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INVESTIGATION OF
BATTERY ACTIVE NICKEL OXIDES

by

P. Ritterman, S. Lerner and H. N. Seiger

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-7620

GULTON INDUSTRIES, INC.
Alkaline Battery Division
Metuchen, New Jersey

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FINAL REPORT

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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CONTRACT NAS 3-7620

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SUMMARY

A study of the structures of the compounds formed on a nickel oxide electrode with respect to charged stand, charge rate, state of charge and during overcharge has been made. This was done by using X-ray diffraction, chemical analysis and spectroscopy. Most of the work was done by means of X-ray diffraction.

It was found that the structure of the discharged state corresponds to ordered $Ni(OH)_2$ and that this structure persists until the electrode is close to the fully charged state. At this point, the structure decays into a randomized NiOOH structure which is essentially amorphous to X-ray diffraction techniques.

Continued high rate overcharging recrystallizes the amorphous material into what is called the γ-NiOOH structure.

Experiments for stabilizing the sintered plate nickel oxide electrode by means of formation at various rates and temperatures indicated that formation procedures have no effect on the charge retention properties of the electrode at elevated temperatures. However, electrodes formed at C/30 and 10°C show an increase in absolute capacity.

The effects of the inclusion of various metal additives to the active material was also investigated as a method of high temperature stabilization. It is shown that the inclusion of cobalt and manganese at the 20 atom percent level significantly increases the charge retention at 65°C, as compared to normal positives and positives containing other metal additives.

INTRODUCTION

A. PURPOSE

The investigations performed under this contract included the following: (1) identification and characterization of nickel oxide electrode materials by a quantitative X-ray diffraction study of the active material as a function of state and rate of charge; (2) an intensive study of stabilization of positive electrode materials at elevated temperatures which included various formation procedures and the inclusion of metal additives to the active material; and (3) studies of the utilization, efficiency, voltage, temperature and cycling characteristics of those positive electrodes stabilized by the most effective method.

B. MEETINGS

Four meetings were held (between Gulton and NASA/Lewis personnel) during the contract period.

The meetings took place on July 28, 1965, December 17, 1965, March 18, 1966, and June 29, 1966, at Gulton Industries, Inc. in Metuchen, New Jersey.

At each meeting, Mr. W. Nagle represented NASA/Lewis, and at the March meeting, he was joined by Mr. H. Schwartz. Drs. R. Shair and H. Seiger and Messrs. P. Ritterman, S. Lerner and R. Michaels were present for Gulton Industries. Professor P. Vaughan, of Rutgers University, consultant to Gulton Industries, was present at the December and March meetings.

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ABSTRACT

A study of the structures of compounds formed on a nickel oxide electrode with respect to charged stand, charge rate, state of charge and during overcharge has been made. This was done by using X-ray diffraction, chemical analysis and spectroscopy. Most of the work was done by means of X-ray diffraction.

It was found that the structure of the discharged state corresponds to ordered $Ni(OH)_2$ and that this structure persists until the electrode is close to the fully charged state. At this point, the structure decays into a randomized NiOOH structure which is essentially amorphous to X-ray diffraction techniques. A theory is presented to account for these structural changes.

Continued high rate overcharging recrystallizes the amorphous material into what is called the γ-NiOOH structure.

Experiments for stabilizing the sintered plate nickel oxide electrode by means of formation at various rates and temperatures indicated that formation procedures have no effect on the charge retention properties of the electrode at elevated temperatures. However, electrodes formed at C/30 and 10°C show an increase in absolute capacity.

The effects of the inclusion of various additives to the active material was also investigated as a method of high temperature stabilization. It is shown that the inclusions of cobalt and manganese at the 20 atom percent level significantly increases the charge retention at 65°C as compared to normal positives and positives containing other metal additives.

I. OUTLINE OF PROGRAM

The program was divided into two parts. The first involved a continuation of the investigation into the qualitative and quantitative nature of the sintered nickel oxide electrode, begun under Contract No. NAS3-4178. This investigation was carried out by the use of chemical, electrochemical, and X-ray diffraction techniques as methods of analysis. The second part concerned itself with methods of stabilizing the nickel compounds formed during charge of the positive electrode. The stabilization methods used included: (1) additives (the inclusion of foreign materials within the structure of nickel oxide crystals; and (2) formation at various currents and temperatures. Plates made by these methods have been evaluated with respect to retention of charge on stand, and performance on charge and discharge (4 cycles).

A. IDENTIFICATION AND CHARACTERIZATION OF BATTERY ACTIVE MATERIAL EXISTING IN THE NICKEL OXIDE ELECTRODE

1. Construction of Test Cells

a. Plates

Positive plates were used, all of which were impregnated at the same time with $Ni(NO_3)_2$ and then chemically converted to $Ni(OH)_2$.

b. Stacks

Single positive plates were surrounded by excess negative capacity in the form of two sintered cadmium electrodes with two layers of non-woven nylon serving as separator and 34% KOH as electrolyte.

2. Formation Treatment

Thirty cores were constructed and cycled using the following regime:

a. Charge at C/10 for 16 hours.
b. Discharge to 0 volt at C/3.
c. Short for 2 hours.

This was repeated 3 times. Twenty cells most alike in capacity were chosen for further testing in Part 3.

Thirty additional cores were constructed and formed for use in Part 4.

3. Effect of State of Charge and Rate of Charge

a. After the third formation cycle was completed, 10 cells were charged at C/2 for 4 hours.

b. Two cells were discharged at C/2 for 1 hour.

c. Two cells were discharged at C/2 to 1.0 V.

d. Two cells were discharged at C/2 for ½ hour.

e. Two cells were allowed to retain their fully charged state.

f. Two cells were charged to the gassing point of the positive plate.

After a 24 hour stand on open circuit, the cells were taken apart and the positive plate analyzed by X-ray diffraction and electrochemical means.

Steps a. to f. were carried out at the C/10 rate.

4. Stand Time at Various Temperatures

After preparing 24 cells chosen from 30 (those most alike in capacity), they were charged at C/10 for 20 hours at room temperature. Twelve of the cells were then disassembled immediately and the positives placed in beakers of 34% potassium hydroxide. The remaining 12 cells remained as they were. Four disassembled cells and four assembled cells were placed in an oven at 50°C. A like number of cells were placed in a cold box at 10°C and the remaining cells were kept at 25°C. After 24 hours, two disassembled positives, along with two positives from the assembled cells, taken from each temperature stand were analyzed. The remaining positives and cells were kept at their respective temperatures for three months and then analyzed.

5. Methods of Analysis

The plates were analyzed by X-ray diffraction and chemical methods.

a. Chemical Means

Emphasis was placed on chemical analysis for quantitative determination of Ni, H, O and the oxidation state of the nickel in the active portion of the plate.

(1) Nickel

In a sintered plate, the interference of pure nickel was eliminated. Total nickel could then be determined by electroplating or precipitation in alkaline solution as nickel dimethylgloxime.

(2) Hydrogen

A washed and dried sample was mixed with K_2CrO_4 and $PbCrO_4$ and heated to 600°. The water vapor then produced was captured in a weighed drying tube.

(3) Oxygen

Oxygen can best be determined by difference, with respect to the total nickel and hydrogen determined.

(4) Nickel Valence

The valence of the active nickel was to be determined by iodometric titration and concurrent analysis for active nickel.

b. X-ray Diffraction

All X-ray diffraction data were obtained using uncovered samples.

Two goniometer scan speeds were used. For qualitative work, a speed of 2° (2θ) per minute (40 minute scan time) was used, and for quantitative structural determinations, a scan speed of 1/8° (2θ) per minute (8 hour scan time) was used.

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation at Various Temperatures and Rates

Cells were constructed using one unformed sintered positive surrounded by two negative plates. Formations were performed at the C/2, C/10, and C/30 rates and at temperatures of 10°, 25° and 80°C for each rate. Three cells were formed at each rate and each temperature for 3 cycles.

2. Additives

Impregnating nickel solutions were prepared containing 20 metal atom percent Li, Na, Be, Mg, Ba, Co and Mn. Additional impregnating solutions containing 5 and 10 metal atom percent of the above additives that yielded optimum results were prepared. A control solution of pure nickel nitrate was also prepared.

For each quantity and additive type, 10 plates were impregnated and formed by the standard procedure.

C. PRELIMINARY EVALUATION

Electrodes stabilized by the above described methods were evaluated in the following manner.

1. Storage and Evaluation

At least three cells of each group were constructed. The capacity was determined as follows:

a. C rate charge for 2 hours.

b. Immediate discharge at C/5 to 0.0 V.

This charge was repeated. After various stand times at different temperatures, the cells were again discharged at C/5 to zero volts.

This was done at 25°C, 50°C, 40°C and 65°C. A check of capacity on immediate discharge at room temperature was made before and after each stand test.

2. Electrochemical Stabilization Tests

Samples of each group were cycled for 4 cycles at C/10 charge--C/5 discharge at room temperature. Methods of evaluation included capacity, reproducibility of results with respect to capacity, efficiency and voltage level.

D. EVALUATION OF IMPROVED MATERIAL

After establishing a superior material, or a group of superior materials, with respect to stabilization, the following tests were made.

1. Decomposition of Charged Positive

Using 15 cells consisting of the superior material, with respect to stabilization, the following tests were performed.

Cells were allowed to stand at temperatures of 20°, 40°, 60°, 80°, and 95°C and after a passage of 1 day, removed and discharged at the C/5 rate to a 1.0 V end point at room temperature. The capacity of all cells was determined immediately after charge at the C rate. This was repeated by charging the same cells at the C rate and extending the stand time to 3 days. The test was repeated allowing just the charged positive plates to be immersed in electrolyte at the various temperatures, the capacity of which, again, had been previously determined. These plates were then surrounded by negatives and discharged to 1.0 V at the C/5 rate. This, too, was repeated, extending the charged stand time if significant differences were noted between the 1 and 3 day stand.

2. Investigation of Sintered Plate parameters

a. Establishment of Optimum Formation Technique

The optimum formation is considered to be the one which produces a plate that, when incorporated into cells, yields the highest voltage level on discharge, the greatest capacity per unit weight and volume, optimum charge efficiency, and most consistent reproducibility of the aforementioned results.

b. Establishment of Charge Acceptance as a Function of Charge Rate, and Determination of Point of Oxygen Evolution at Various Rates

The characteristics of positive plates could be established with one experiment. A positive plate is contained in a sealed chamber of known volume together with an oxygen consuming electrode. Both the oxygen electrode and the positive plate have external connections allowing for charge. The sealed chamber is filled with pure oxygen and a pressure gauge records oxygen pressure. As current is passed to charge the positive plate and cause oxygen reduction at the appropriate electrode, the rate of oxygen pressure decay should be in direct proportion to the charging current provided that no oxygen is produced at the positive. The deviation from the theoretical slope not only establishes the charge acceptance, but also indicates the point at which oxygen evolution begins.

c. Determination of Utilization Factors at Various Rates of Discharge.

The three plate cells, consisting of 1 positive and 2 negative electrodes, were again employed here. All charges were done at the 1 hour rate. Discharges were performed at the 10 minute, 1 hour, two hour five hour, and the 10 hour rates. Capacities were determined to 1.0 V and 0.0 V.

d. Determination of Utilization Factors for Depth of Discharge at 25%, 35%, 50%, 75% and 100%

A group of three plate cells were charged at the C rate. After the initial charge, the cell was discharged for 15 minutes at the C rate. It was then charged for 15 minutes at the C rate and finally discharged to 1.0 V and 0.0 V at C rate. This was repeated for a 21 minute discharge, a 30 minute discharge, and similarly to obtain the other stated depths of discharge. A comparison was made of the capacities obtained when discharging to 1.0 V and 0.0 V versus the various depths of discharge.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. EXPERIMENTAL PROCEDURES

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State of Charge and Rate of Charge

(1) Construction of cells

Thirty cells consisting of 1 positive and 2 negatives were assembled as described in Section I. Each positive plate had the dimensions of 1-7/8 x 2-1/8 x .035" and contained 3.4 grams of $Ni(OH)_2$.

(2) Formation Procedure

All cells were charged at 100 ma for 16 hours and discharged immediately at 400 ma to 0.0 V. Upon completion of discharge, cells were shorted for 2 hours. This procedure was repeated twice more.

(3) Selection of Cells and Test Procedures

Based on the capacity of the third formation cycle, 20 cells were chosen for further testing. Six of the 20 cells were charged at 500 ma for 4 hours. Two of these were discharged at the same rate for ½ hour. Two others were discharged at 500 ma to 1.0 V. The remaining two cells were kept at their fully charged state.

All six cells stood on open circuit for a period of 24 hours after which time they were disassembled and their positives placed in separate polyethylene bags. Just before being placed in the goniometer of the X-ray diffraction apparatus, each positive was removed from its polyethylene container. Thus, X-ray diffraction patterns were obtained from plates wet with KOH and uncovered.

Six other plates were charged at 100 ma for period of 20 hours. Two were discharged at 100 ma for 2½ hours; two were discharged at the same rate to 1.0 V; and two retained their fully charged state. Upon completion of their electrochemical treatment, all six cells were disassembled, their positives placed in polyethylene bags which were removed before X-ray diffraction patterns were taken.

b. Effect of Stand Time at Various Temperatures

(1) Construction of Cells

Thirty cells, consisting of 1 positive and 2 negatives, were assembled. Each positive plate had dimensions of 1-7/8" x 2-1/8" x .035" and contained 3.4 grams of $Ni(OH)_2$.

(2) Formation Procedure

All cells were formed at 100 ma. The charge lasted for 15 hours, then discharged until the cells reached zero volts. Upon completion of discharge, the cells were shorted for 2 hours. This procedure was repeated twice more.

(3) Selection of Cells and Test Procedures

Based on the capacity of the third formation cycle, the 24 cells most alike in capacity were charged at 100 ma for 20 hours at room temperature. Twelve of the cells were then disassembled in the charged state and their positives placed in beakers of 34% potassium hydroxide. The other 12 cells remained as they were. Four plates and four cells were placed in an oven at 50°C. A like number of cells and plates were placed in a cold box at 10°C, and the remaining cells and plates were kept at room temperature. After a stand of 24 hours, a plate and a cell were removed from each temperature ambient, the cells disassembled, and all plates X-rayed. After 48 hours, another cell and plates were removed from each ambient and the positive plates X-rayed. The remaining cells and plates were retained at their respective temperatures for a three month period at which time the positives were X-rayed.

c. Methods of Analysis

Various methods of chemical analysis were attempted to determine quantitatively the amounts of active nickel, oxygen and hydrogen content and the average nickel valence on the sintered plate.

(1) Analysis of Active Nickel

Active nickel can be determined by heating the electrode in a solution of ammonium hydroxide-ammonium acetate. This solution will dissolve only the oxidized nickel leaving the sintered substrate unattacked.

(2) Analysis of Hydrogen

The amount of hydrogen in a sample of pure $Ni(OH)_2$ was determined by means of oxidation of the hydrogen by K_2CrO_4 and $PbCrO_4$. The details of the analysis are given below.

A combustion tube was set up in the following manner. At the exit end was one inch of copper gauze, then 12 inches of lead chromate, followed by 4 inches of copper gauze. The sample crucible was placed in next, followed by another four inches of copper gauze. The section of the combustion tube was heated first to 300°C while dry air passed through the system. When all moisture had been removed, the section under the sample cruxible was heated to 700°C. The exiting stream of water vapor was caught in a weighed drying tube containing Drierite. The flow of air was adjusted to 2 ml/sec. The amount of hydrogen in a sample was determined from the weight of water trapped in the Drierite tube.

(3) Analysis of Oxygen

Oxygen content is determined by difference with respect to the total nickel and hydrogen content.

(4) Analysis for the Oxidation State of Nickel

The oxidation state of nickel was determined in the following manner.

The sample was placed in a beaker of alkaline KI. The sample was then dissolved by addition of dilute sulfuric acid to Ph 1.5. The iodine liberated by the reduction of nickel in oxidation states greater than 2 to Ni^{++} is titrated with a standard solution of $Na_2S_2O_3$. The total amount of nickel present was determined by electroplating on a platinum grid. A sintered plate was also analyzed by this method.

d. Preparation of $Ni(OH)_2$

Pure $Ni(OH)_2$ was prepared as another X-ray standard by addition of KOH to $Ni(NO_3)_2$ solution. The resulting precipitate was filtered through a Buchner funnel, washed and dried. It was analyzed for nickel valence using the method described above.

e. High Valence Nickel Oxide

With the hope of producing a standard for X-ray, a nickel oxide compound was prepared by slow addition of a solution consisting of .34N NaOCl and 6.45N in KOH to 200 ml of .17N $Ni(NO_3)_2$ solution. When the resulting precipitate had settled, the supernatant liquid was removed by decantation and the solid washed twice with fresh base. The sample was stored in a beaker of 34% KOH.

f. γ-NiOOH ($Ni_2O_3 \cdot H_2O$)

With the intent of preparing an X-ray standard, a compound was prepared by the method of Cairns and Ott(8) which was analyzed by them and found to have the composition of $Ni_2O_3 \cdot H_2O$. This compound is a dimer of NiOOH and the reported X-ray data are similar to that given by Glemser and Einerhand(7) for γ-NiOOH.

2. Stabilization of Nickelic Oxides and Hydroxides

a. Formation

(1) Construction of Test Cells

Thirty standard cells consisting of 1 positive and 2 negatives were assembled. Each positive plate contained 3.4 grams of $Ni(OH)_2$.

(2) Formation Procedure

Cells were formed in groups of 10 at 100 ma at 25°C, 35 ma at 10°C, and 100 ma at 80°C. The charge at each rate was of such duration as to equal 150% of the theoretical capacity of the cell, which amounted to 15 hours for the 100 ma charges and 45 hours for the 35 ma charges. The discharge was to zero volts, followed by a minimum of a 2 hour short.

Cells received 3 formation cycles.

(3) Effect of Stand

The evaluation of the positive plates formed at 10°C-35 ma, 25°C-100 ma, and 80°C-100 ma was performed in the following manner.

Six cells from each group of ten were charged at 1 ampere for 2 hours and then immediately discharged at 200 ma and room temperature to 0.0 V. After an overnight short, they were again charged at 1 ampere for 2 hours. The cells were disassembled and the positives allowed to stand in separate beakers of KOH, at room temperature, for a period of 3 days, and then discharged at 200 ma at room temperature to 0.0 V. Cells were again shorted overnight and test procedure described above was repeated at a 50°C and 65°C three day stand for the charged positives.

(4) Effect of Cycling

The four remaining cells from each group were cycled 4 times. Each charge was for a period of 16 hours at 100 ma, followed immediately by a discharge at 200 ma to a cell voltage of 0.0 V. All cells were shorted for 2 hours between cycles.

b. Additives

(1) Impregnation of Sintered Plates

Sintered plates, 1-7/8 x 2-1/8 x 0.035" were vacuum impregnated with nitrate solutions containing 80 metal atom % Ni and 20 metal atom % of the additives Li, Na, Be, Mg, Ba, Co and Mn. Ten plates were prepared for each additive. In addition, 10 plates were impregnated with pure nickel nitrate. Conversion to the hydroxide was done in 25% KOH at 70°C. The impregnation and conversion procedure was repeated until the plates had gained approximately 3 grams.

(2) Construction of Test Cells

The eighty test cells were prepared using the standard three plate cell technique. Each group of ten cells was then sub-divided into two groups; one of six cells and one of four cells.

(3) Effect of Cycling

Four cells from each group were cycled 4 times. Each charge was for a period of 16 hours at 100 mA, followed immediately by a discharge at 200 ma to a cell voltage of 0.0 V. All cells were shorted overnight between cycles.

(4) Effect of Stand

The remaining six cells from each group were charged at 1 ampere for two hours and were then immediately discharged to 0.0 V at 200 ma at room temperature. The cells were then shorted overnight and again charged at 1 ampere for 2 hours. The cells were allowed to stand in the charged state for 3 days at room temperature; following this stand, the cells were discharged at 200 ma to 0.0 V and shorted overnight. This cycle was repeated for a 3 day stand at 65°C and again for a 7 day stand at 65° for a group of cells containing selected additives.

B. EXPERIMENTAL RESULTS

1. Determination of Battery Active Materials Existing in the Sintered Plate Nickel Oxide Electrode

a. Effect of State and Rate of Charge

(1) Formation

The discharge capacities obtained during formation of the 30 sintered plates are shown in Table I. The check marks indicate the 20 cells chosen for further testing.

(2) Preparation for and X-ray Analysis of Positive Plates at Various States of Charge

(a) C/2 Rate - The six cells used for this test were numbers 7, 8, 9, 10, 11 and 12. Cells 7 and 8 were left fully charged and the X-ray diffraction pattern obtained from their positives is shown in Figures 1 and 2 respectively. Cells 9 and 10 were discharged for ½ hour (C/2 rate) and the X-ray patterns from their 3/4 charged positives are shown in Figures 3 and 4. The remaining two cells were discharged to 1.0 V (C/2) rate), cell number 11 requiring 125 minutes to reach that voltage. Figure 5 and 6 are the respective X-ray diffraction patterns obtained for these positive electrodes.

(b) C/10 Rate - Cell numbers 22, 23, 24, 25, 26 and 27 were used for this test. The patterns obtained from the positives of these cells appear in Figures 7 through 12 respectively. Cells 24 and 25, which were discharged to 1.0 V, required 10 hours and 28 minutes and 9 hours 22 minutes, respectively, to reach their required voltage. Cells 22 and 23 were discharged 2½ hours and the remaining two cells retained in the fully charged state.

The major peaks and their intensities are shown in Table II for both rates.

(3) Quantitative Structure Determination

Figure 13 shows X-ray diffraction patterns obtained by slow scan between 10° and 40°. Three peaks obtained correspond to the three major peaks of $Ni(OH)_2$. Patterns of the discharged state, 75% charged, 90% charged, and 100% charged and 133% charged are shown.

Figure 14 shows the diffraction patterns obtained from 200% to 550% charged.

(a) Effect of Stand at Various Temperatures

The capacities of the additional 30 cells on their final formation discharge are listed in Table III. Numbers marked with an asterisk indicate the 24 cells chosen.

Figures 15 to 31 are the X-ray patterns from positive electrodes stored at various ambient temperatures for 24 and 48 hours and 3 months.

b. Chemical Analysis of a Discharged Electrode

(1) Active Nickel

An impregnated discharged electrode of known weight was treated with a mixture of ammonium hydroxide and ammonium persulfate. After two hours in solution, the plate was washed, dried and reweighed. The impregnated plate weighed 8.583 g initially, and after treatment 5.427 g. Since the weight gain during impregnation was 2.963 g, approximately 190 mg of sinter was converted to active nickel. The $NH_4(OH)-(NH_4)_2S_2O_8$ solution was then electrolyzed at 3.0 V between a platinum wire anode and a platinum grid cathode. The electrolysis was continued until the solution tested negative for nickel with dimethylglyoxime. The total amount of active nickel was determined to be 1.934 grams. The total active material equals

$$2.963 + 0.190 = 3.153 \text{ grams}$$

Thus, the percent Ni = 1.934/3.153 = 61%

(2) Hydrogen

A plate containing 2.831 grams of active material yielded 0.0666 grams of hydrogen.

Assuming about the same percentage of nickel sinter was converted to active material as in the above case, then the total active material is is 3.013. The percent hydrogen equal to 0.0666/3.013 = 2.2%

(3) Oxygen

Oxygen is determined by difference.

$$\% \text{ O} = 100 - (61\% + 2.2\%) = 36.8\%$$

(4) Formula Weight

By dividing these percents by the atomic weights H = 1, Ni = 58.7, O = 16 we obtain

$$\frac{6.1\%}{58.7} = 1.04 \qquad \frac{2.2\%}{1} = 2.2 \qquad \frac{36.8\%}{16} = 2.3$$

On this basis, the discharged plate has the formula $Ni(OH)_{2.2}$

c. Average Nickel Valence

From the values of the oxidation state, shown in Table IV and the duplicate determination of one of the charged states, it is apparent that the fraction of trivalent nickel is precise to ± 20%. At the 50% charge level, average valence is 2.3, and at the fully charged (100%) level, the average valence is 2.5. The composition at 500% charged, at which state the electrode has previously been shown to be composed of γ-NiOOH(4), is 2.75.

d. Nickel Hydroxide Standard

Three major peaks from the X-ray diffraction pattern of $Ni(OH)_2$ are shown in Figure 32.

e. High Valence Nickel Oxide and Oxidation State

The oxidation state of the nickel in the high valence oxide was determined to be 3.07. Table V shows the data used in determining the average valence.

The X-ray pattern, shown in Figure 33 shows the compound to be amorphous.

f. γ-NiOOH ($Ni_2O_3 \cdot H_2O$)

The X-ray pattern for this compound is shown in condensed form in Figure 34 and the X-ray "d" spacings and integrated intensities were obtained by measuring the areas under the peaks with a mechanical integrator, as shown in Table VI.

The oxidation state of the nickel oxide was determined to be 2.79 ± 20%.

2. Stabilization of Nickelic Oxides and Hydroxides

a. Formation

(1) Capacities

The capacities to 0.0 V during each formation cycle of plates formed at different rates and temperatures is shown in Table VII.

(2) Effect of Stand

The capacities obtained from the cells with different formation histories are listed in Table VIII for immediate discharges and discharges after a 3 day stand at room temperature, 50°C and 65°C. The immediate discharge capacities were taken initially and before each elevated temperature testing.

The effect of stand is shown in graphic form in Figure 35 using the average value of the immediate discharge capacity as 100% charge retention.

(3) Effect of Cycling

Table IX shows the capacities of 4 cells in each group for 4 consecutive cycles. Figure 36 shows a typical discharge curve for each formation group.

b. Additives - 20% Level

(1) Preparation of Plates

Tables X through XVII list the weight gain, theoretical capacity and experimental capacity on the third formation cycle of cells with positives containing, respectively, 20 metal atom percent of beryllium, magnesium, lithium, sodium, manganese, cobalt, and barium along with the control cells.

(2) Effect of Cycling

Table XVIII shows the capacities of 4 cells in each group for 4 consecutive cycles. Figures 37 and 38 show a typical discharge curve for each group.

(3) Effect of Stand

Table XIX shows the capacities of 6 positives from each additive and control group on immediate discharge, 3 day stand at 25°C, 3 day stand at 65°C, and for selected additives on 7 day stand at 65°C. The data for the positives containing cobalt are for 1 and 7 days at 65°C.

c. Additives at Other Levels

Based on the data presented in Section b. above, the additives cobalt and manganese were chosen to be evaluated at the 5 and 10 metal atom percent level.

(1) Preparation of Plates and Cells

Positive plates and laboratory cells were prepared in the manner previously described. The formation capacities are shown in Tables XX through XXIII.

(2) Effect of Cycling

Table XXIV shows the capacities of 4 cells in each group for 4 consecutive cycles. Figures 39 and 40 show typical discharge curves for each group.

(3) Effect of Stand

Table XXV shows the capacities of 6 positives from each additive group on immediate discharge, 3 day stand at 25°C, 3 day stand at 65°C and a 7 day 65°C stand for the 10% cobalt cells.

III. EVALUATION OF IMPROVED MATERIALS

With their superiority, with respect to high temperature charge retention, established, positive electrodes containing 20 metal atom percent cobalt and 20 metal atom percent manganese were selected as improved materials and, along with control cells, were subjected to further evaluation.

A. UTILIZATION FACTORS OF VARIOUS RATES OF DISCHARGE

1. Experimental Procedure

Four cells with cobalt containing positives, four with manganese containing positives, and four controls were chosen. The cells were charged at 1 ampere for two hours and then discharged at the 6C rate to 0.0V and shorted overnight. This procedure was repeated except that the discharge rate was changed to the C rate, C/2 rate, C/5 rate and C/10 rate.

2. Results

The results of the above experiment are summarized in Table XXVI and shown graphically in Figures 41 through 44.

B. UTILIZATION FACTORS AT VARIOUS DEPTHS OF DISCHARGE

1. Experimental Procedure

The cells were charged at 1 ampere for 2 hours, discharged to a given depth at 1 ampere, recharged at 1 ampere for the same length of time as the discharge and then discharged at 1 ampere to 0.0 volts.

2. Results

The results are summarized in Table XXVII.

C. STAND AT ELEVATED TEMPERATURES

1. Experimental Procedure

Eighteen cells, 6 each of 20% manganese and 20% cobalt doped and control cells were placed in an oven at 80°C for 3 days.

2. Results

At the elevated temperatures, the cells containing positives doped with 20 atom percent cobalt and manganese had no capacity, while the control cells did. Disassembly of the cells revealed that the separator bags around the doped positives were completely disintegrated and the active material had shed from the substrate. The control cells, while showing some shedding of active material, did not attack the separator.

Figure 45 shows the attack on the separator of a manganese positive and the shedding of the active material on a cobalt positive.

D. DETERMINATION OF CHARGE EFFICIENCY

1. Experimental Procedure

In order to determine the charging efficiency and oxygen gassing point of both doped and control cells, a sealed cell concept was used.

The cell consisted of two 1 ampere-hour positive plates, four negative plates and an oxygen consuming electrode connected to the negative terminal.

The cell was then pressurized with oxygen and a pressure vs. time decay curve was obtained. The cell was then repressurized and charged at a given rate and the pressure decay curve obtained. From these conditions, along with the void volume of the cell and the Faradaic equivalent to convert rate of pressure change to current, the fraction of charging current which goes into producing oxygen can be determined, as shown below.

$$\frac{dP}{dt}\text{ evolution} = \frac{dP}{dt}\text{ net} + kP \qquad (1)$$

$$I_{O_2} = \frac{4FV}{RT}\frac{dP}{dt}\text{ evolution} \qquad (2)$$

Where:

I_{O_2} = the fraction of the current producing oxygen
F = the Faraday
V = the void volume of the cell
R = the gas constant
T = the absolute temperature

Therefore, by using equation (2) the fraction of the current used for the parasitic reaction (production of oxygen) and also the point in the charge where this becomes significant can be determined. However, this method could not be used because of unexpected hydrogen evolution from the negative electrode at all current densities tested. Therefore, an alternate scheme was devised and is shown below.

2. Determination of Charge Efficiency

Consider an experimental cell. It has a gas volume, V, it is charged at I amperes at an absolute temperature, T, and is pressured with oxygen to P atmospheres. When the oxygen is consumed at the blank electrode, it must do so at a rate proportional to the current. Using the ideal gas law, we may write the pressure decay as:

$$\frac{dP}{dt} = \frac{RT}{V}\frac{dn}{dt} \qquad (3)$$

where n is the number of moles of oxygen consumed and the other symbols have their usual significance. Multiplying by the number of electrons required to produce a molecule of oxygen, 4N, and using the relationship (N = Avogadre's number)

$$I = zF \frac{dn}{dt}, \tag{4}$$

where F is the faraday of electricity,

$$\frac{dP}{dt} = \frac{RT}{4FV} I \tag{5}$$

Equation (5), therefore, represents the theoretical rate of oxygen consumption and is expected to hold until the oxygen pressure decreases to the point where this process no longer occurs. At this time, it is expected that the potential will increase as the blank electrode changes from an oxygen consumption electrode into a hydrogen evolution electrode at a cell voltage of 1.5 volts.

The cells prepared for this experiment consisted of 2 positive electrodes and 5 oxygen consuming electrodes. One cell contained control positives, another contained positives with 20 atom percent cobalt, and a third contained positives with 20 atom percent manganese. The cell volumes were determined by a gas expansion procedure.

The cells were evacuated, then pressurized with oxygen to 65 PSIA. During a C/10 charge (0.2 A), the pressure decay rates were measured.

3. Results

Figure 46 shows the theoretical and actual oxygen decay rates for the control cell. From this curve, the charging efficiency is 80% at C/10.

If, in Figure 47 (cobalt cell), we concentrate on the lower portion of the experimental curve (after 20 minutes), we find that at the C/10 rate, the cobalt positives are, within experimental error and under the conditions of this experiment, 100% efficient in receiving charge. The upper portion of the curve, before twenty minutes, may be due to a redistribution of water and a change in effective void volume.

The manganese containing positives shown in Figure 48 show an experimental curve divided into two sections, A and B. In section A, the efficiency is 75%. However, after 10% of its capacity is returned, the efficiency drops off sharply to about 40%.

IV. DISCUSSION

A. DETERMINATION OF BATTERY ACTIVE MATERIAL EXISTING IN THE SINTERED PLATE NICKEL OXIDE ELECTRODE

1. Effect of Stand On Structure

The results of Figures 15 through 31 are summarized in Table XXVIII with respect to an estimate of the intensities of the reflections of the 001, 100 and 101 planes of the $Ni(OH)_2$ structure, corresponding to the nominal "d" values of 4.62, 2.73 and 2.32 Å. The intensities are given as a function of area under the curve. The results show that at 10°, 25° and 50°C there is considerably less self discharge in positive electrodes stored without their antipodes (negative electrodes) than those positives stored as cells.

2. Chemical Analysis

a. Nickel, Oxygen and Hydrogen

While the analytical methods described above are inherently accurate much difficulty is encountered in analyzing the active material on the sintered plate. The hydrogen determinations are complicated by the fact that there is only 2.14% hydrogen in $Ni(OH)_2$ and half that amount in NiOOH. This means, for example, that in a discharged one ampere-hour electrode the amount of hydrogen to be determined is less than 0.07 grams.

The nickel-analysis is complicated by the conversion of the nickel sinter to active material.

For these reasons, chemical analysis was not pursured further than the discharged electrode study.

b. Oxidation State of the Active Material on the Sintered Electrode

The determination of the oxidation state of nickel in high valence oxides has been accurately measured by use of an iodometric titration. However, when this method is applied to the active material on the sintered plate positive electrode the results do not agree with the electrochemical data. For example, a fully charged electrode yields an average nickel valence of 2.5, whereas the electrochemical data indicates that the average valence should be between 2.8 and 2.9. From these data it is apparent that the method for determining the average oxidation state of nickel in high valence oxides by iodometric titration has not yet been developed to the point where it is applicable to sintered electrodes. See Table XXIX.

3. Structure of Nickelous Hydroxide (Figure 13)

The discharged state of the positive nickel oxide electrode has been shown to yield the same x-ray pattern as that of pure nickel hydroxide as has been described in the literature and as prepared in our laboratories (Figure 32).

Pure nickelous hydroxide crystallizes with a hexagonal layer structure of closest packed oxygen layers having the space group C $\bar{3}$ M. In this structure, the Ni^{2+} ions occupy the octahedral interstices between every other layer. Thus, the sequence of layers may be described as:

$$\begin{array}{lcccc} \text{O:} & B|A \ \vdots & B|A \ \vdots & B|A \ \vdots & \cdots\cdot \\ \text{Ni:} & C & C & C & \end{array}$$

in which the hydrogen atoms probably occupy tetrahedral positions between pairs of layers as indicated by the dotted lines.

4. Effect of State of Charge on Structure

A quantitative study of the effect of state of charge on structure was made by obtaining the integrated intensities (areas under the peaks) of the X-ray reflections shown in Figures 13 and 14. These intensities are tabulated in Table XXX and were obtained by normalizing the areas under the various peaks by setting the 001 reflection (d = 4.60-4.70Å) equal to 100.

During the charging process, the active material is oxidized from Ni^{2+} to Ni^{3+} with the simultaneous loss of a proton to the electrolyte solution.

As shown in Figures 13 and 14, and Table XXX, no structural changes discernible by X-ray techniques occur until the electrode is close to fully charged.

It can now be shown that for the discharged $[Ni(OH)_2]$ state the structure factors F, (whose square multiplied by the multiplicity and Lorenz polarization factors are proportional to the intensities) for the reflections in question are:

$$F_{001} = f_{Ni}, \quad F_{002} = f_{Ni} - 2f_O, \quad F_{100} = f_{Ni} - f_O \quad \text{and}$$

$$F_{101} = f_{Ni} + \sqrt{3}\, f_O$$

Where f_{Ni} is the atomic scattering factor for nickel and f_O is the atomic scattering factor for oxygen.

When sufficient protons have been lost and the structure nears the composition NiOOH, the intensity data indicate that a randomization of the structure occurs, probably due to a shearing motion of the layers caused by hydrogen bonding. Evidence for the existence of hydrogen bonds has been shown by Kober by use of infrared spectroscopy. Figure 49 is an infrared reflectance spectrum of a discharged electrode. The absorption peak at 3730 cm^{-1} is indicative of free hydroxyl groups as one would find in $Ni(OH)_2$. This peak is missing in Figure 50 which is the charged electrode. This indicates that there are no free hydroxyl groups in NiOOH and, therefore, those hydroxyl groups which are present are most probably tied up as hydrogen bonds.

This shearing motion causes the ordered arrangement to be replaced by a random arrangement of layers of the type:

$$\begin{array}{llll} O: & B|A, & C|B, & A|C \\ Ni: & C & A & B \end{array}$$

Figure 51 schematically diagrams the transformation from the ordered to the random layer structure. Figure 52A is a ball and stick model of 2 layers of the ordered $Ni(OH)_2$ structure. The random arrangement of NiOOH shown in Figure 52B corresponds to a structure which, on the average, has 1/3 Ni at 000, 1/3 2/3 0, 2/3 1/3 0, and 1/3 O at 00 ± 1/4, 1/3 2/3 ± 1/4 and 2/3 1/3 ± 1/4. This structure has structure factors:

$$F_{001} = f_{Ni}, F_{100} = F_{101} = 0 \text{ and}$$

$$F_{002} = f_{Ni} - 2f_{O}$$

These structure factors agree well with those indicated by the observed intensities. Figure 14 illustrates the fact that at 200% charged the electrode is essentially amorphous and that further high rate overcharge causes the amorphous material to recrystallize into what has been described as the γ-NiOOH phase.

5. Depth of X-ray Penetration

A calculation revealed that the depth of penetration corresponding to 95% of the diffracted intensity was many orders of magnitude greater (0.01") than the expected size of a crystal. This eliminates the possibility of the partially discharged surface of a crystal of active material accounting for the similarity of patterns obtained from 90% charged and completely discharged electrodes.

The thickness of the sintered plate is 0.035". The grid material is 0.01" thick, leaving the sintered nickel and active material with a thickness of .013" for each side. For a mixture of nickel and of active material, the depth of penetration which yields 95% diffraction, corresponds to slightly less than 0.01" but certainly more than .003". Since we are dealing with a porous material, the penetration probably exceeds .01". The remote possibility of discharged material existing within the depth of the sintered plate as a cause of the patterns is thus negated.

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation

The results of comparison of charge retention characteristics of plates formed at various rates and temperatures are summarized in Figure 36. No significant differences are shown with respect to stability at room, or elevated temperatures between plates with different formation treatments. On the basis of capacity, however, the results given in Tables III, IV and Figure 17 indicate that a slightly greater capacity for plates formed at C/30, and 10C was exhibited than the control, while those formed at C/10 and 80° exhibit a lower capacity. The reproducibility of capacity with cycling is not affected by different formation conditions.

2. Additives 20% Level

The additives, Li, Na, Be, Mg, Ba, Co and Mn were added to the positive electrodes in order that their effect on cycling and charge retention at elevated temperatures could be studied.

a. Cycling

As can be seen from Table XVIII cycling, at least for four cycles, has little effect on the capacities of the positives. Except for magnesium containing positives whose capacity decreases sharply on cycling, the capacity of other cells containing doped positives and the control cells remain constant or tend to increase somewhat. This increase in capacity is probably due to attack on the sinter.

b. Effect of Stand

(1) Initial Capacity

The initial no stand capacities of all the positive plates containing additives were higher than were expected from the weight of the impregnated nickel hydroxide. In the cases of cobalt and manganese this is to be expected since these additives are most probably electrochemically active. However, as far as the other additives are concerned this increase in capacity is probably due to attack of the nickel sinter. The most pronounced effect is that caused by the addition of lithium to the positive. The capacities of such positives are on the order of 0.3 AH higher than expected. Chemical analysis of the lithium doped positives for active material showed that enough of the sinter had been attacked to cause the increase in capacity.

(2) Stand at Room Temperature

All of the additives with the exception of magnesium showed good charge retention after three days at room temperature.

(3) Stand at 65°C

Figure 53, which is a graphical summary of the 65°C stand show in Table XIX, clearly shows the superiority of charge retention by both the cobalt and manganese additions to the positive over all other additive materials and the controls. In addition to its charge retention properties, the cobalt containing positives have greater absolute capacities (Figures 37 and 38) than the controls or positives containing other additives.

3. Additives - Other Levels

a. Cycling

As is shown in Table XXIV there is little capacity change on cycling of the positives containing either cobalt or manganese at either the 5 or 10 atom percent level.

b. Effect of Stand

Table XXV shows large losses in capacity on stand at room temperture and at 65°C for positives with 5 and 10 atom percent manganese and 5 percent cobalt. The 10% cobalt positives show a loss in capacity after 3 days at 65°C comparable with that of the 20% cobalt positives. However, after 7 days at 65°C the 10% cobalt plates have a capacity equal to the original no stand capacity. A subsequent charge and discharge of the plates yielded on the average, a capacity 13% higher than the initial capacity (Table XXXI). This increase in capacity is most likely due to attack on the sintered nickel plaque.

C. EVALUATION OF IMPROVED MATERIALS

1. Utilization Factors at Various Rates of Discharge

For all rates of discharge, the capacity of the cobalt containing positives is higher than that of the manganese and control positives. The control positives have, again, a somewhat higher capacity than the manganese containing positives. In Figure 54 there is a plot of percent change in capacity using the value at 100 ma for normalization vs. discharge rate. The effect of charge rate on these electrodes is similar. In fact, the manganese and control electrodes are essentially identical, while the slope for the cobalt containing plates is less than that of the other two. Between the amount of capacity and the slope for the discharge rate, plates with cobalt are, indeed, attractive.

2. Utilization Factors at Variois Depths of Discharge

The results of this test show that there is almost no difference in the utilization factors for either the positives containing additives or the control positives.

3. Stand at Elevated Temperatures

Shorting of cells with additions of 20% cobalt and manganese occurred on stand at 80°C due to severe attack on the separator material.

4. Determination of Charge Efficiency

The charge efficiency of positives containing 20 atom percent cobalt, 20 atom percent manganese and control plates at the C/10 rate has been determined by the method outlined in Section IV-D.

At this rate the most efficient positives were those containing 20% cobalt followed by the control and manganese positives. Rates above C/10 were not studied since it was not possible to keep the voltage low enough to prevent hydrogen gassing.

We have not refined the method sufficiently, as yet, to determine the point in the charge of the positive (near full charge) where oxygen gassing becomes perfuse.

V. CONCLUSIONS

A. DETERMINATION OF BATTERY ACTIVE MATERIALS EXISTING IN THE SINTERED PLATE NICKEL OXIDE ELECTRODE

1. X-ray diffraction studies of the positive nickel oxide electrode have shown that the discharged $Ni(OH)_2$ structure is present until the electrode is almost fully charged. . At that point the structure begins to randomize and at 200% of charge the active material is almost completely amorphous.

B. STABILIZATION OF NICKELIC OXIDES AND HYDROXIDES

1. Formation

The effect of various formation rates and temperatures has been studied and it has been determined that formation at C/30 and 10°C yields electrodes with somewhat improved capacity.

2. Additives

It has been determined that positive electrodes containing 20 atom percent cobalt are far superior to conventional positive electrodes with respect to absolute capacity, utilization of various rates of discharge charging efficiency and charge retention in the range 25 - 65°C.

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TABLE I

CAPACITIES OF SINTERED PLATES DISCHARGED AT 400 ma to 1.0 V and 0.0 V

CELL NO.	CYCLE 1		CYCLE 2		CYCLE 3	
	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt
1	.92 AH	.93 AH	.97 AH	1.02 AH	.91 AH	.94 AH
2	.91	.92	.97	.99	.89	.91
* 3	.94	.95	1.01	1.05	.94	.97
* 4	.88	.91	.93	1.03	.88	.95
5	.95	.95	1.08	1.15	1.02	1.06
6	.94	.95	1.07	1.07	.92	.93
* 7	.96	.97	.98	.99	.93	.95
* 8	1.01	1.02	1.03	1.07	.98	1.00
* 9	1.01	1.02	1.05	1.05	.98	.99
* 10	.94	.96	.98	1.01	.92	.94
* 11	.98	.98	1.03	1.05	.95	.96
* 12	.94	.94	1.04	1.05	.98	.99
13	.92	.92	.97	.99	.91	.91
* 14	.90	.90	1.04	1.05	.97	.97
15	1.01	1.02	.99	1.00	.90	.91
* 16	1.04	1.05	.98	.98	.93	.94
17	.93	.94	1.01	1.03	.97	1.00
18	1.05	1.06	.91	.95	.84	.85
19	1.01	1.01	1.05	1.06	1.01	1.01
* 20	.94	1.03	.99	.99	.94	.95
* 21	1.02	1.05	.94	.95	.89	.93
* 22	1.02	1.05	1.00	1.03	.96	1.00

TABLE I - Continued

	CELL NO.	CYCLE 1		CYCLE 2		CYCLE 3	
		1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt	1.0 Volt	0.0 Volt
*	23	.99 AH	1.00 AH	.96 AH	.96 AH	.93 AH	.94 AH
*	24	1.03	1.04	1.01	1.02	.96	.98
*	25	1.05	1.06	1.01	1.02	.98	.99
*	26	1.05	1.06	1.01	1.01	.98	.98
*	27	1.02	1.03	.99	.99	.95	.96
*	28	1.03	1.03	1.01	1.01	.97	.98
	29	1.05	1.06	1.01	1.03	.99	1.00
*	30	1.01	1.01	.98	.99	.94	.95

TABLE II

LIST OF "d SPACINGS AND PEAK HEIGHTS AT VARIOUS STATES OF CHARGE OF SINTERED POSITIVE ELECTRODES

FIGURE	STATE OF CHARGE	RATE	"d" SPACINGS AND INTENSITIES *				
1	Fully Charged	500 ma	4.61(8)				
2	Fully Charged	500 ma	4.66(10)				
3	One quarter Discharged	500 ma	4.63(13)	2.67(7)	2.32(15)	1.56(3)	
4	One quarter Discharged	500 ma	4.73(13)	2.68(5)	2.34(12)		
5	Discharged to 1.0 V	500 ma	4.73(8)	2.72(6)	2.36(10)	1.57(3)	
6	Discharged to 1.0 V	500 ma	4.61(18)	2.69(8)	2.32(17)	1.56(5)	1.49(5)
7	Discharged to 1.0 V	100 ma	4.66(18)	2.71(7)	2.34(14)	1.58(4)	
8	Discharged to 1.0 V	100 ma	4.66(16)	2.71(8)	2.34(12)	1.57(3)	1.48(3)
9	One quarter Discharged	100 ma	4.63(18)	2.71(6)	2.34(12)	1.57(3)	
10	One quarter Discharged	100 ma	4.61(13)	2.68(4)	2.34(8)	1.56(3)	
11	Fully Charged	100 ma	4.66(15)				
12	Fully Charged	100 ma	4.63(13)				

* "d" Spacings in Angstroms; relative intensities are indicated in brackets; nickel lines omitted.

TABLE III

CAPACITY ON FINAL FORMATION - STAND CELLS

CELL NUMBER	CAPACITY	
	To 1.0V	To 0.0V
* 1	.98	.98
* 2.	1.03	1.03
* 3	.93	.94
* 4	.97	.97
* 5	.95	.95
* 6	.98	.98
* 7	1.01	1.01
* 8	1.04	1.04
* 9	.95	.95
* 10	.99	.99
* 11	.98	.98
12	.91	.92
* 13	1.00	1.00
14	.85	.85
15	.83	.83
16	.90	.91
* 17	.93	.93
* 18	.94	.95
* 19	.94	.95
20	.65	.72
* 21	.92	.92
22	1.08	1.08
* 23	.96	.96
* 24	1.00	1.00
* 25	.97	.97
* 26	.96	.96
* 27	.98	.98
* 28	1.01	1.01
* 29	.97	.97
* 30	.96	.96

* Cells Chosen - Most alike in capacity

TABLE IV

DETERMINATION OF AVERAGE VALENCE OF SINTERED NICKEL OXIDE ELECTRODES AT VARIOUS STATES OF CHARGE

PERCENT CHARGED	WEIGHT-ACTIVE NICKEL (gms)	MILLIEQUIVALENTS ACTIVE NICKEL	MILLIEQUIVALENTS $Na_2S_2O_3$ = MILLIEQUIV. Ni^{3+}	$\frac{\text{MILLIEQUIVALENTS } Ni^{3+}}{\text{MILLIEQUIVALENTS } Ni}$	AVERAGE VALENCE
50	1.22	20.85	7.06	0.34	2.34
100	1.19	20.32	9.93	0.49	2.49
100	1.21	20.54	8.34	0.41	2.41
300	1.16	19.70	11.60	0.60	2.60
500	1.29	21.84	16.34	0.75	2.75
γ-NiOOH ($Ni_2O_3 \cdot H_2O$)	0.13	2.18	1.72	0.79	2.79

TABLE V

DETERMINATION OF AVERAGE VALENCE OF HIGH VALENCE NICKEL OXIDE

SAMPLE NO.	WEIGHT NICKEL (gms)	MILLI-EQUIVALENTS NICKEL	MILLI-EQUIVALENTS $Na_2S_2O_3$ USED	$\frac{\text{MILLIEQUIVALENTS } Na_2S_2O_3}{\text{MILLI-EQUIVALENTS Ni}}$	AVERAGE VALENCE
1	0.0234	0.3986	0.4822	1.21	3.10
2	0.0263	0.4479	0.4822	1.08	3.04
Avg.	0.0249	0.4241	0.4822	1.15	3.07

TABLE VI

X-RAY DIFFRACTION PATTERN
γ-NiOOH ($Ni_2O_3 \cdot H_2O$)

2θ	d	I/I_o	hkl (γ-NiOOH)	MATERIAL
12.3	7.19	100B	003	γ-NiOOH - $Ni_2O_3 \cdot H_2O$
24.9	3.57	18B	006	γ-NiOOH - $Ni_2O_3 \cdot H_2O$
33.3	2.69	14B		$Ni_2O_3 \cdot H_2O$
36.5	2.47	8B	101	γ-NiOOH - $Ni_2O_3 \cdot H_2O$
38.0	2.37	12B	102	γ-NiOOH - $Ni_2O_3 \cdot H_2O$

B = Broad

TABLE VII

FORMATION DISCHARGE CAPACITIES AT VARIOUS TEMPERATURES & RATES

DISCHARGE RATE	TEMPERATURE	CAPACITY TO 0.0 V		
		CYCLE 1	CYCLE 2	CYCLE 3
100 ma	25°C	.94 AH	.98 AH	.97 AH
100 ma	25°C	.95	.99	.99
100 ma	25°C	.91	.96	.94
100 ma	25°C	.95	.99	.98
100 ma	25°C	.95	.99	.98
100 ma	25°C	.91	.96	.94
100 ma	25°C	.96	1.00	.99
100 ma	25°C	.94	.99	.98
100 ma	25°C	.94	.98	.97
100 ma	25°C	.91	.98	.94
100 ma	80°C	.70	.70	.72
100 ma	80°C	.67	.68	.70
100 ma	80°C	.75	.77	.75
100 ma	80°C	.68	.67	.69
100 ma	80°C	.72	.72	.73
100 ma	80°C	.76	.77	.78
100 ma	80°C	.77	.77	.79
100 ma	80°C	.79	.77	.79
100 ma	80°C	.75	.77	.76
100 ma	80°C	.59	.60	.61

TABLE VII (Continued)

DISCHARGE RATE	TEMPERATURE	CAPACITY TO 0.0 V		
		CYCLE 1	CYCLE 2	CYCLE 3
35 ma	10°C	1.02	1.09	1.05
35 ma	10°C	1.02	1.06	1.05
35 ma	10°C	1.02	1.06	1.11
35 ma	10°C	1.02	1.06	1.00
35 ma	10°C	1.02	1.09	1.05
35 ma	10°C	1.02	1.12	1.05
35 ma	10°C	1.02	1.10	1.05
35 ma	10°C	1.02	1.16	1.11
35 ma	10°C	1.02	1.18	1.12
35 ma	10°C	1.02	.93	.96

TABLE VIII

CAPACITIES OF VARIOUS FORMED PLATES AFTER VARIOUS STANDS

FORMATION TREATMENT	CAPACITY TO 0.0 V					
	NO STAND			3 DAY STAND AT ROOM TEMP.	3 DAY STAND AT 50°C	3 DAY STAND AT 65°C
10°C-35 ma	1.11 AH	1.12 AH	.95 AH	1.04 AH	.79 AH	.55 AH
	1.11	1.10	.95	.94	.73	.55
	1.11	1.13	1.02	1.03	.78	.51
	1.07	.97	.91	.91	.68	.48
	.97	1.05	.96	.85	.69	.60
	1.04	1.08	1.00	.90	.66	.48
25°C-100ma	.87	.93	.89	.86	.66	.51
	.98	1.04	.87	.87	.72	.55
	.94	1.07	.80	.87	.51	.54
	.98	1.11	.79	.84	.61	.59
	1.10	1.11	.83	1.01	.48	.56
	.95	1.05	.89	.86	.59	.54
80°C-100ma	.87	.96	.86	.73	.62	.48
	.91	.97	.87	.78	.62	.49
	.89	.95	.80	.81	.51	.46
	.85	.86	.79	.71	.43	.42
	.87	.91	.79	.76	.48	.46
	.83	.87	.70	.74	.33	.47

TABLE IX

CYCLING DATA - PLATES WITH VARIOUS FORMATION TREATMENT

FORMATION TREATMENT	CAPACITY							
	CYCLE 1		CYCLE 2		CYCLE 3		CYCLE 4	
	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V
10°C - 35ma	.94	.96	.93	.97	.91	1.00	.87	.90
	1.01	1.08	1.00	1.09	.99	1.09	.95	1.01
	1.01	1.08	.98	1.08	.96	1.09	.91	.92
	.91	.92	.89	.92	.90	.96	.86	.91
25°C - 100ma	.98	1.05	.97	1.06	.95	1.05	.87	.91
	.97	.99	.99	1.03	.98	1.04	.87	.91
	.91	.92	.91	.98	.83	.91	Shorted	
	.96	.98	.98	.99	.83	.89	.90	.91
80°C - 100 ma	.70	.77	.71	.79	.69	.77	.65	.70
	.76	.82	.86	.94	.86	.93	.80	.82
	.60	.70	.61	.83	.67	.84	.63	.72
	.58	.69	.64	.74	.59	.73	.53	.65

TABLE X

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL ATOM % BERYLLIUM

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
1	2.98	2.72	0.75 AH	0.76 AH	0.79 AH
2	3.11	2.84	0.75	0.75	0.82
3	2.99	2.73	0.74	0.75	0.79
4	3.09	2.82	0.75	0.76	0.82
5	3.04	2.78	0.75	0.78	0.80
6	3.06	2.80	0.76	0.78	0.81
7	3.00	2.74	0.75	0.77	0.79
8	2.94	2.69	0.75	0.76	0.78
9	3.07	2.81	0.75	0.80	0.81
10	2.95	2.70	0.75	0.78	0.78

TABLE XI

FORMATION CAPACITIES OF POSITIVES CONTAINING 20 METAL ATOM % MAGNESIUM

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
1	3.05	2.67	0.67 AH	0.68 AH	0.77 AH
2	3.06	2.67	0.66	0.67	0.77
3	3.00	2.62	0.65	0.66	0.76
4	3.06	2.67	0.68	0.70	0.77
5	3.06	2.67	0.68	0.71	0.77
6	3.02	2.64	0.67	0.68	0.76
7	3.10	2.71	0.67	0.69	0.79
8	3.01	2.63	0.66	0.69	0.76
9	3.01	2.63	0.66	0.67	0.76
10	2.99	2.63	0.68	0.70	0.76

TABLE XII

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL ATOM PERCENT LITHIUM

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0V	0.0V
1	3.07	2.91	0.95 AH	0.95 AH	0.84 AH
2	2.96	2.81	0.91	0.91	0.81
3	3.04	2.88	0.93	0.94	0.83
4	3.05	2.89	0.90	0.91	0.84
5	3.06	2.90	0.93	0.94	0.84
6	2.97	2.82	0.92	0.93	0.82
7	2.97	2.82	0.90	0.91	0.82
8	2.99	2.83	0.91	0.92	0.82
9	2.97	2.82	0.93	0.93	0.82
10	2.98	2.83	0.90	0.92	0.82

TABLE XIII

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL ATOM PERCENT SODIUM

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0V	0.0 V
1	3.03	2.77	0.94 AH	0.96 AH	0.80 AH
2	3.10	2.83	0.91	0.92	0.82
3	2.99	2.73	0.89	0.92	0.79
4	3.12	2.85	0.92	0.93	0.82
5	3.03	2.77	0.87	0.87	0.80
6	2.99	2.73	0.94	0.95	0.79
7	3.00	2.74	0.89	0.92	0.79
8	2.96	2.71	0.95	0.96	0.78
9	3.05	2.79	0.93	0.94	0.80
10	2.95	2.70	0.89	0.91	0.78

TABLE XIV

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL PERCENT MANGANESE

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma EXPERIMENTAL CAPACITY 1.0 V	DISCHARGED AT 100 ma EXPERIMENTAL CAPACITY 0.0 V	DISCHARGED AT 100 ma THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$ 0.0 V
1	3.20	2.58	0.82 AH	0.88 AH	0.75 AH
2	3.09	2.50	0.81	0.87	0.72
3	3.13	2.53	0.82	0.88	0.73
4	3.07	2.48	0.81	0.87	0.72
5	3.04	2.47	0.78	0.85	0.71
6	3.27	2.64	0.85	0.88	0.76
7	3.08	2.49	0.81	0.86	0.72
8	3.17	2.57	0.84	0.87	0.74
9	3.11	2.51	0.81	0.86	0.73
10	3.07	2.48	0.80	0.85	0.72

TABLE XV

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL ATOM PERCENT COBALT

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
1	3.13	2.50	0.91 AH	0.92 AH	0.72 AH
2	3.09	2.47	0.90	0.90	0.71
3	2.95	2.36	0.87	0.87	0.68
4	2.90	2.32	0.85	0.85	0.67
5	2.96	2.37	0.86	0.86	0.68
6	3.17	2.54	0.92	0.93	0.73
7	3.15	2.52	0.92	0.93	0.73
8	2.88	2.30	0.83	0.84	0.66
9	2.95	2.36	0.87	0.87	0.68
10	3.13	2.50	0.92	0.93	0.72

TABLE XVI

FORMATION CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 METAL ATOM PERCENT BARIUM

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	
1	2.87	1.81	0.90 AH	0.91 AH	0.52 A
2	2.87	1.81	0.94	0.94	0.52
3	2.92	1.84	0.92	0.93	0.53
4	2.90	1.83	0.92	0.92	0.53
5	2.96	1.86	0.89	0.90	0.54
6	3.02	1.90	0.96	0.97	0.55
7	2.99	1.88	0.92	0.92	0.54
8	2.98	1.88	0.93	0.94	0.54
9	3.07	1.93	0.92	0.93	0.55
10	3.14	1.98	0.93	0.94	0.57

TABLE XVII

FORMATION CAPACITIES - CONTROL CELLS

CELL NO.	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
		EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
		1.0 V	0.0 V	0.0 V
1	2.98	0.92 AH	0.93 AH	0.86 AH
2	3.00	0.92	0.93	0.87
3	3.15	0.93	0.94	0.91
4	3.06	0.90	0.91	0.88
5	3.04	0.92	0.93	0.88
6	3.03	0.93	0.93	0.88
7	3.12	0.93	0.93	0.90
8	3.01	0.94	0.94	0.87
9	3.00	0.93	0.94	0.87
10	2.97	0.89	0.90	0.86

TABLE XVIII

CYCLING DATA FOR CELLS WITH POSITIVES CONTAINING 20 ATOM % METAL AND CONTROL CELLS

CELL NO.	DISCHARGED AT 200 ma							
	CYCLE I		CYCLE II		CYCLE III		CYCLE IV	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Be-1	0.79 AH	0.85 AH	0.82 AH	0.85 AH	0.81 AH	0.86 AH	0.81 AH	0.87 AH
Be-1	0.81	0.84	0.84	0.88	0.82	0.85	0.82	0.85
Be-3	0.78	0.83	0.79	0.83	0.78	0.82	0.78	0.82
Be-4	0.81	0.85	0.82	0.84	0.82	0.85	0.82	0.86
Mg-1	0.72	0.74	0.68	0.71	0.64	0.67	0.59	0.62
Mg-2	0.68	0.72	0.65	0.69	0.61	0.68	0.58	0.63
Mg-3	0.70	0.72	0.65	0.68	0.61	0.65	0.58	0.59
Mg-4	0.71	0.72	Short	Short	0.67	0.69	0.59	0.62
Li-1	0.94	0.96	0.97	0.98	0.96	1.00	0.99	1.03
Li-2	0.93	0.94	0.97	0.97	0.94	0.99	0.97	1.01
Li-3	0.93	0.95	0.96	0.97	0.94	0.94	0.97	1.01
Li-4	0.90	0.92	0.93	0.97	0.92	0.97	0.96	1.00
Na-1	0.94	0.97	0.93	1.06	0.91	1.04	0.96	1.02
Na-2	0.88	0.95	0.86	0.95	0.86	0.97	0.88	0.99
Na-3	0.89	0.96	0.86	0.96	0.86	0.98	0.89	1.00
Na-4	0.93	0.97	0.88	1.01	0.84	0.96	0.87	0.98
Mn-1	0.89	0.98	0.97	0.98	0.89	0.97	0.87	0.94
Mn-2	0.90	0.97	0.90	0.96	0.87	0.95	0.85	0.93
Mn-3	0.90	0.99	0.90	0.97	0.87	0.96	0.85	0.93
Mn-4	0.88	0.96	0.88	0.95	0.87	0.94	0.84	0.92
Co-6	0.85	0.88	0.87	0.89	0.91	0.94	0.91	0.94
Co-7	0.89	0.91	0.92	0.95	0.97	0.99	0.96	0.98
Co-8	0.88	0.91	0.91	0.93	0.95	0.99	0.94	0.97
Co-9	0.82	0.84	0.85	0.87	0.91	0.94	0.91	0.92
Ba-1	0.74	0.76	0.78	0.80	0.79	0.81	0.77	0.80
Ba-2	0.78	0.81	0.80	0.82	0.82	0.84	0.80	0.82
Ba-3	0.78	0.79	0.80	0.81	0.82	0.83	0.80	0.82
Ba-4	0.76	0.78	0.79	0.80	0.81	0.83	0.78	0.80
Cont-11	0.94	1.07	0.92	1.06	0.92	1.06	0.94	1.04
Cont-12	0.90	1.01	0.90	1.00	0.88	1.03	0.92	1.02
Cont-13	0.92	1.01	0.92	1.01	0.91	1.03	0.94	1.02
Cont-14	0.90	0.97	0.86	0.95	0.84	0.92	0.86	0.93

TABLE XIX

CAPACITIES OF CELLS WITH POSITIVES CONTAINING 20 ATOM % METAL ADDITIVES AND CONTROL CELLS AT VARIOUS TEMPERATURES

CELL NUMBER	DISCHARGED AT 200 ma							
	NO STAND		3 DAYS 25°C		3 DAYS 65°C		7 DAYS 65°C	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Be-5	0.83 AH	0.87 AH	0.77 AH	0.80 AH	0.55 AH	0.56 AH	---	---
Be-6	0.79	0.84	0.72	0.75	0.55	0.56	---	---
Be-7	0.75	0.84	0.73	0.74	0.56	0.57	---	---
Be-8	0.77	0.80	0.72	0.73	0.59	0.59	---	---
Be-9	0.79	0.84	0.74	0.77	0.58	0.58	---	---
Be-10	0.77	0.86	0.77	0.78	0.59	0.59	---	---
Mg-5	0.89	0.93	0.73	0.75	0.65	0.65	---	---
Mg-6	0.88	0.93	0.72	0.73	0.57	0.57	---	---
Mg-7	0.86	0.88	0.69	0.69	0.53	0.53	---	---
Mg-8	0.89	0.93	0.72	0.73	0.56	0.56	---	---
Mg-9	0.90	0.95	0.73	0.75	0.61	0.63	---	---
Mg-10	0.90	0.95	0.77	0.78	0.60	0.62	---	---
Li-5	1.13	1.19	1.03	1.03	0.75	0.83	0.27 AH	0.28 AH
Li-6	1.14	1.21	1.06	1.07	0.66	0.85	0.28	0.29
Li-7	1.04	1.07	0.94	0.94	0.69	0.86	0.27	0.28
Li-8	1.13	1.17	1.05	1.05	0.66	0.89	0.27	0.28
Li-9	1.19	1.24	1.00	1.00	0.90	0.95	---	---
Li-10	1.12	1.17	1.05	1.06	0.81	0.86	0.33	0.34
Na-5	0.97	0.99	0.81	0.82	0.48	0.52	---	---
Na-6	0.96	0.99	1.00	1.00	0.74	0.77	---	---
Na -7	1.01	1.03	0.94	0.94	0.66	0.73	---	---
Na-8	0.85	0.96	1.01	1.01	0.85	0.90	---	---
Na-9	1.00	1.04	0.83	0.83	0.77	0.80	---	---
Na-10	0.93	0.97	0.87	0.88	0.74	0.77	---	---
Mn-5	0.88	0.98	0.82	0.93	0.95	0.95	0.54	0.72
Mn-6	0.97	1.05	0.93	0.98	0.86	0.87	0.71	0.80
Mn-7	0.93	1.03	0.88	0.96	0.82	0.85	0.70	0.78
Mn-8	0.95	1.03	0.89	0.95	0.85	0.85	0.76	0.76
Mn-9	0.94	1.03	0.89	0.97	0.85	0.85	0.79	0.82
Mn-10	0.94	1.02	0.88	0.92	0.73	0.75	0.47	0.48

.....Continued

TABLE XIX - Continued

CELL NUMBER	DISCHARGED AT 200 ma							
	NO STAND		3 DAYS 25°C		3 DAYS 65°C		7 DAYS 65°C	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Co-1	1.15AH	1.25AH	---	---	1.02(1 day)	1.03 (1 day)	0.88AH	0.92AH
Co-2	1.16	1.28	---	---	1.04 "	1.08 "	0.92	0.94
Co-3	0.98	1.07	---	---	0.93 "	0.94 "	0.72	0.77
Co-4	1.00	1.07	---	---	0.95 "	0.97 "	0.72	0.81
Ba-5	0.71	0.72	0.67	0.68	0.64	0.66	---	---
Ba-6	0.83	0.84	0.72	0.73	0.68	0.70	---	---
Ba-7	0.67	0.68	0.61	0.65	0.50	0.53	---	---
Ba-8	0.79	0.81	0.72	0.73	0.56	0.60	---	---
Ba-9	0.64	0.66	0.62	0.63	0.43	0.47	---	---
Ba-10	0.55	0.58	0.47	0.47	0.38	0.42	---	---
Control-15	1.09	1.09	1.03	1.03	0.75	0.80	0.52	0.57
Control-16	1.11	1.11	1.06	1.06	0.78	0.85	0.63	0.70
Control-17	1.06	1.06	1.00	1.01	0.72	0.81	0.58	0.70
Control-18	1.08	1.08	1.06	1.06	0.93	0.97	0.80	0.85
Control-19	1.11	1.11	1.06	1.07	0.90	0.94	0.45	0.45
Control-20	1.05	1.06	1.02	1.03	0.88	0.92	0.80	0.89

TABLE XX

FORMATION CAPACITIES OF CELLS WITH PLATES CONTAINING 5 METAL ATOM % MANGANESE

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
11	3.17	3.02	0.94 AH	0.98 AH	0.87 AH
12	3.26	3.10	0.90	0.93	0.90
13	3.23	3.07	1.00	1.01	0.89
14	3.30	3.14	0.98	1.00	0.91
15	3.24	3.08	1.00	1.01	0.89
16	3.11	2.96	0.88	0.91	0.86
17	3.17	3.02	0.91	0.94	0.87
18	3.21	3.06	0.97	1.01	0.88
19	3.27	3.11	0.93	1.00	0.90
20	3.32	3.16	0.91	0.95	0.91

TABLE XXI

FORMATION CAPACITIES OF CELLS WITH PLATES CONTAINING 5 METAL ATOM PERCENT COBALT

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT $Ni(OH)_2$ (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
21	3.23	3.07	0.99 AH	1.05 AH	0.89 AH
22	3.33	3.16	0.99	1.04	0.91
23	3.10	2.94	0.94	0.99	0.85
24	2.97	2.82	0.91	0.96	0.82
25	2.90	2.75	0.98	1.04	0.80
26	3.25	3.09	0.91	0.97	0.89
27	3.36	3.19	0.94	0.99	0.92
28	3.44	3.27	0.96	1.00	0.95
29	3.02	2.87	0.93	0.98	0.83
30	3.17	3.01	0.90	0.95	0.87

TABLE XXII

FORMATION CAPACITIES OF CELLS WITH PLATES CONTAINING 10 METAL ATOM % MANGANESE

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT Ni(OH) (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
21	3.01	2.72	0.85 AH	0.91 AH	0.79 AH
22	3.00	2.71	0.83	0.89	0.78
23	3.03	2.74	0.86	0.92	0.79
24	3.10	2.80	0.83	0.90	0.81
25	3.11	2.81	0.89	0.95	0.81
26	3.02	2.73	0.86	0.92	0.79
27	3.12	2.82	0.92	0.93	0.82
28	3.10	2.80	0.92	0.95	0.81
29	3.01	2.72	0.89	0.95	0.79
30	2.98	2.69	0.92	0.95	0.78

TABLE XXIII

FORMATION CAPACITIES OF CELLS WITH PLATES CONTAINING 10 METAL ATOM PERCENT COBALT

CELL NO.	TOTAL WT. GAIN (gms)	WEIGHT Ni(OH) (gms)	DISCHARGED AT 100 ma		
			EXPERIMENTAL CAPACITY		THEORETICAL CAPACITY BASED ON WEIGHT $Ni(OH)_2$
			1.0 V	0.0 V	0.0 V
31	3.18	2.86	0.95 AH	0.99 AH	0.83 AH
32	3.03	2.73	0.96	1.00	0.79
33	3.35	3.01	0.92	0.95	0.87
34	3.21	2.89	0.96	0.99	0.84
35	3.08	2.78	0.96	1.00	0.80
36	3.21	2.89	0.96	1.00	0.84
37	3.11	2.80	0.96	1.00	0.81
38	3.34	3.01	0.95	0.99	0.87
39	3.22	2.90	0.95	1.00	0.84
40	3.23	2.91	0.96	1.00	0.84

TABLE XXIV

CAPACITIES OF CELLS WITH POSITIVES CONTAINING 5 & 10 METAL ATOM % MANGANESE & COBALT AFTER CYCLING

CELL NUMBER	DISCHARGED AT 200 ma							
	CYCLE I		CYCLE II		CYCLE III		CYCLE IV	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Mn-5%								
11	0.80 AH	0.89 AH	0.94 AH	1.03 AH	0.95 AH	1.05 AH	0.90 AH	1.00 AH
12	0.89	0.97	0.91	0.99	0.94	1.02	0.90	0.99
13	0.99	1.07	1.01	1.10	1.02	1.11	0.98	1.07
14	0.97	1.04	0.98	1.07	0.99	1.09	0.96	1.05
Co-5%								
21	0.95	1.05	0.96	1.05	1.01	1.10	0.97	1.07
22	0.94	1.07	0.94	1.02	0.97	1.06	0.94	1.04
23	0.88	0.99	0.88	0.94	0.92	1.01	0.89	0.99
24	0.87	0.97	0.84	0.95	0.88	0.99	0.84	0.94
Mn-10%								
21	0.81	0.89	0.83	0.95	0.87	0.98	0.85	0.97
22	0.79	0.88	0.82	0.94	0.81	0.94	0.80	0.94
23	0.83	0.95	0.80	0.95	0.81	0.95	0.80	0.92
24	0.74	0.90	0.79	0.92	0.78	0.92	0.75	0.88

continued....

TABLE XXIV
(Continued)

CELL NUMBER	DISCHARGED AT 200 ma							
	CYCLE I		CYCLE II		CYCLE III		CYCLE IV	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Co-10%								
31	0.88	0.97	0.94	0.98	0.97	1.02	0.94	1.00
32	0.88	0.95	0.88	0.96	0.93	0.99	0.90	0.98
33	0.83	0.89	0.81	0.86	0.88	0.89	0.82	0.86
34	0.78	0.89	0.87	0.97	0.91	0.99	0.84	0.96

TABLE XXV

CAPACITIES OF CELLS WITH POSITIVES CONTAINING 5 & 10 METAL ATOM % MANGANESE AND COBALT

Cell No.	DISCHARGED AT 200 ma					
	No Stand		3 Days 25°C		3 Days 65°C	
	1.0V	0.0V	1.0V	0.0V	1.0V	0.0V
Mn-5%						
15	1.02 AH	1.05 AH	0.98 AH	0.98 AH	0.50 AH	0.60 AH
16	.61	.62	.45	.45	.38	.40
17	.58	.61	.46	.48	Short	Short
18	.89	.93	.81	.89	.44	.48
19	.77	.84	.74	.78	.20	.22
20	.70	.73	.57	.41	.23	.37
Co-5%						
25	.96	1.02	.88	.88	.87	.88
26	.73	.82	.59	.64	.30	.33
27	.81	.84	.71	.73	.30	.33
28	.89	.96	.82	.82	.73	.79
29	.77	.84	.68	.70	.63	.68
30	.50	.60	.52	.53	.50	.53
Mn-10%						
25	.81	.81	.68	.70	.41	.43
26	.74	.81	.58	.60	.29	.35
27	.69	.72	.46	.57	Short	Short
28	.84	.89	.73	.74	.54	.56
29	.83	.93	.78	.83	.63	.67
30	.86	.96	.83	.83	.72	.74

continued.....

TABLE XXV
(Continued)

CELL NUMBER	DISCHARGED AT 200 ma							
	NO STAND		3 DAYS 25°C		3 DAYS 65°C		7 DAYS 65°C	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Co-10%								
35	0.94	0.97	0.94	0.95	0.75	0.78	1.05	1.11
36	0.88	0.88	0.89	0.90	0.64	0.70	0.81	0.95
37	0.86	0.87	0.88	0.89	0.63	0.73	0.68	0.86
38	0.99	1.03	Short	Short	0.73	0.83	0.94	1.07
39	0.90	0.95	Short	Short	0.75	0.81	0.73	0.83
40	0.89	0.93	0.85	0.85	0.78	0.83	Short	Short

TABLE XXVI

UTILIZATION FACTORS AT VARIOUS RATES OF DISCHARGE

CELL NUMBER	RATE									
	6C (6.0 A)		C (1.0 A)		C/2 (0.5 A)		C/5 (0.2 A)		C/10 (0.1 A)	
	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V	1.0 V	0.0 V
Mn-1	---	.50	.67	.89	.67	.79	.75	.97	.99	1.17
Mn-2	---	.60	.75	.95	.71	.83	.78	.95	.97	1.12
Mn-3	---	.50	.67	.89	.63	.79	.75	.94	.89	1.07
Mn-4	---	.50	.67	.95	.68	.83	.75	.94	.94	1.08
Co-11	---	.90	1.00	1.22	1.01	1.12	1.23	1.31	1.26	1.32
Co-12	---	.60	.85	1.14	.83	1.06	1.14	1.23	1.19	1.25
Co-13	---	1.00	.92	1.17	.93	1.06	1.15	1.23	1.19	1.26
Co-14	---	1.00	.85	1.15	.88	1.02	1.10	1.22	1.17	1.23
Control-11	---	.60	.80	.92	.73	.85	.85	1.09	1.03	1.15
Control-12	---	.60	.80	.92	.71	.85	.88	1.09	1.03	1.16
Control-13	---	.60	.80	.92	.75	.82	.87	1.07	1.01	1.13
Control -14	---	.60	.67	.85	.66	.77	.83	1.01	.95	1.06

TABLE XXVII

AVERAGE UTILIZATION (%) FOR MANGANESE DOPED, COBALT DOPED AND CONTROL POSITIVES AT VARIOUS DEPTHS OF DISCHARGE

	INITIAL CAPACITY	DEPTH OF DISCHARGE (%)				
		25	35	50	75	87
CELL	0.0 V	0.0 V	0.0 V	0.0 V	0.0 V	0.0 V
Mn	0.92AH	82	82	87	80	73
Co	1.17AH	90	85	90	85	74
Control	0.92AH	96	82	90	80	69

TABLE XXVIII

X-RAY DIFFRACTION LINES AND THEIR INTEGRATED INTENSITIES OBTAINED FROM PLATES STORED AT VARIOUS TEMPERATURES FOR VARIOUS TIMES

FIGURE NO.	STAND TIME	STORED AS	TEMPERATURE	X-RAY "D" SPACINGS & INTENSITIES		
15	24 Hrs.	Plate	10°C	Amorphous	Amorphous	Amorphous
16	48 Hrs.	Plate	10°C	4.67(16)		
17	3 Mo.	Plate	10°C	4.77(8)	2.71(4)	2.34(12)
18	24 Hrs.	Cell	10°C	4.60(25)		2.32(8)
19	48 Hrs.	Cell	10°C	4.72(13)	2.69(7)	2.32(19)
20	3 Mo.	Cell	10°C	4.62(10)	2.70(15)	2.34(17)
21	24 Hrs.	Plate	25°C	4.72(10)		
22	48 Hrs.	Plate	25°C	4.67(12)	2.71(3)	2.34(7)
23	3 Mo.	Plate	25°C	4.55(5)	2.68(3)	2.32(10)
24	24 Hrs.	Cell	25°C	4.60(6)		
25	48 Hrs.	Cell	25°C	4.67(19)	2.71(4)	2.37(13)
26	24 Hrs.	Plate	50°C		2.73(12)	2.32(11)
27	48 Hrs.	Plate	50°C	4.55(7)	2.75(20)	2.34(19)
28	3 Mo.	Plate	50°C	4.60(3)	2.69(5)	2.34(12)
29	24 Hrs.	Cell	50°C	4.72(14)	2.73(6)	2.34(7)
30	48 Hrs.	Cell	50°C	4.55(6)	2.71(19)	2.32(6)
31	3 Mo.	Cell	50°C	4.60(15)	2.71(10)	2.32(18)

TABLE XXIX

DETERMINATION OF AVERAGE VALENCE OF SINTERED NICKEL OXIDE ELECTRODES AT VARIOUS STATES OF CHARGE

PERCENT CHARGED	WEIGHT-ACTIVE NICKEL (gms)	MILLIEQUIVALENTS ACTIVE NICKEL	MILLIEQUIVALENTS $Na_2S_2O_3$ = MILLIEQUIV. Ni^{3+}	$\frac{\text{MILLIEQUIVALENTS } Ni^{3+}}{\text{MILLIEQUIVALENTS } Ni}$	AVERAGE VALENCE
50	1.22	20.85	7.06	0.34	2.34
100	1.19	20.32	9.93	0.49	2.49
100	1.21	20.54	8.34	0.41	2.41
300	1.16	19.70	11.60	0.60	2.60
500	1.29	21.84	16.34	0.75	2.75
γ-NiOOH ($Ni_2O_3 \cdot H_2O$)	0.13	2.18	1.72	0.79	2.79

TABLE XXX

INTEGRATED INTENSITIES OF X-RAY REFLECTIONS Vs. STATE OF CHARGE

STATE OF CHARGE %	I/I_o 001	I/I_o 100	I/I_o 101-002	I/I_o 002	I/I_o 003-γ-NiOOH
0	100	19	78	---	---
75	100	25	70	---	---
90	100	27	73	---	---
100	100	11	34	---	---
133	100	0	0	15B	---
200	100	0	0	60B	24B

γ-NiOOH

STATE OF CHARGE %	I/I_o 001-$Ni(OH)_2$	I/I_o 003	I/I_o 006	I/I_o 101-102	I/I_o 104-105
550	4	100	36	31B	11B

B = Broad

TABLE XXXI

IMMEDIATE DISCHARGE CAPACITIES OF CELLS WITH POSITIVES CONTAINING 10 METAL ATOM PERCENT COBALT SUBSEQUENT TO DISCHARGE AFTER 3 DAY 65° STAND

CELL NUMBER	DISCHARGED AT 200 ma CAPACITY 1.0 V	DISCHARGED AT 200 ma CAPACITY 0.0 V
25	1.19 AH	1.32 AH
26	1.00	1.14
27	0.92	1.17
28	1.08	1.29
29	1.00	1.21
30	0.86	1.12

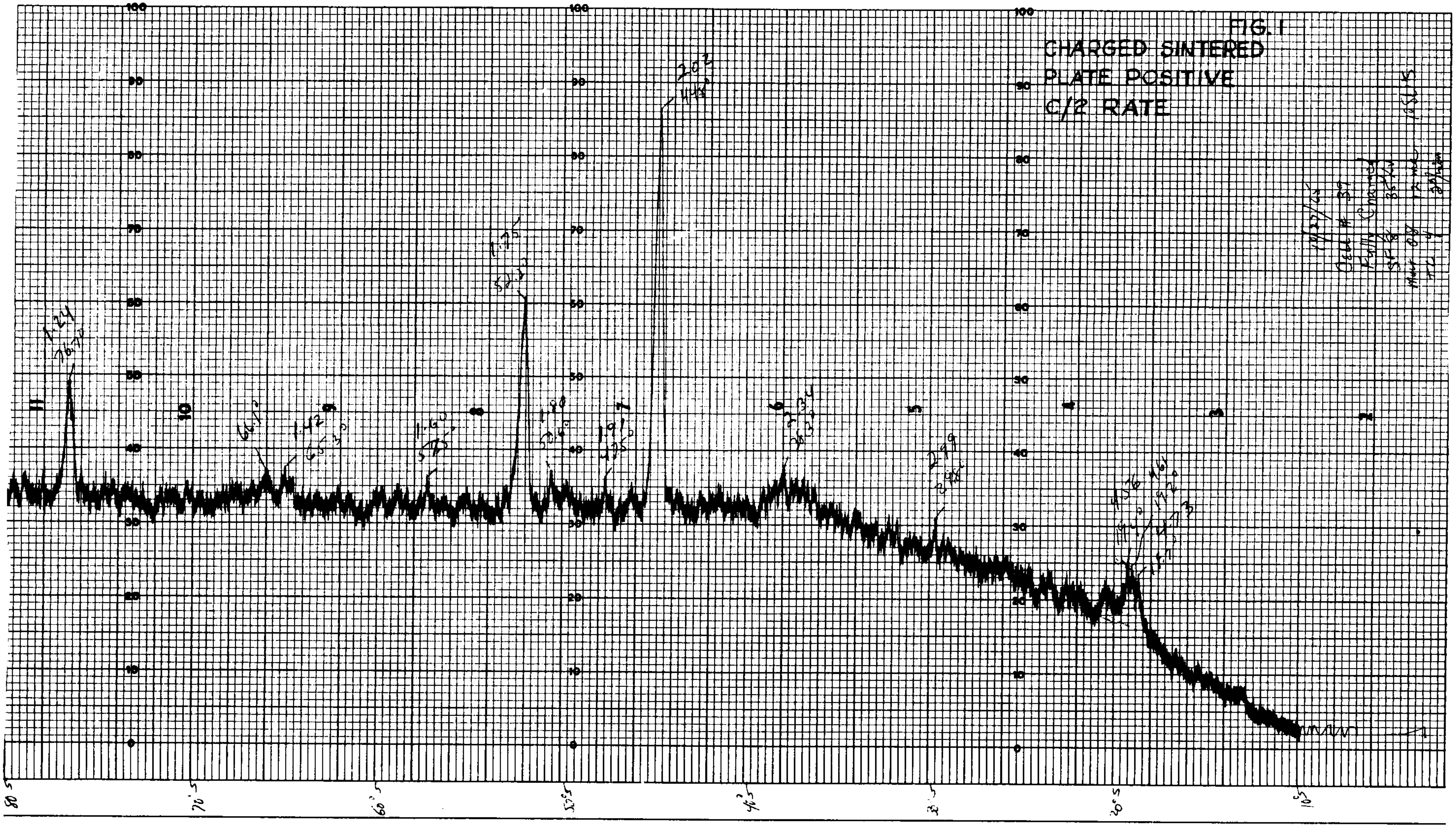
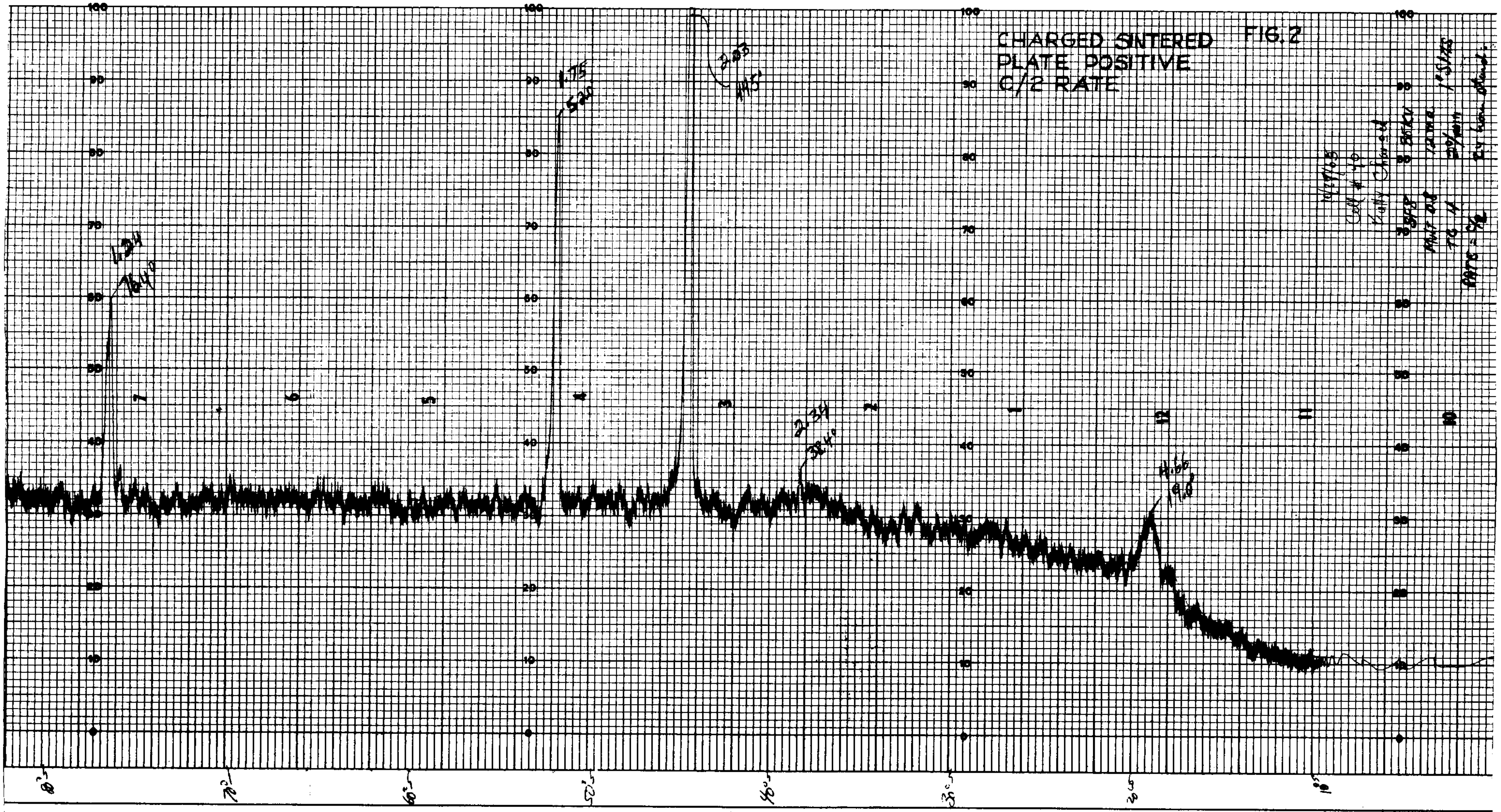


FIG. I
CHARGED SINTERED
PLATE POSITIVE
C/2 RATE
10/27/65
Cell # 39
Fully Charged
SF 8 85 kv
mat 08 12 ma
TC 4 3°/min
1.24
76.70
1.42
65.35
1.60
57.45
1.75
52.20
1.88
48.40
1.91
47.55
2.02
44.8
2.34
38.35
2.99
29.8
4.36
4.61
100
90
80
70
60
50
40
30
20
10
0
2
3
4
5
6
7
8
9
10
11
80°
70°
60°
55°
45°
35°
20°
10°
GRAPHIC CONTROLS CORPORATION BUFFALO, N.Y.
NO. 6270
PRINTED IN U.S.A.



CHARGED SINTERED PLATE POSITIVE C/2 RATE

FIG. 2

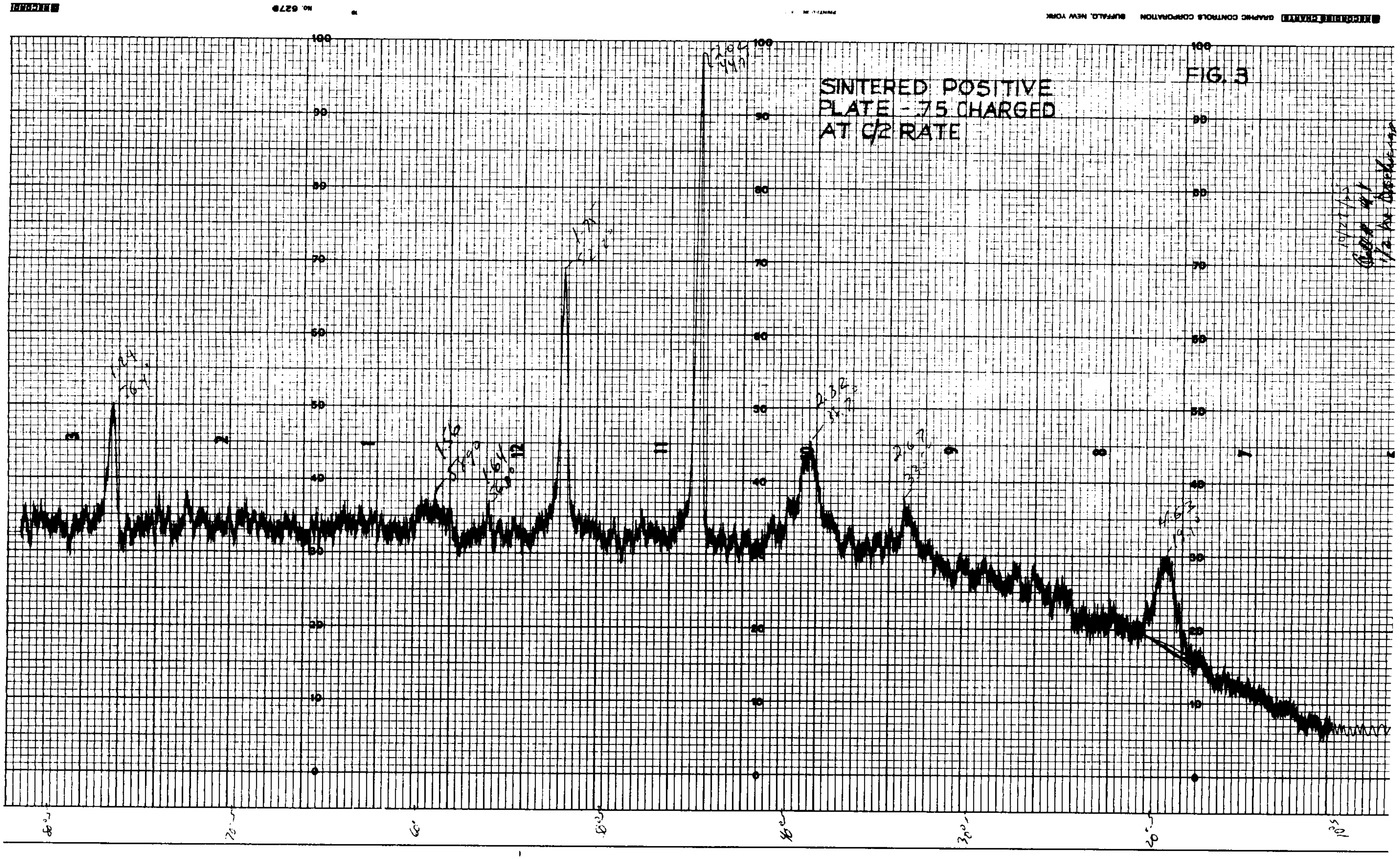


FIG. 3

SINTERED POSITIVE
PLATE -.75 CHARGED
AT C/2 RATE

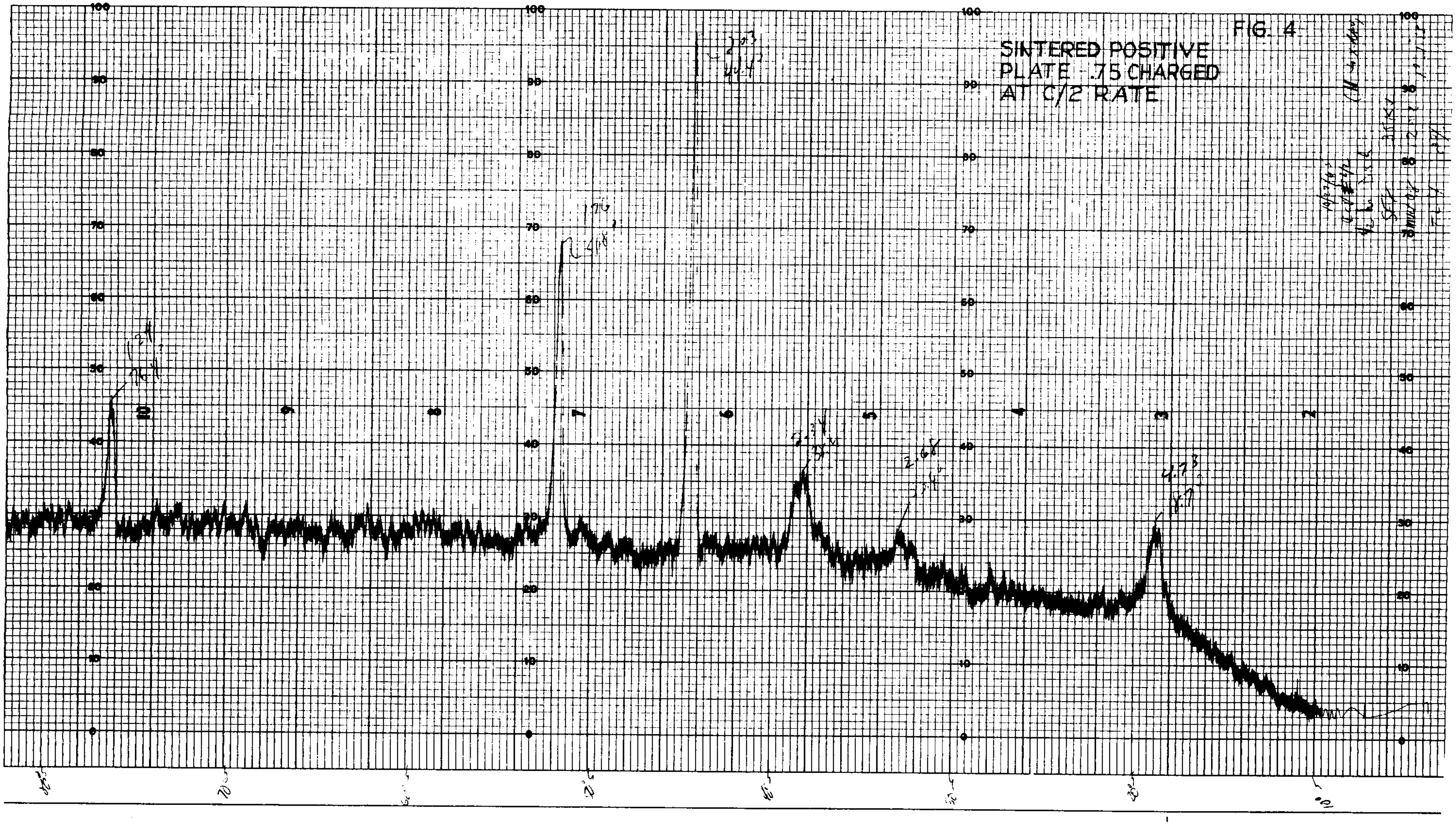


FIG. 4

SINTERED POSITIVE PLATE .75 CHARGED AT C/2 RATE

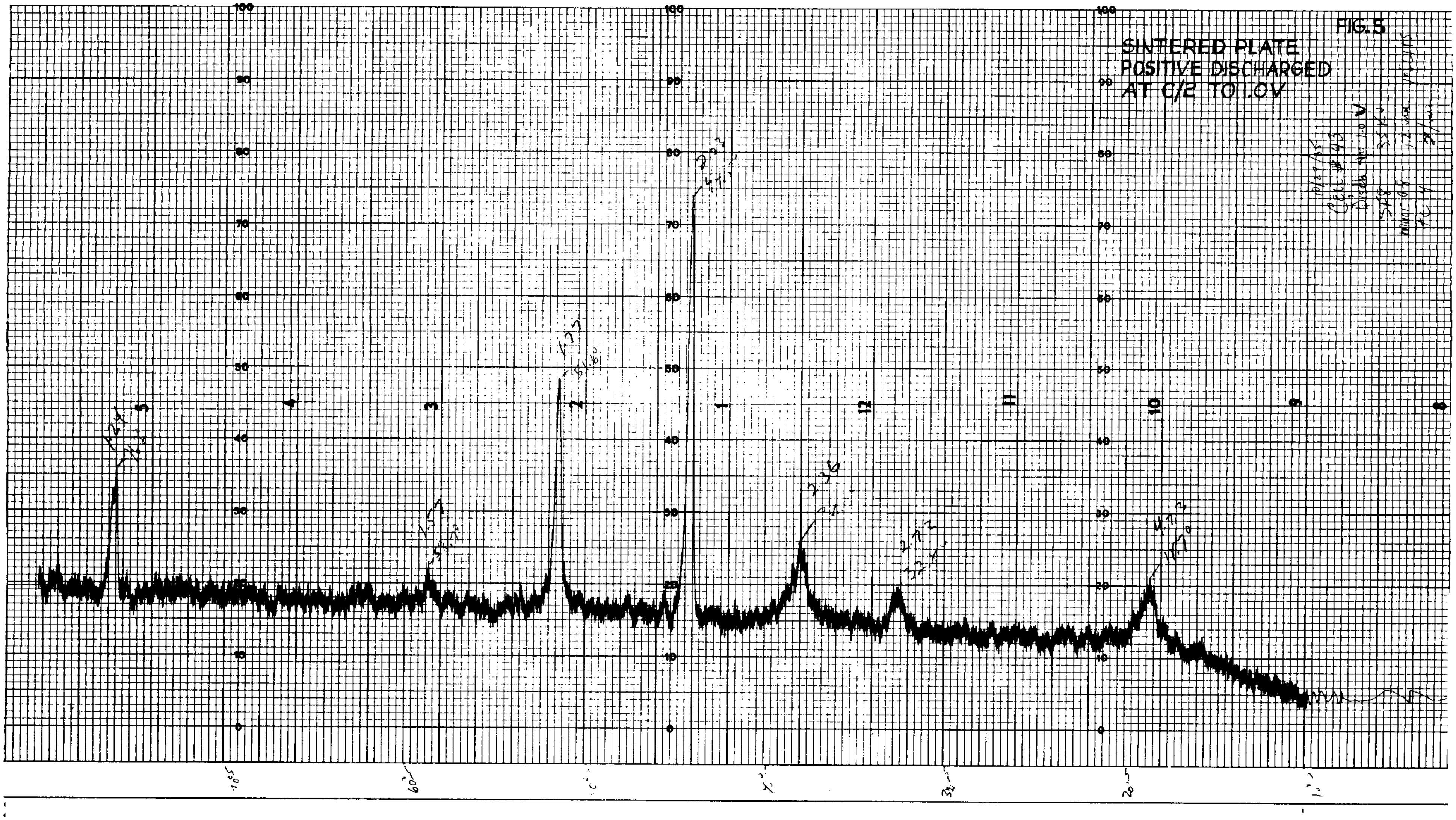
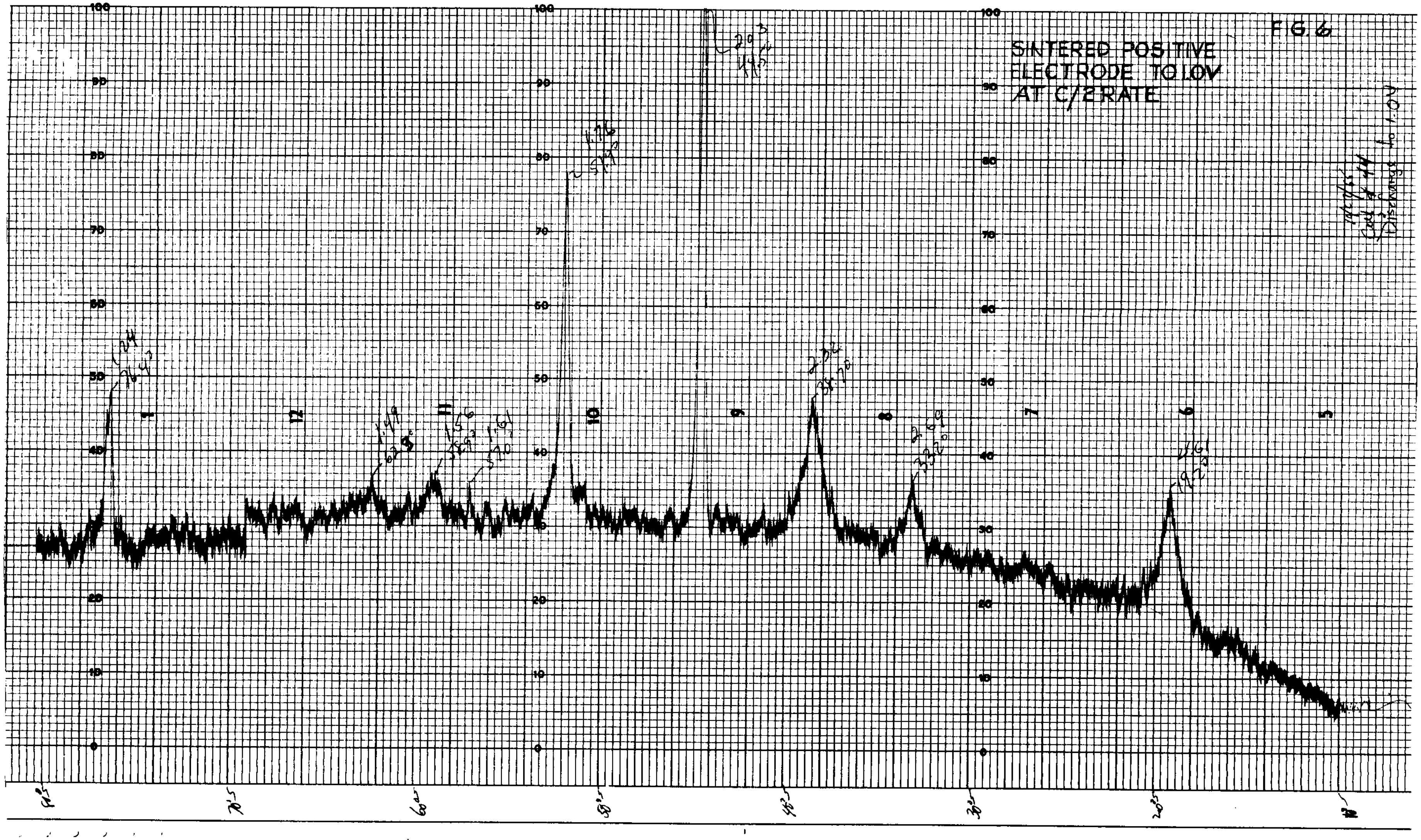


FIG. 5

SINTERED PLATE
POSITIVE DISCHARGED
AT C/2 TO 1.0V

FIG. 6



SINTERED POSITIVE ELECTRODE TO 1.0V AT C/2 RATE

10/21/65
Cell # 44
Discharge to 1.0V

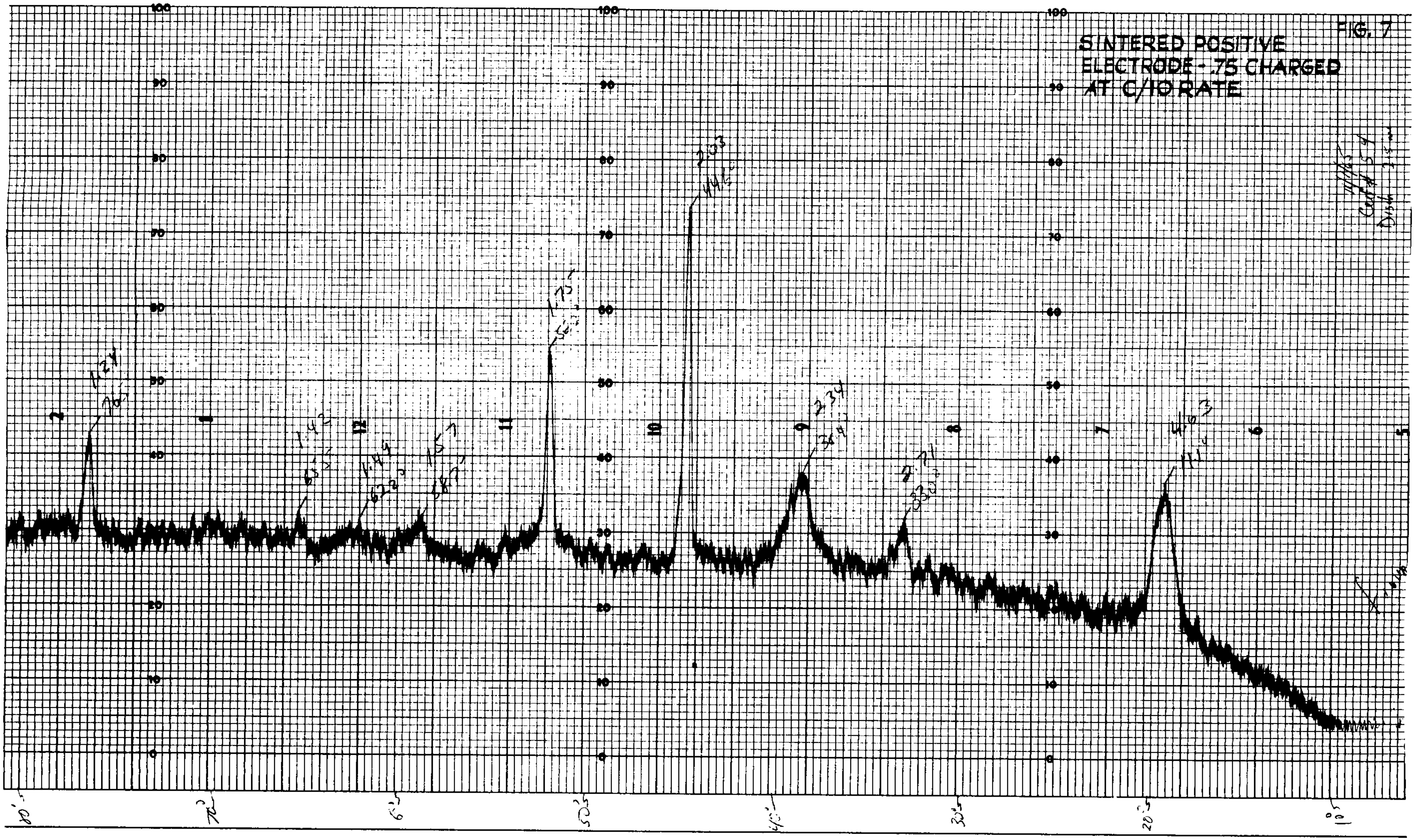


FIG. 7

SINTERED POSITIVE ELECTRODE - .75 CHARGED AT C/10 RATE

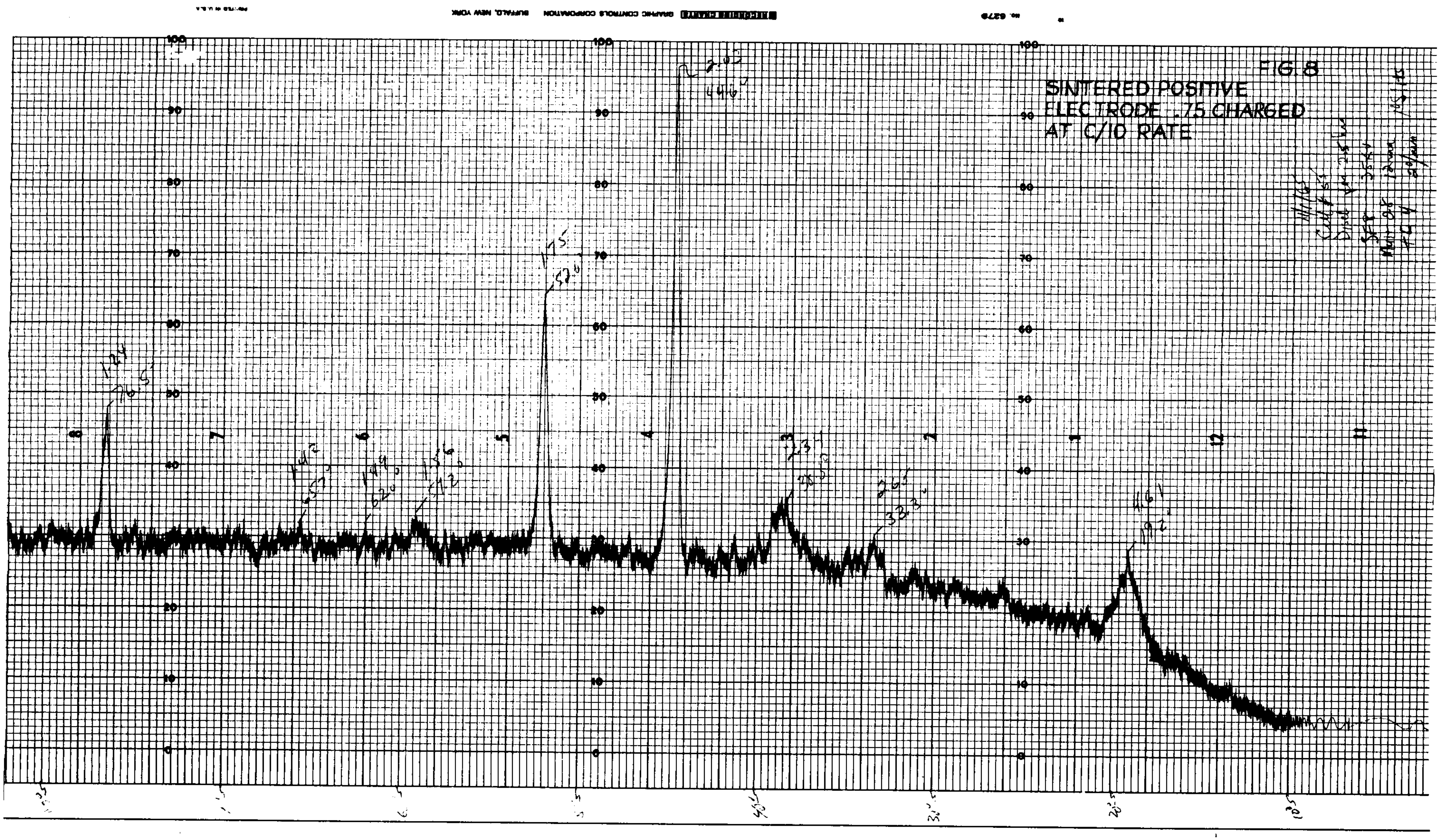


FIG 8

SINTERED POSITIVE ELECTRODE .75 CHARGED AT C/10 RATE

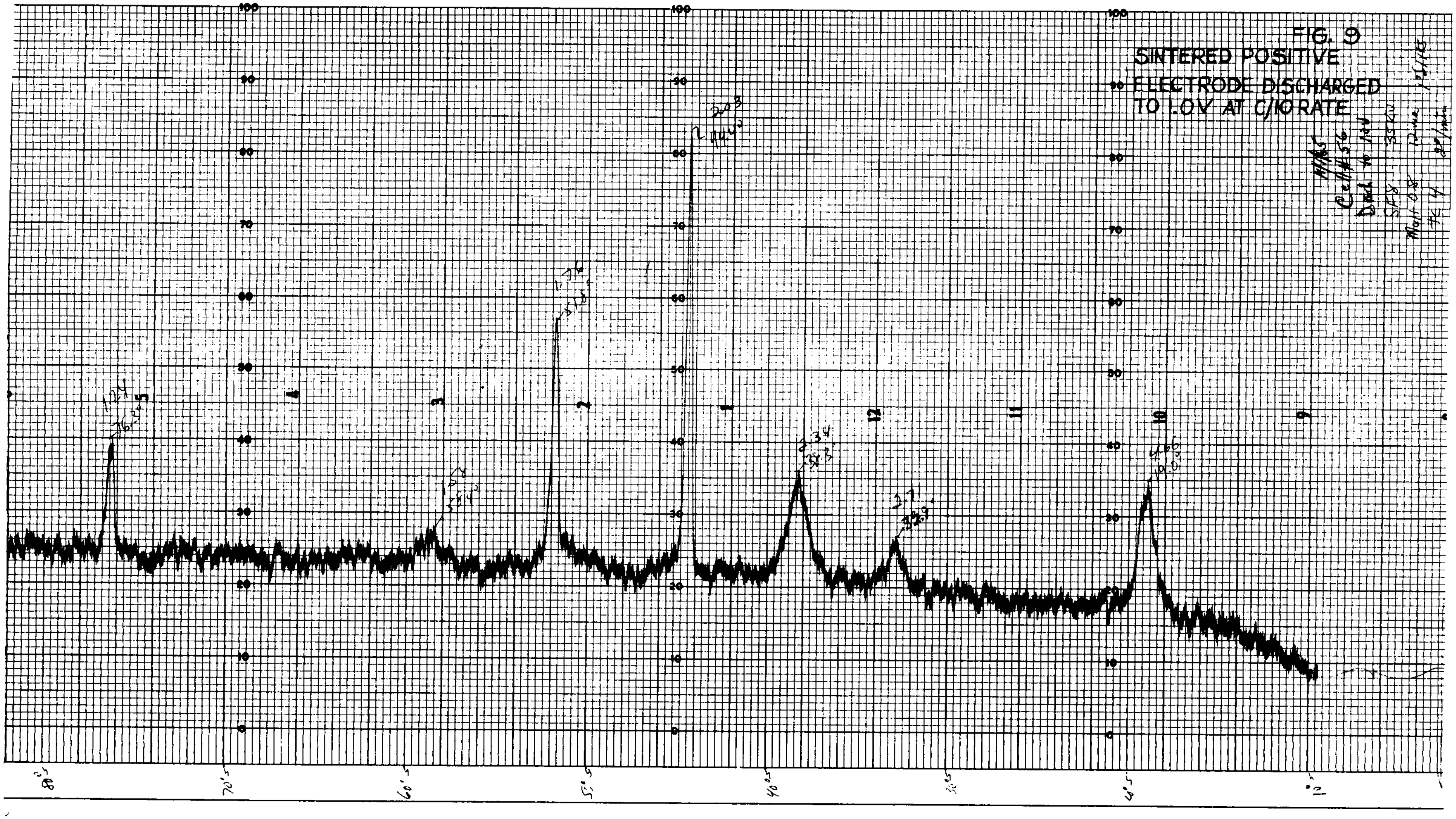


FIG. 9

SINTERED POSITIVE ELECTRODE DISCHARGED TO 1.0V AT C/10 RATE

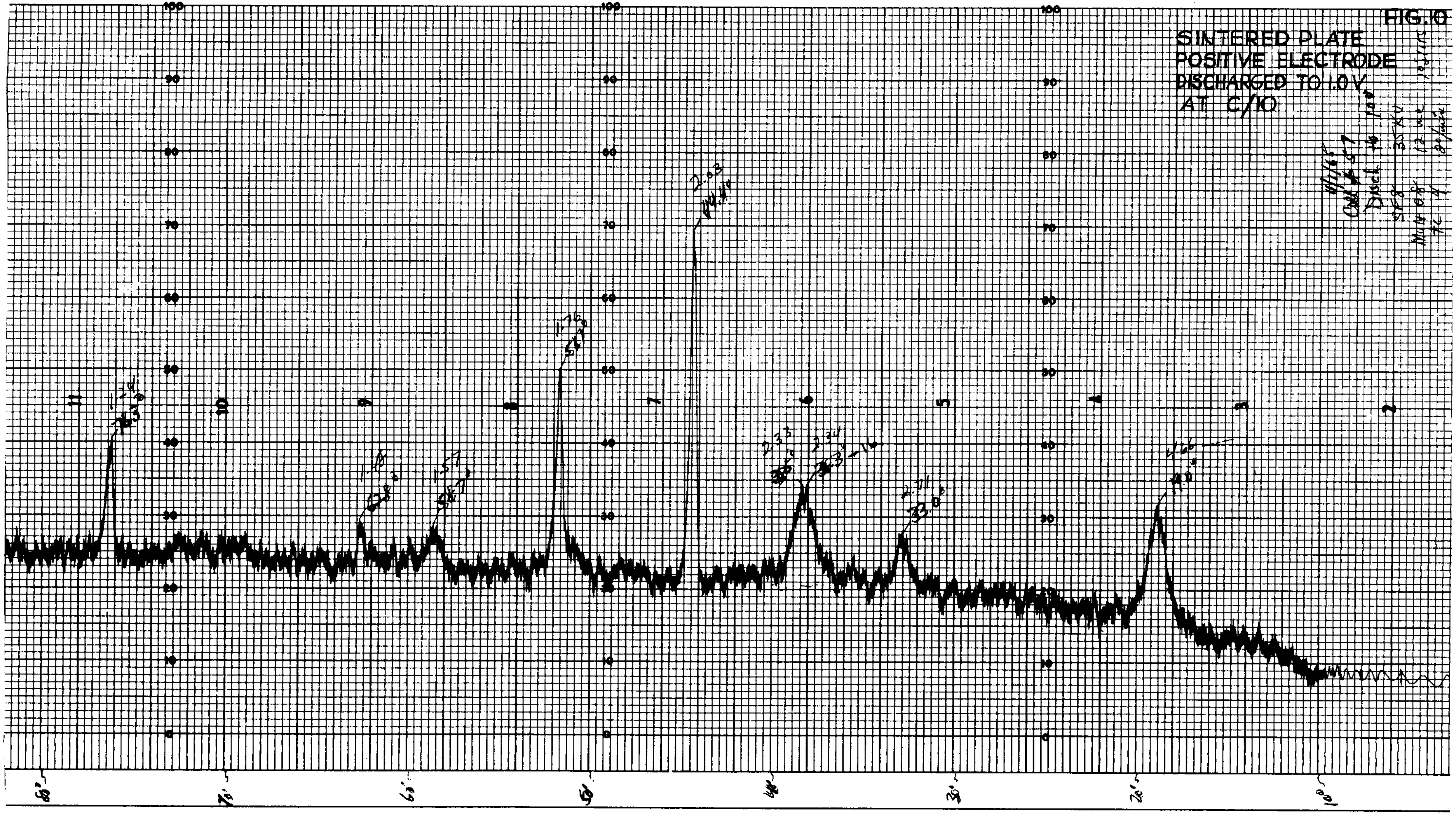


FIG. 10

SINTERED PLATE
POSITIVE ELECTRODE
DISCHARGED TO 1.0 V
AT C/10

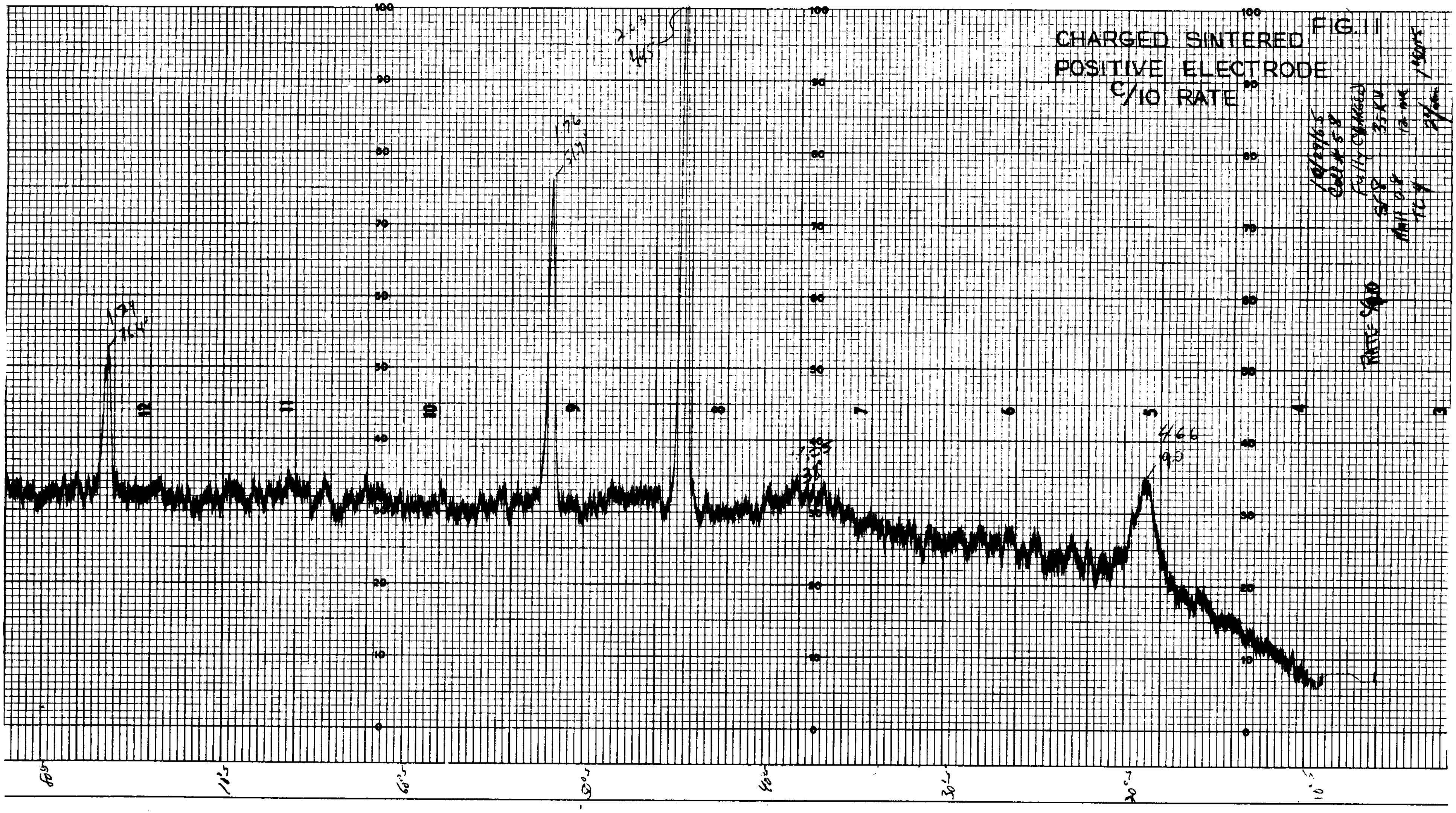


FIG. 11

CHARGED SINTERED POSITIVE ELECTRODE C/10 RATE

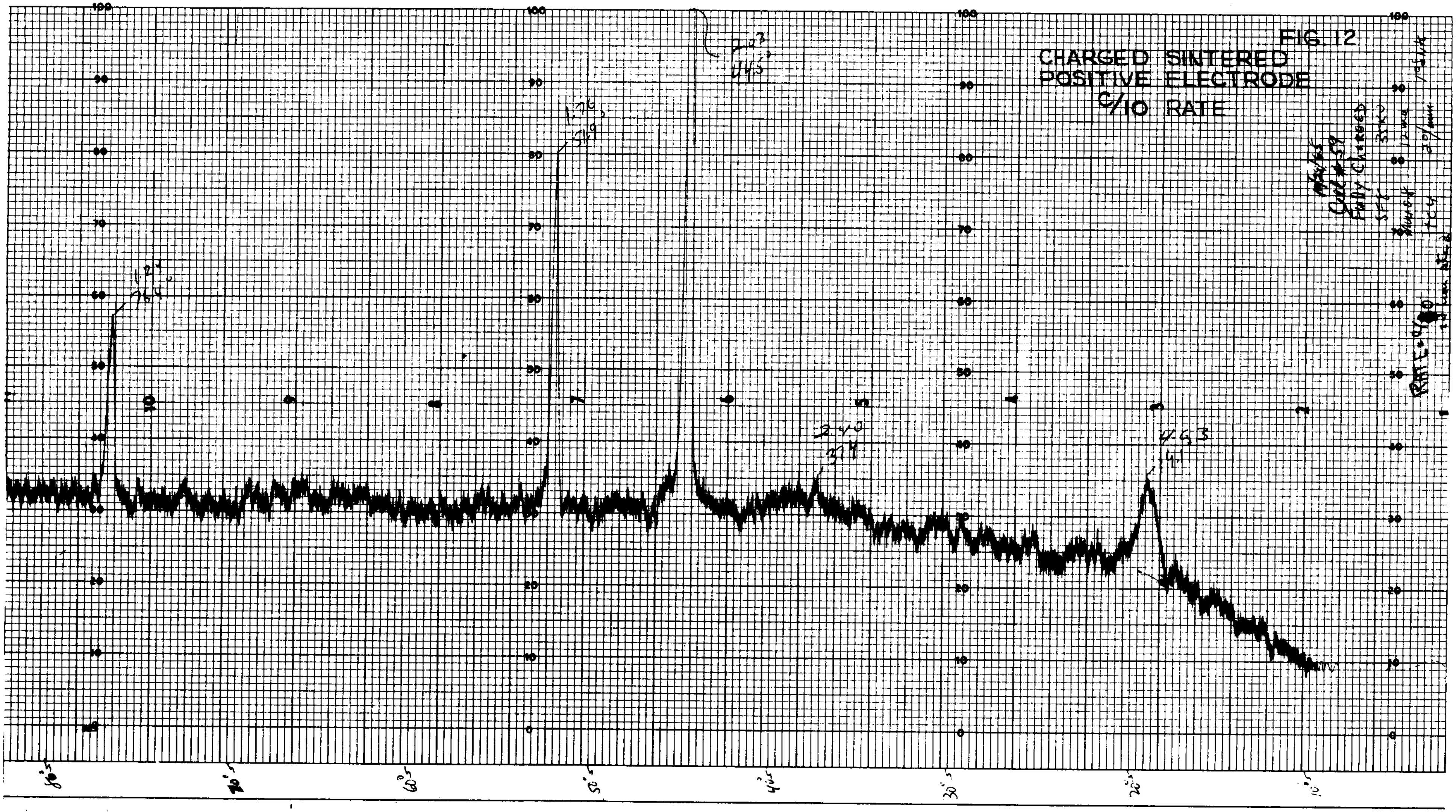


FIG. 12
CHARGED SINTERED
POSITIVE ELECTRODE
C/10 RATE

FIGURE 13.

X-RAY PATTERNS vs. STATE OF CHARGE

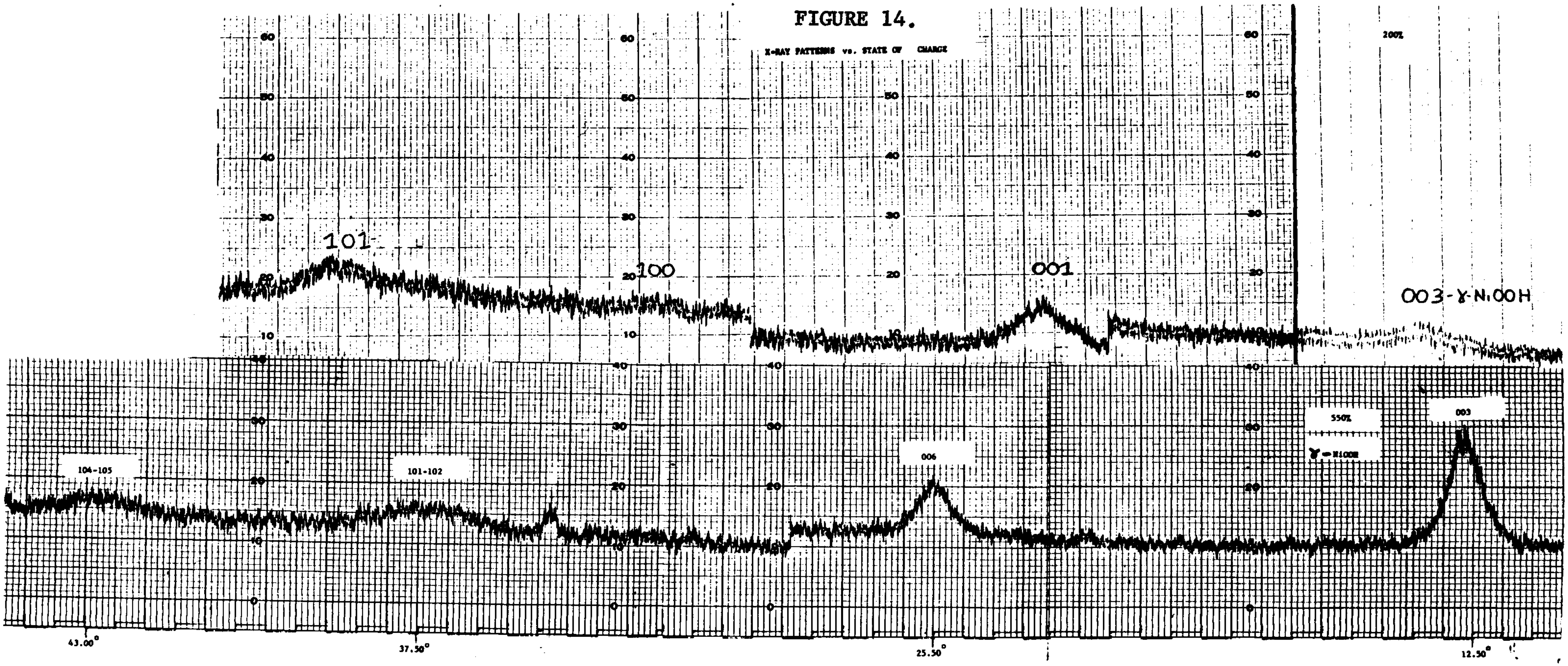


FIGURE 14.

X-RAY PATTERNS vs. STATE OF CHARGE

FIGURE 15.

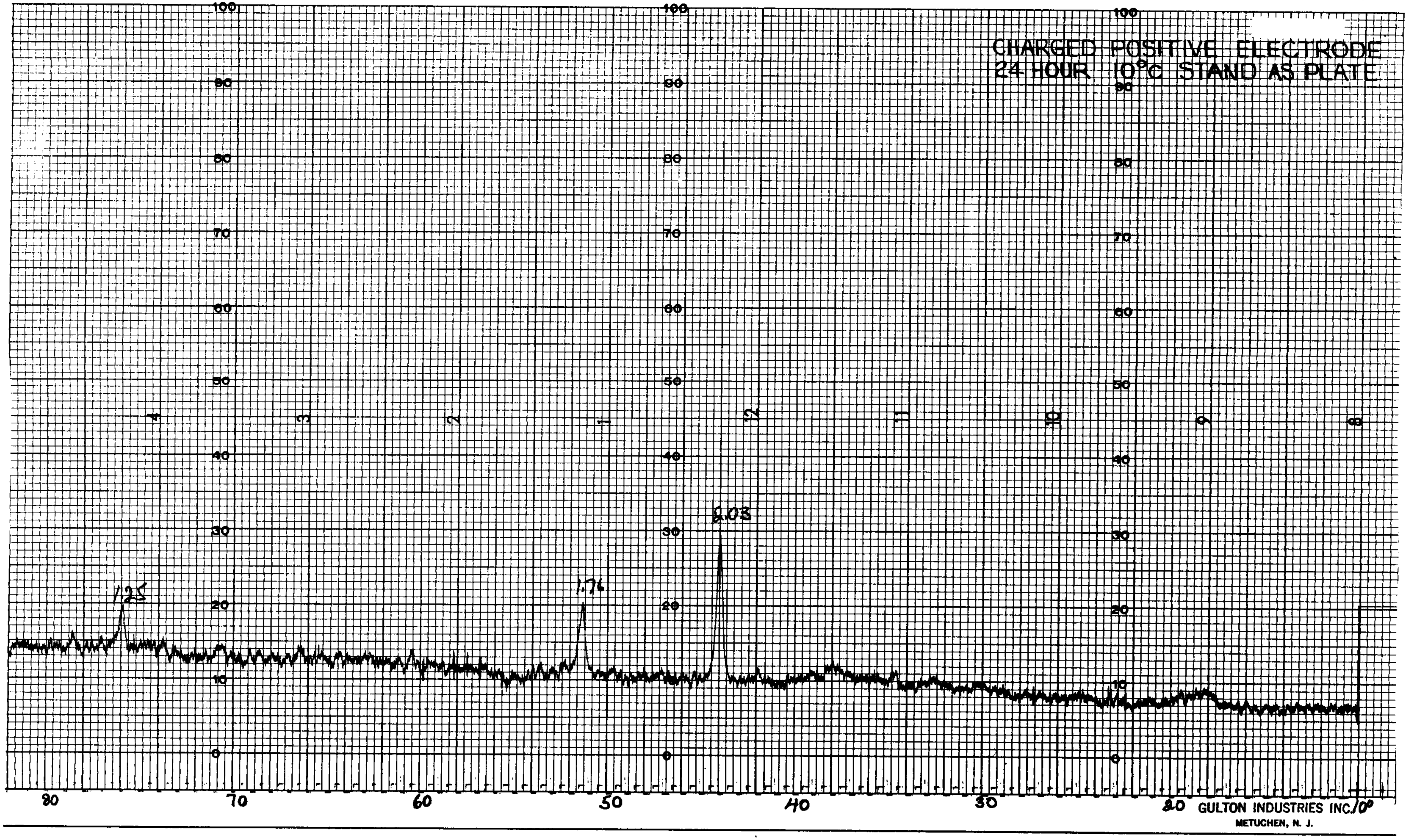

CHARGED POSITIVE ELECTRODE
24 HOUR 10°C STAND AS PLATE
1.25
1.76
2.03
100
90
80
70
60
50
40
30
20
10
0
4
3
2
1
12
11
10
9
8
80
70
60
50
40
30
20
10°
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIGURE 16.

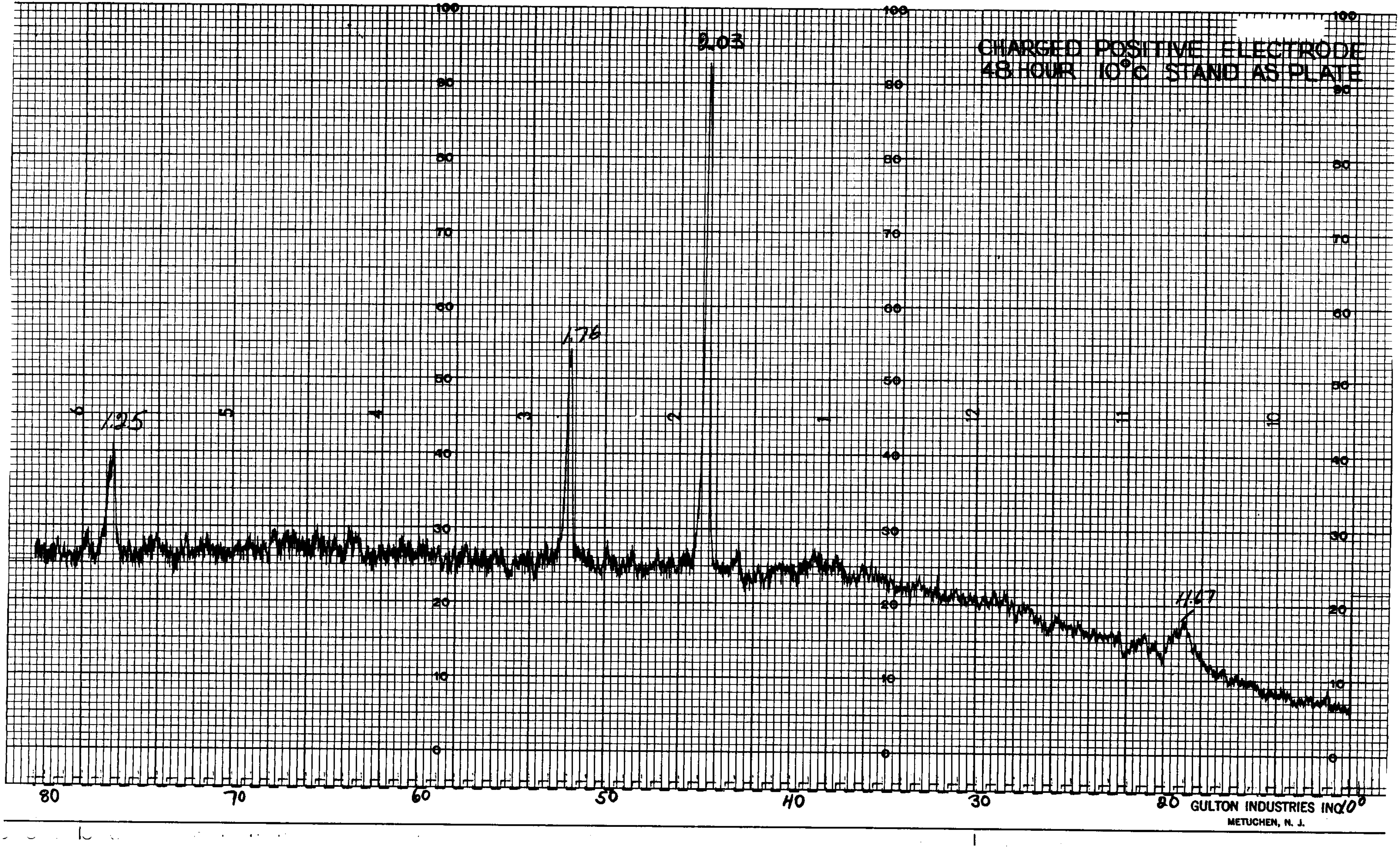

CHARGED POSITIVE ELECTRODE
48 HOUR 10°C STAND AS PLATE
2.03
1.76
1.25
4.47
100
90
80
70
60
50
40
30
20
10
0
80
70
60
50
40
30
20
10
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIGURE 17.

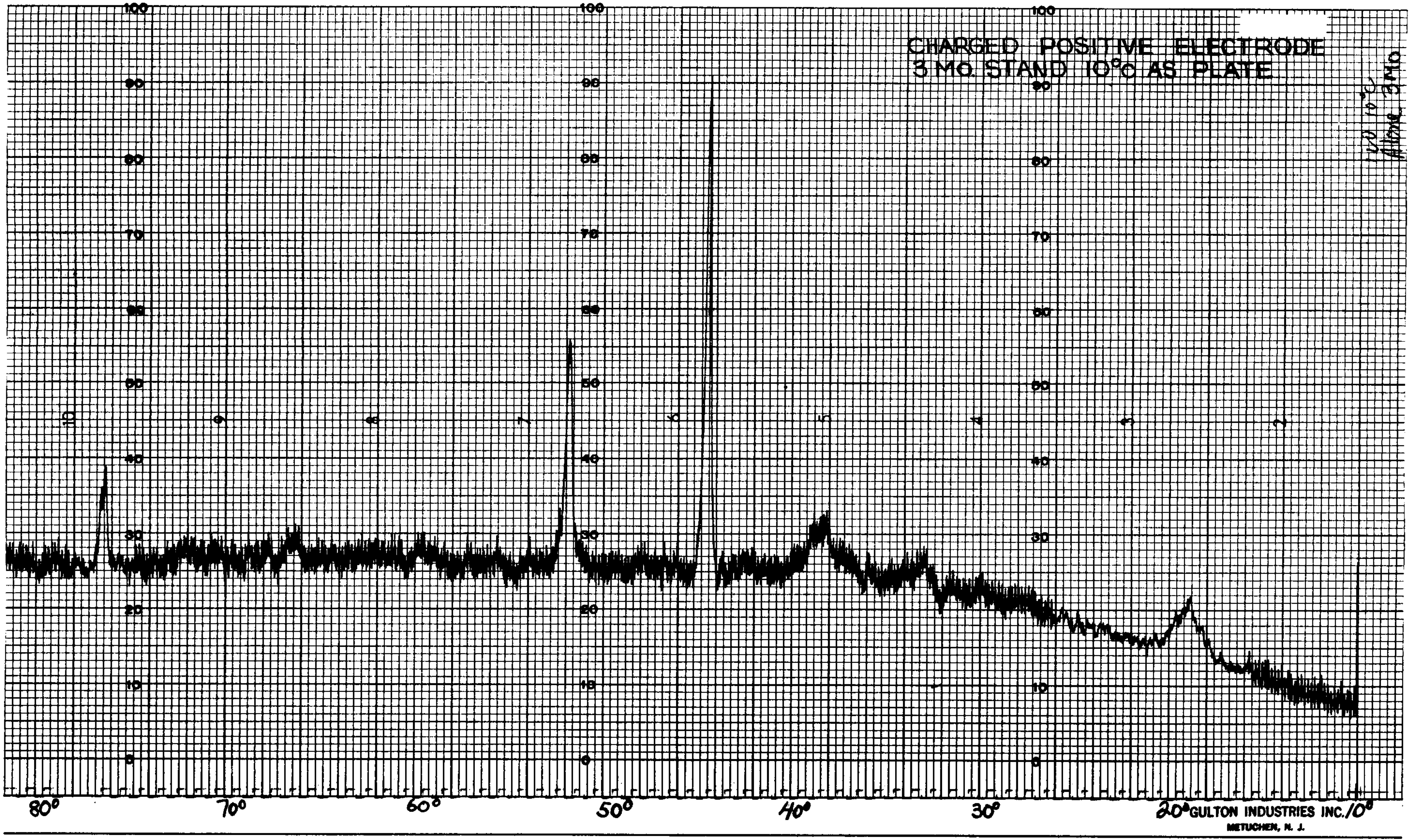
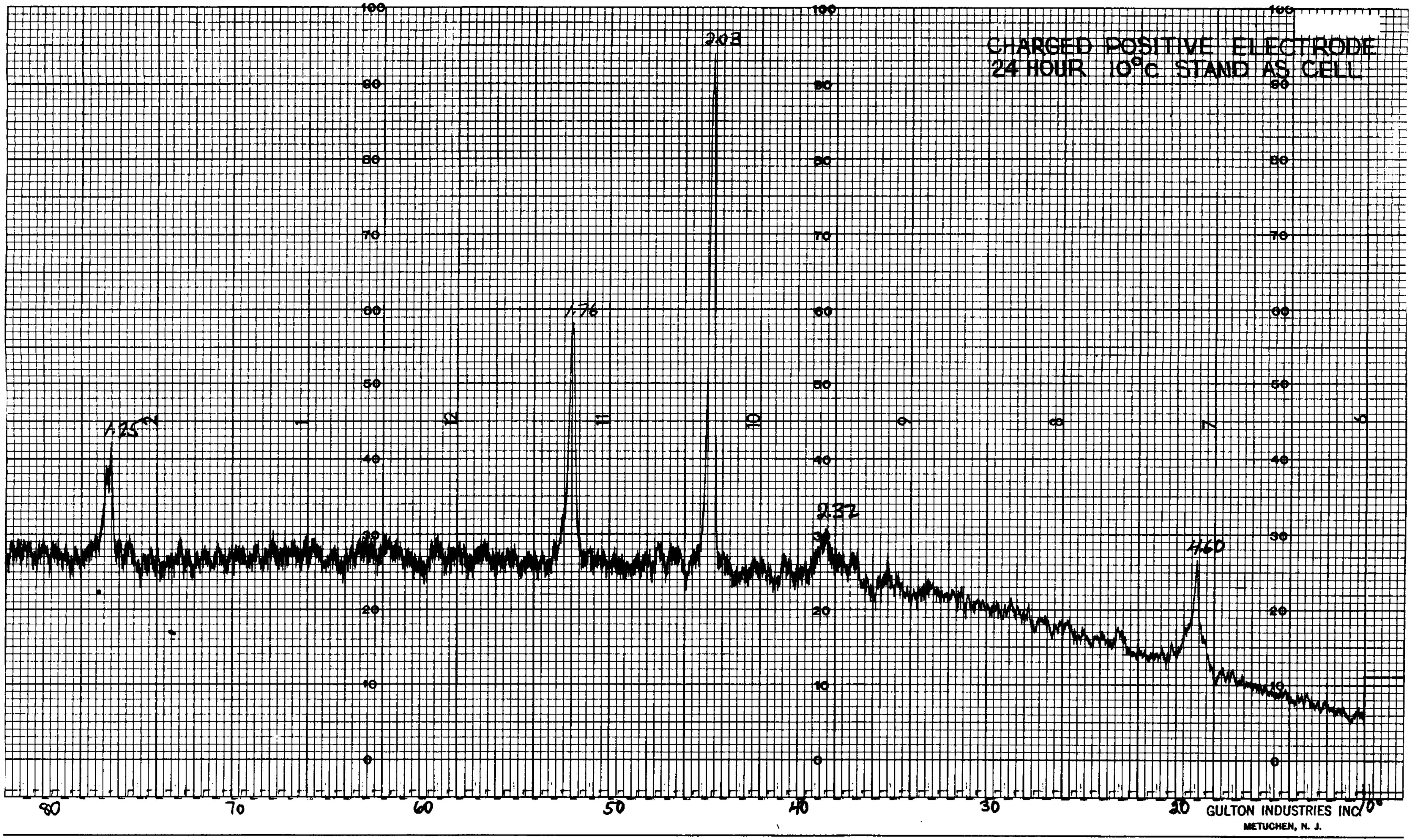
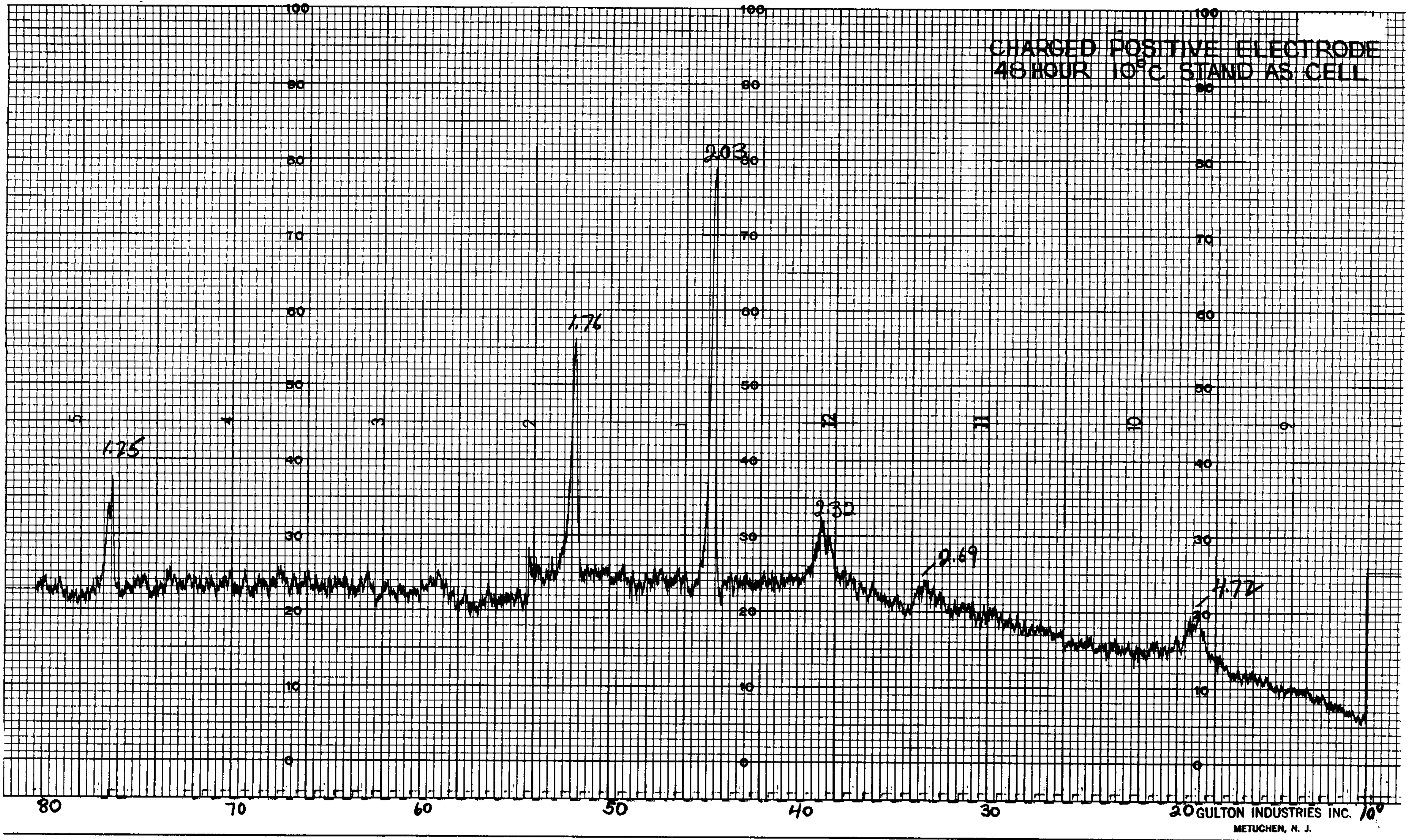

CHARGED POSITIVE ELECTRODE
3 MO. STAND 10°C AS PLATE
120 10°C
Alone 3Mo
100
90
80
70
60
50
40
30
20
10
0
10
9
8
7
6
5
4
3
2
80°
70°
60°
50°
40°
30°
20°
10°
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIGURE 18.



CHARGED POSITIVE ELECTRODE
24 HOUR 10°C STAND AS CELL

FIGURE 19.



CHARGED POSITIVE ELECTRODE
48 HOUR 10°C STAND AS CELL

FIGURE 20.

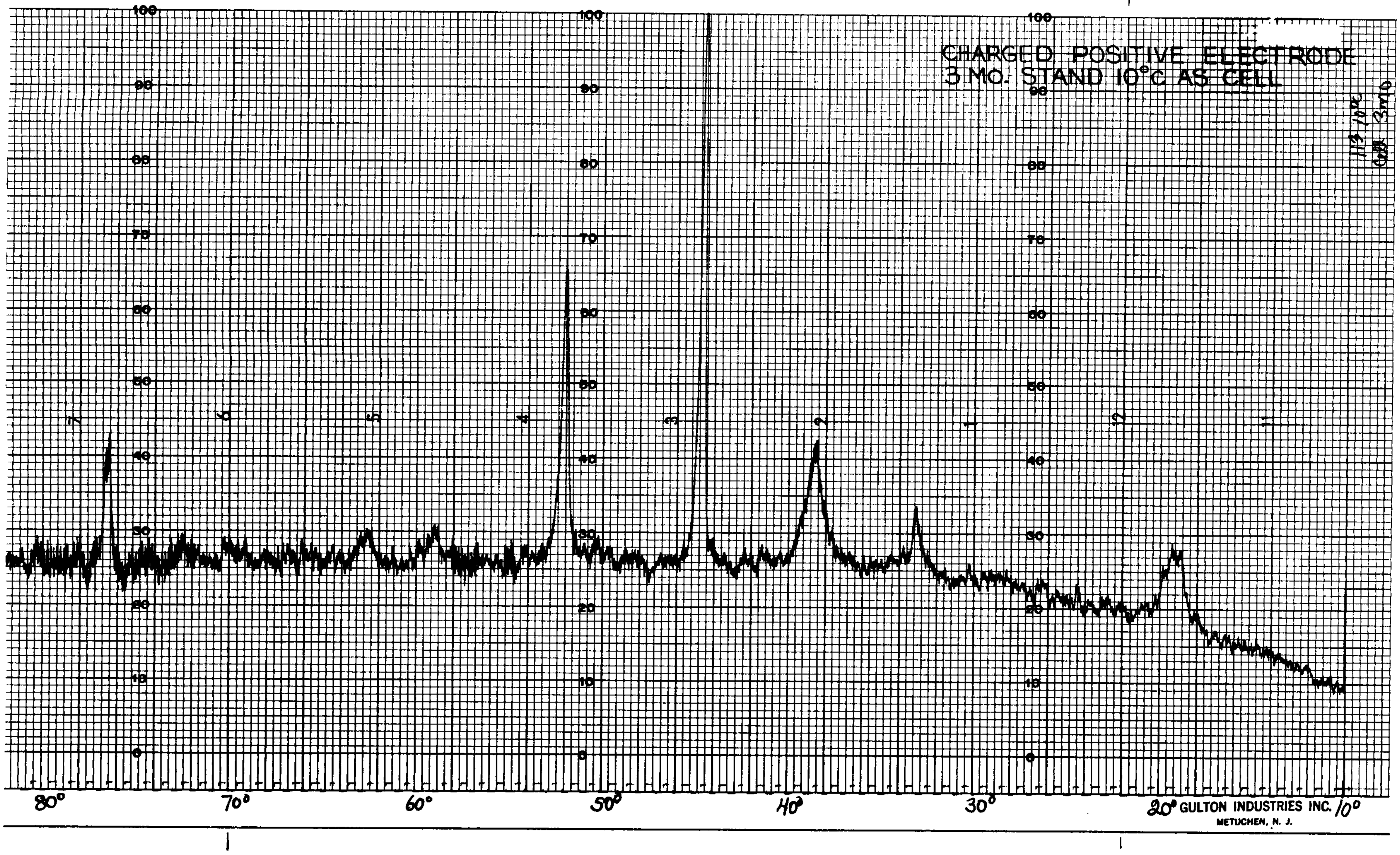
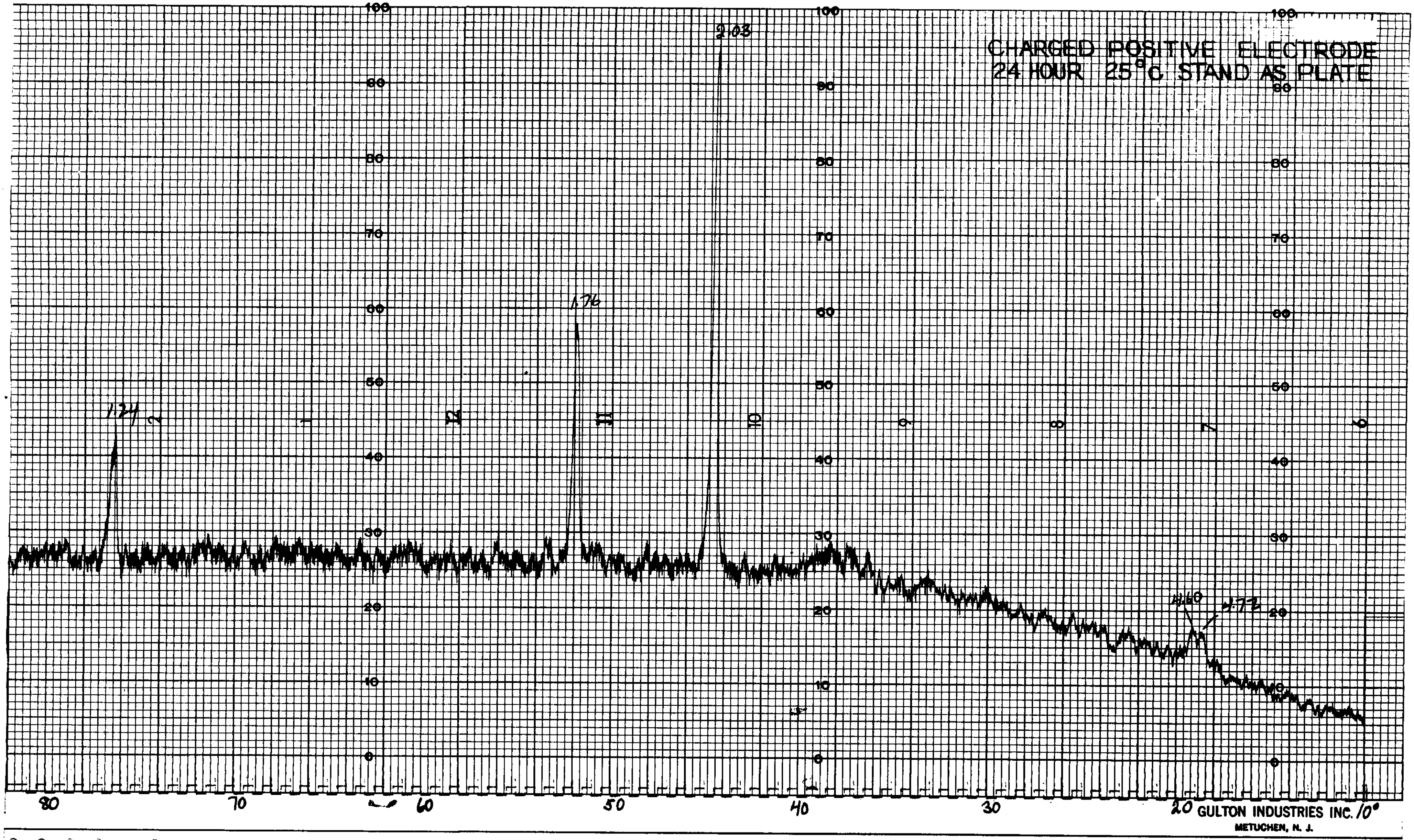
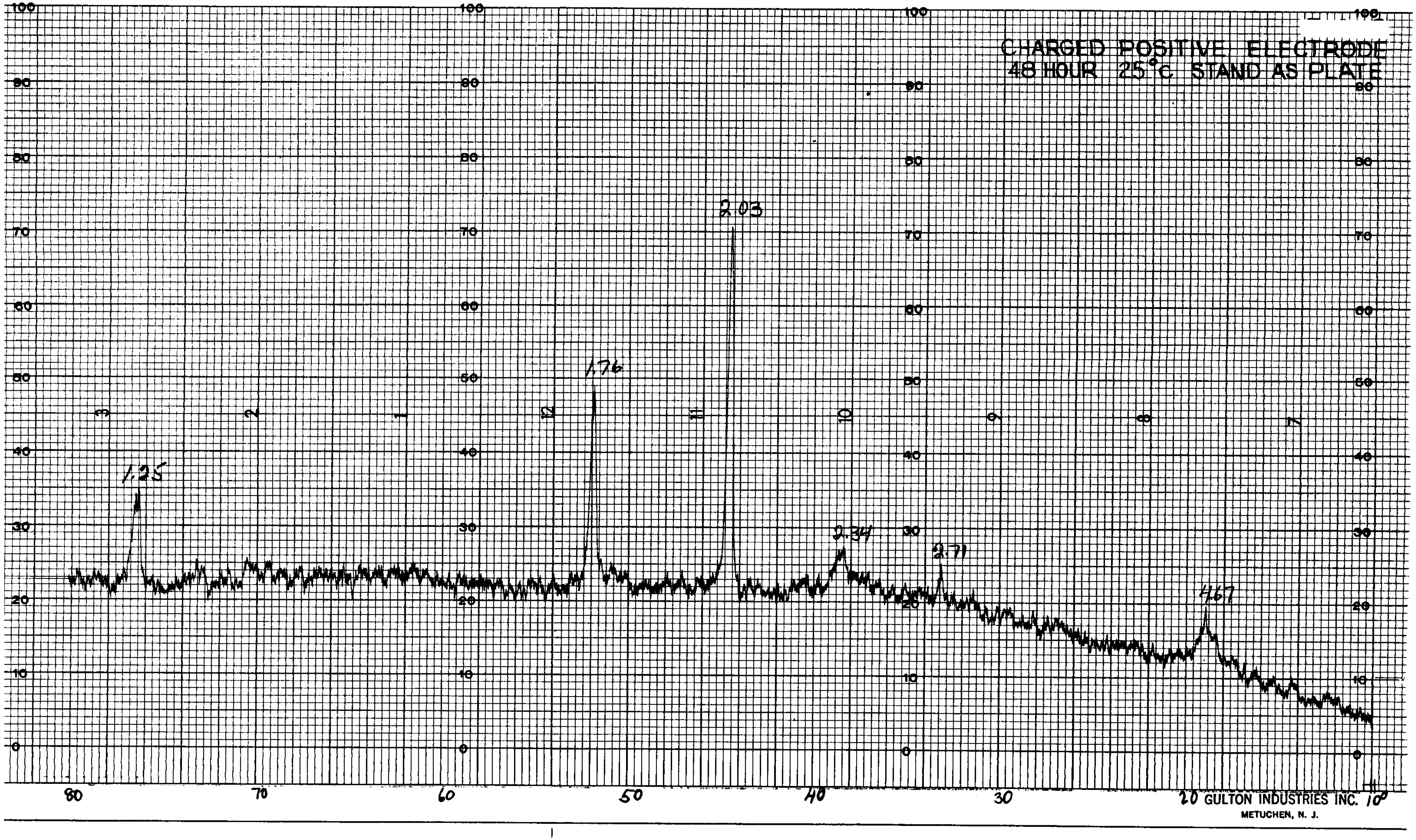

CHARGED POSITIVE ELECTRODE
3 MO. STAND 10°C AS CELL
113 10°C
cell 3mo
100
90
80
70
60
50
40
30
20
10
0
7
6
5
4
3
2
1
12
11
80°
70°
60°
50°
40°
30°
20°
10°
GULTON INDUSTRIES INC.
METUCHEN, N. J.

FIGURE 21.



CHARGED POSITIVE ELECTRODE
24 HOUR 25°C STAND AS PLATE

FIGURE 22.



CHARGED POSITIVE ELECTRODE
48 HOUR 25°C STAND AS PLATE

FIGURE 23.

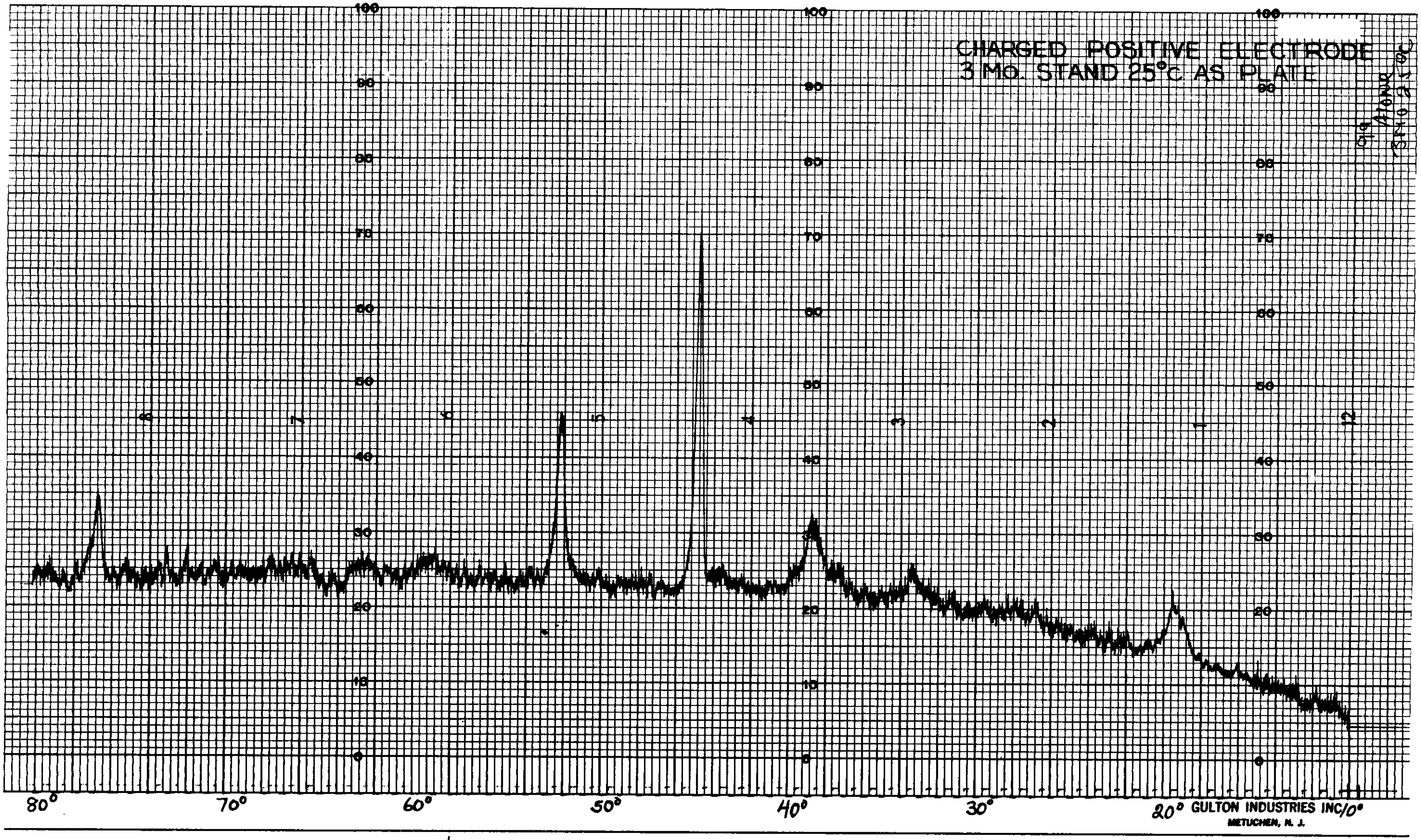
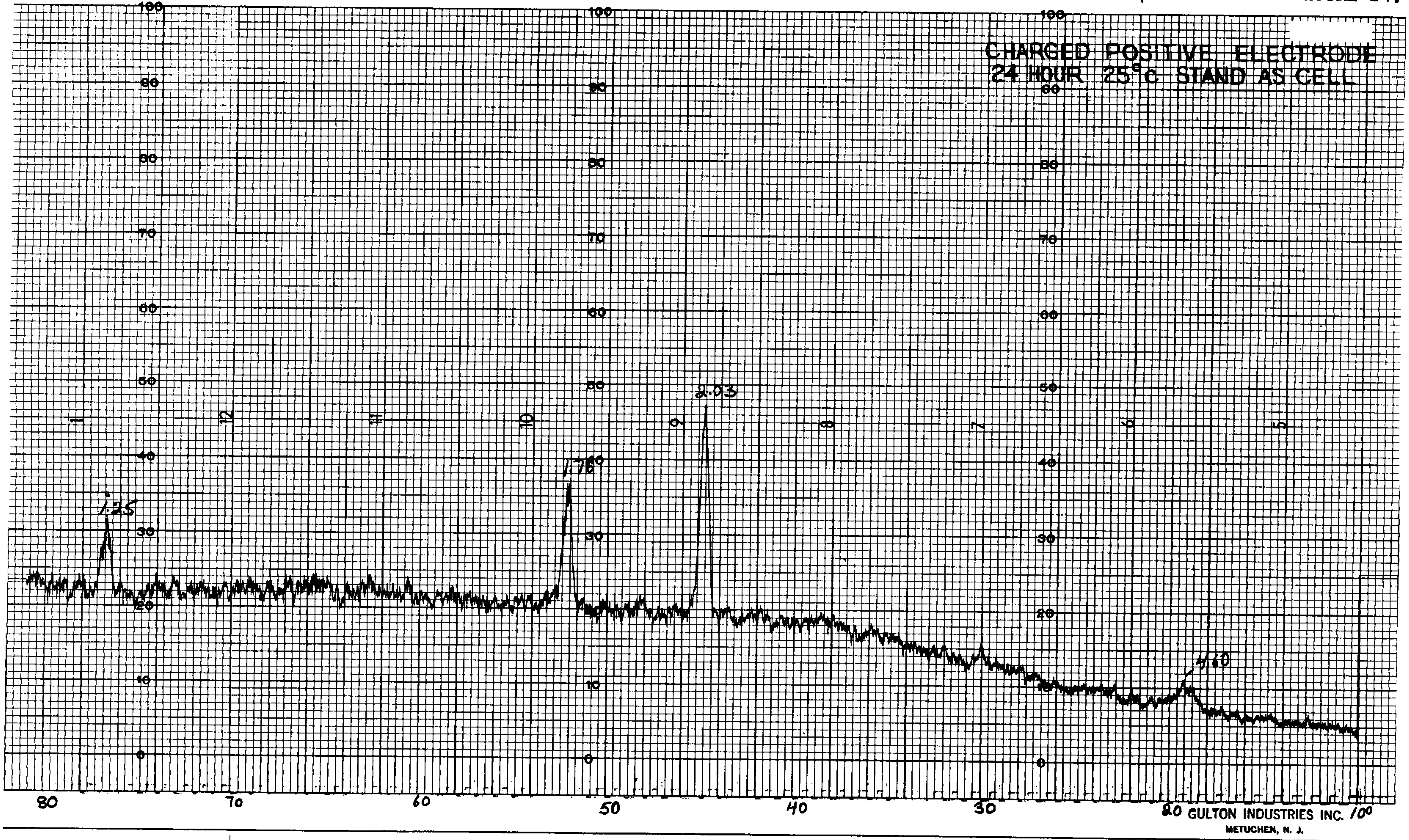
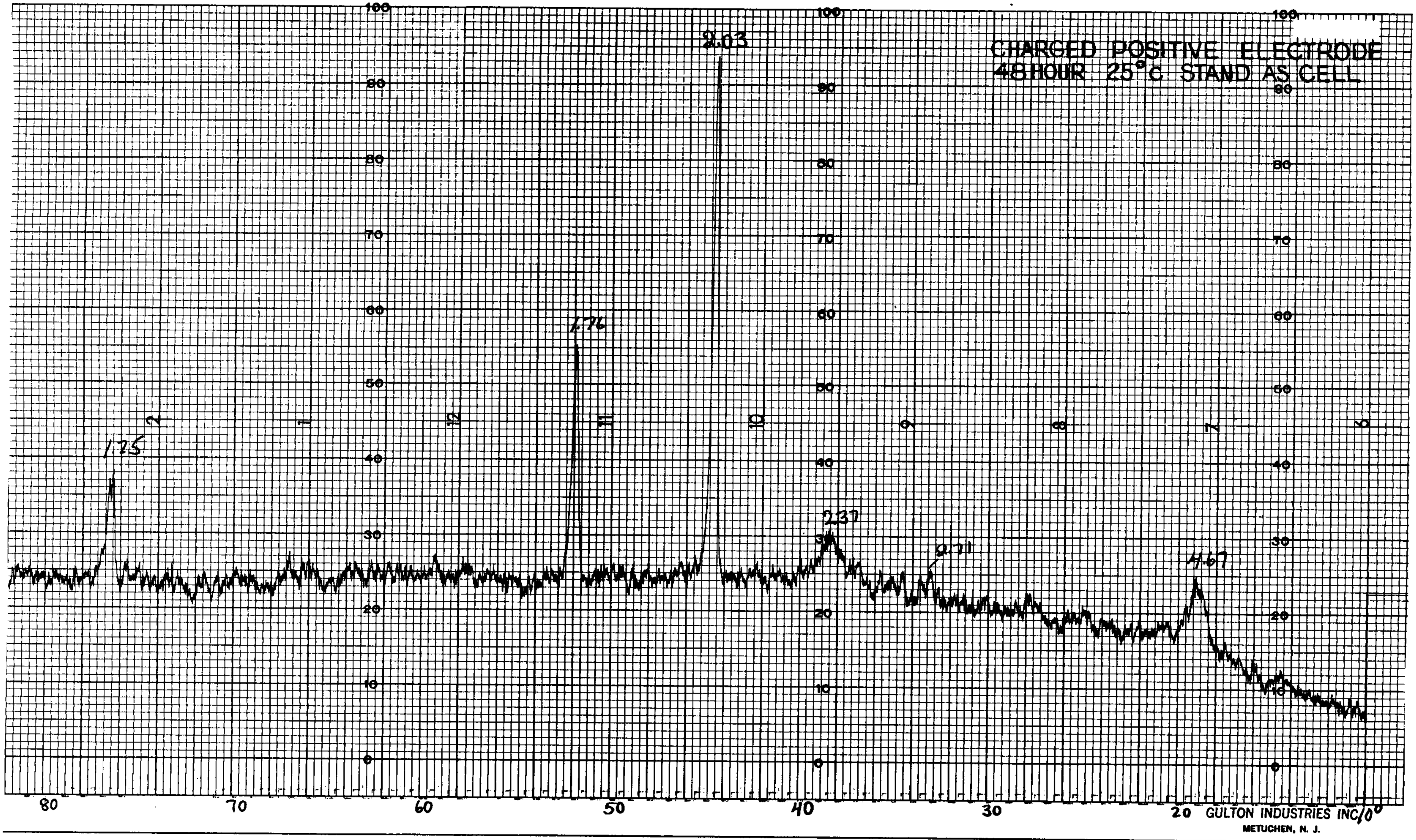

CHARGED POSITIVE ELECTRODE
3 MO. STAND 25°C AS PLATE
916
Alone
100
90
80
70
60
50
40
30
20
10
0
80°
70°
60°
50°
40°
30°
20°
GULTON INDUSTRIES INC/0°
METUCHEN, N. J.
8
7
6
5
4
3
2
1
12

FIGURE 24.



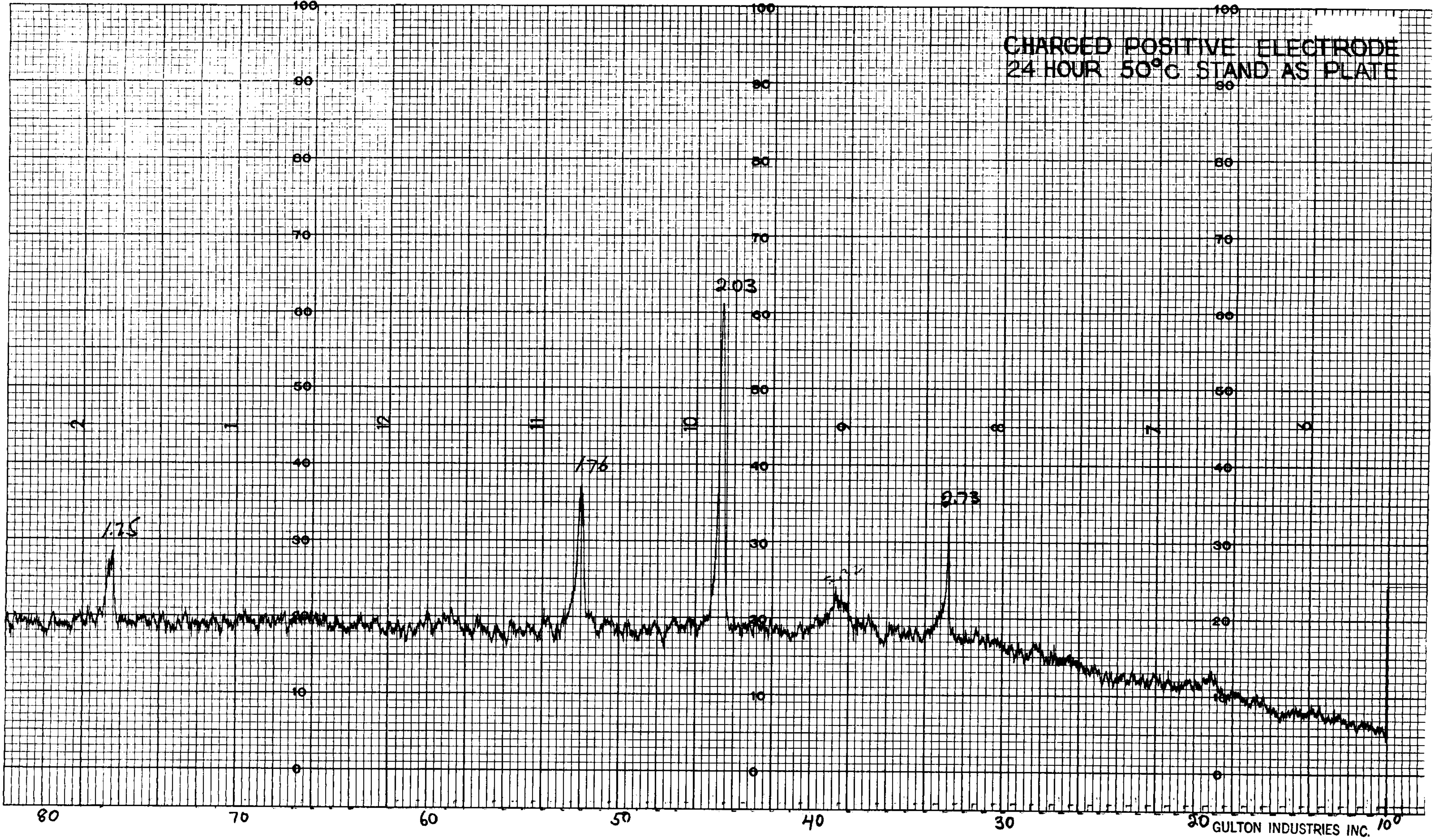
CHARGED POSITIVE ELECTRODE
24 HOUR 25°C STAND AS CELL

FIGURE 25.



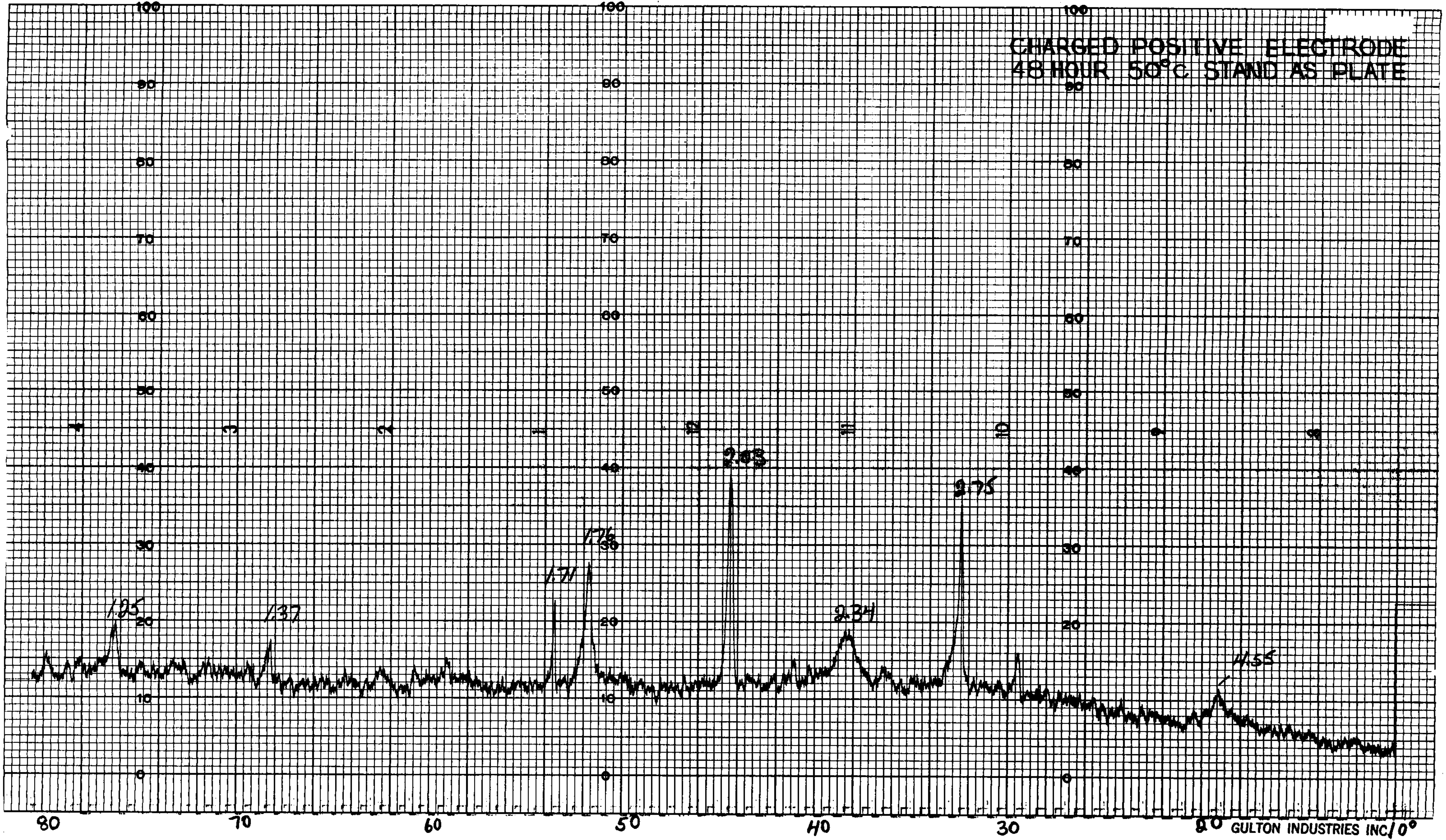
CHARGED POSITIVE ELECTRODE
48 HOUR 25°C STAND AS CELL

FIGURE 26.



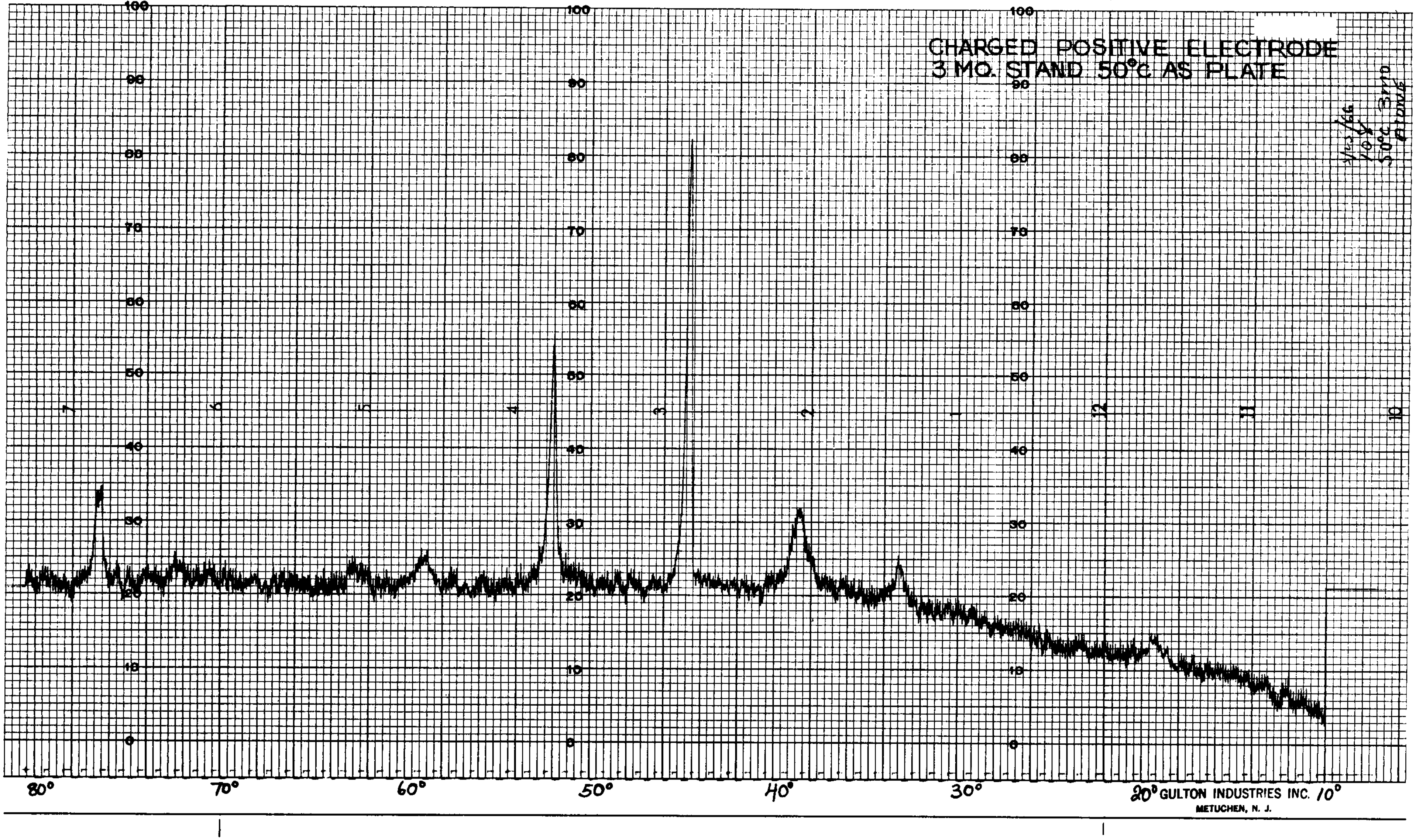
CHARGED POSITIVE ELECTRODE
24 HOUR 50°C STAND AS PLATE

FIGURE 27.



CHARGED POSITIVE ELECTRODE
48 HOUR 50°C STAND AS PLATE

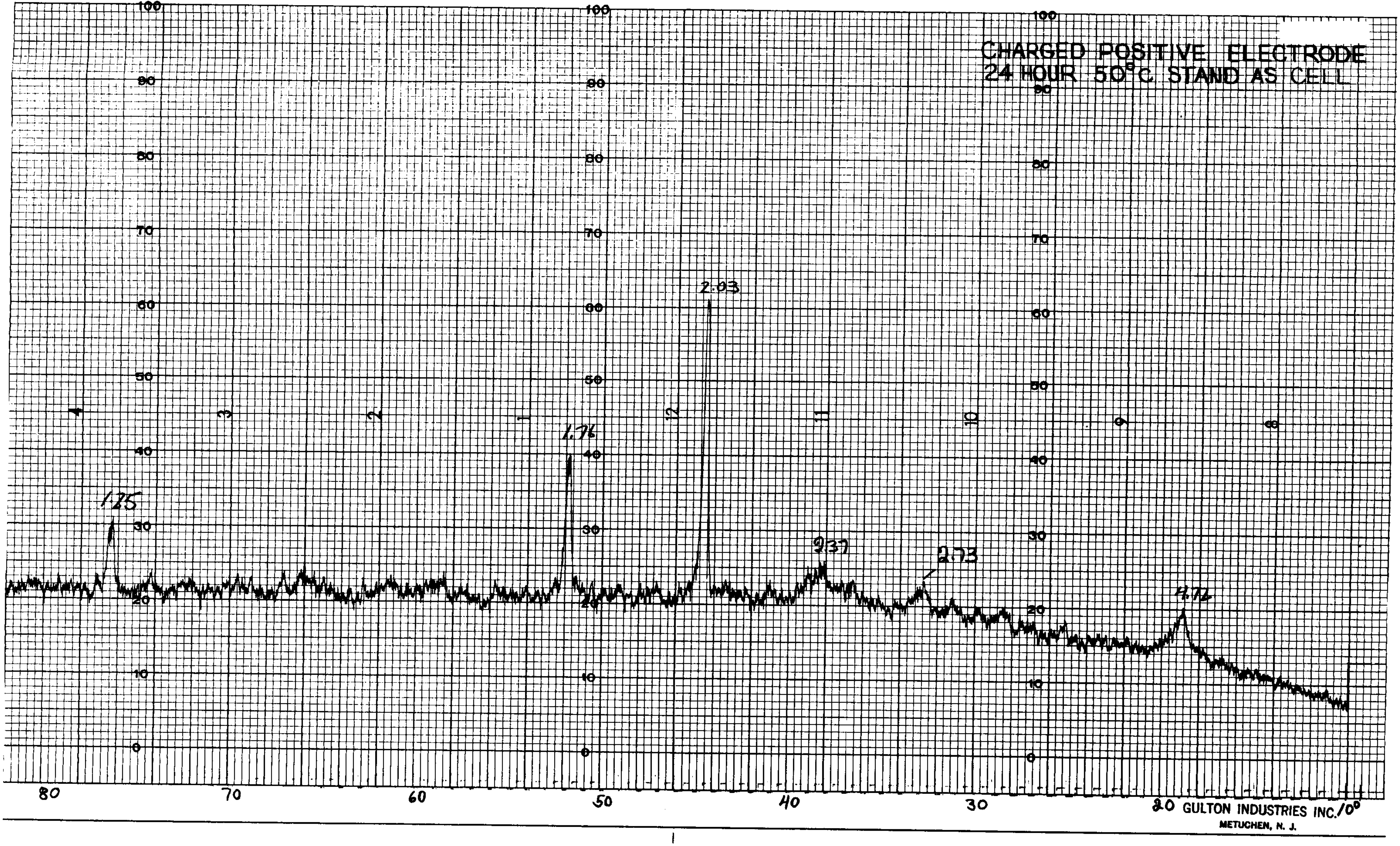
FIGURE 28.



CHARGED POSITIVE ELECTRODE
3 MO. STAND 50°C AS PLATE

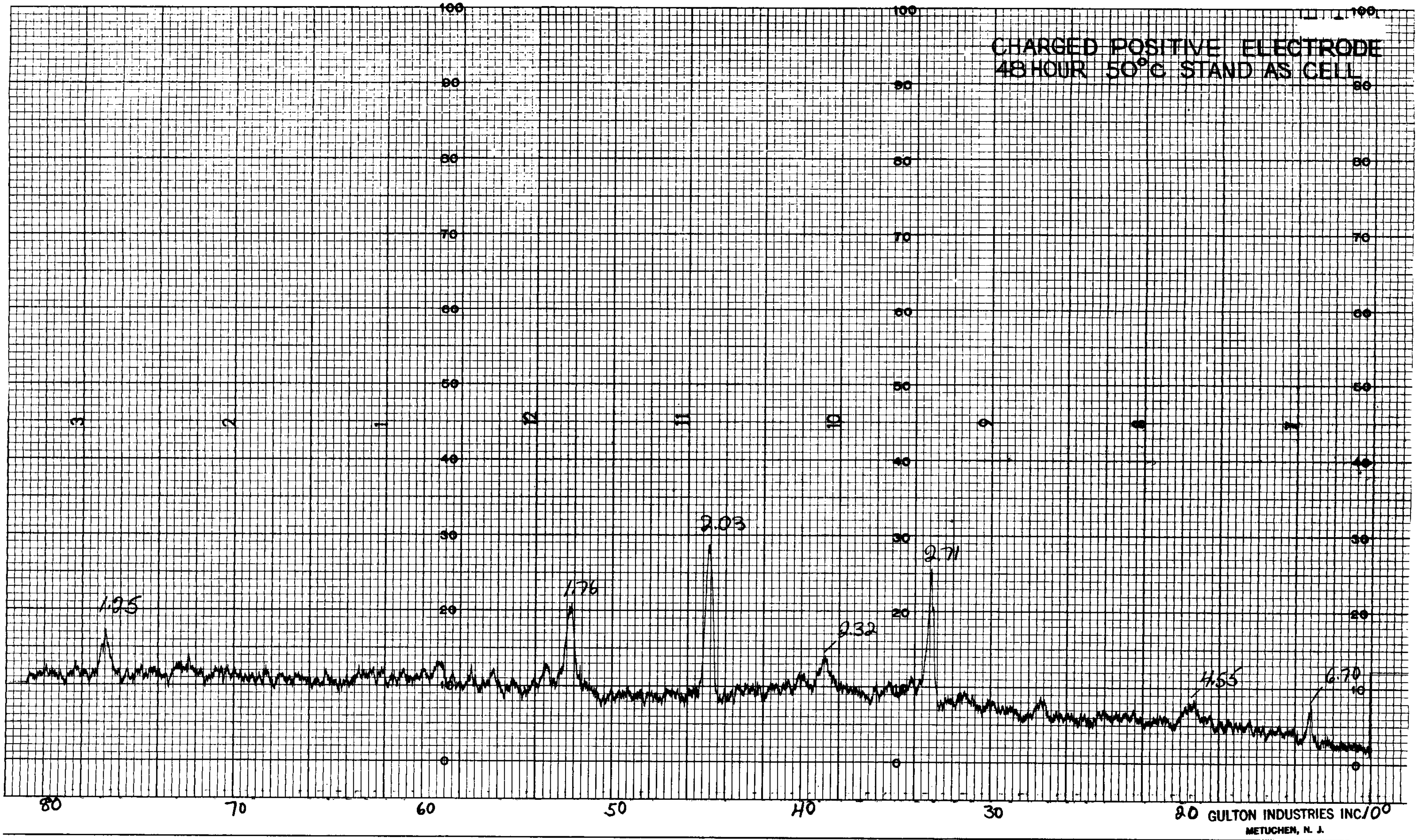
1/25/66
10 #
50°C 3 mo
Plate

FIGURE 29.



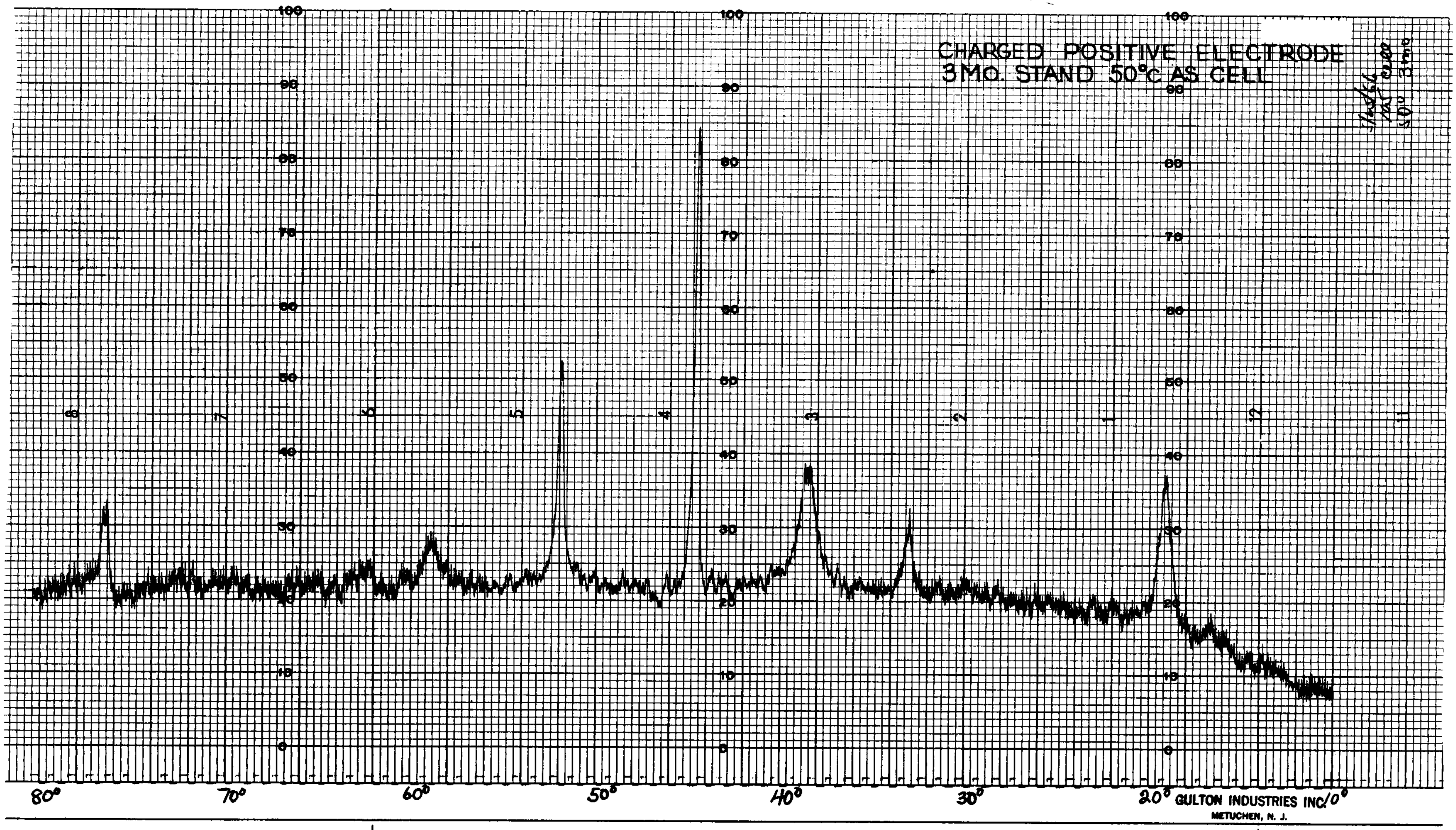
CHARGED POSITIVE ELECTRODE
24 HOUR 50°C STAND AS CELL

FIGURE 30.



CHARGED POSITIVE ELECTRODE
48 HOUR 50°C STAND AS CELL

FIGURE 31.



CHARGED POSITIVE ELECTRODE
3MO. STAND 50°C AS CELL

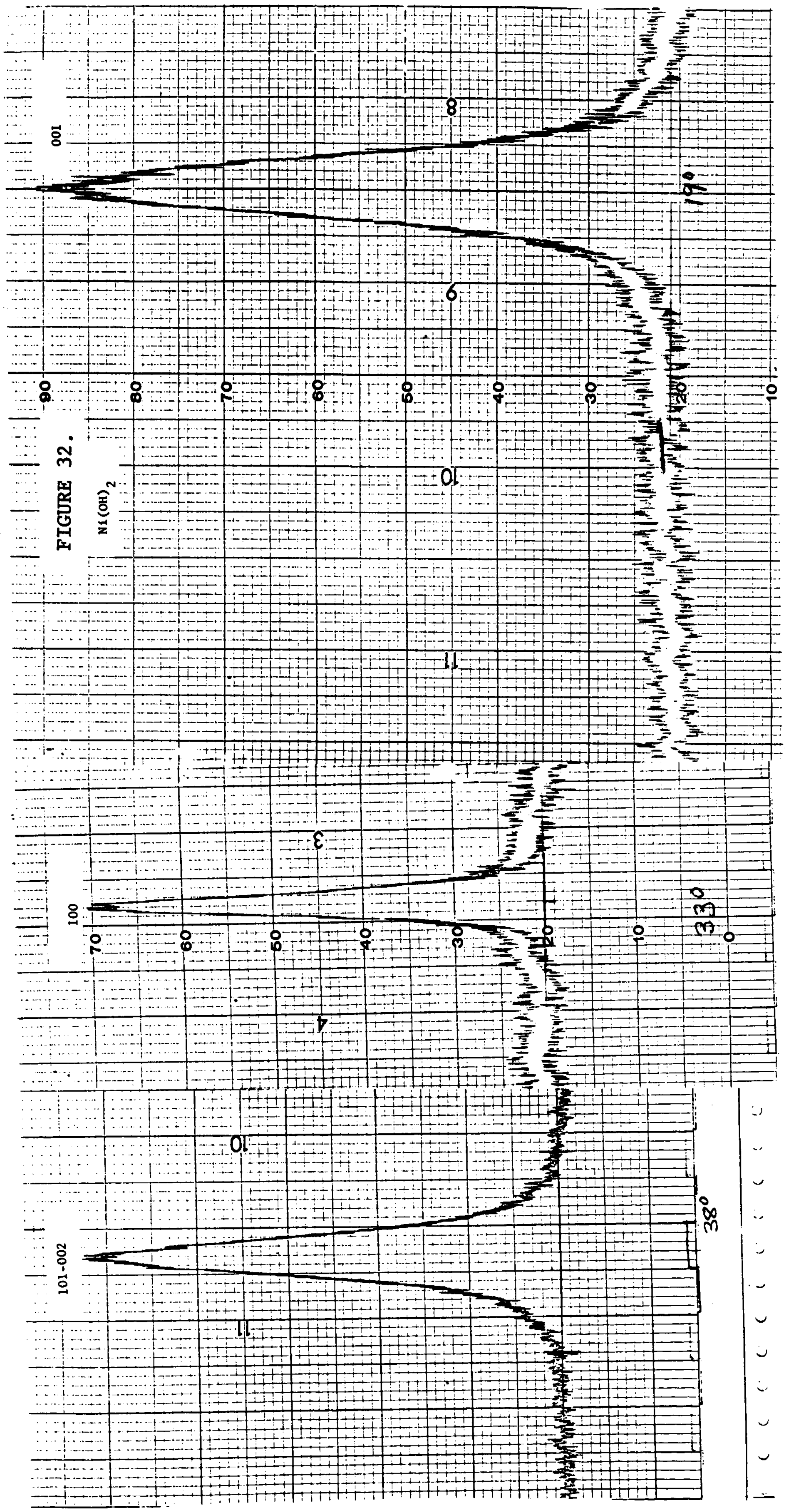
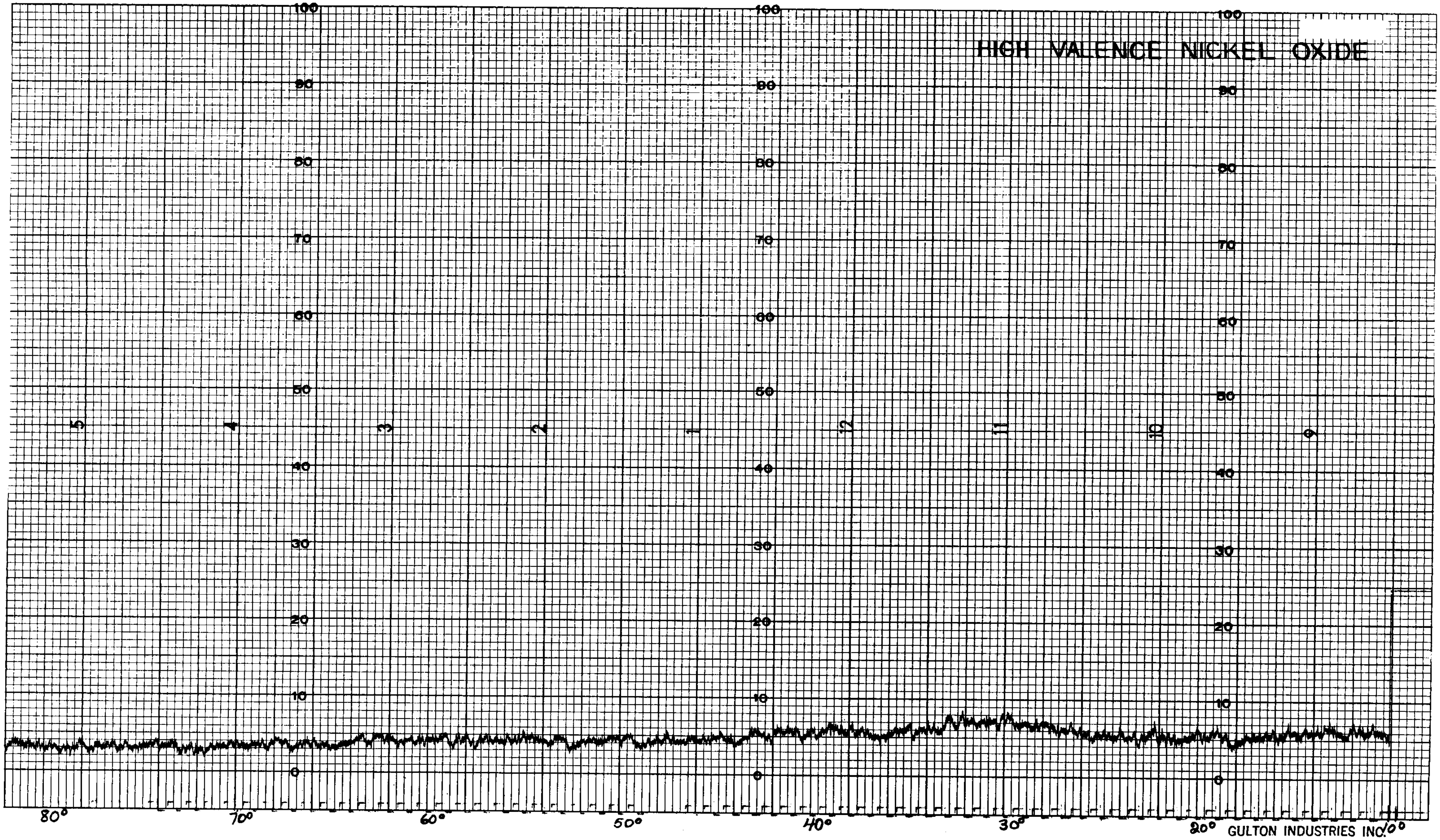


FIGURE 32.

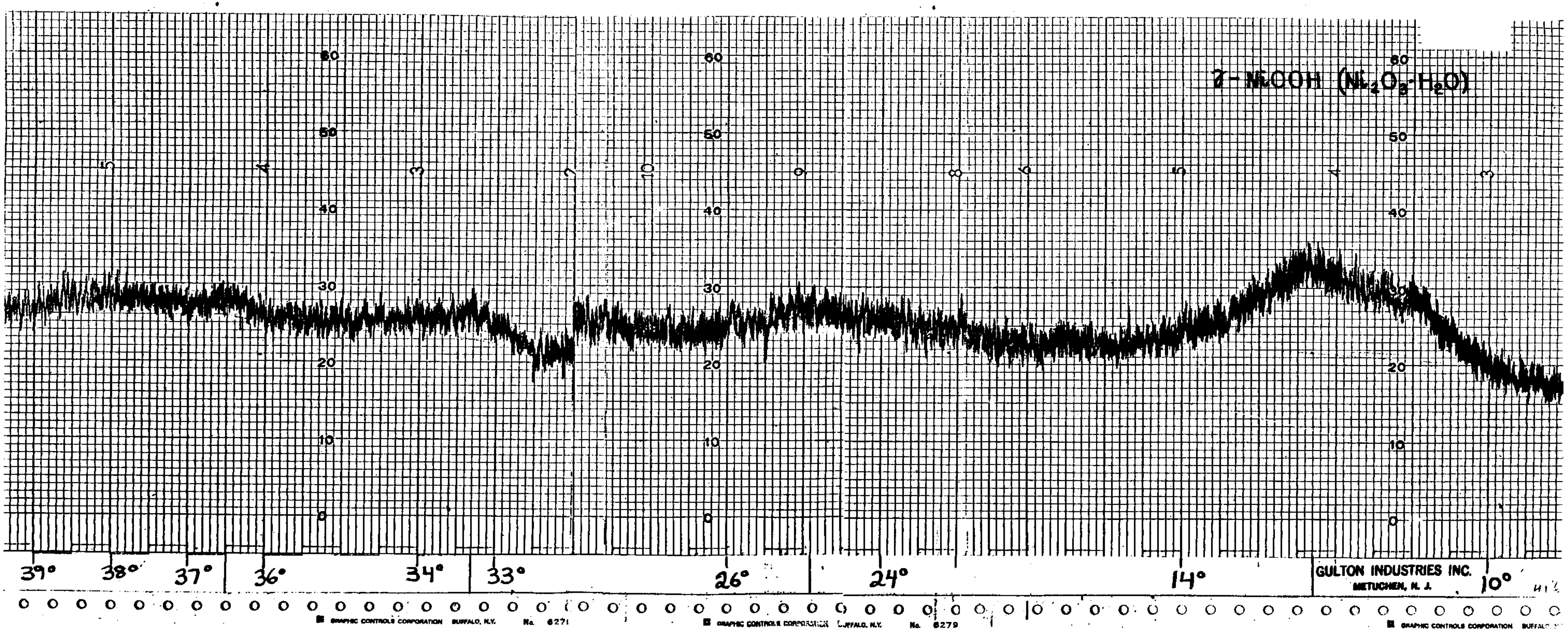
$Ni(OH)_2$

FIGURE 33.



HIGH VALENCE NICKEL OXIDE

FIGURE 34.


γ-NiOOH ($Ni_2O_3 \cdot H_2O$)
60
50
40
30
20
10
0
39°
38°
37°
36°
34°
33°
26°
24°
14°
10°
GULTON INDUSTRIES INC.
METUCHEN, N. J.
GRAPHIC CONTROLS CORPORATION BUFFALO, N.Y. No. 6271
GRAPHIC CONTROLS CORPORATION BUFFALO, N.Y. No. 6279

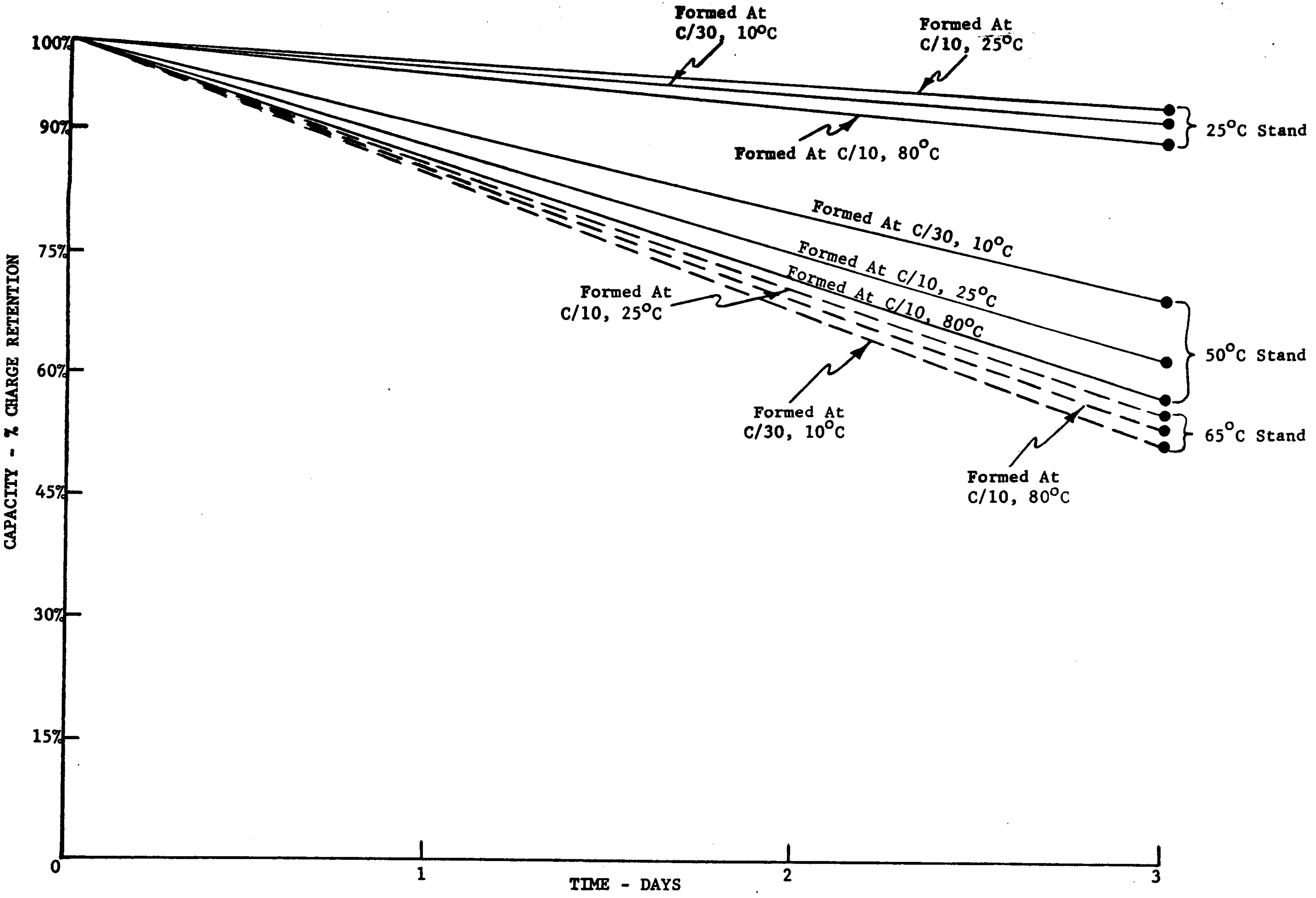


FIGURE 35 STABILITY OF POSITIVE PLATES AT VARIOUS TEMPERATURES

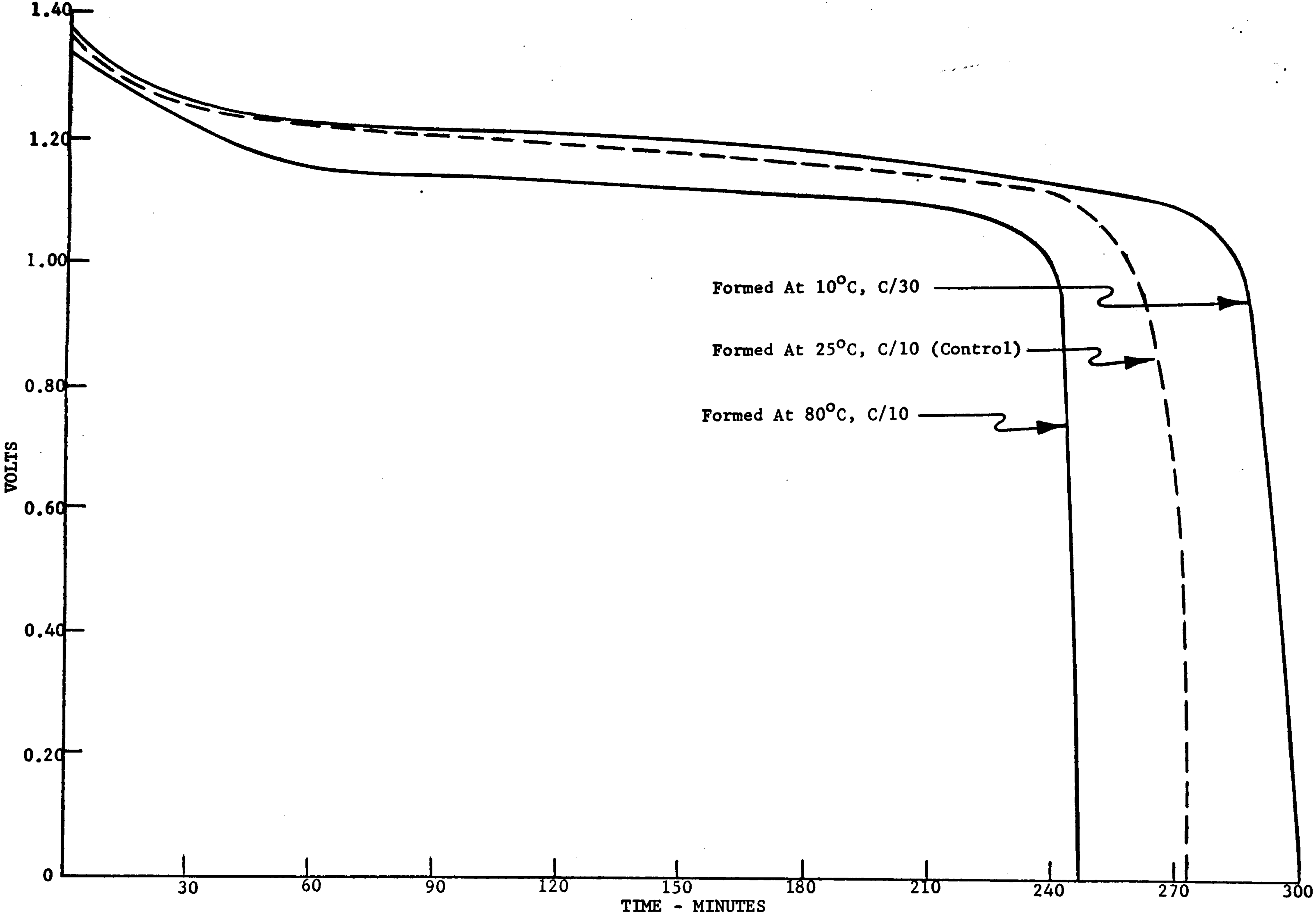


FIGURE 36 DISCHARGE CURVES OF CELLS WHOSE POSITIVES HAVE BEEN FORMED AT VARIOUS RATES & TEMPERATURES

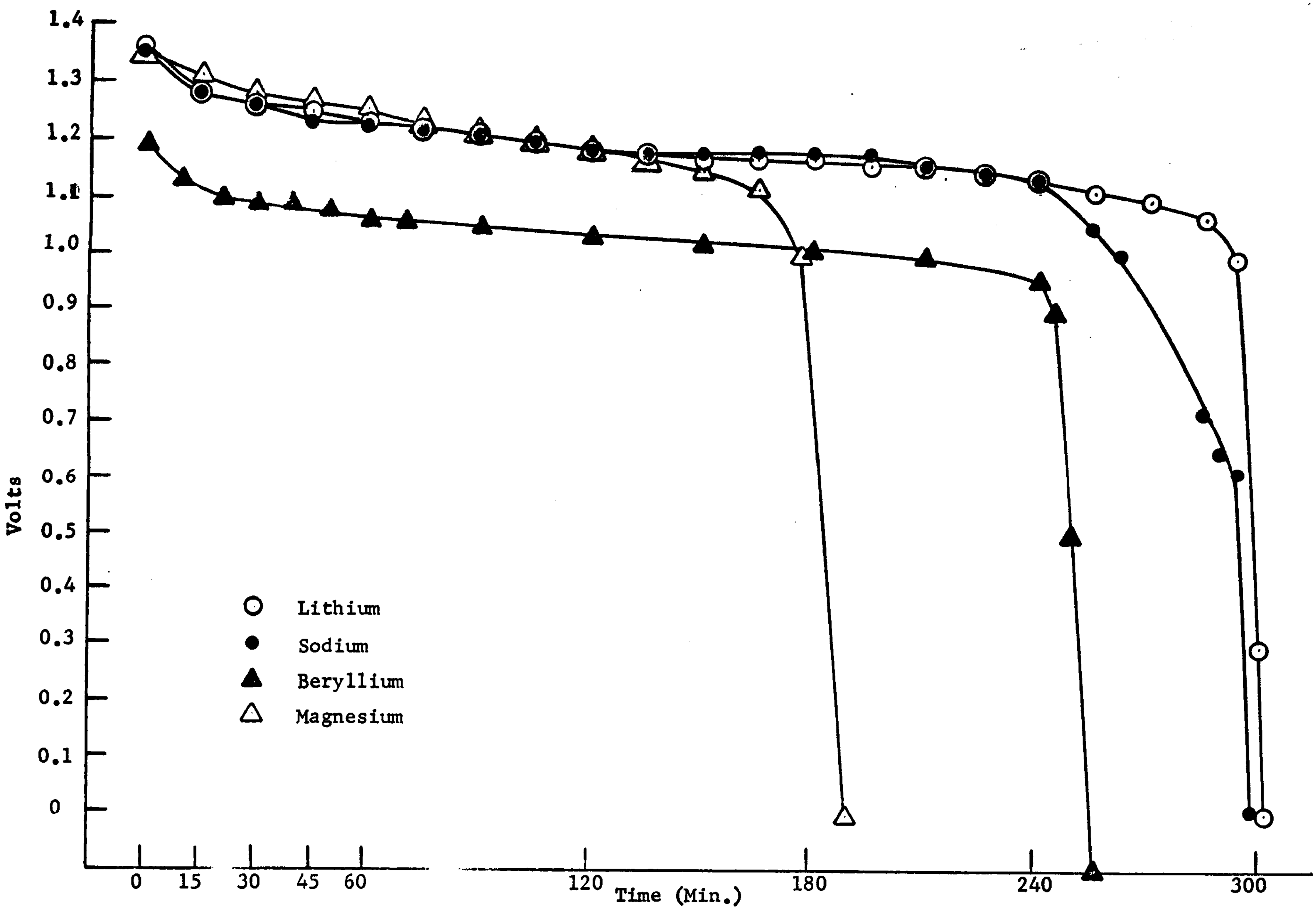


FIGURE 37. DISCHARGE CURVES (200 ma) OF CELLS WITH POSITIVES CONTAINING 20 ATOM % LITHIUM, SODIUM, BERYLLIUM AND MAGNESIUM ADDITIONS

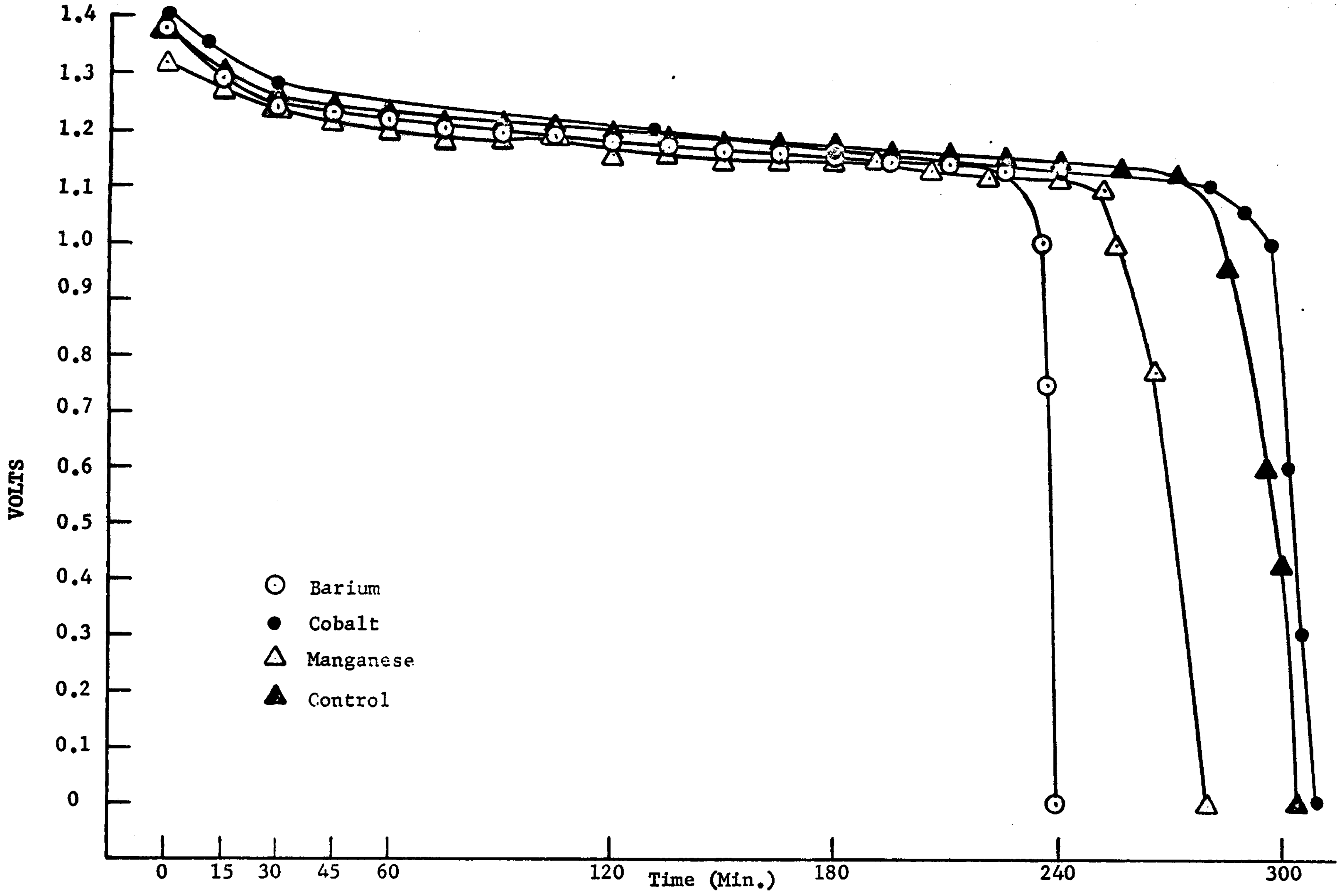


FIGURE 38. DISCHARGE CURVES (200 ma) OF CELLS WITH POSITIVES CONTAINING 20 ATOM PERCENT BARIUM, COBALT, AND MANGANESE ADDITIONS AND CONTROL CELLS

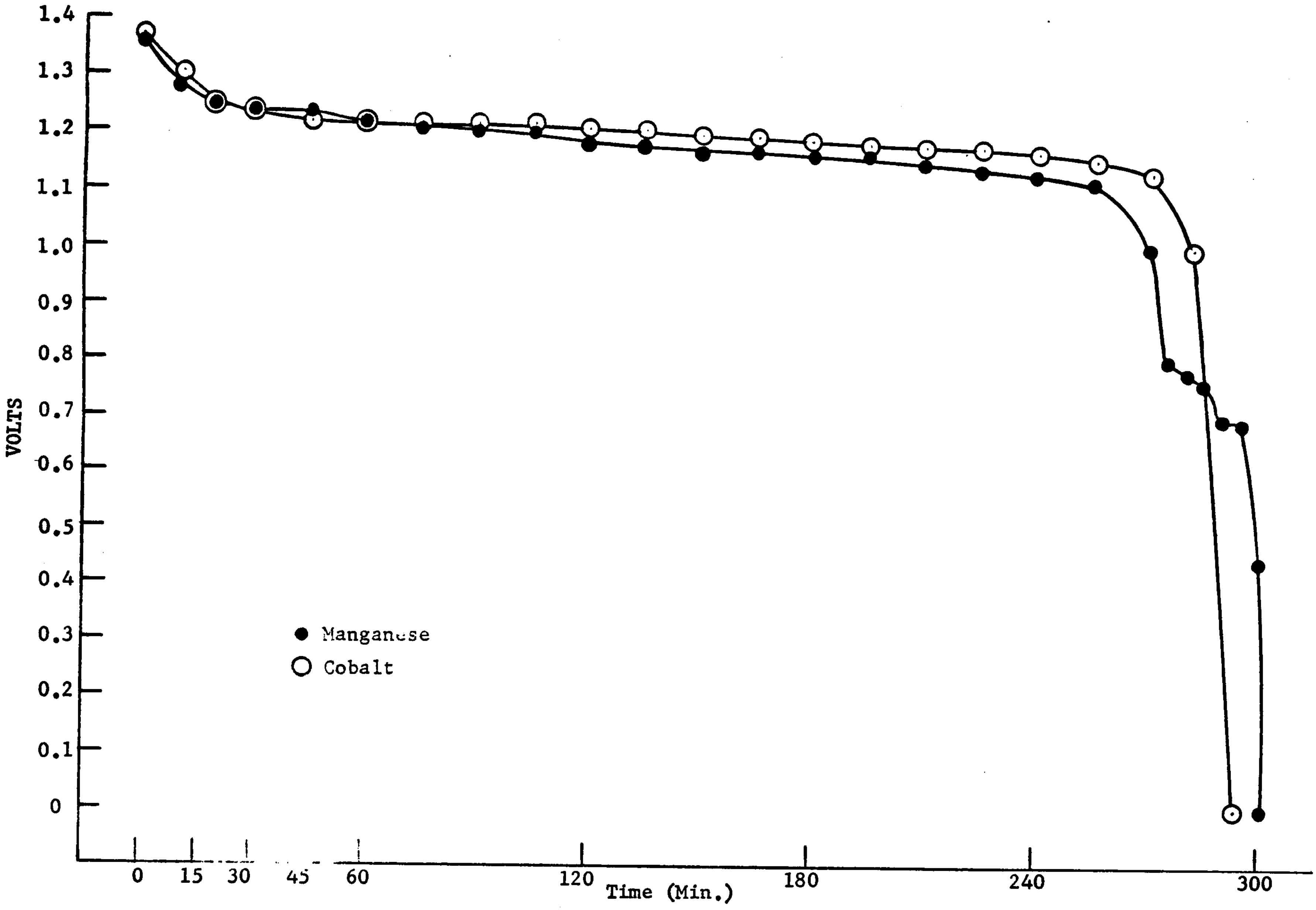


FIGURE 39. DISCHARGE CURVES (200 ma) OF CELLS WITH POSITIVES CONTAINING 5 METAL ATOM PERCENT COBALT AND MANGANESE

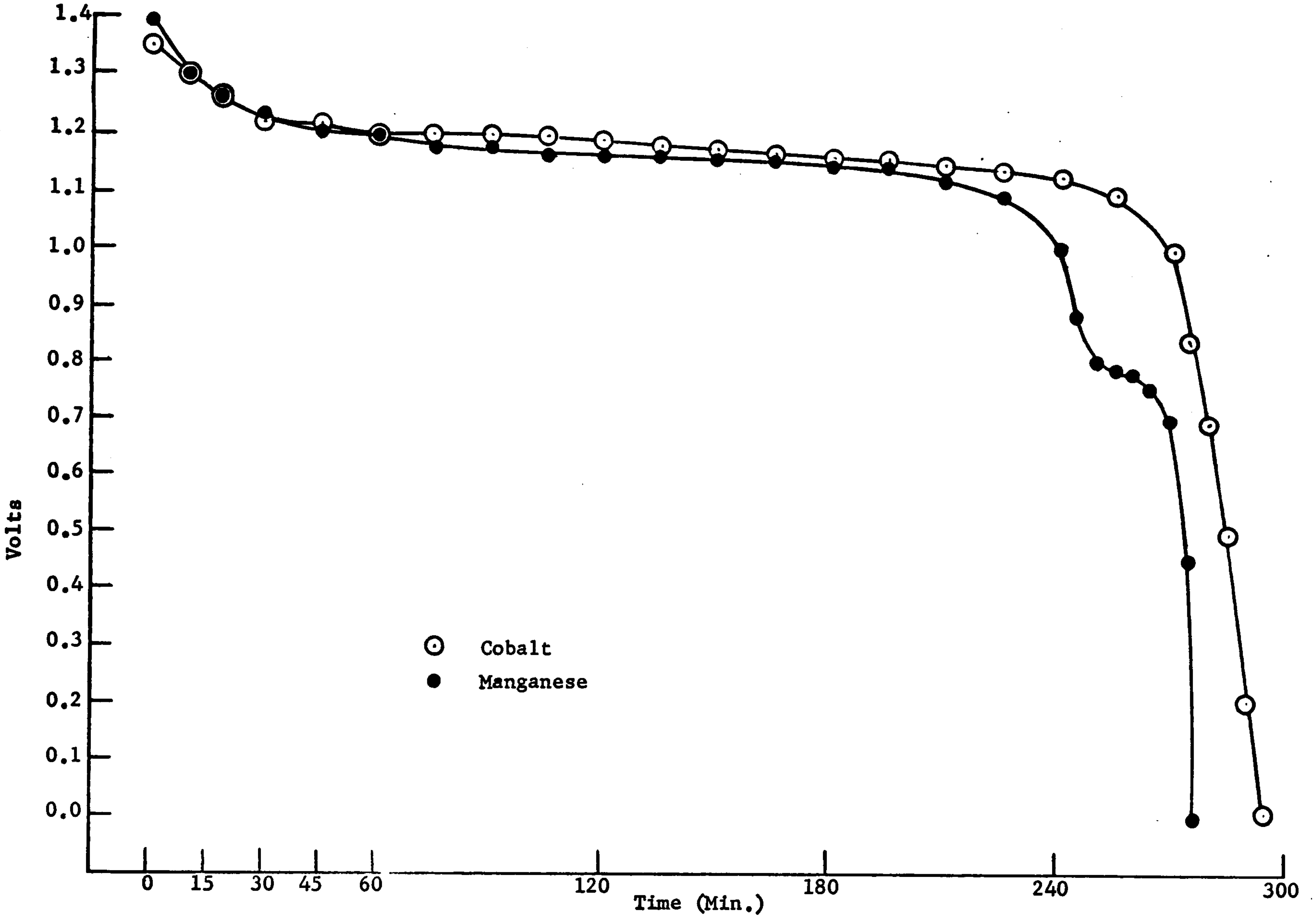


FIGURE 40. DISCHARGE CURVES (200 ma) OF CELLS WITH POSITIVES CONTAINING 10 METAL ATOM PERCENT COBALT AND MANGANESE

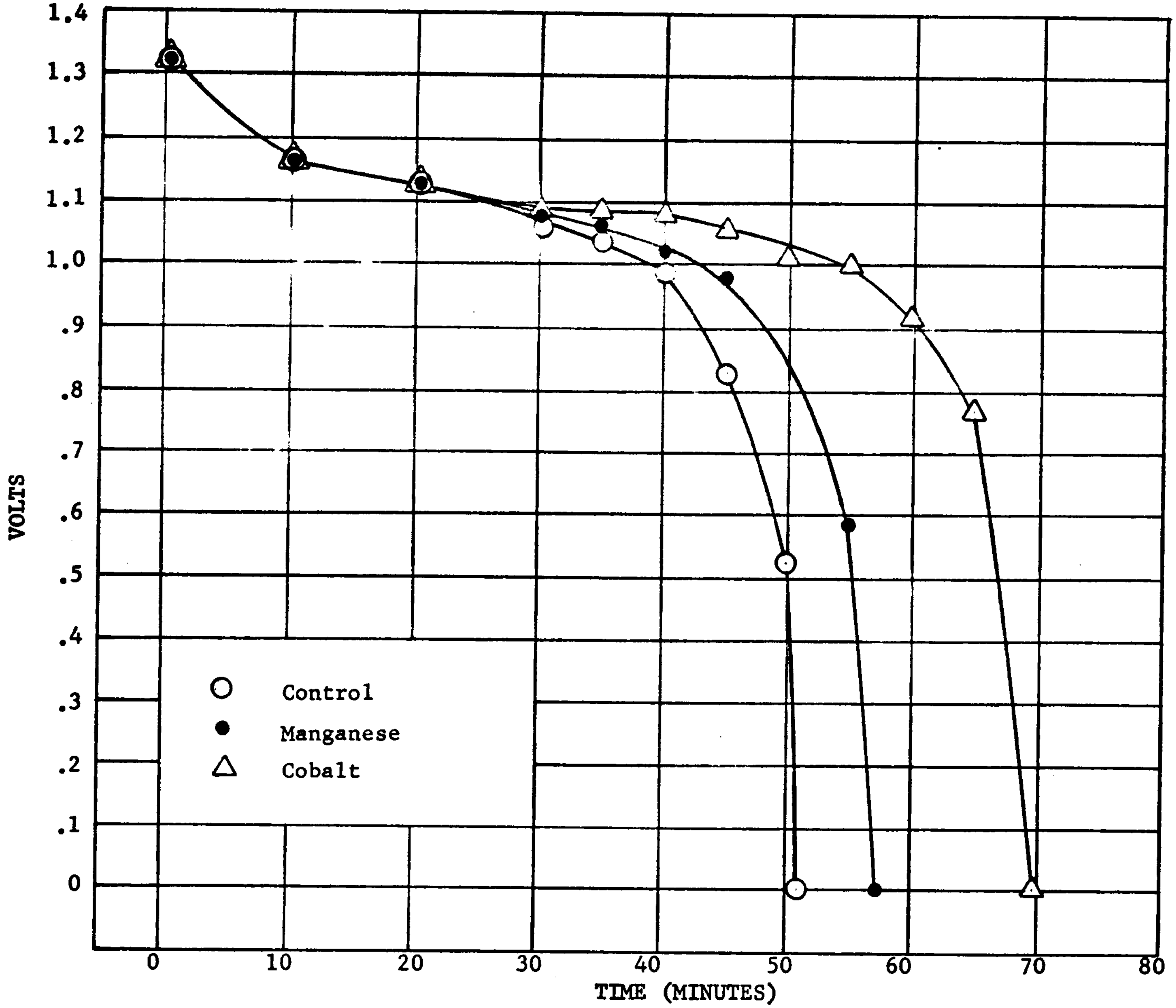


FIGURE 41 C RATE DISCHARGE - 20 ATOM % DOPED POSITIVES & CONTROL

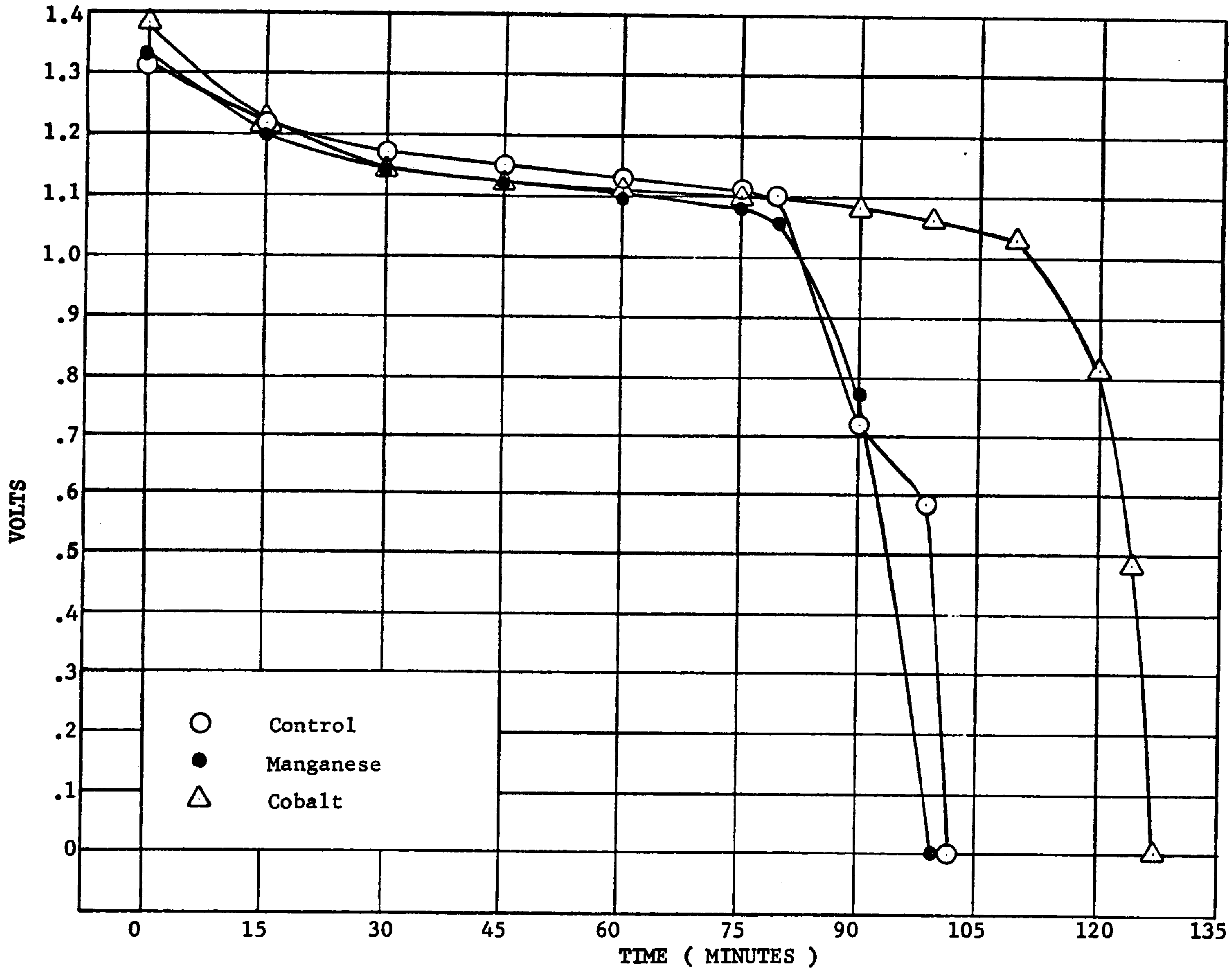


FIGURE 42 C/2 DISCHARGE - 20 ATOM % DOPED POSITIVES & CONTROLS

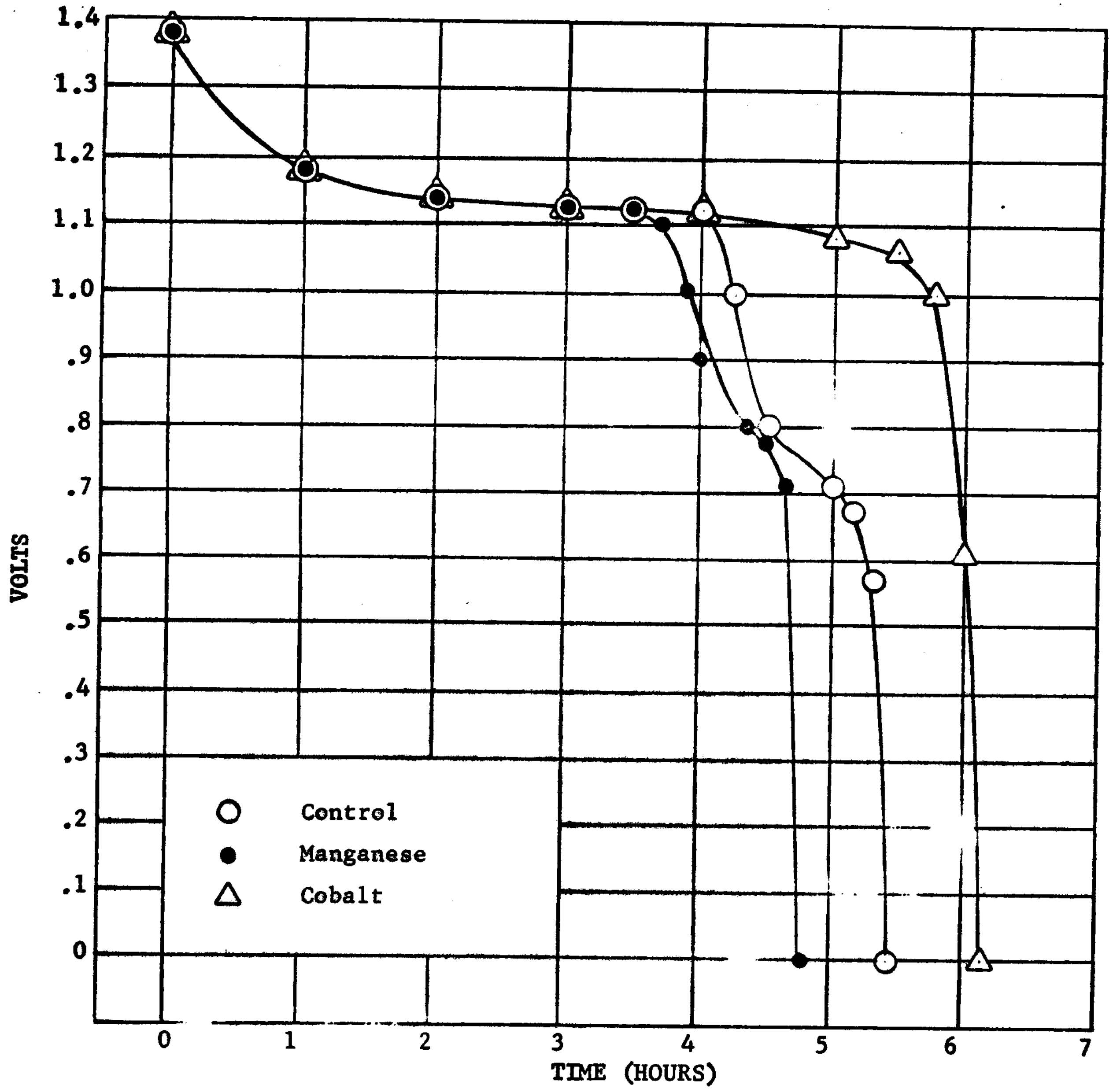


FIGURE 43 . C/5 DISCHARGE - 20 ATOM % DOPED POSITIVES & CONTROL

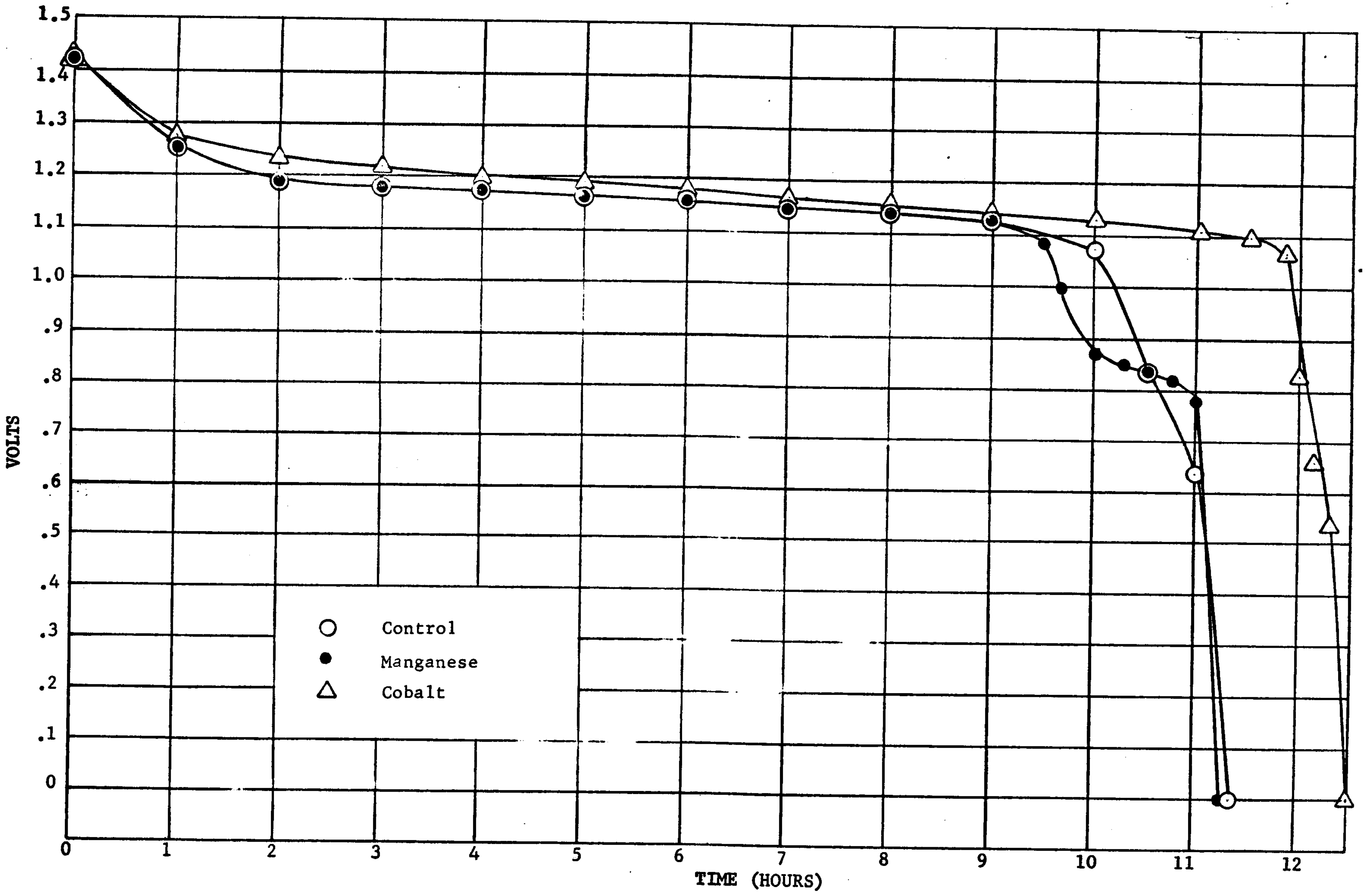
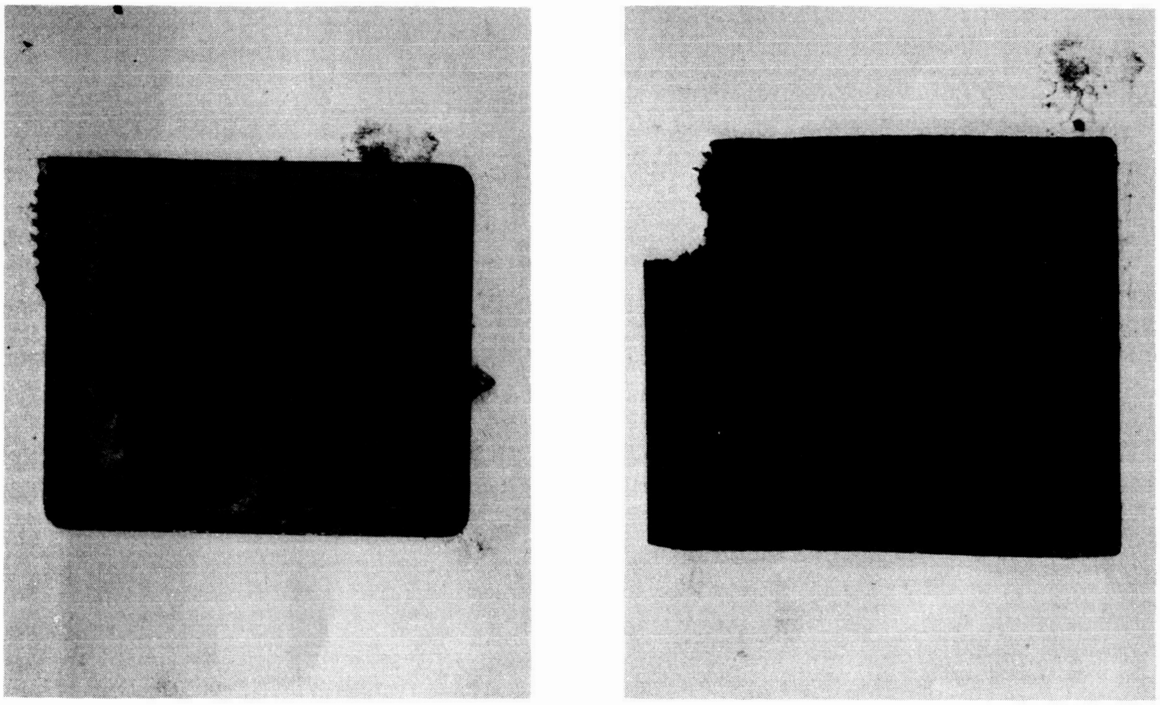


FIGURE 44 C/10 DISCHARGE - 20 ATOM % DOPED POSITIVES & CONTROL



A

B

FIGURE 45. A - MANGANESE DOPED POSITIVE SHOWING REMAINS OF SEPARATOR

B - COBALT DOPED POSITIVE SHOWING LOSS OF ACTIVE MATERIAL

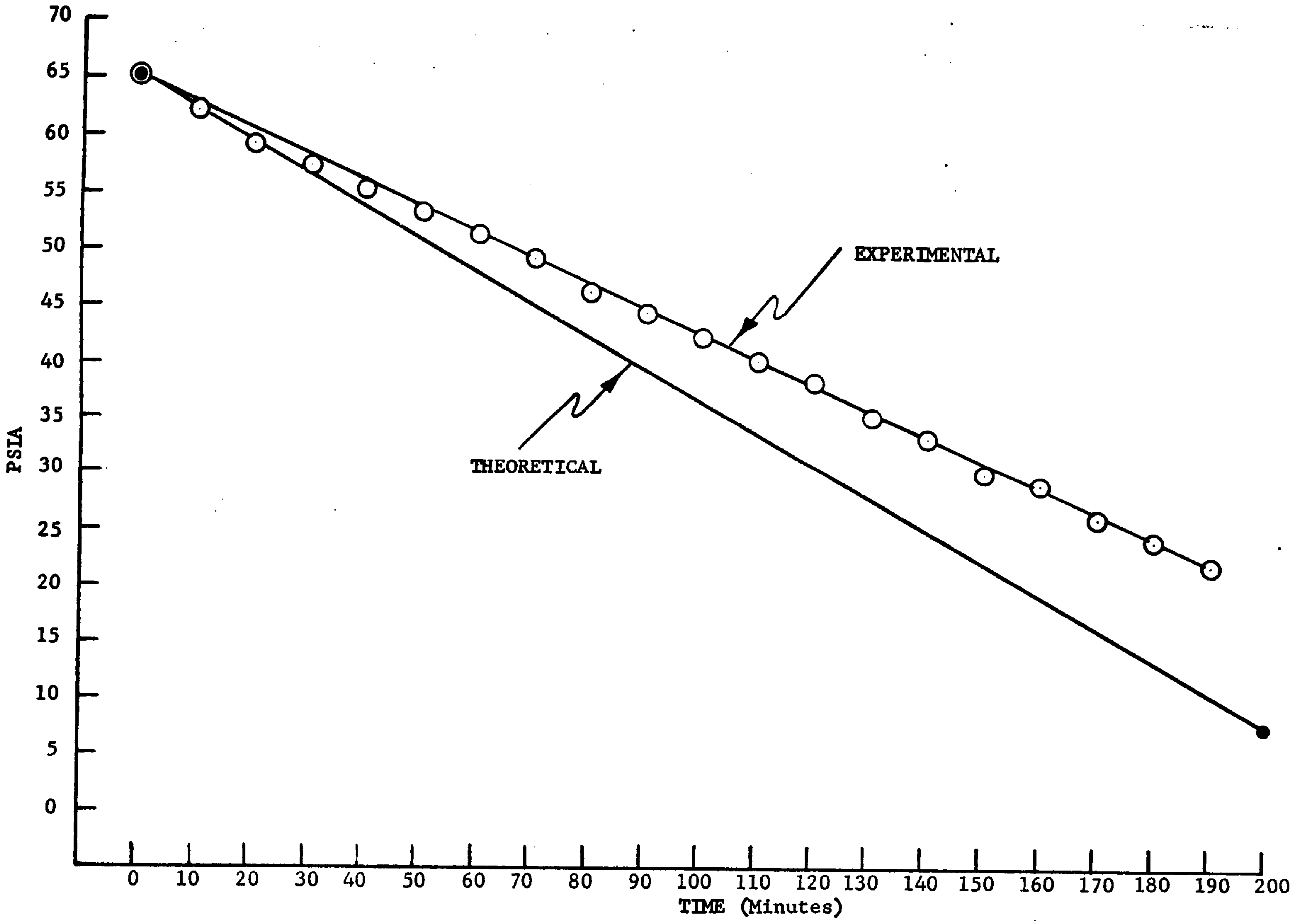


FIGURE 46 O_2 DECAY RATE (C/10) CONTROL CELLS

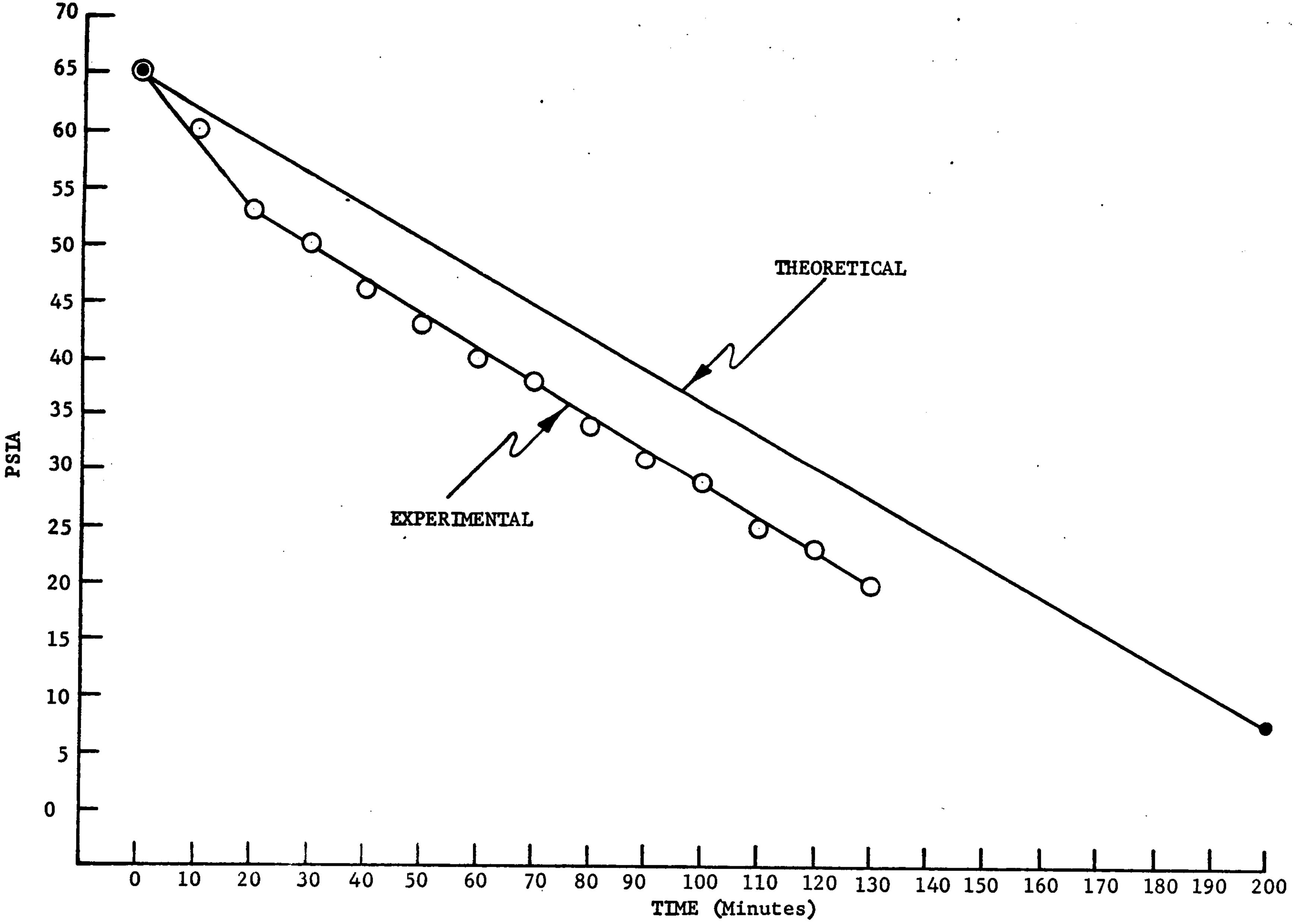


FIGURE 47 O_2 DECAY RATE (C/10) COBALT CELLS

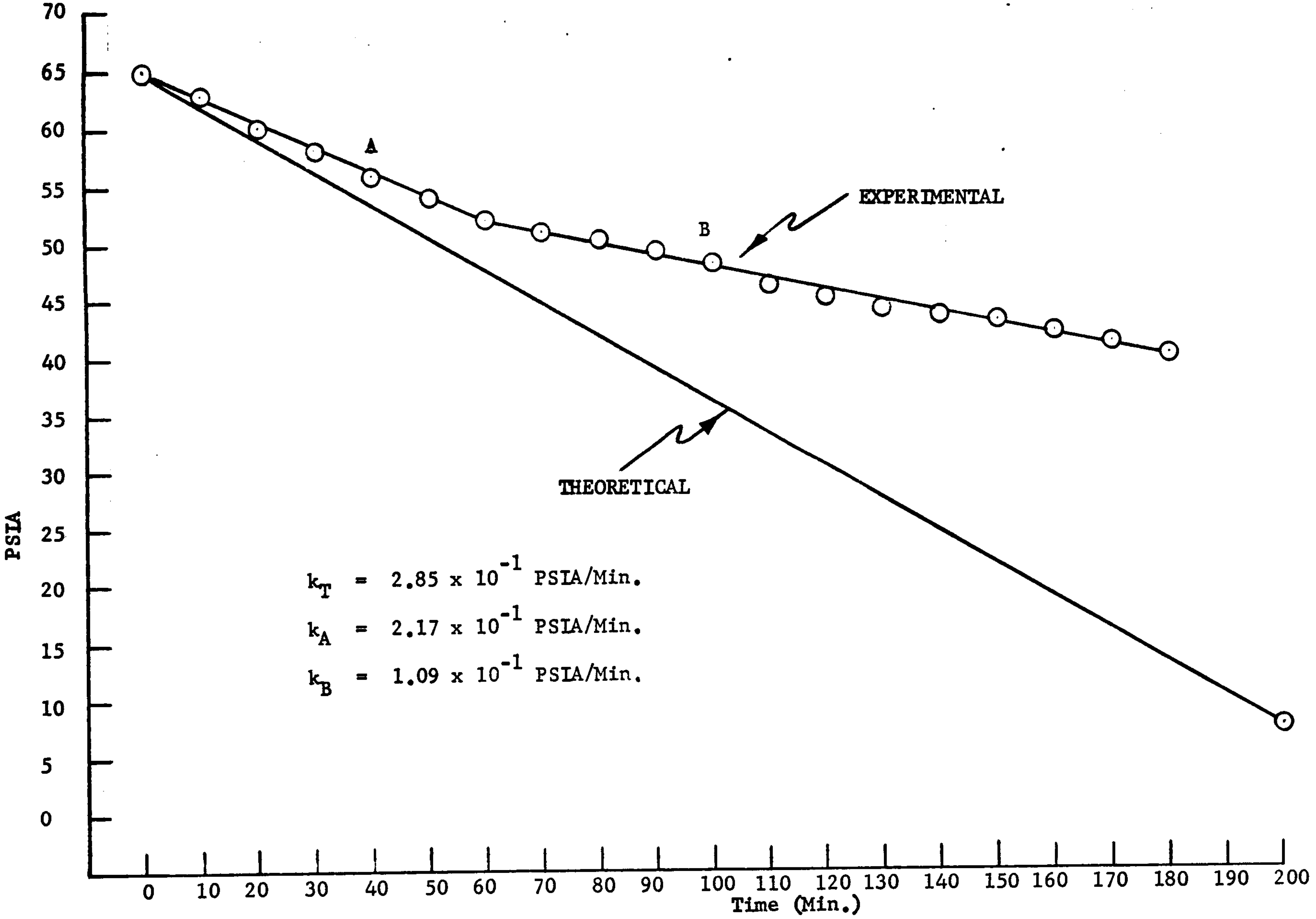
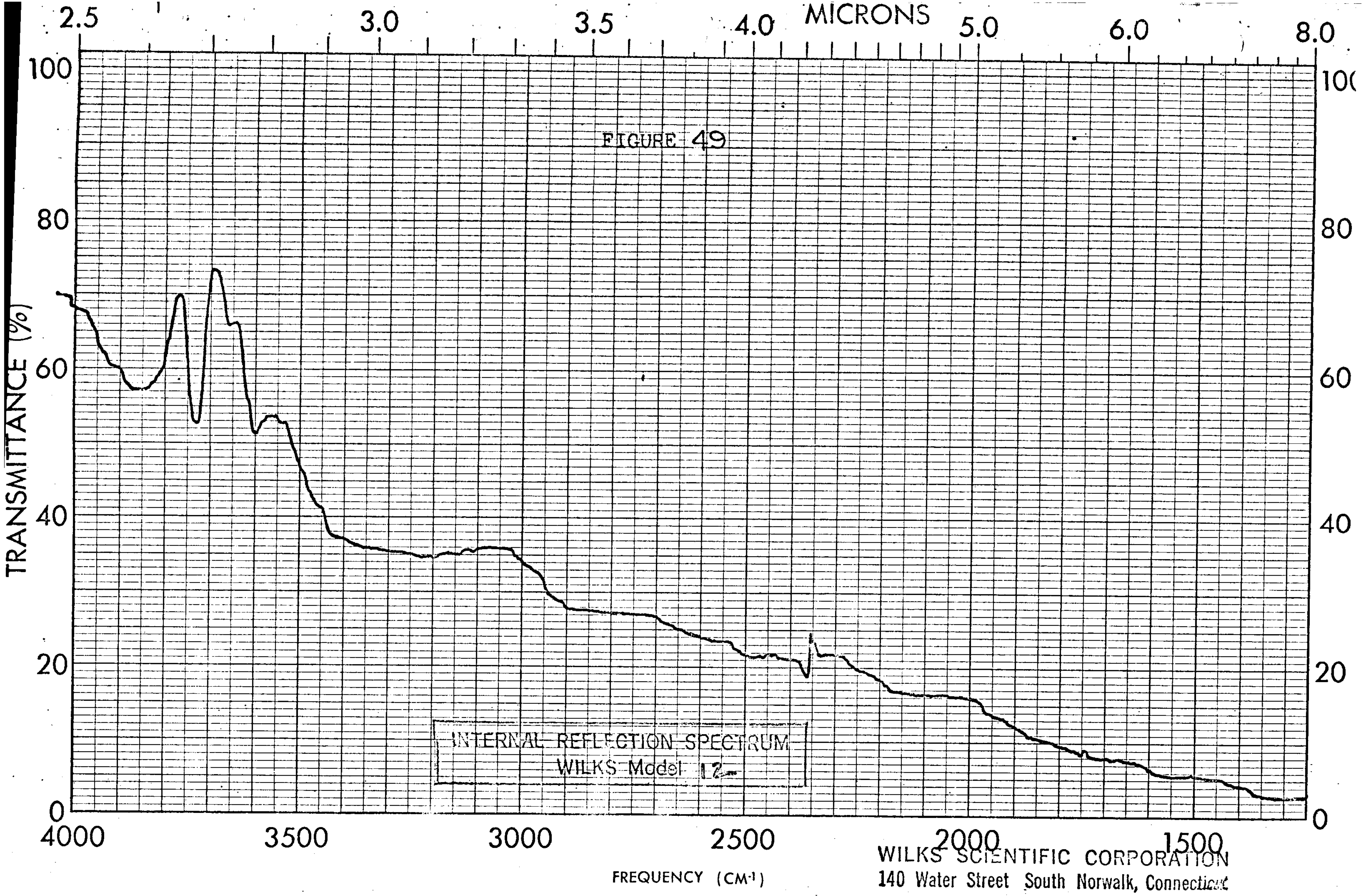


FIGURE 48. O_2 DECAY RATE - C/10 - 20% MANGANESE CELLS

FIGURE 49



WILKS SCIENTIFIC CORPORATION
140 Water Street South Norwalk, Connecticut

SAMPLE Nickel Electrode #3
discharged
ORIGIN Gulton Industries
SOLVENT

CURVE NO. 302-2
CONC.
CELL PATH KRS-5 50x20x2mm 45°
REFERENCE

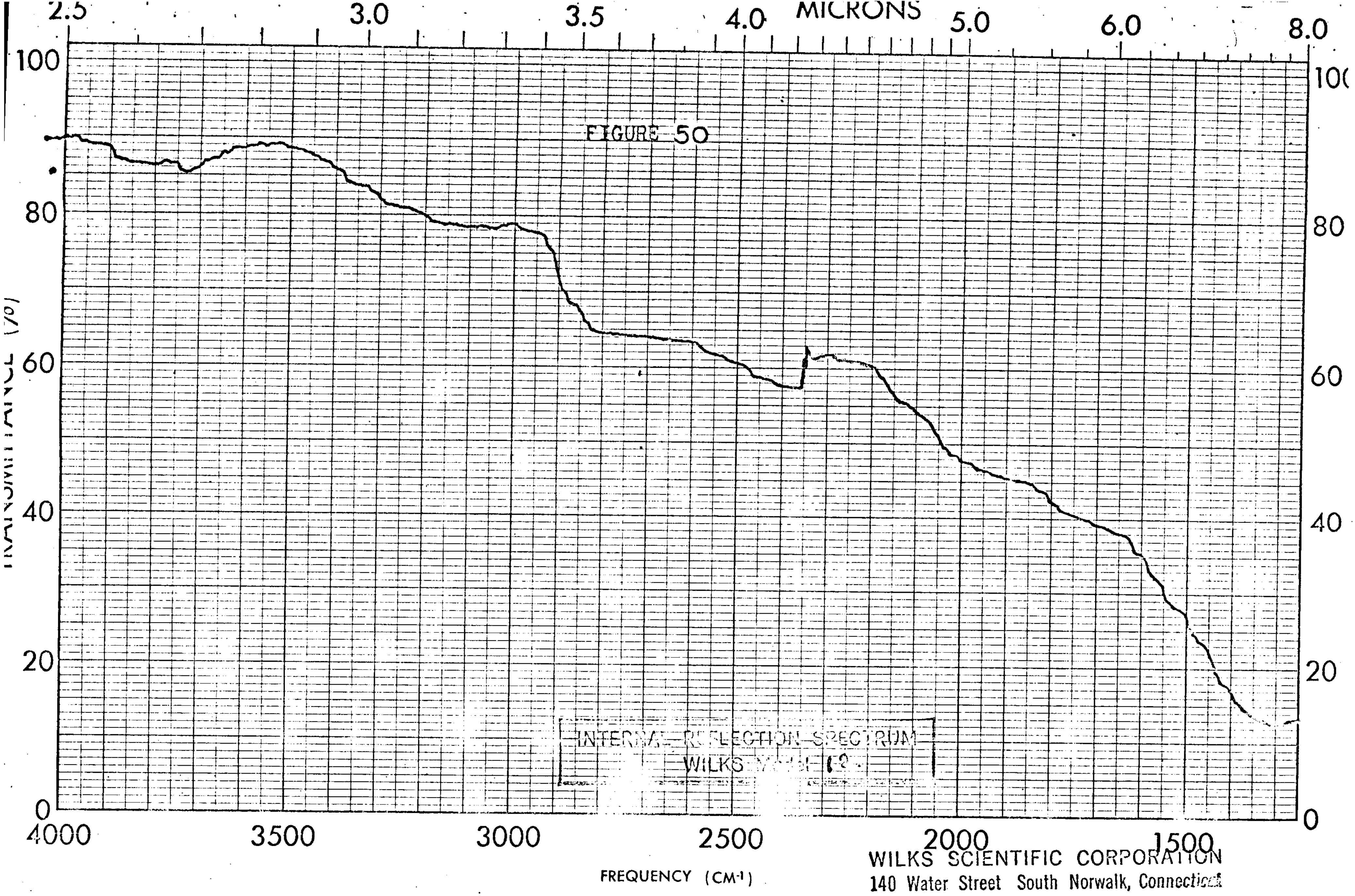
SCAN SPEED F
SLIT N
REMARKS

OPERATOR G.D.P.
DATE 7·26·66

PART NO. 237-1034

PERKIN-ELMER

FIGURE 50



WILKS SCIENTIFIC CORPORATION
140 Water Street South Norwalk, Connecticut

SAMPLE Nickel Electrode #2
Charged State
ORIGIN Gulton Industries
SOLVENT

CURVE NO. 302-1
CONC.
CELL PATH KRS-5 50x20x2mm 45°
REFERENCE KRS-5

SCAN SPEED F
SLIT N
OPERATOR GDP
DATE 2·26·66
REMARKS

PART NO. 237-1034 PE®

PERKIN-ELMER

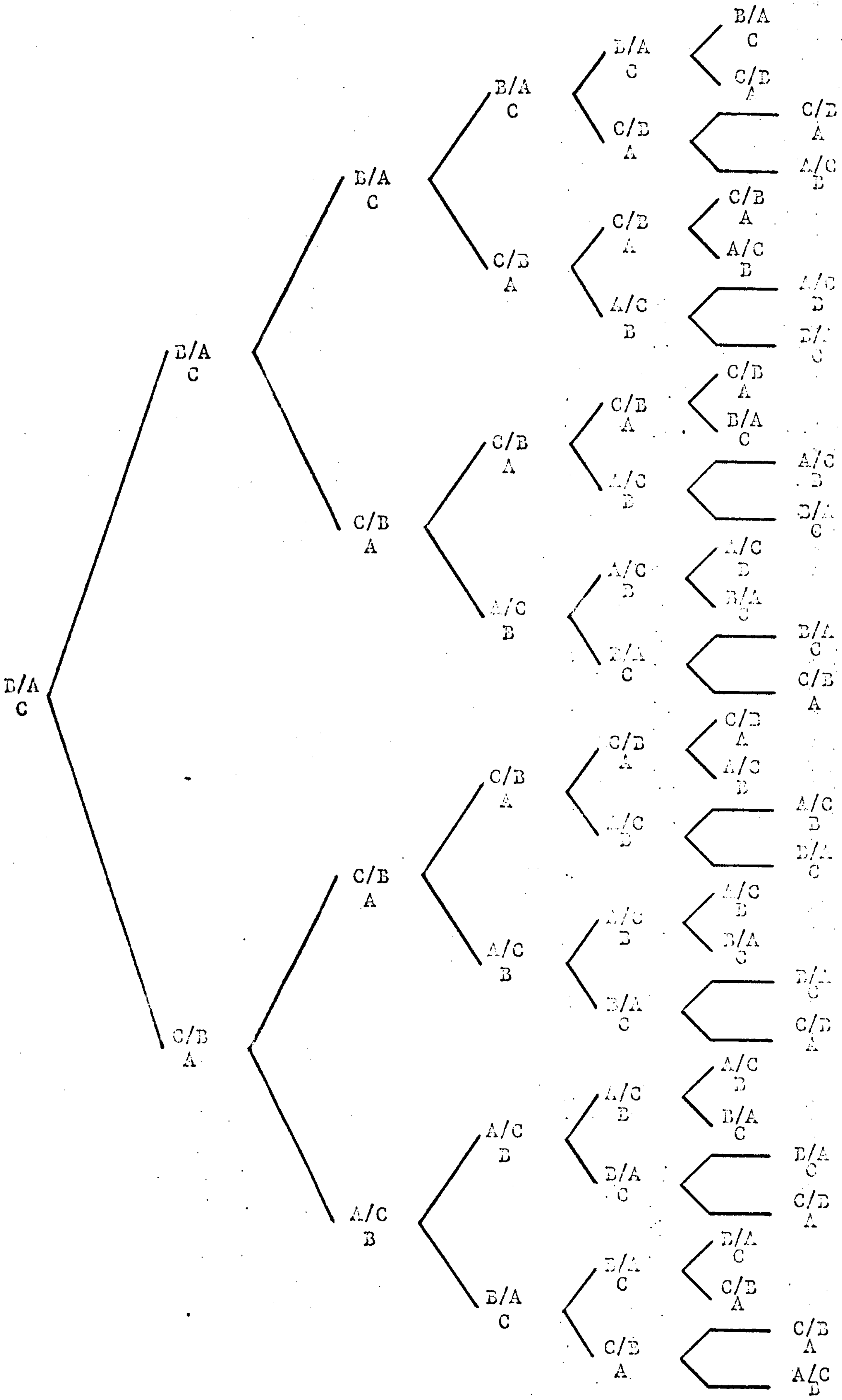
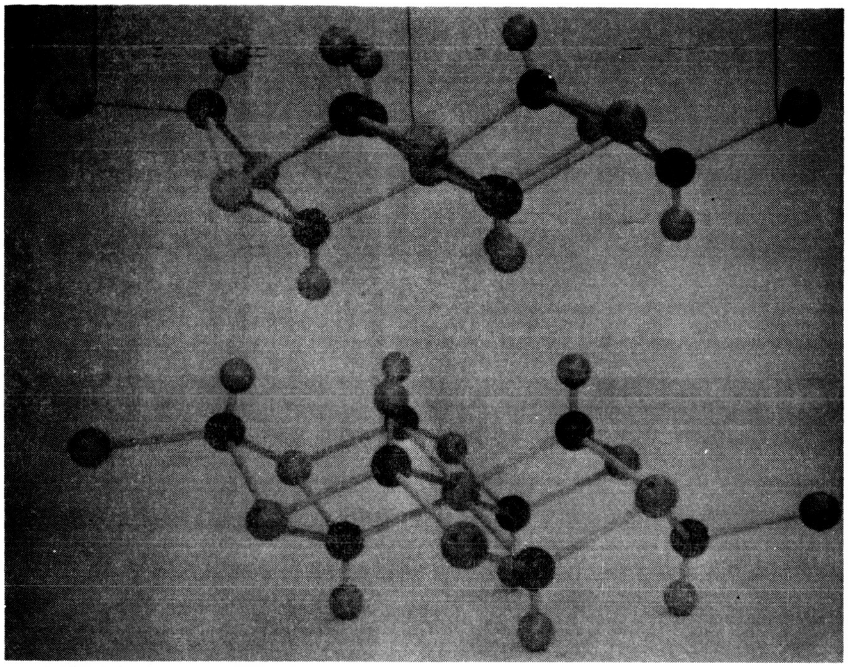
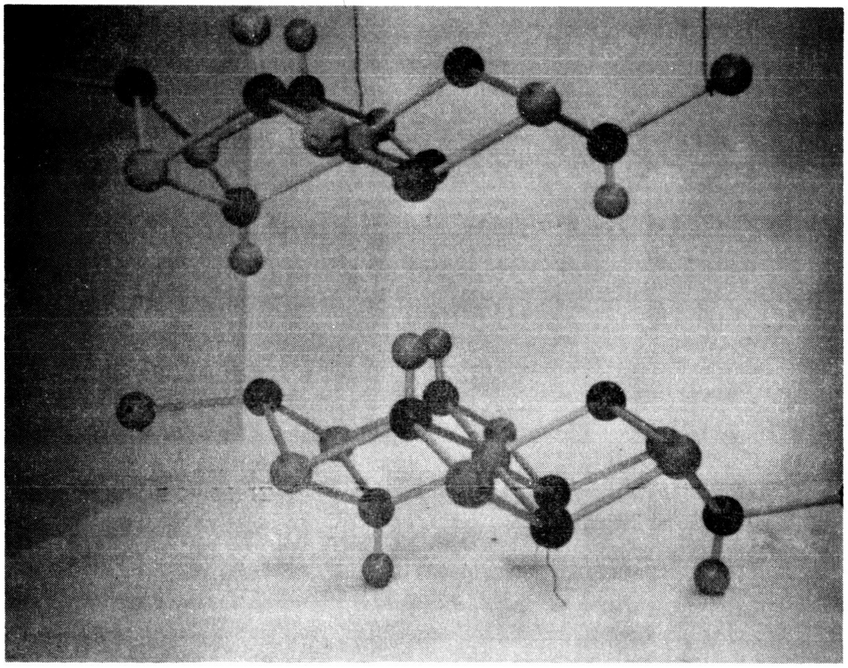


FIGURE 51. RANDOMIZATION OF THE LAYER STRUCTURE



A



B

FIGURE 52. BALL AND STICK MODELS

A - $Ni(OH)_2$

B - NiOOH

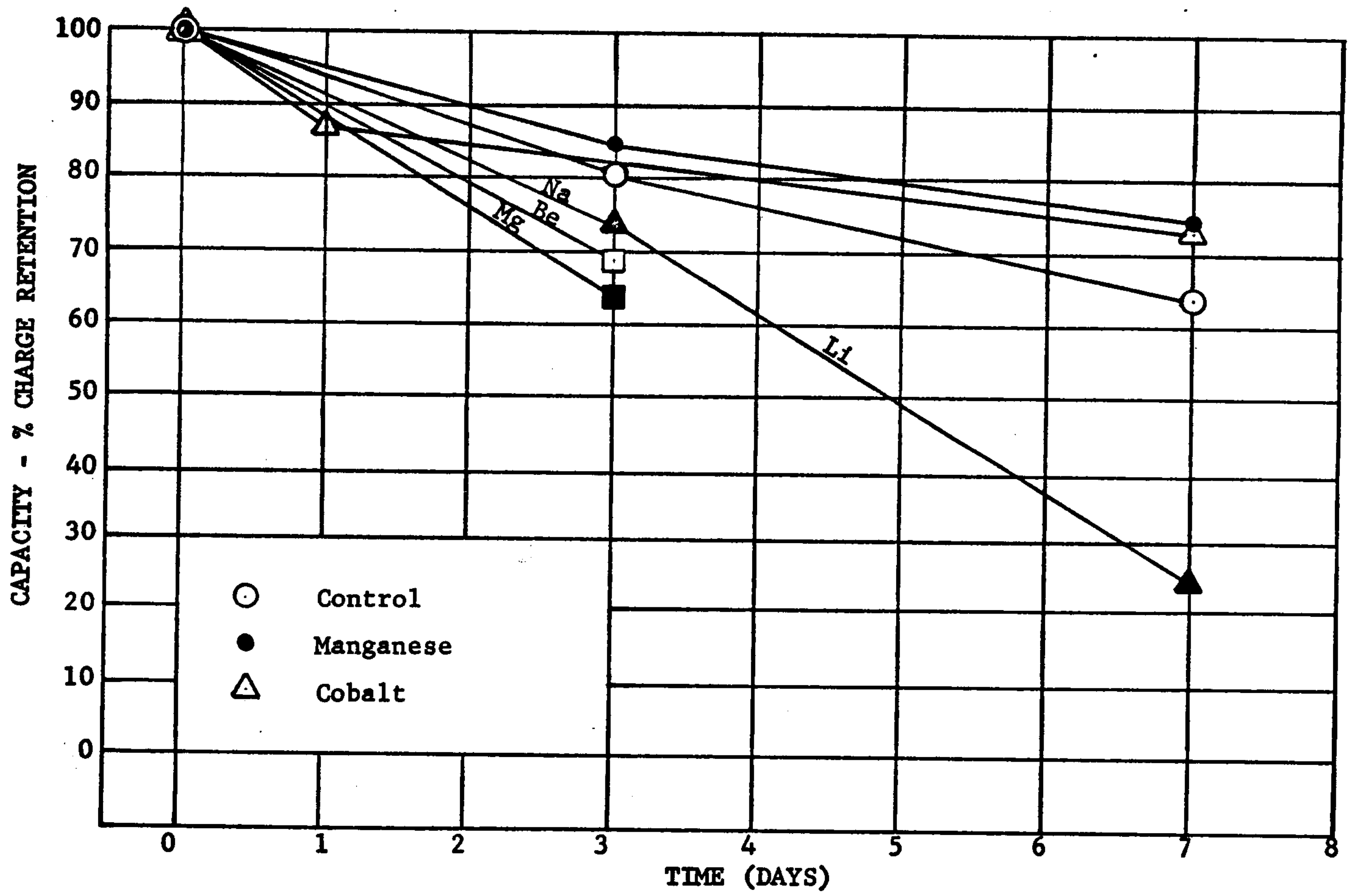


FIGURE 53. COMPARISON OF POSITIVES CONTAINING ADDITIVES WITH CONTROL POSITIVES - STABILITY AT 65°C

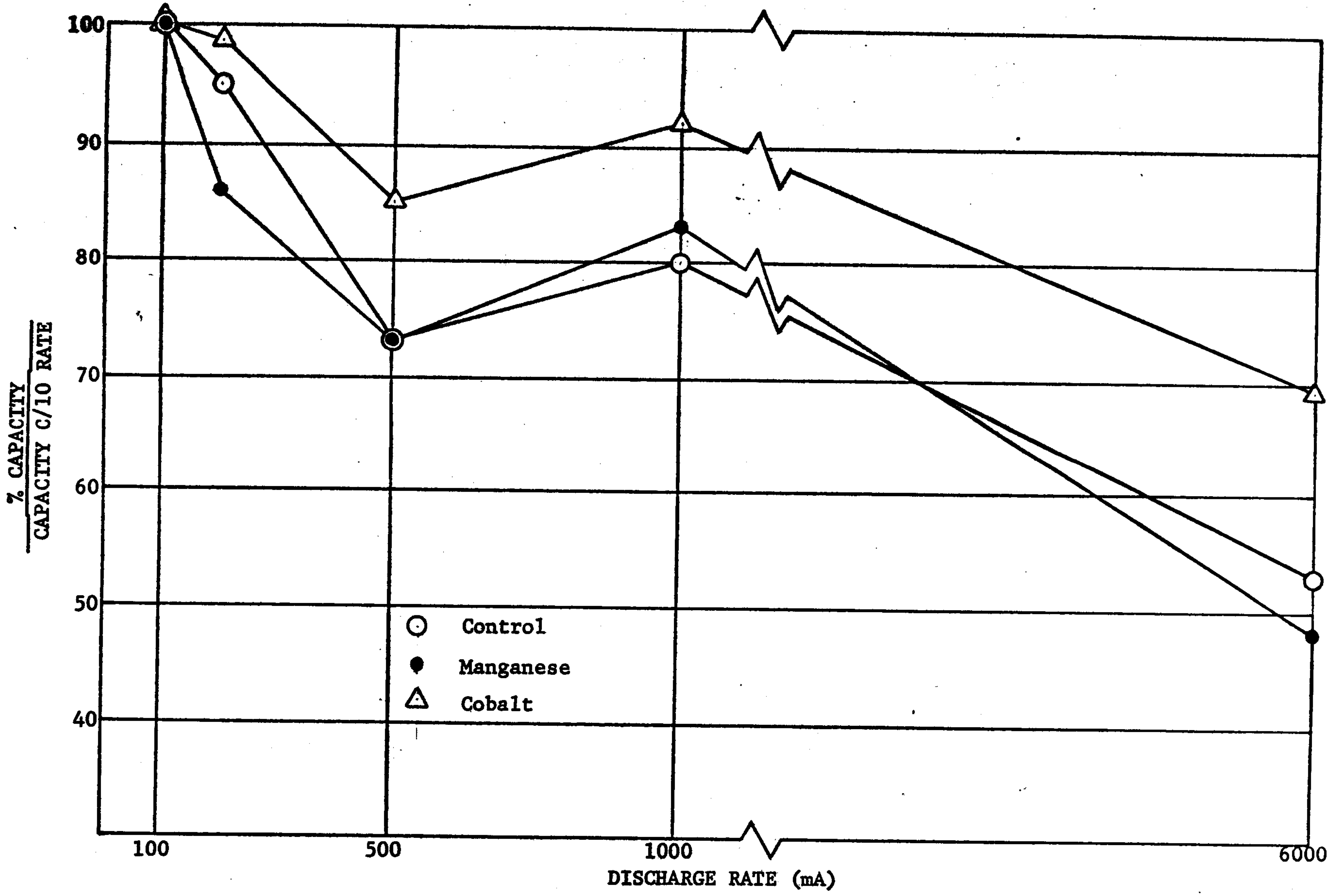


FIGURE 54. UTILIZATION OF CELLS WITH POSITIVES CONTAINING 20 ATOM % METAL AND CONTROLS AT VARIOUS RATES