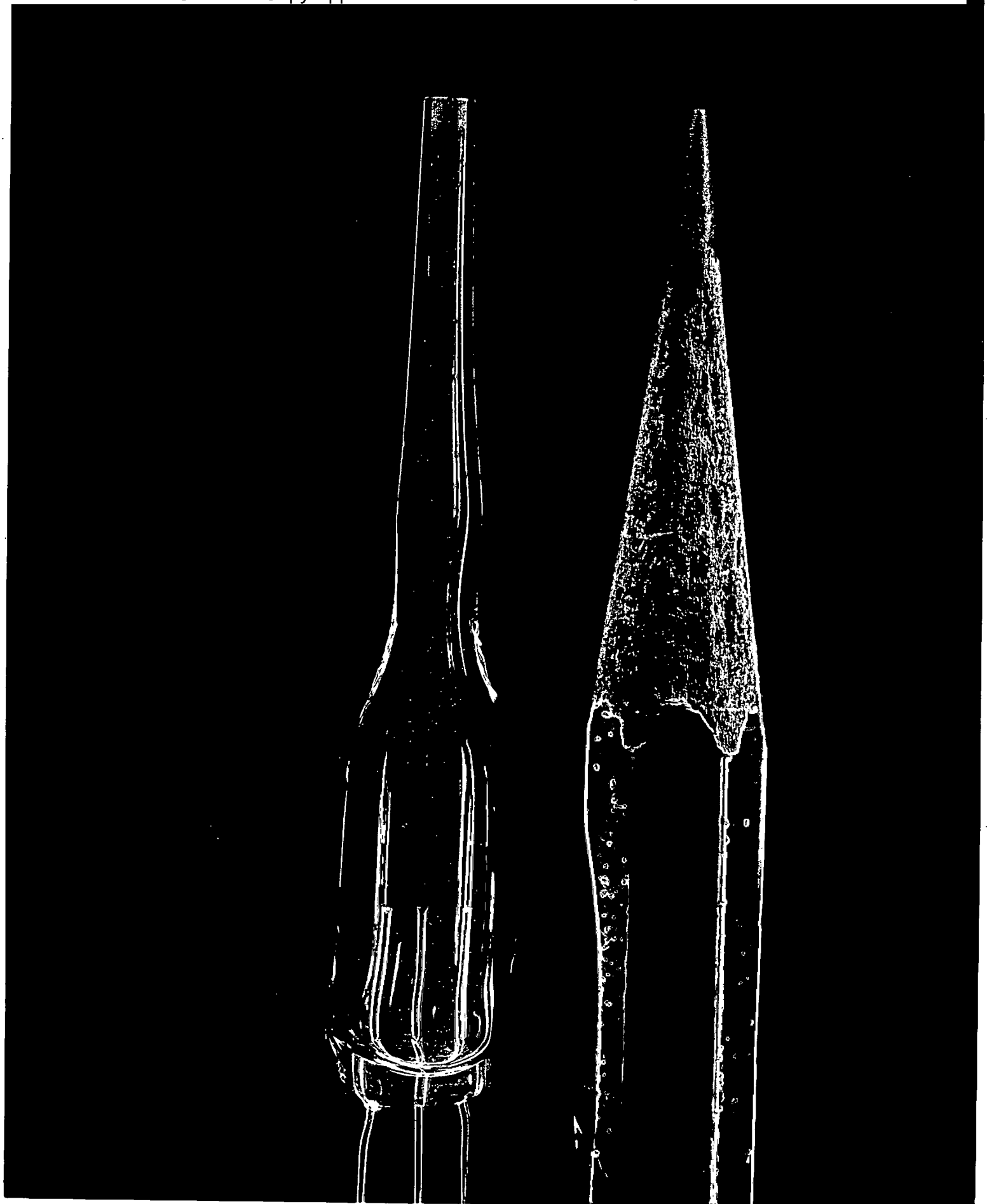

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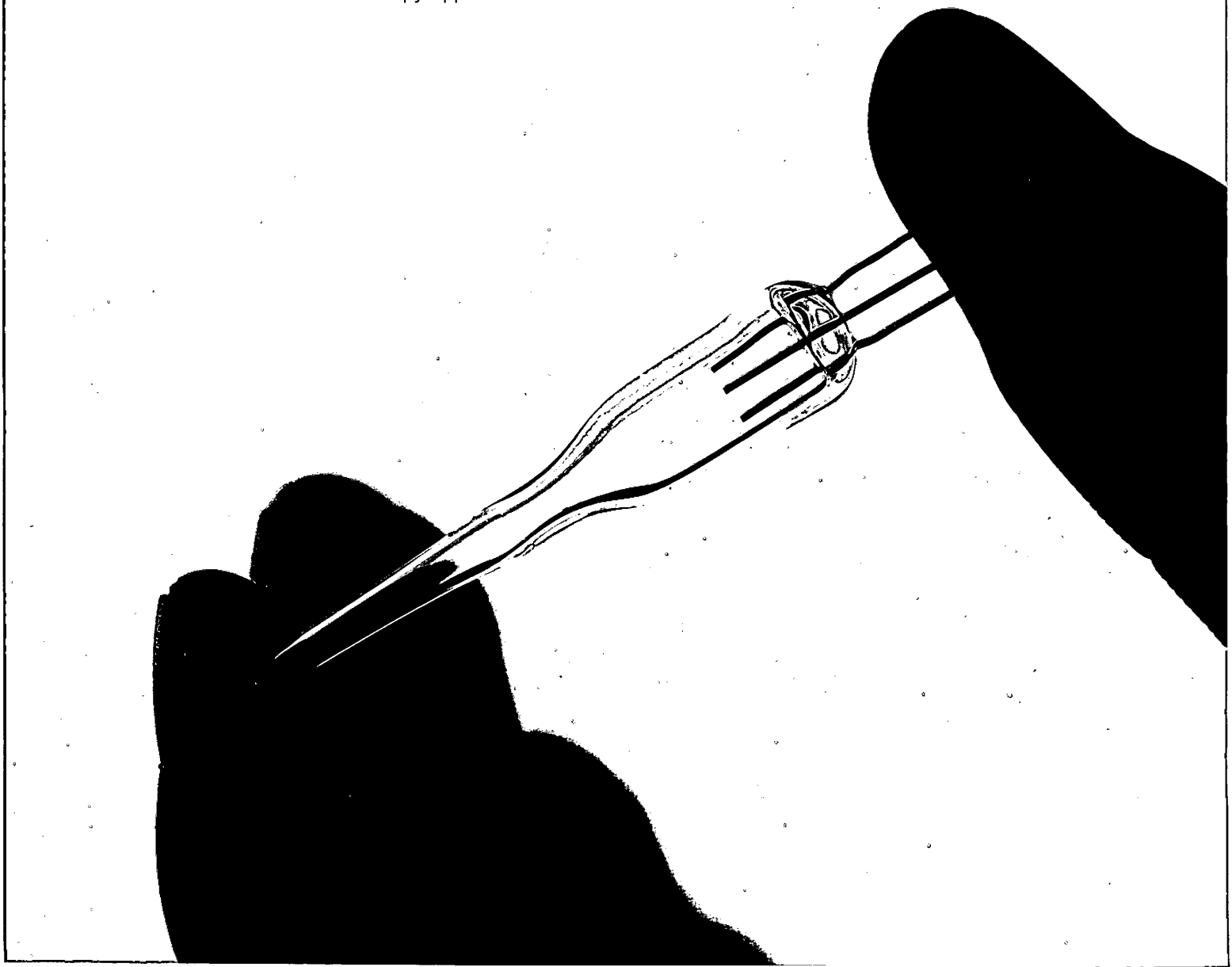

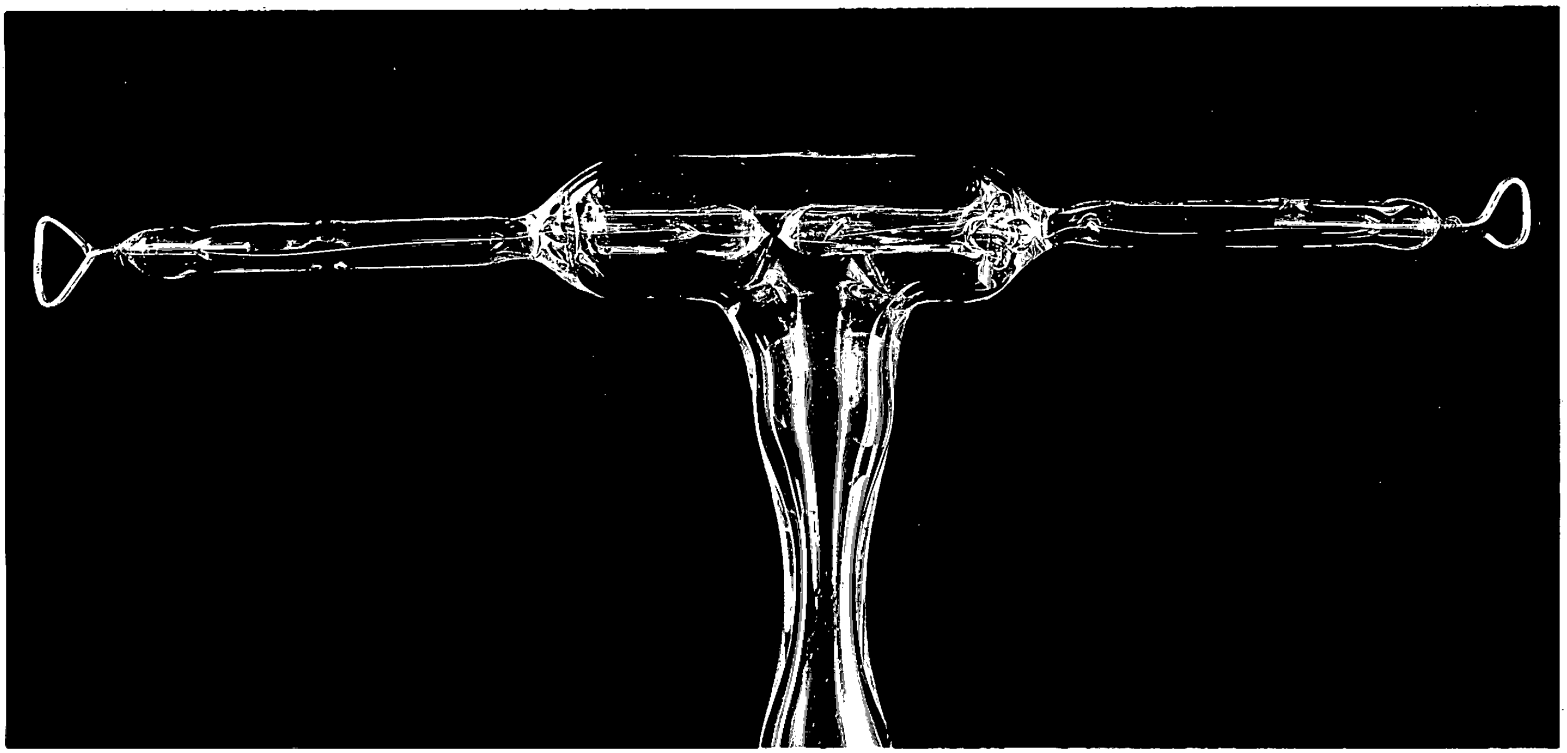

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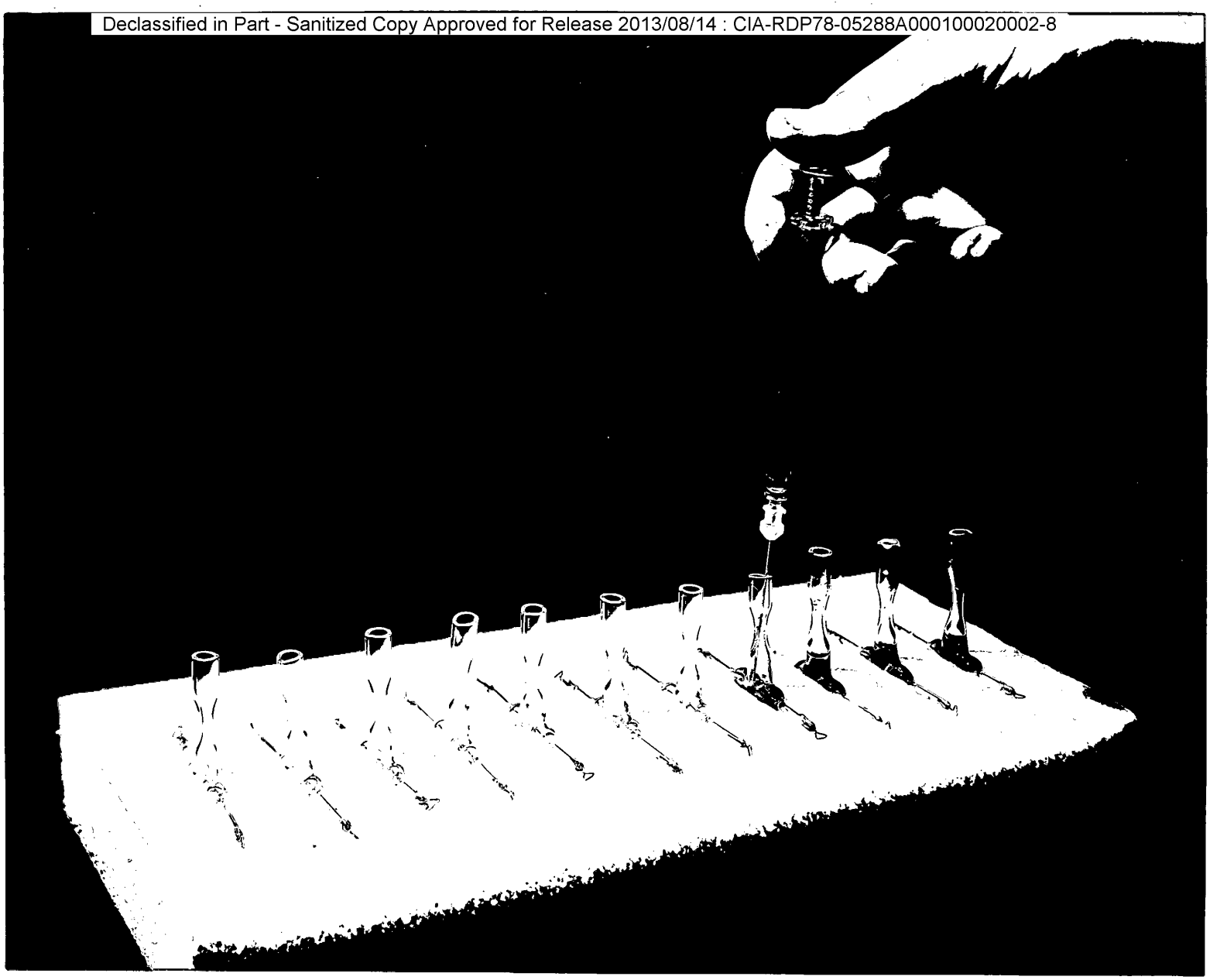

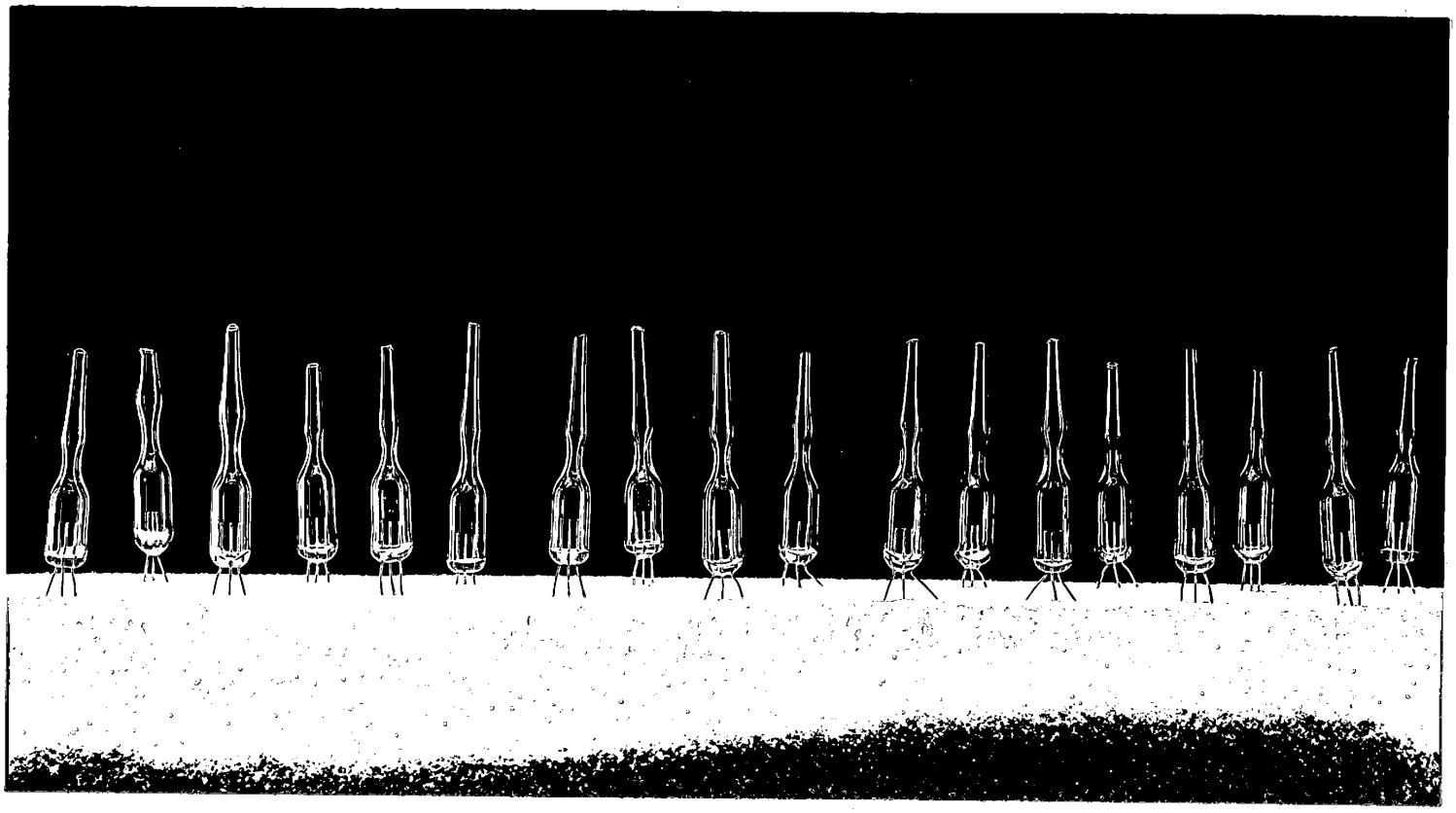

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