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THE EFFECT OF SURFACE PROTRUSIONS ON SELF-SUSTAINED THERMAL OSCILLATIONS DURING HYDROGEN OXIDATION ON A NICKEL FOIL

BY

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ABSTRACT

The effects of surface pretreatment on the presence and form of self-sustained oscillations during hydrogen oxidation on a nickel foil is examined. Nickel foil samples were subjected to a series of pretreatments then put in a reactor and run under conditions where oscillations were expected. A rapid ignition to a high temperature state was observed with some of the catalysts, while others produced oscillations at the same conditions. Some of the oscillations occurred with a regular pattern, while others were chaotic. Examination of the catalysts revealed that in all the cases where oscillations were observed, there were 1-10 micron protrusions on the surface of the catalyst while no such protrusions were seen for the samples that did not catalyse the oscillations. The regular oscillations occurred when the protrusions all looked similar while chaotic oscillations were seen when there were protrusions of many different sizes and shapes. There were no significant differences between the surface compositions of the various catalysts. These results are discussed in the context of the fuzzy wire model of Jensen and Ray.

Introduction

Over the last thirteen years, many researchers have studied the problem of oscillations in catalytic oxidation in an attempt to determine the essential factors influencing this phenomena. Since oscillations are due to the periodic extinction and ignition of the oxidation reaction, the investigation of oscillatory phenomenon will contribute to the understanding of basic extinction and ignition processes. Also, studies of catalytic oscillations will help in understanding catalytic behavior in general.

The occurrence of oscillations in catalytic oxidation has been known since the appearance of a paper by Liljenroth (1) in 1918. However, it has not been until the last thirteen years that the problem has recieved a great deal of attention. A vast majority of the work to date has involved carbon monoxide oxidation of platinum, and hydrogen oxidation on nickel or platinum. Platinum foils, wires, meshes, and supported particles have been used, while work with nickel catalysts has been limited to nickel foils (2). Review articles which summarize the results of various researchers are available (2,3).

Oscillations in the oxidation of hydrogen on a nickel foil have been observed by Belyaev, et al. (4,5,6), and Schmitz, et al. (7,8). Belyaev, et al. have observed oscillations under isothermal conditions where the reaction rate varied in a simple harmonic fashion. Foil temperatures between 180°C and 300°C produced oscillations when the inlet oxygen concentration was less than 0.3 percent. Schmitz, et al., observed oscillations when the temperature, flow rate and composition of the feed gas were held constant, and the catalyst temperature was allowed to vary. They found that the catalyst temperature oscillated when the feed temperature was between 230°C and 250°C and the inlet oxygen concentration was below five percent. These oscillations began as simple periodic oscillations, but became chaotic as the reaction progressed. The amplitude of the oscillations varied, with a maximum of 250°C.

Many models have been proposed which are capable of predicting observed oscillatory behavior. These models have focused mainly on the reaction kinetics since oscillations have been observed under conditions where heat and mass transfer effects are not important (5,9,10). Mechanisms which have been able to predict oscillations include a "buffer" whose adsorption and desorption are slow relative to the reaction dynamics (11); the presence of two different forms of adsorbed reactant, one active and one inactive (9,12);the periodic reduction and oxidation of the surface (2,7); changes in mechanism with surface coverage (13); variation of the activation energy with surface coverage (4,5,14,15); the dissolution of reactants in the bulk metal (4,17); a Langmuir-Hinshelwood mechanism with vacant sites (16); and hot spots on the surface due to protrusions (18). In order to predict the very low frequency oscillations sometimes observed in hydrogen oxidation, it is necessary to include processes which are slow relative to the mean reaction rate (17). Mechanisms which involve the participation of deeper layers of the catalyst satisfy this requirement.(4,17).

Presented here are the results of a study of the effects of surface structure and composition on the self-sustained oscillations which occur in the oxidation of hydrogen on a polycrystalline nickel foil. Catalysts were prepared using a number of different procedures, placed in a reactor similar to that used by Schmitz, et al. (7,8), and reactants were introduced under conditions which were expected to produce oscillations. The temperature of the catalyst was recorded as a function of time. Periodically, the catalyst was removed from the reactor and its surface structure and composition were examined with a scanning auger microprobe. It was found that it was possible to correlate changes in the surface structure with changes in oscillatory behavior.

APPARATUS

A schematic diagram of the apparatus is shown in Figure 1. Compressed gas cylinders purchased from the Linde Division of Union Carbide Corporation are used as a source of hydrogen and oxygen. Each of these gases flows from the cylinders through a one-foot long, one-half inch copper tube filled with Drierite anhydrous calcium sulfate, through calibrated Roger Gilmont flowmeters (size #1 for oxygen, size #2 for hydrogen), and into a check valve. The gases are then mixed at a tee, passed through a third check valve, and admitted to the reactor through a one-quarter inch pyrex ball joint. An on-off valve allowed the oxygen flow to be shut off quickly in an emergency. All connecting lines in the system were of one-quarter inch copper tubing.

The reactor, which is shown in Figure 2, was modeled after the one used by Schmitz, et al., (6,7). It was constructed entirely of glass, and consisted of a bottom section, a top section and a connection between the two. The bottom section of the reactor was a 43 centimeter long tube with a diameter of 4.95 centimeters. The top section of the reactor was 23 centimeters long with a diameter of 2.19 centimeters. A constriction with a diameter of 0.6 centimeters connected the two sections. Reactants entered the bottom of the reactor through a one-quarter inch ball joint. The bottom section of the reactor was filled with glass wool up to the level of the gas inlet. A mixture of three, four, and five millimeter glass beads was then used to fill the reactor approximately two-thirds full. A glass wool plug was placed just above the constriction, and more glass beads were used to fill the top section of the reactor to within six centimeters of the outlet. Two eight-foot Glas Cal Cords were wrapped around the reactor in order to preheat the reactants, and the entire reactor was insulated with asbestos tape. The voltage to the heating tapes was controlled using two Variac Autotransformers.

Although the reactor was designed to provide a uniform gas flow, it was found that the gas temperature decreased with distance from the center. The reactor outlet was covered with glass wool in an attempt to alleviate this problem, but the success of this measure is doubtful.

The nickel catalysts used in this study were discs with diameters of three-eighths of an inch. These discs were cut from a sheet of nickel foil with a thickness of five-thousandths of an inch. The temperature of the catalyst was measured using a three-thousandths inch chromel-alumel thermocouple obtained from Omega Engineering Inc. A twelve centimeter ceramic insulator kept the thermocouple wires separated. The thermocouple was attached to a Linear recorder which was calibrated with an Omegatemp digital thermometer manufactured by Omega Engineering Inc.

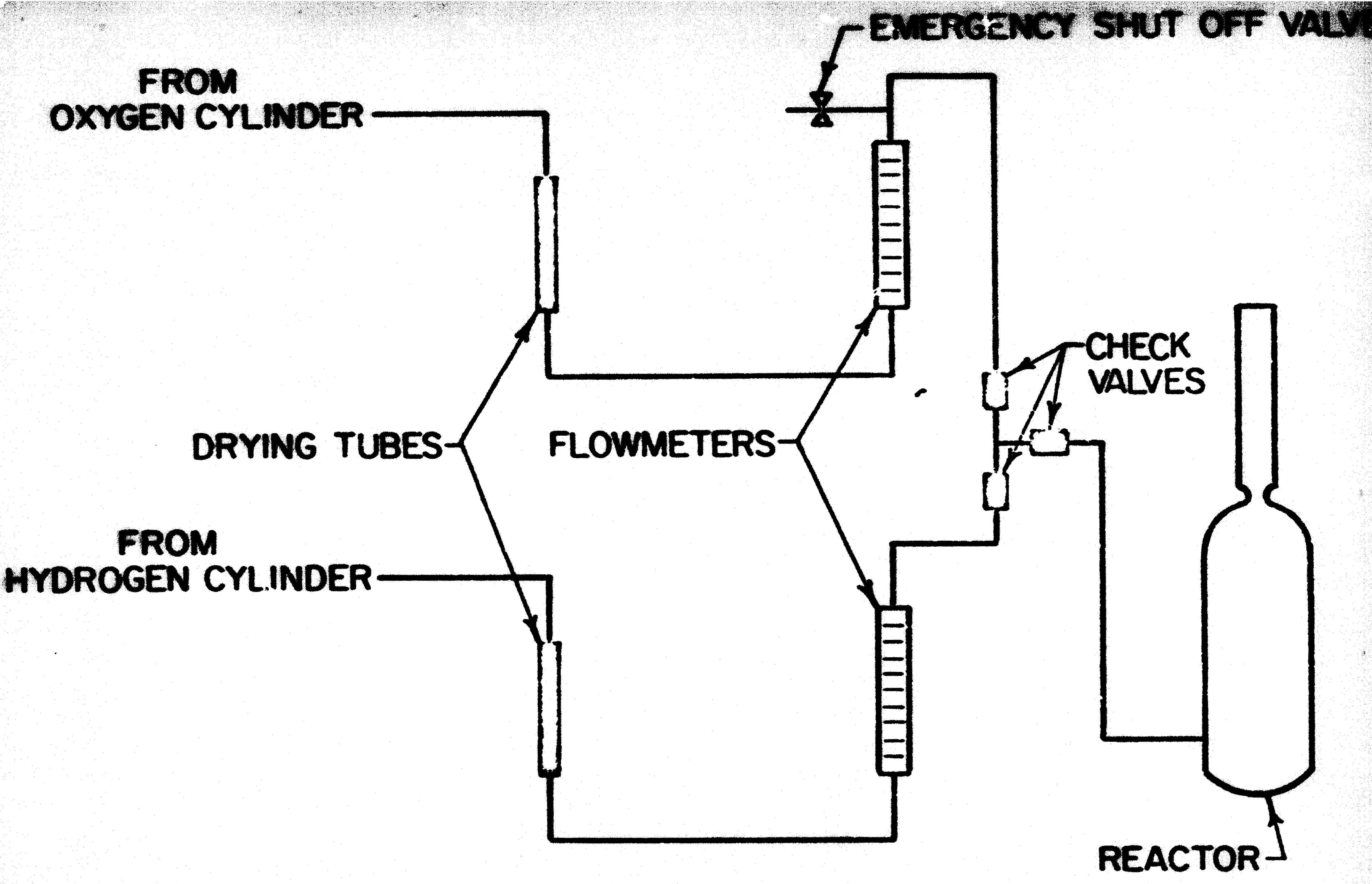


Figure 1: Experimental Apparatus

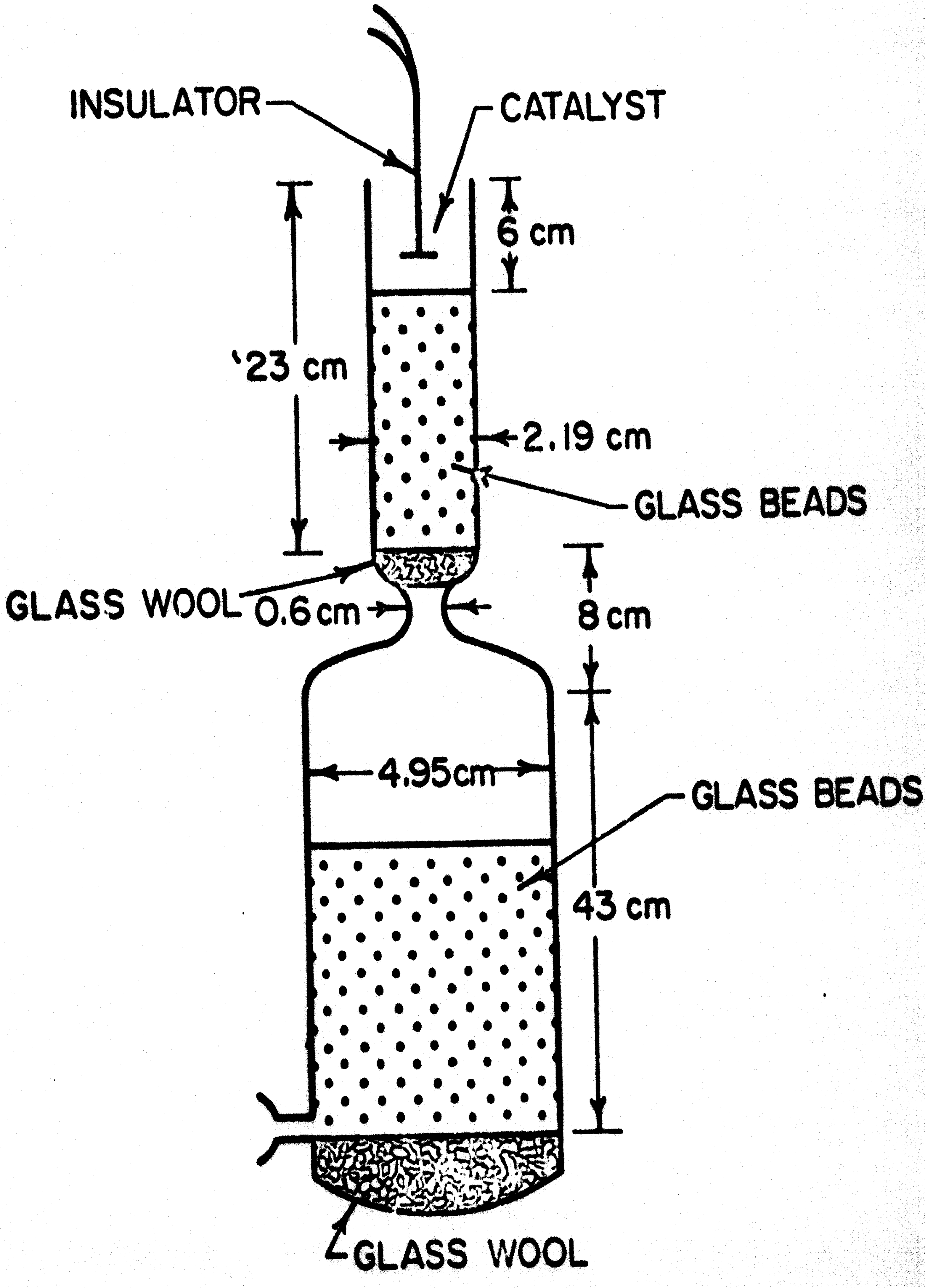


Figure 2: Experimental Reactor

PROCEDURE

A. Experimental

The procedure varied somewhat from run to run. In general, the catalysts were treated, loaded in the reactor, and activated. Then the reaction was started at conditions which were expected to produce oscillations. The behavior of the catalyst was watched closely, and the reaction was stopped and the catalyst removed for analysis after any significant change in behavior.

Three different treatment procedures, which were labeled I, II and III, and summarized in Table 1, were used to prepare the catalyst. Procedure I was to mechanically polish the face of the catalyst with various sizes of diamond paste down to 6 microns, spotweld on the thermocouples, and position the catalyst in the reactor about 2cm above the level of the glass beads. Procedure II was to polish the catalyst as in I, place it in air in a furnace at 500°C for one hour, cool the catalyst down, spotweld on the thermocouples, and position the catalyst in the reactor. Procedure III was to take a catalyst sample, with no treatment, spotweld on the thermocouples and position it in the reactor. No steps were taken to poison the back of the catalyst or the thermocouple leads in any run.

The activation procedure was the same in all the runs. The oxygen flow rate was adjusted to the highest value allowed by the flowmeter (about 300 ml/min), and the Variac voltages were adjusted to raise the catalyst temperature to between 340°C and 370°C. After one hour, the oxygen flow was terminated, and the reactor was purged with nitrogen for five minutes. After purging, hydrogen was introduced to the system at a rate of 2100 ml/min, and the Variacs were readjusted to maintain the catalyst temperature at 340°C to 370°C. After one-half hour, the oxygen flow was turned on at a rate of 63 ml/min, resulting in a gas mixture of three percent oxygen by volume. For the duration of a given experiment, temperature versus time data were collected by the recorder. The length of the experiments varied from a few minutes to four hours. After any significant change in behavior, the oxygen flow and the Variacs were turned off, and the catalyst cooled to 150°C or less in hydrogen. The catalyst was then removed from the reactor, separated from the thermocouple wires, and carried to a scanning auger spectrometer for analysis.

Table I

Pretreatment of the Nickel Samples

Treatment Type	Treatment before putting the catalyst in the reactor
I	Polished
II	Polished and calcined at 500°C for one hour
III	None

B. Analysis

A Physical Electronics 595 scanning Auger microprobe was used for all the analysis. The 595 combines the high resolution electron optics of a scanning electron microscope with the surface analysis capabilities of a standard Auger spectrometer. All of the analyses reported here were done with a beam energy of 10 kEV. High resolution photographs of the surface were taken with a beam current of 0.4 na and a magnification setting of 100,000. Low resolution photographs of the surface were taken with a beam current of 10-50na and a magnification setting of 500. General Auger spectra were taken by defocusing the beam with a beam current of 100 na. Component maps were done by setting the beam current to 100 na and the magnification to 500, then scanning an energy window around the appropriate Auger peak at each point on a 256 x 256 array on the surface of the catalyst. The map was calculated by computing the difference in the maximum and minimum in the undifferentiated Auger spectrum and normalizing to the minimum. The later procedure allows one to differentiate between variations in composition over the surface, and variations in reflectivity due to morphological features.

RESULTS

A. Catalytic Behavior

Results for one of the catalysts prepared by Procedure I are shown in Figure 3. Before the introduction of oxygen the catalyst temperature was 693°F. When the oxygen flow started the temperature rose to 785°F over a period of three minutes and an oscillation with an amplitude of about 100°F occurred. Two minutes later a very large amplitude oscillation occurred which raised the catalyst temperature to 1105°F and then back down to 740°F. The temperature then rose slowly over a period of 4 minutes with some small oscillations at which point the temperature rose quickly to 1135°F and did not return. Turning off the oxygen flow and restarting it after the catalyst had cooled resulted in a direct jump to the high temperature state with no oscillations. Similar results were obtained for all catalysts prepared using Procedures I and II. At most, two oscillations occurred before the catalyst went to the high temperature state.

Catalysts of Type III, which were not polished or calcined, exhibited sustained oscillations. Figures 4 through 7 show the temperature versus time data for a typical catalyst of this type. After the behavior shown in each figure the catalyst was removed from the reactor, analyzed, and placed back in the reactor.

Figure 4 shows the initial behavior of the catalyst. After the oxygen flow was started the temperature rose from 670°F to 770°F over a period of 38 minutes. At this point, a small oscillation with an amplitude of about 20°F occurred. Eight minutes later, the temperature had risen to 770°F, where a second oscillation occurred. During this oscillation, the temperature rose to 900°F, and dropped back down to 780°F. A slow temperature rise to 800°F over the next eight minutes resulted in a third oscillation, which increased the temperature to 920°F, and then decreased it to 780°F. Two more oscillations occurred over the next ten minutes which were similar to the third one. Peak widths were about ten seconds for all of the oscillations. The sample was then removed for analysis.

Figure 5 shows the second type of behavior exhibited by the catalyst. The temperature rose from 640°F to 750°F over a period of 20 minutes at the beginning of the experiment. Oscillations then began to occur with amplitudes of around 100°F, and periods of three to five minutes. A gradual decrease in period and increase in amplitude occurred over the first 100 minutes of the experiment. These changes were found to be due to drifting of the hydrogen flowrate. Readjustment of the flowrate resulted in a reproduction of the original behavior. The gas temperature was increased after 105 minutes in order to induce a behavioral change. As the temperature increased, the periods became smaller, and lower limit of the oscillations increased. The amplitude of the oscillations remained at about 100°F. Seventeen minutes after the temperature increase began, the lower oscillation limit was at 825°F, and the period of the oscillations was about 30 seconds. At this point, the behavior became chaotic with peak amplitudes varying from 15°F to 200°F. The lower limit stayed constant at 835°F. The chaotic behavior was allowed to continue for 30 minutes before the experiment was ended and the sample removed for analysis. It should be noted that the time scale in Figure 5 changes at 122.5 and 148 minutes. Also, the small temperature variations at times of 16, 101, and 104 minutes were caused by oxygen flowrate adjustments, not catalytic behavior.

The third type of behavior exhibited by the catalyst is shown in Figure 6. Within 5 minutes of the introduction of oxygen, the temperature had risen from 680°F to 785°F. Several small oscillations of 5°F to 10°F occurred followed by a larger oscillation in which the temperature rose to 945°F and then fell to 755°F. The temperature rose slowly to 803°F over the next eight minutes, followed by another oscillation. This oscillation had a much larger amplitude and peak width than any previously observed oscillation. The maximum temperature reached was 1055°F, and the peak width was about 80 seconds. Subsequent oscillations also had unusually large amplitudes and peak widths. The upper temperature limit varied from 1040°F to 1100°F, while the lower limit remained essentially constant at around 755°F. The peak widths varied from 20 to 60 seconds. Several of the oscillations were preceded by some small amplitude (2-5°F), small period (20 seconds) oscillations. The amplitude of these oscillations gradually increased for one to two minutes before the large oscillation occurred. For the fourth, and twelfth and fourteenth peaks, three to four small amplitude oscillations were superimposed on the large oscillation at the top of the peak. The period between the large oscillations varied from six to seventeen minutes. Some of the variation in period may have been due to drift in the hydrogen flowrate. The experiment was ended after 150 minutes, and the sample was removed for analysis.

In Figure 7, the transition to the high temperature state is shown. For the first 120 minutes of this experiment, the behavior was very similar to that shown in Figure 6. Consequently, the gas temperature was increased in an attempt to force the reaction into the high temperature state. The result of this was an increase in both the upper and lower temperature limits, and a decrease in the period. The lower limit increased to 835°F and the upper limit went from 1080°F to 1100°F. The period decreased to four minutes. After four oscillations at the increased temperature, the high temperature state was reached. The temperature of this state was nearly the same as the upper limit of the preceding oscillations. The catalyst was again removed for analysis.

A fifth experiment was also done with this catalyst. In this experiment, the catalyst was brought to the high temperature state and left there for five hours and then removed. No oscillations were observed.

These experiments were repeated for three other catalysts prepared in Procedure III. In general, the results looked similar to those in Figures 3 through 7. Oscillations were observed with a range of periods of 20 to 1000 seconds, and a range of amplitudes of 5°F to 350°F.

B. Auger Analysis

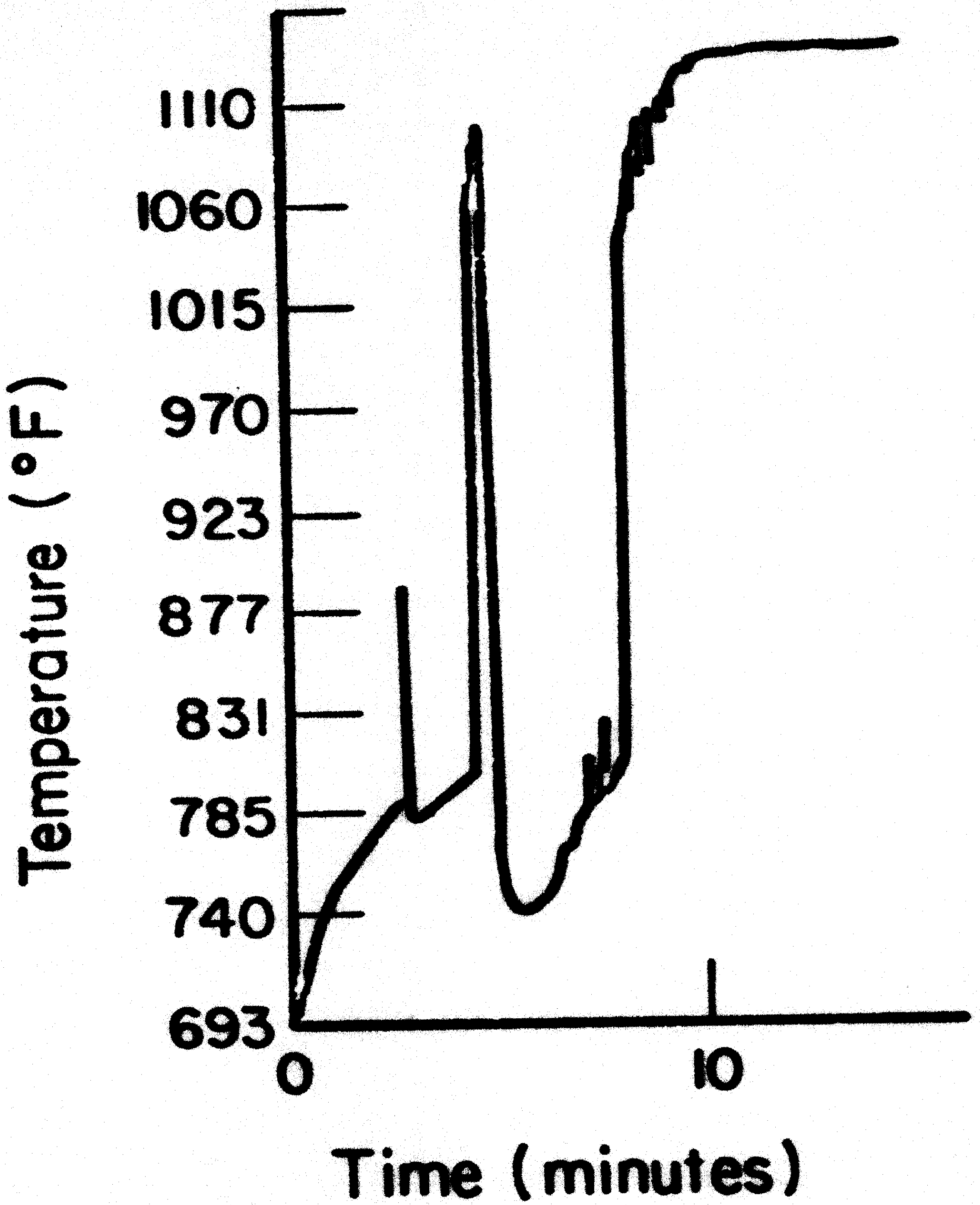
A low magnification picture of the catalyst whise behavior was shown in Figure 3 is shown in Figure 8. The surface shows some small scratches which were caused by polishing, but no large ridges or valleys. At a higher magnification, shown in Figure 9, small peaks and valleys with a size on the order of 0.02 microns can be seen, but no gross features exist. All catalysts prepared by Procedures I and II looked qualitatively similar. The catalysts looked relatively flat on the scale of 10 microns, but there were some small features on the order of hundredths of microns in diameter.

An Auger scan of one of the catalysts prepared by Procedure I is shown in Figure 10. The analysis shows large amounts of oxygen (483EV and 513EV) and nickel (716EV, 783EV, 848EV), with a small amount of carbon (272EV) and trace impurities. Sputtering with Argon for three and a half minutes at a voltage of 2kV, a current of 0.1na, and an Argon pressure of 4×10^{-7} torr resulted in the spectrum shown in Figure 11, Most of the impurities have been removed along with a fraction of the oxygen. Auger analysis of all of the other catalysts prepared by Procedures I and II showed similar features. The surfaces contained large amounts of nickel and oxygen, small amounts of carbon, and trace amounts of other components. Not shown are oxygen and carbon maps, which indicated that the oxygen and carbon concentrations are essentially constant over the surface.

Low magnification pictures of the catalyst whose behavior was shown in Figures 4 through 7 are given in Figures 12 through 15. After the simple periodic oscillations in Figure 4, the surface exhibited mountains and ridges with an average diameter of about 8 microns with some relatively flat areas as shown in Figure 12 . After the chaotic behavior shown in Figure 5, the surface still had some large ridges as before, but the previous flat areas were covered by small pits and spots as shown in Figure 13. The very large amplitude oscillations in Figure 6 occurred when the surface had smaller mountains, and some very tiny cracks as shown in Figure 14. Just after the catalyst went to the high temperature state, Figure 15 shows that the surface was much smoother than originally, with few large mountains.

Higher magnification pictures of an oscillating catalyst are shown in Figures 16 and 17. Figure 16 shows a medium magnification picture of several of the ridges. The ridges appear to be fairly round, with some small grooves cut into them. Figure 17 shows a high magnification picture of a flat area on the catalyst. On the day this picture was taken, the resolution of the auger was not as good as that in Figure 9. (It was only on rare occasions that the resolution was high enough to allow the magnification shown in Figure 9.) However, it is still possible to see small ridges and valleys with sizes on the order of tenths of a micron.

Auger analysis of an oscillating catalyst is shown in Figures 18 and 19. There are large oxygen and nickel peaks, a much smaller carbon peak, and some trace impurities. Comparison with Figures 10 and 11 showed that the surface composition was very similar to that for nonoscillating catalysts shown previously. Sputtering at the same conditions as before, again removed the impurities and some of the oxygen. In one case, sputtering appeared to increase the carbon content, but this occurred on a day when the Auger system was dirty and depositing carbon.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1060
1015
970
923
877
831
785
740
693
0
10
Time (minutes)

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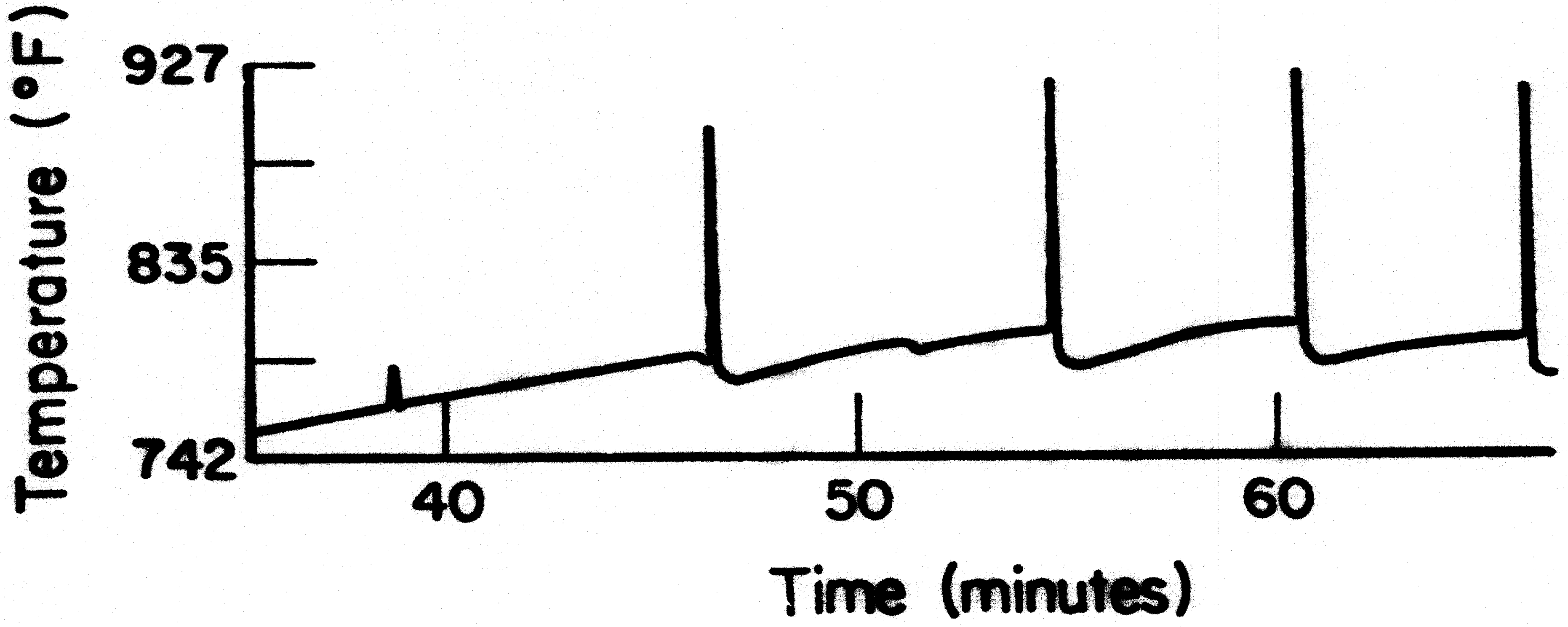
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742
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50
60
Time (minutes)

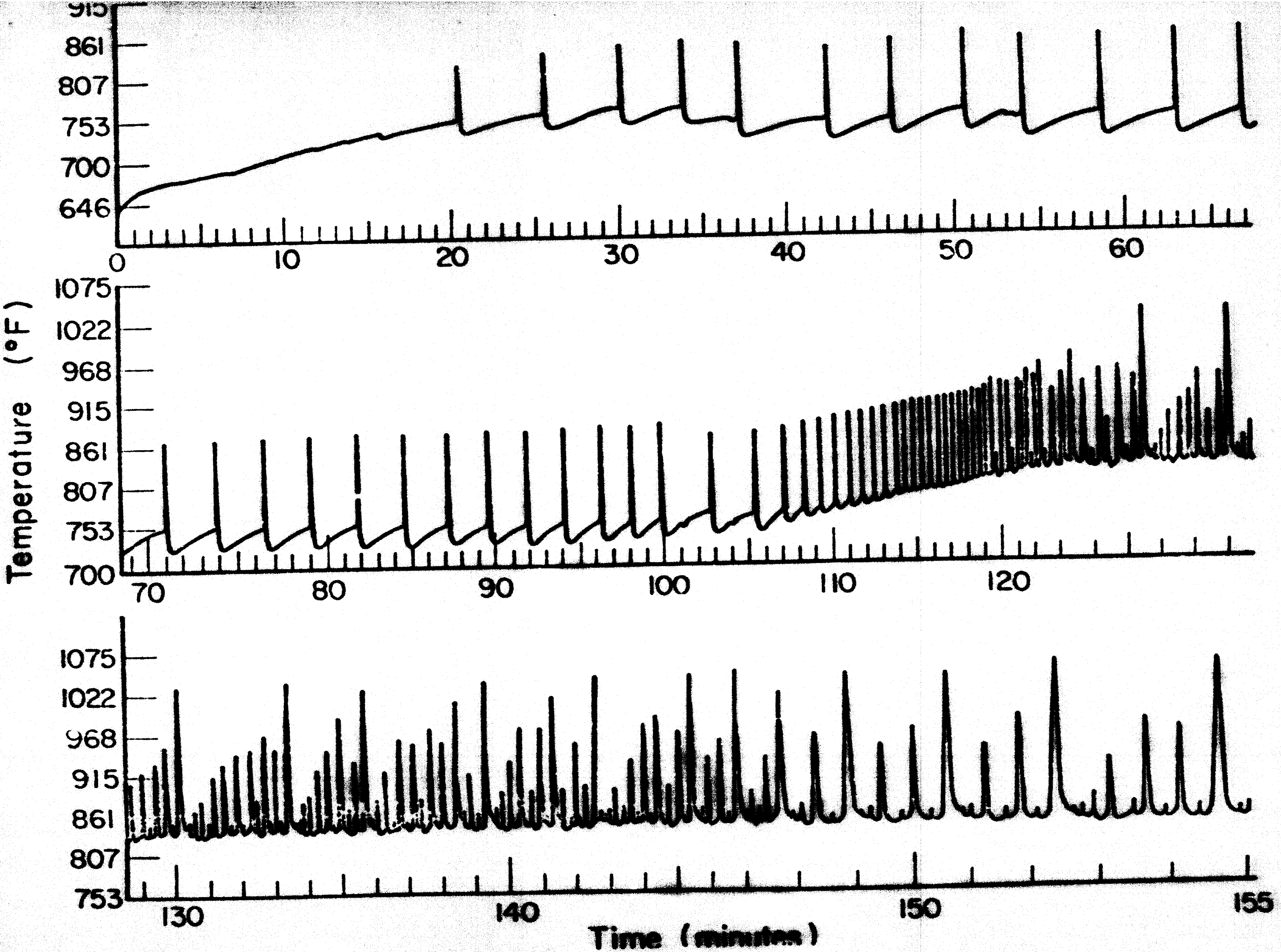

Figure [illegible]: Reaction of a Catalyst Prepared by Procedure III, Second Experiment

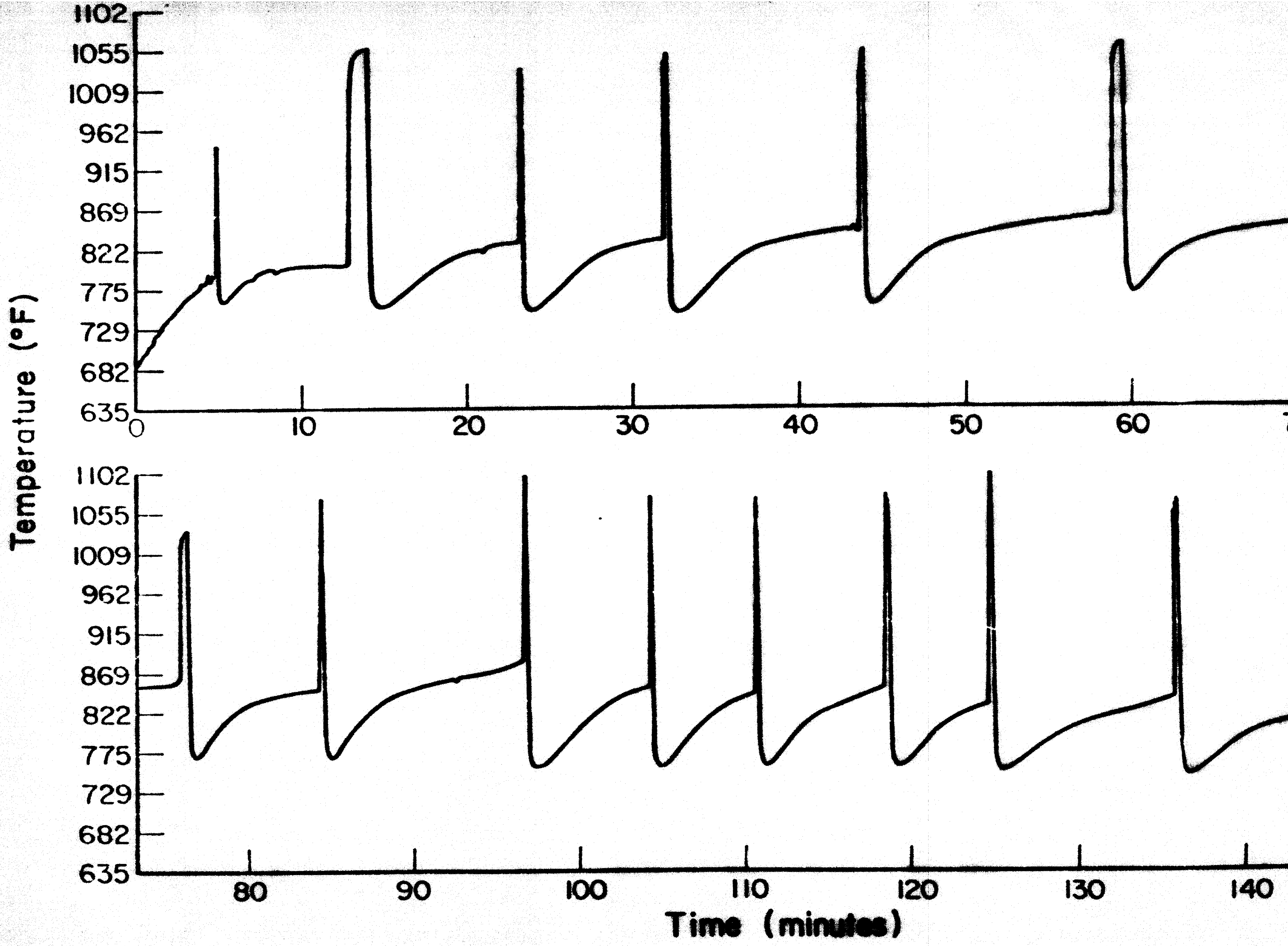

Figure [illegible] : [illegible]
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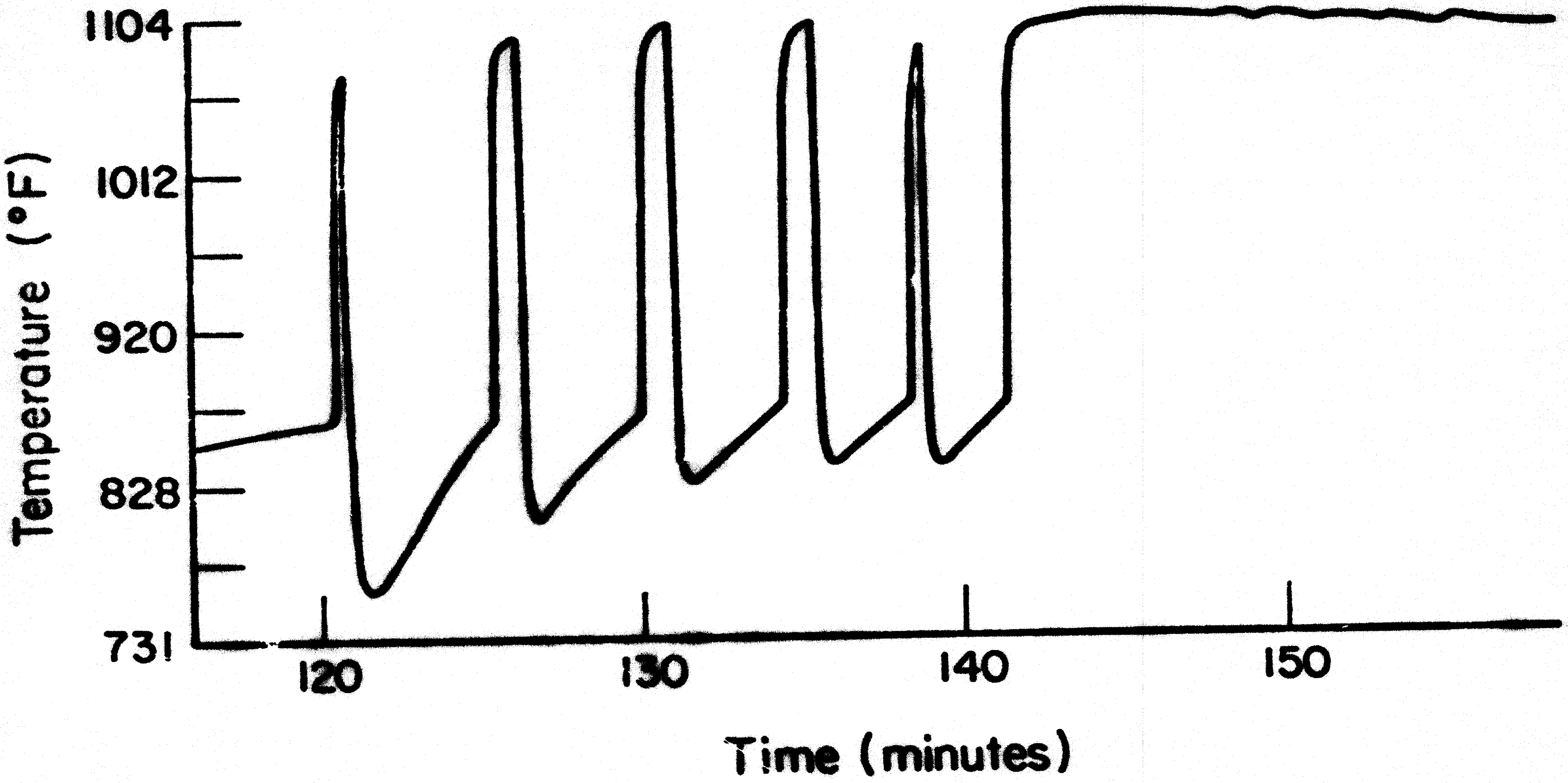
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1012
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828
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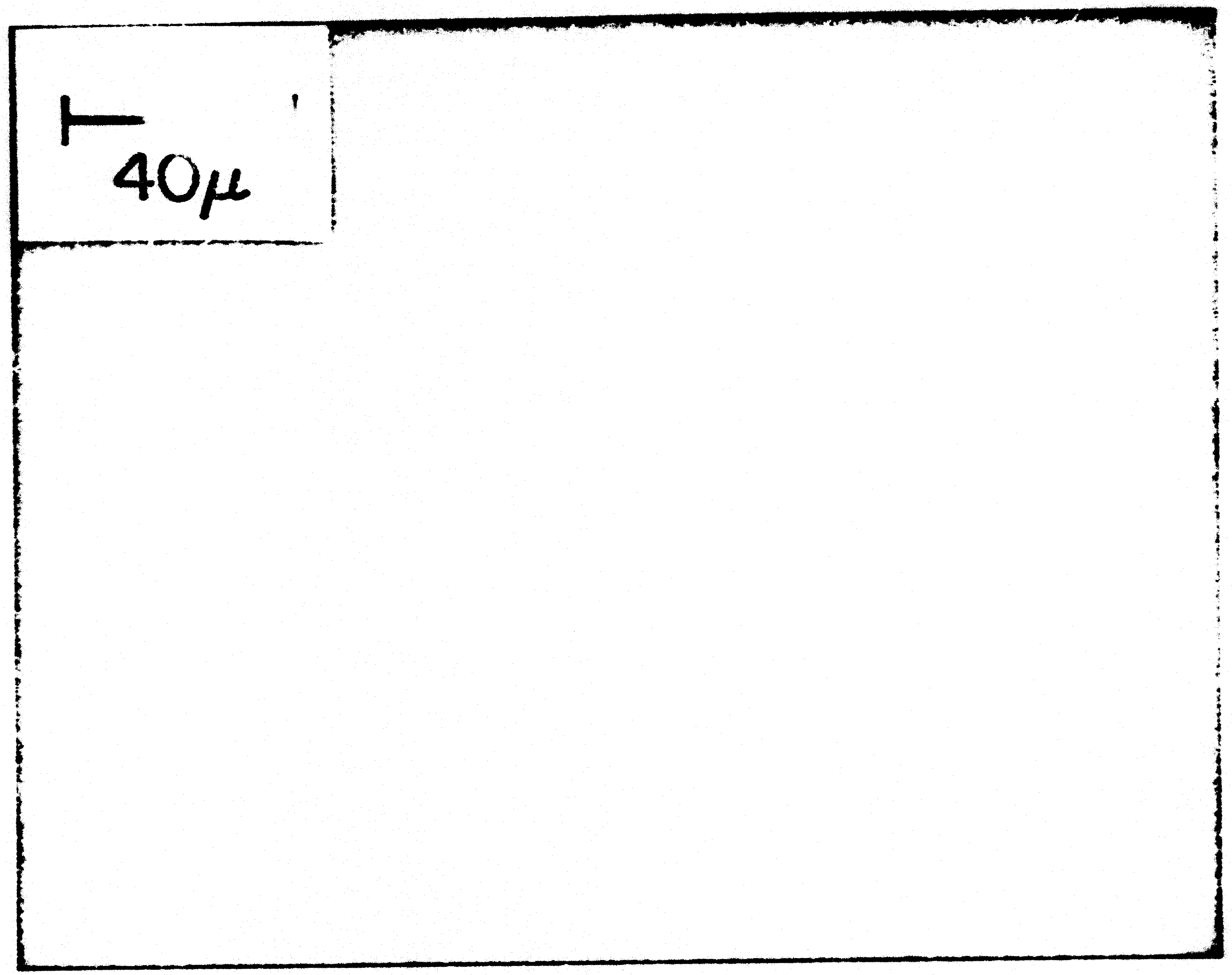
130
140
150
Time (minutes)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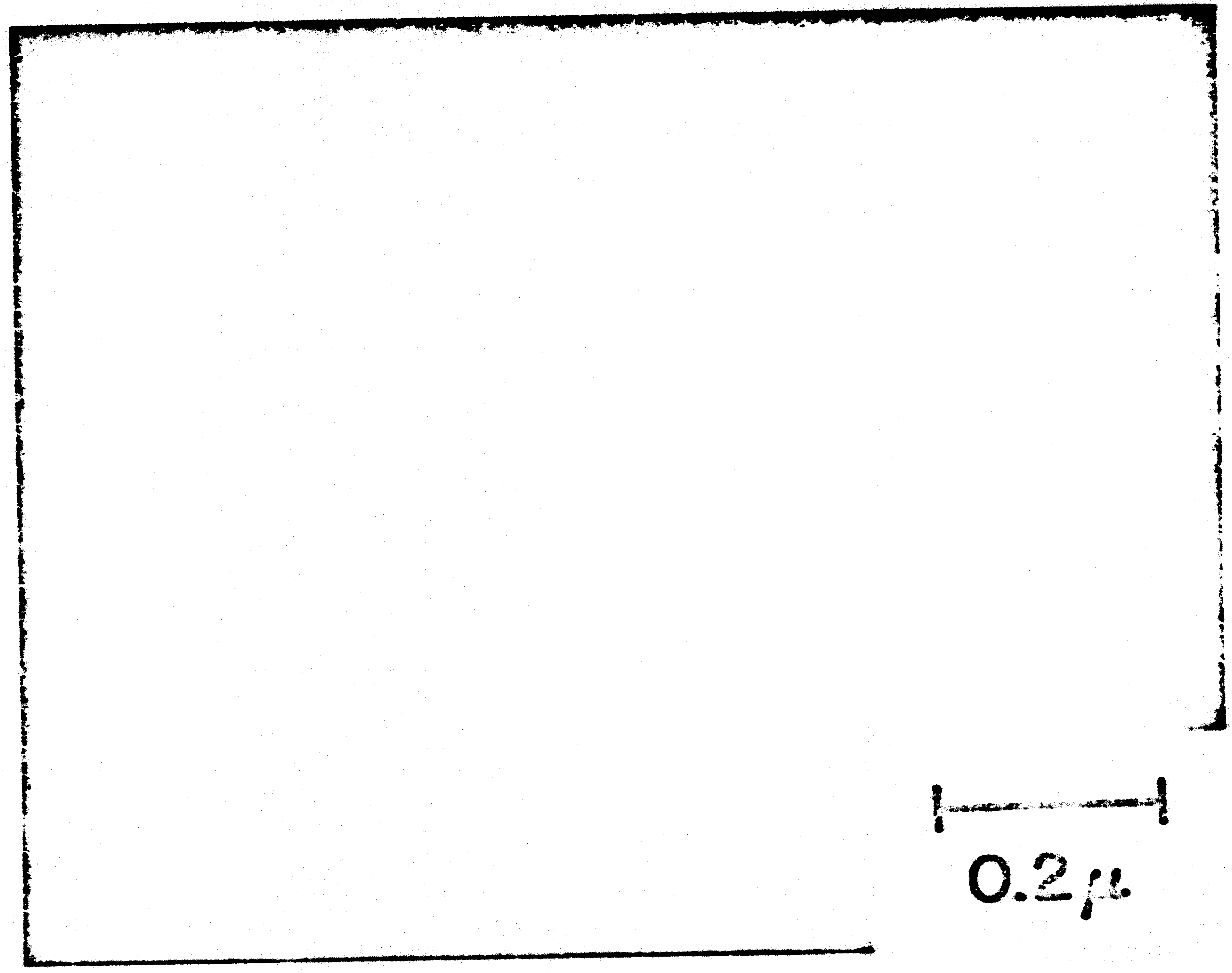
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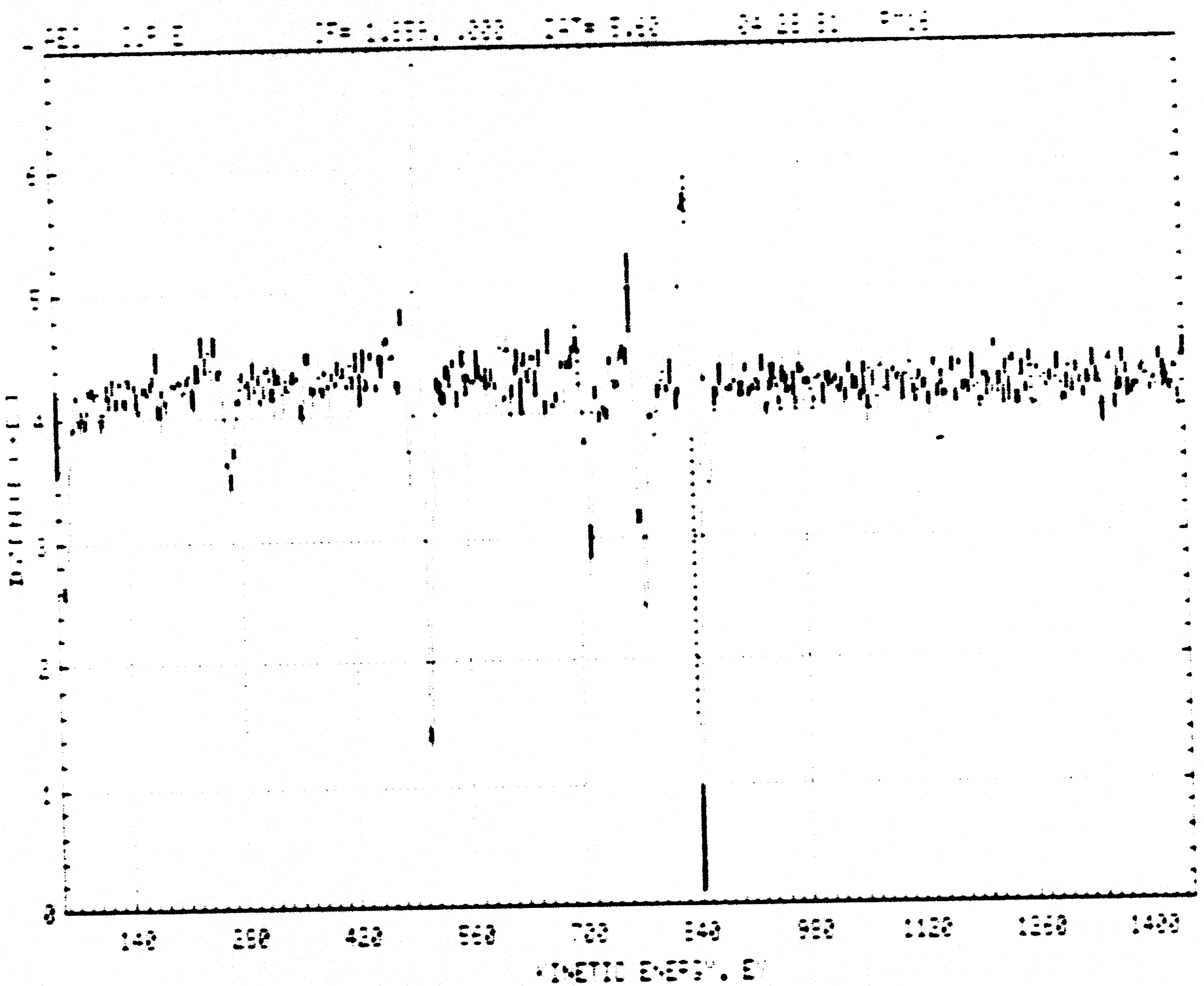


Figure 10: Auger Scan of a Catalyst Prepared by Procedure I

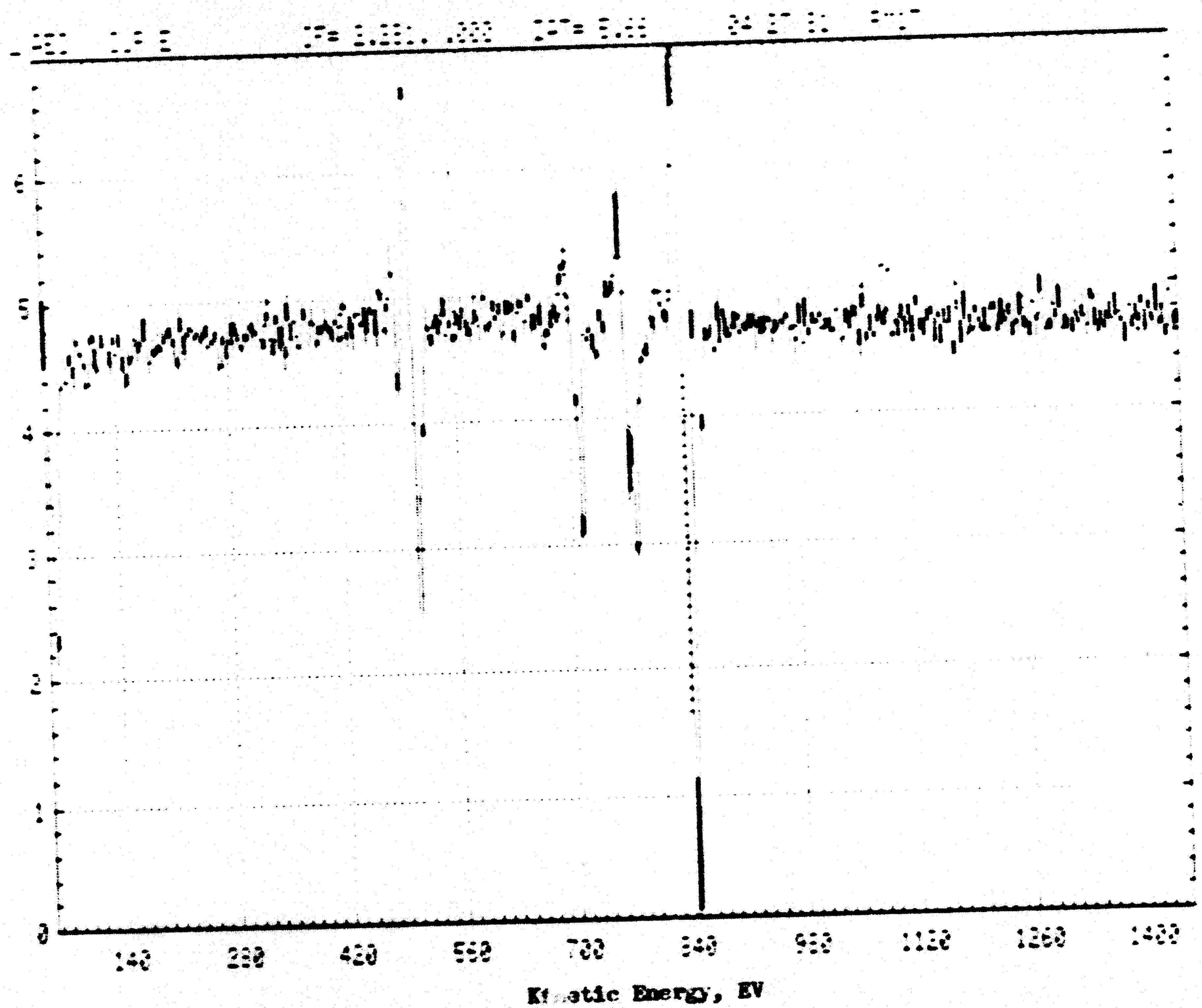
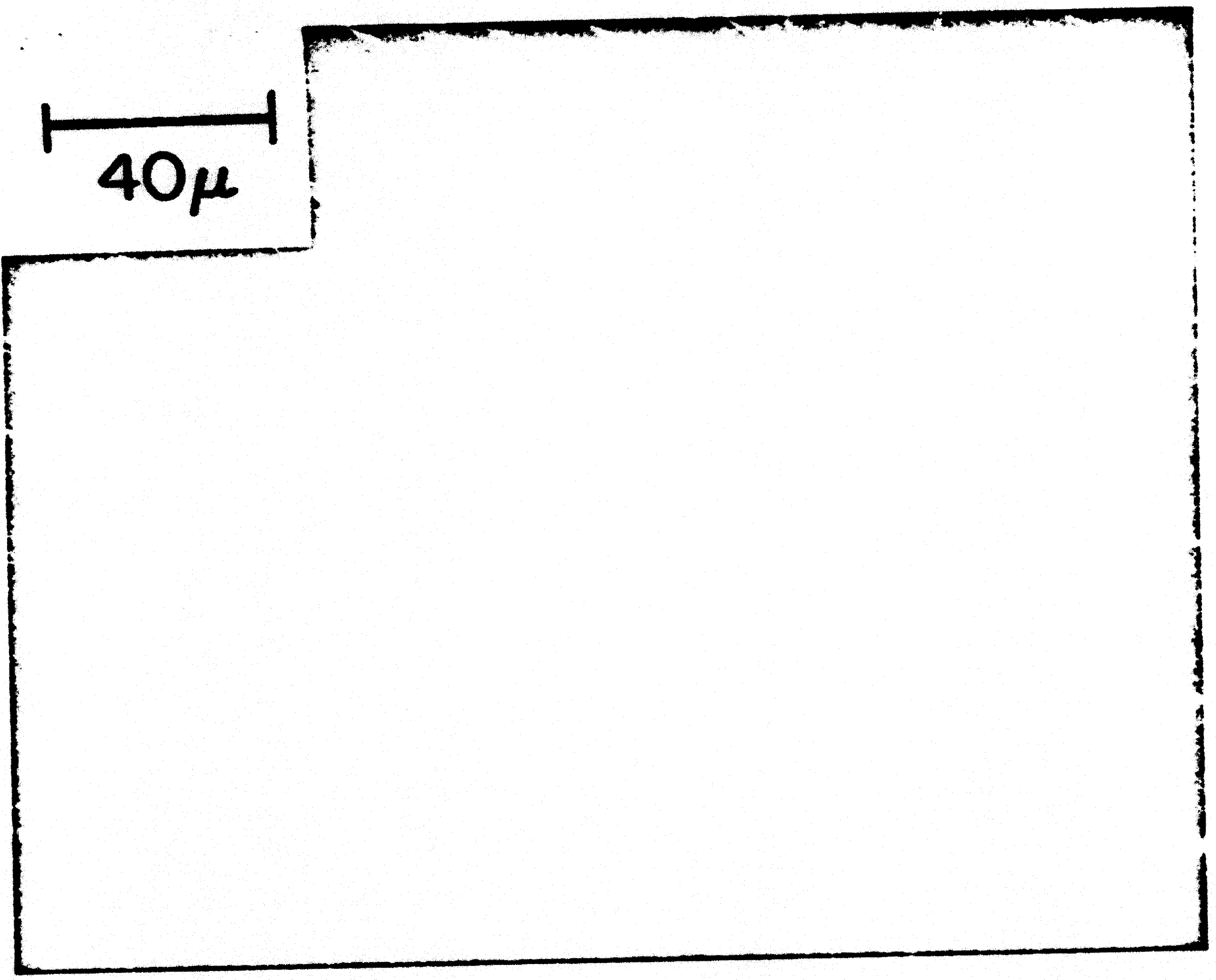


Figure 11: Auger Scan of a Catalyst Prepared
by Procedure I
After Sputtering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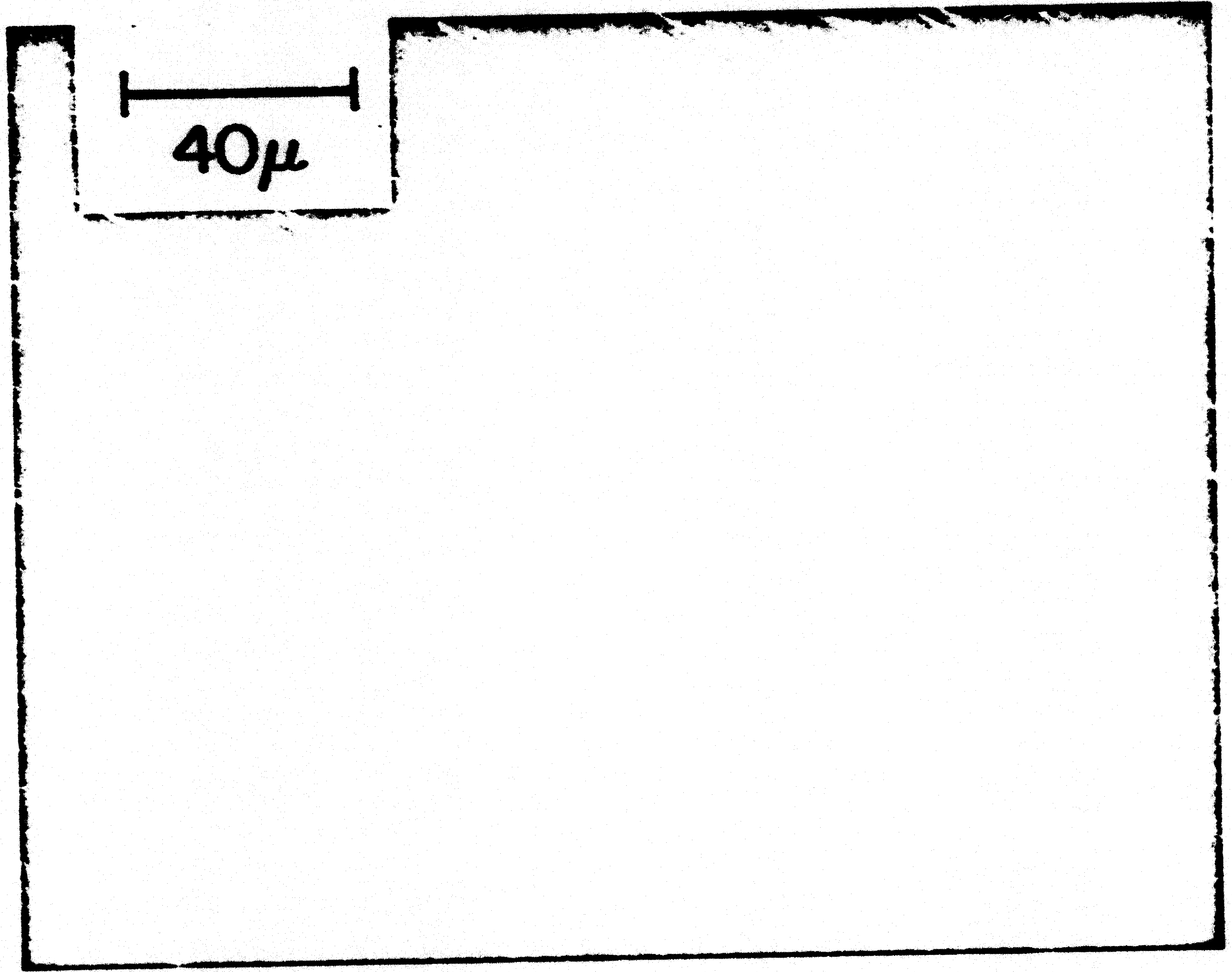
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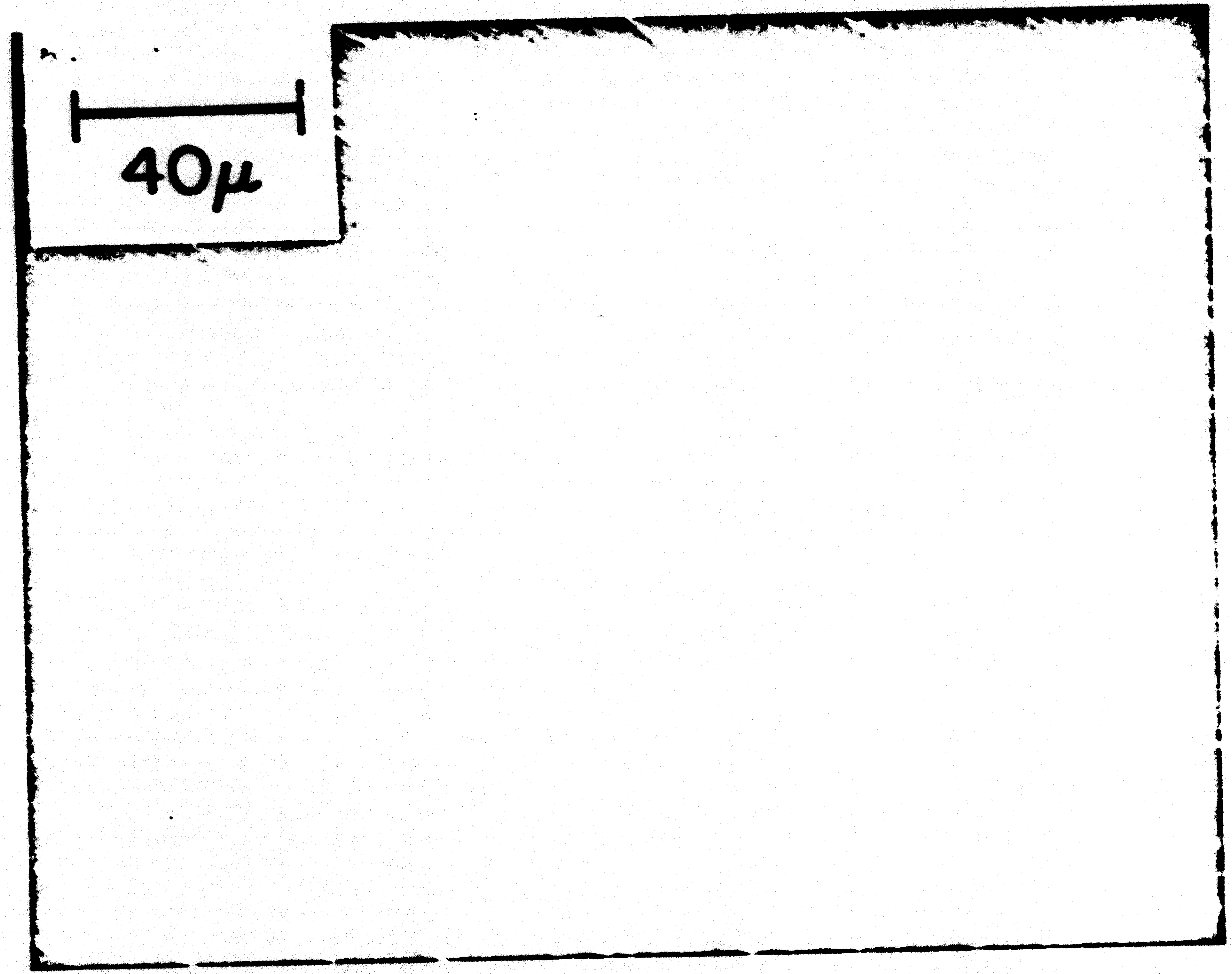

Figure [illegible]: [illegible]
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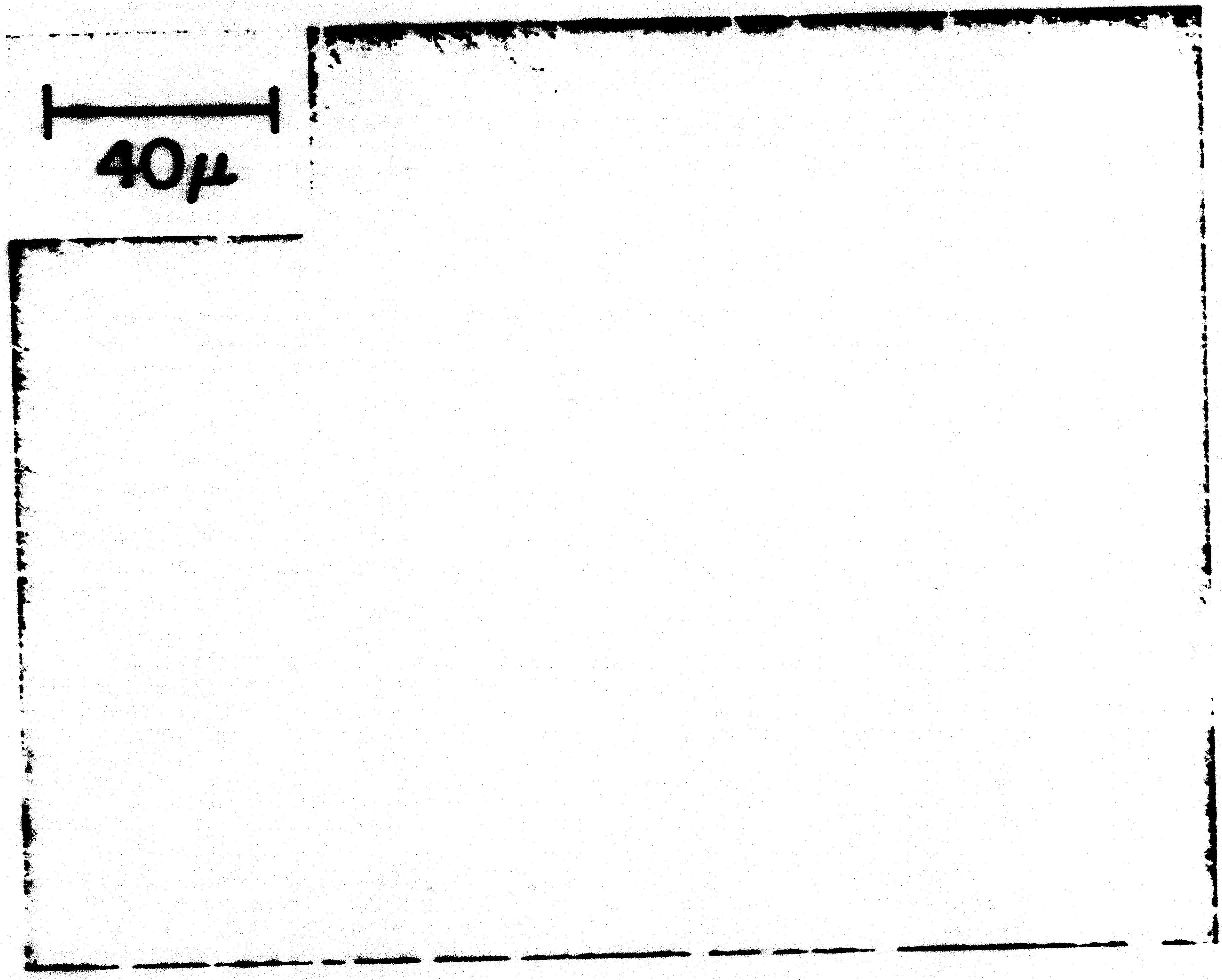
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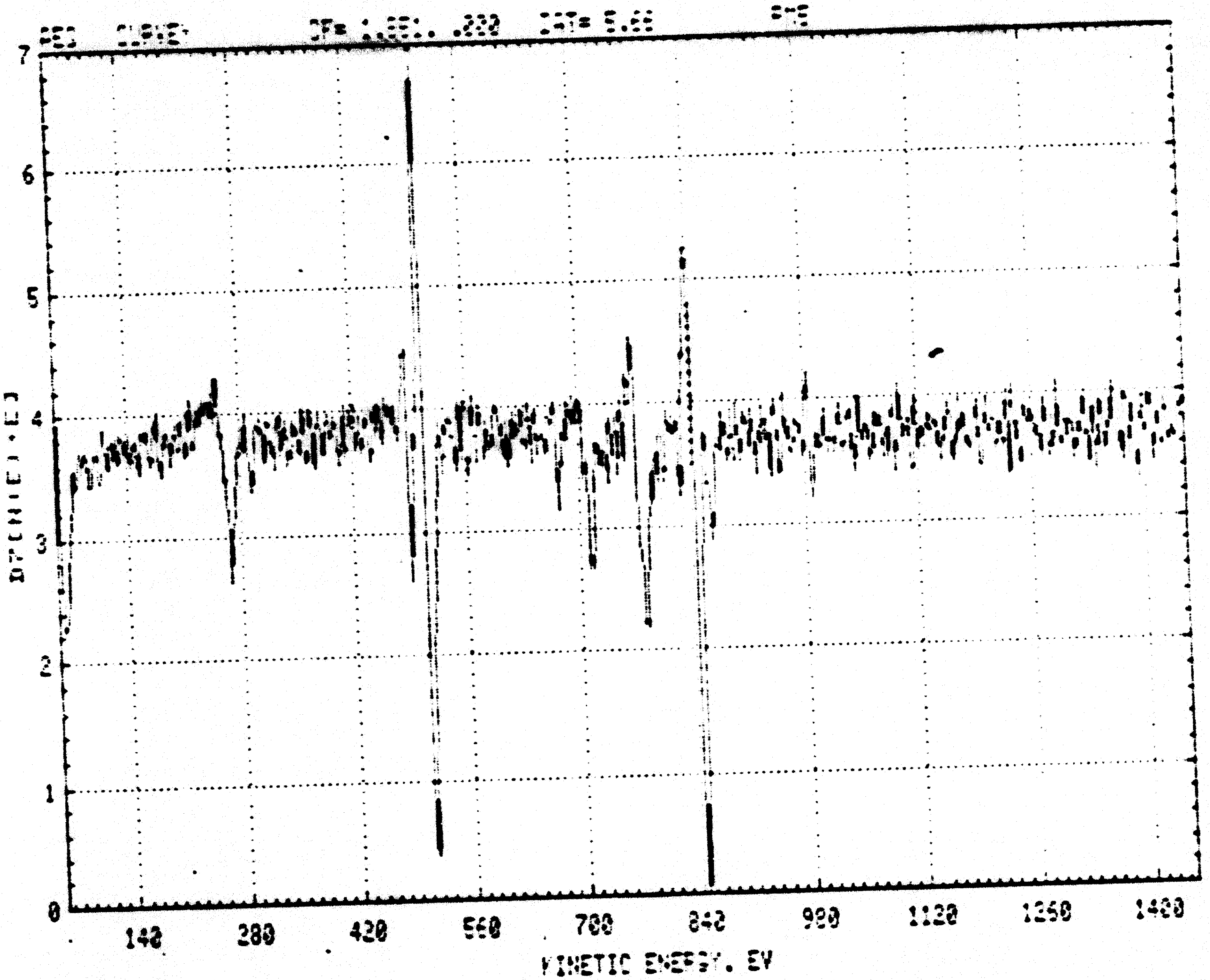

Figure 18: Auger Scan of a Catalyst Prepared by Procedure III

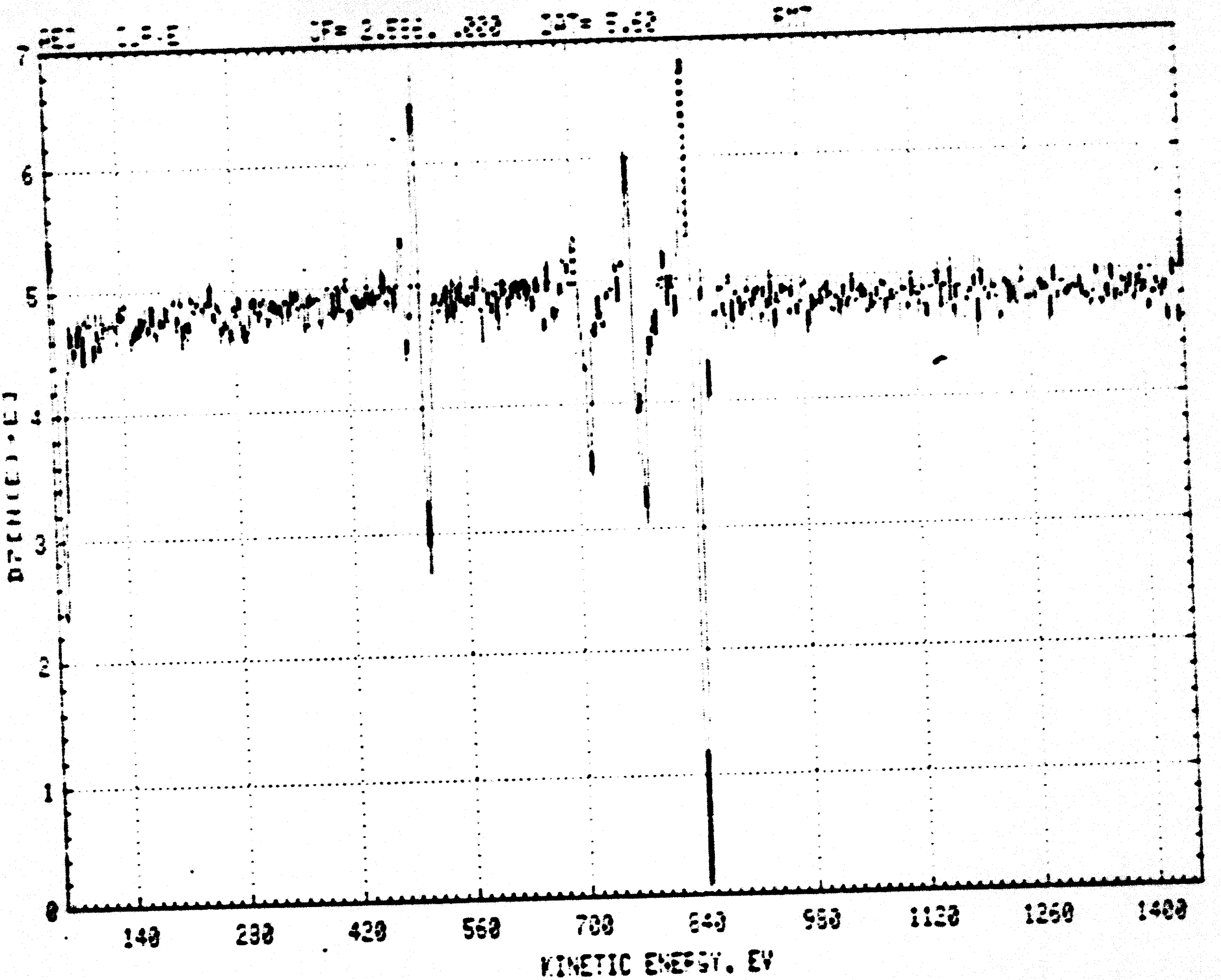

Figure 19: Auger Scan of a Catalyst Prepared
by Procedure III
After Sputtering

Discussion

The data in the last section indicate that the pretreatment procedure has a large effect on whether the system exhibits sustained oscillations, and on the form of the oscillations. No sustained oscillations were observed for catalysts which were polished or annealed, while self-sustained oscillations were observed for catalysts which were loaded directly into the reactor with no pretreatment. A different pretreatment procedure was used by Schmitz, et al. (7,8) which left the surface visibly rough, and resulted in a different form for the oscillations than was seen here. All of the oscillations observed here were similar in form in that the catalyst spent a majority of the time at a low temperature, with a rapid increase and subsequent decrease in the catalyst temperature during an oscillation. In the oscillations observed by Schmitz, et al., the catalyst spent a majority of the time at a high temperature, with a rapid decrease and subsequent increase in the temperature during an oscillation. Schmitz, et al., painted the backs of their samples with an aluminum paint and used a large thermocouple, so that the thermal mass of their samples was larger than the thermal mass of the samples used here. Jensen and Ray (18) have shown that differences in thermal mass can change the form of the oscillations. Consequently, a comparison of the data of Schmitz, et al., with our data is complicated.

From the data in the last section, it is apparent that the pretreatment greatly affected the morphology of the surface, but [illegible] taken in this study show that the surfaces of the catalysts were covered by a thick layer of nickel and oxygen. The relative amounts of these two components did not vary significantly from catalyst to catalyst, and while the amounts of impurities varied slightly, no correlation was found between the presence of any impurity and the occurence of sustained oscillations.

A comparison was made between the spectra taken here, and the spectra of a sample which had been cleaned in vacuum, and subjected to the same transfer procedure as used here. This comparison showed that a great deal more oxygen was present on our samples, indicating that the presence of oxygen was not due entirely to the transfer procedure. Also, the oxygen on our samples was less easily removed by sputtering. The comparison suggests that the surfaces of the catalysts used here were covered by a layer of nickel oxide. This result is surprising since the reaction was run under net reducing conditions. However, the data of Larson and Smith (19) indicates that when hydrogen is oxidized on nickel, the oxidation reaction persists long after the oxygen is turned off.

The morphological changes caused by the pretreatment procedure are seen by comparing figures 8 and 12. Catalysts such as the one in figure 8, which did not produce sustained oscillations, were flat, while catalyst such as the one in figure 12, which did produce sustained oscillations , looked very rough. Figures 13 through 16 show that as the catalytic behavior gets more complicated, the catalyst surface gets progressively rougher. As the ability of the catalyst to sustain the oscillations decreases, the surface becomes smoother. High resolution pictures, such as the ones in figures 9 and 17, show that only large scale differences are involved. All of the samples looked the same on a scale of tenths to hundredths of microns. This result was expected since the only differences between the catalysts was the degree of polishing, and a six micron paste was used to do the polishing.

The data given here is consistent with the model of Jensen and Ray (18) which shows that the presence of protrusions on the surface can lead to sustained oscillations. This model also predicts that the presence of several different sized protrusions will lead to complex catalytic behavior, while a surface with only one size protrusion will exhibit simple periodic oscillations. In figure 12 the height of the protrusions is fairly constant, and the catalyst exhibited very simple behavior, as shown in figure 4. In figure 13 there is a large variation in the height of the protrusions, and the behavior shown in figure 5 is very complex, as predicted by the model. In figure 14, the surface has smoothed out somewhat, resulting in a more uniform distribution of protrusion heights, and a similar type of behavior, as shown in figure 6. In figure 15, the surface is much smoother than originally, and the catalyst no longer oscillates. Thus, it appears that a minimum peak height is necessary for oscillations to occur.

One problem with Jensen and Ray's model is that they assumed that the protrusions were porous. Figure 16 shows that this assumption is not valid for our catalysts. However, the qualitative agreement of our results with the model of Jensen and Ray suggests that the role of surface protrusions in catalytic oscillations is important.

Conclusions

The results presented here suggest that the occurence of oscillations in catalytic oxidation is due to a physical rather than a chemical mechanism. The lack of compositional differences between catalysts which exhibited very different behavior is strong evidence that the presence of surface impurities in small amounts does not have an effect on the form or the occurence of oscillations. On the other hand, the large scale morphological differences which accompanied changes in catalytic behavior implies that the surface structure is an extremely important factor in catalytic oscillations. The data given here shows that the presence of surface protrusions or ridges is necessary for the occurence of oscillations. Also, the form of the oscillations is very dependent on the size distribution of the protrusions. The lack of any morphological differences on a molecular level, as shown by the similarity of the catalysts on a submicron scale, shows that the influence of surface protrusions is important only when the size of the protrusions is above a certain critical height. Taken together, the data in this study suggests that further research in the area of oscillations in catalytic oxidation should be directed toward the understanding of the influence of surface morphology on this phenomenon.

Acknowledgments

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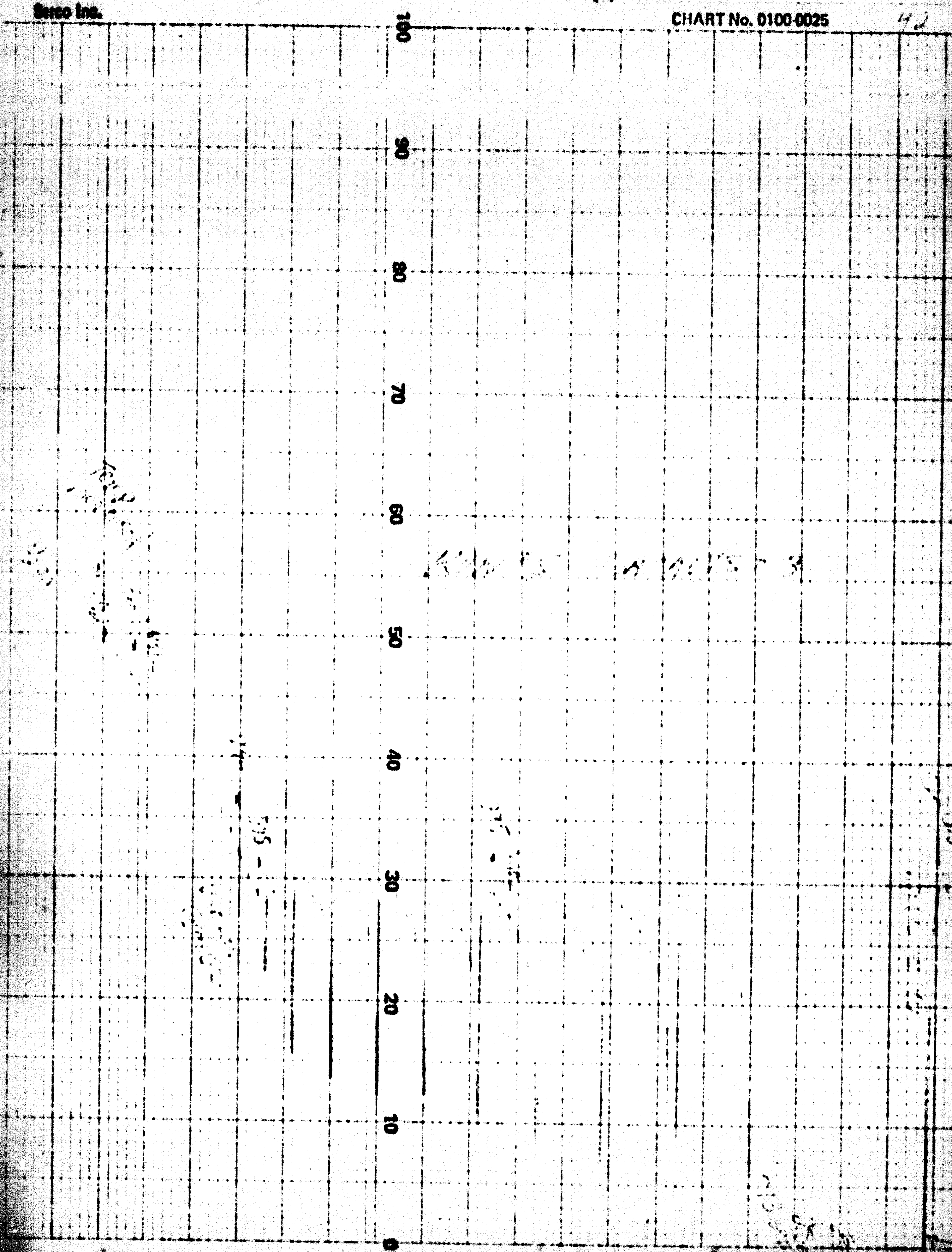
Appendix A: Additional Calibration Behavior

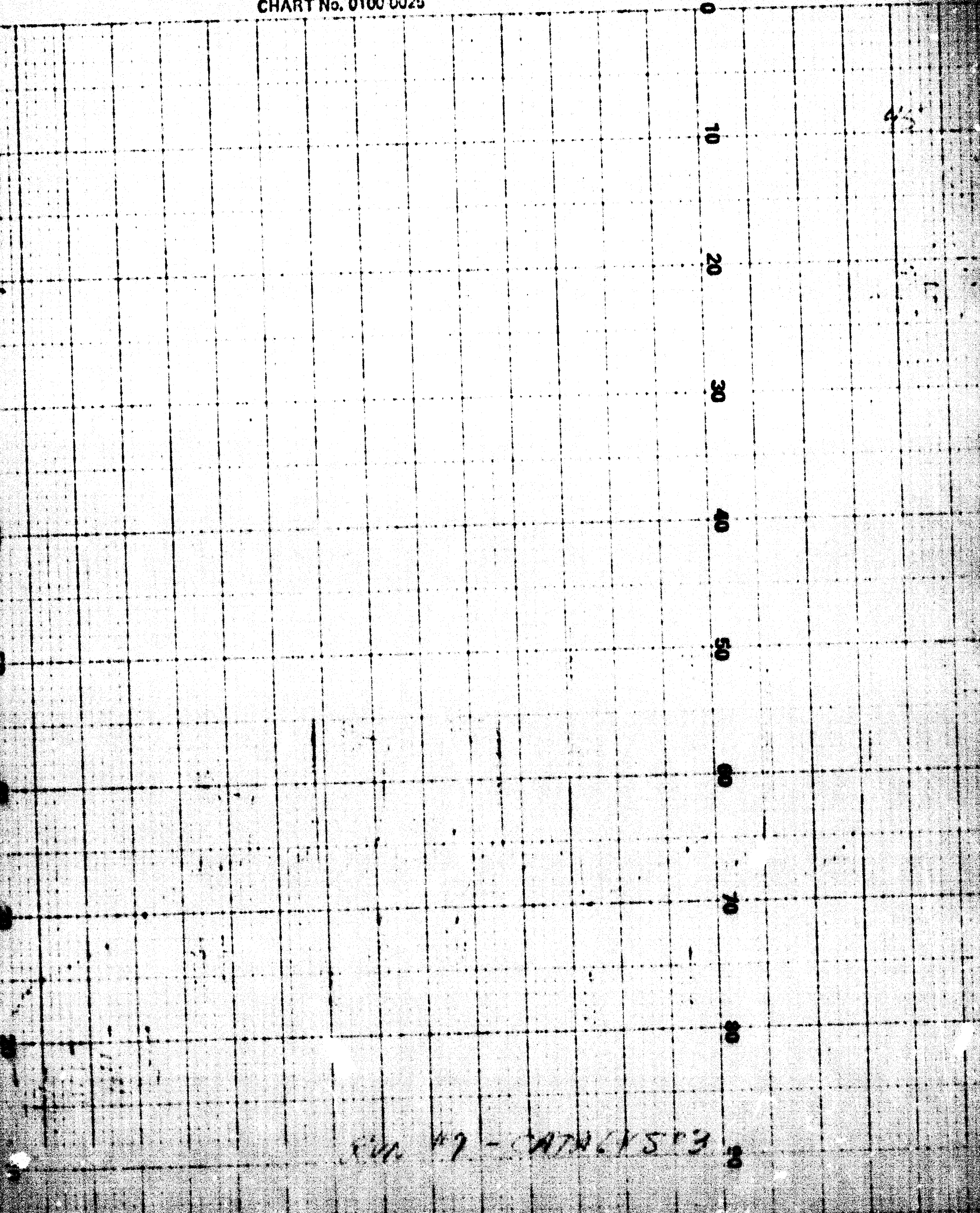


Serco Inc.

[illegible]

4/4

Run #3 AT&T 5 3



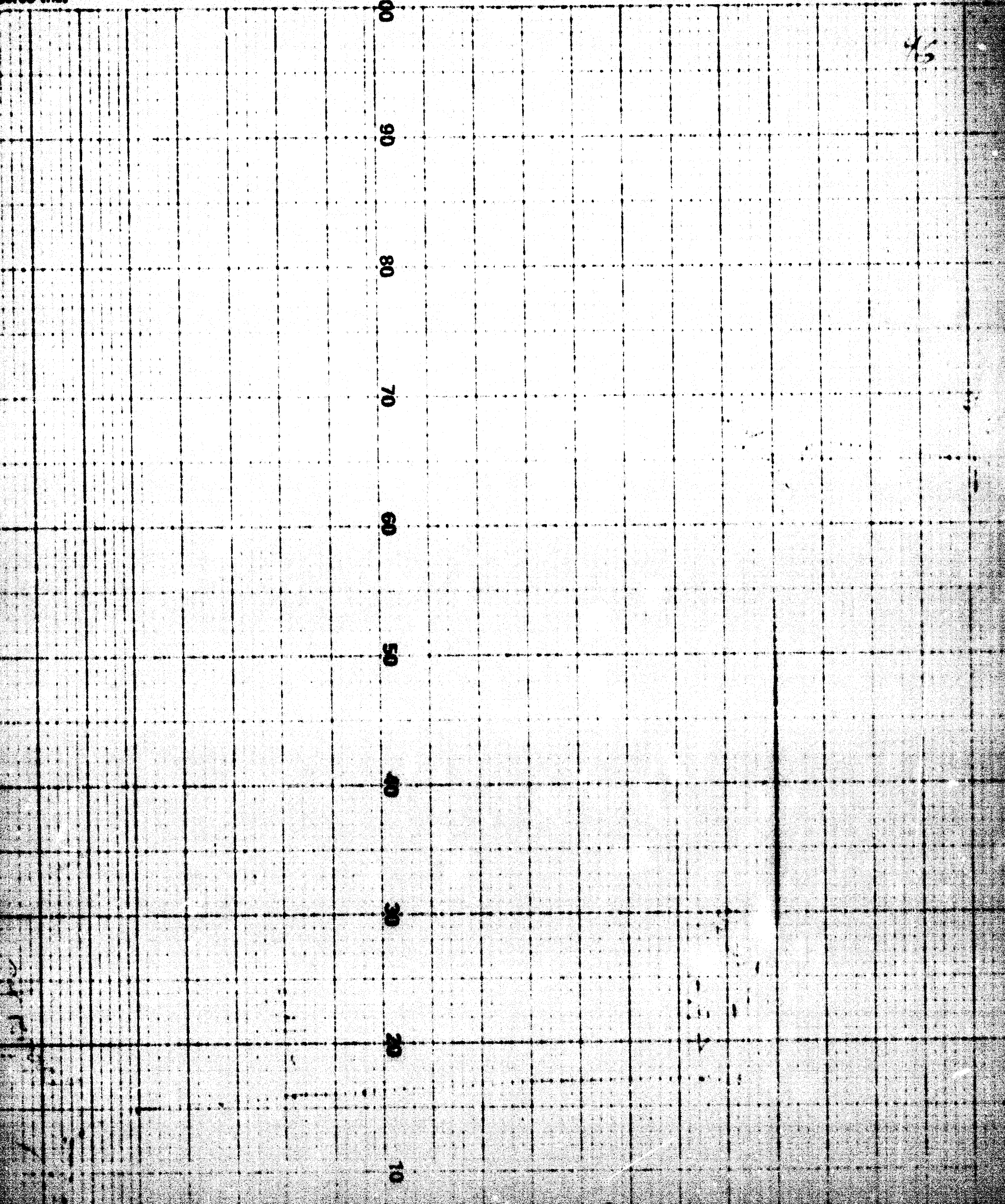
4:2

CM 47 - CATW.1 S 3

Serco Inc.

CHART No. 0100 0025

45



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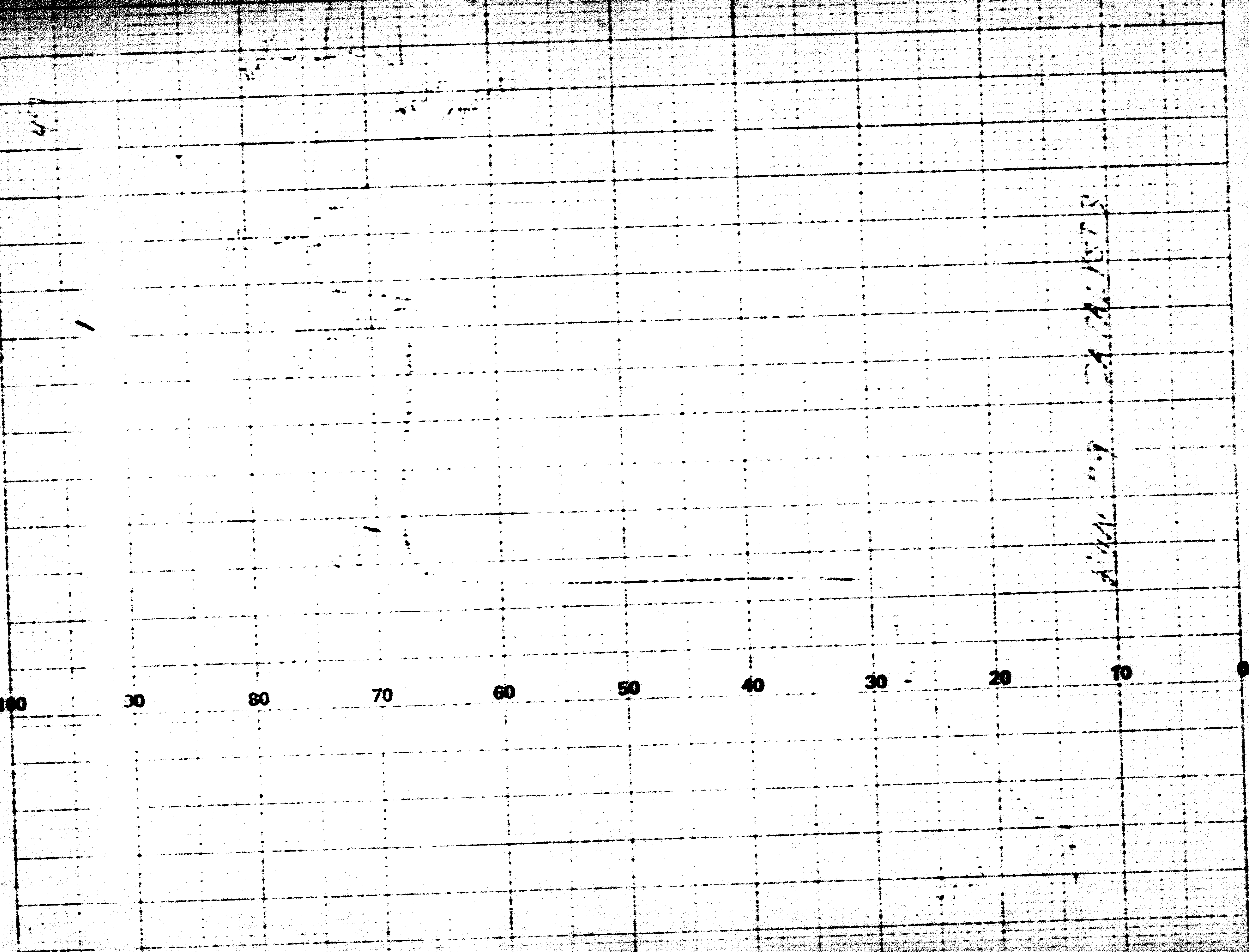
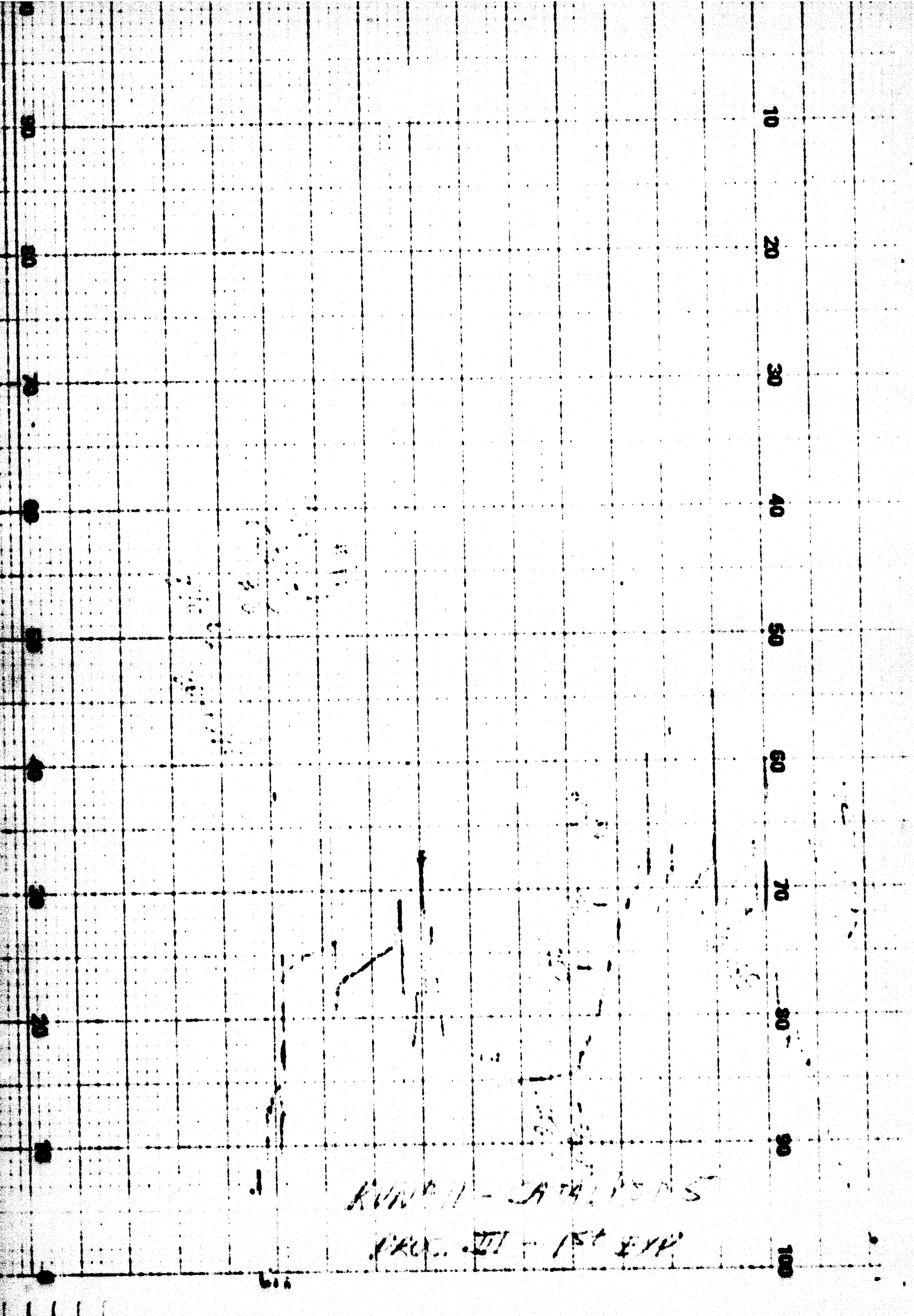
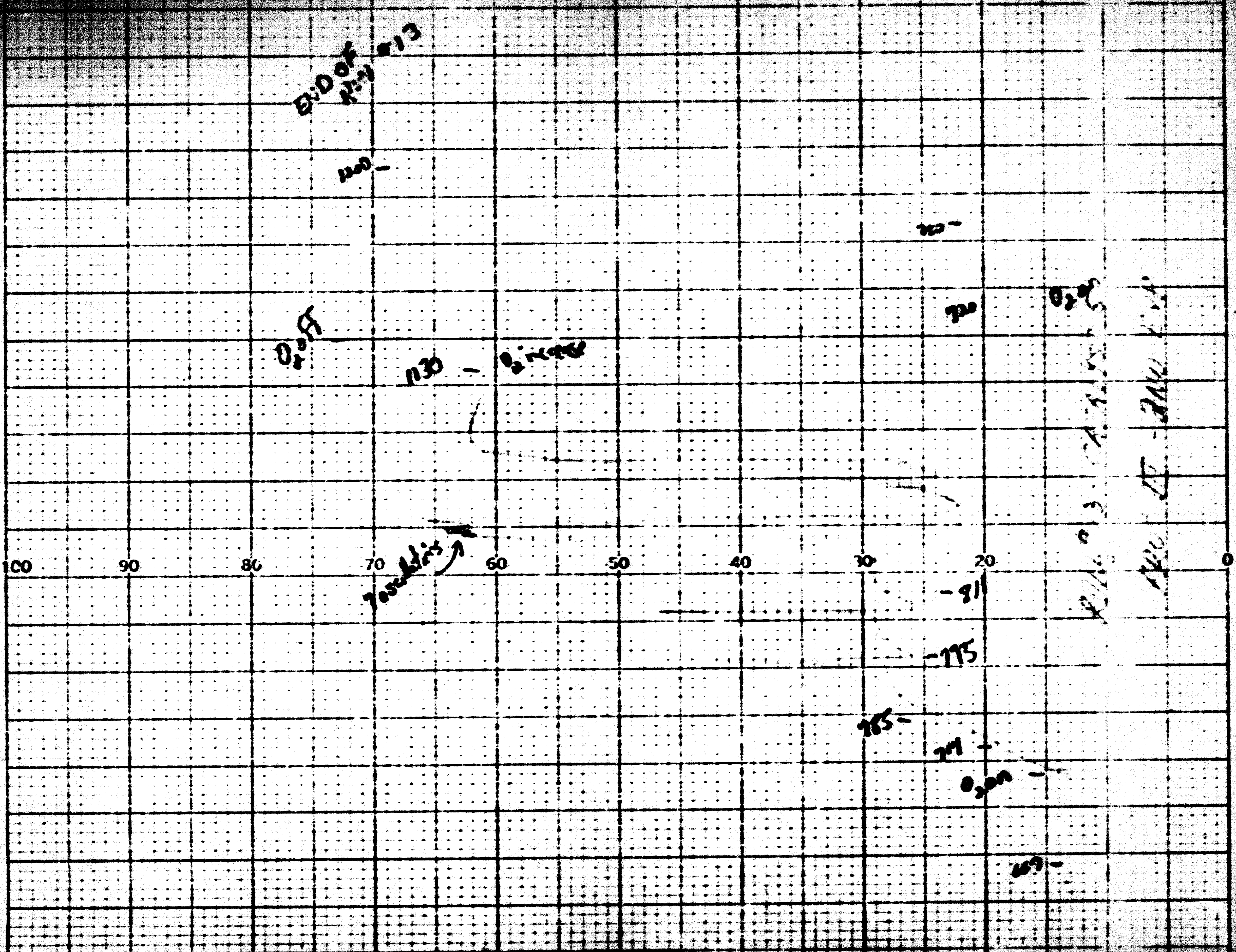


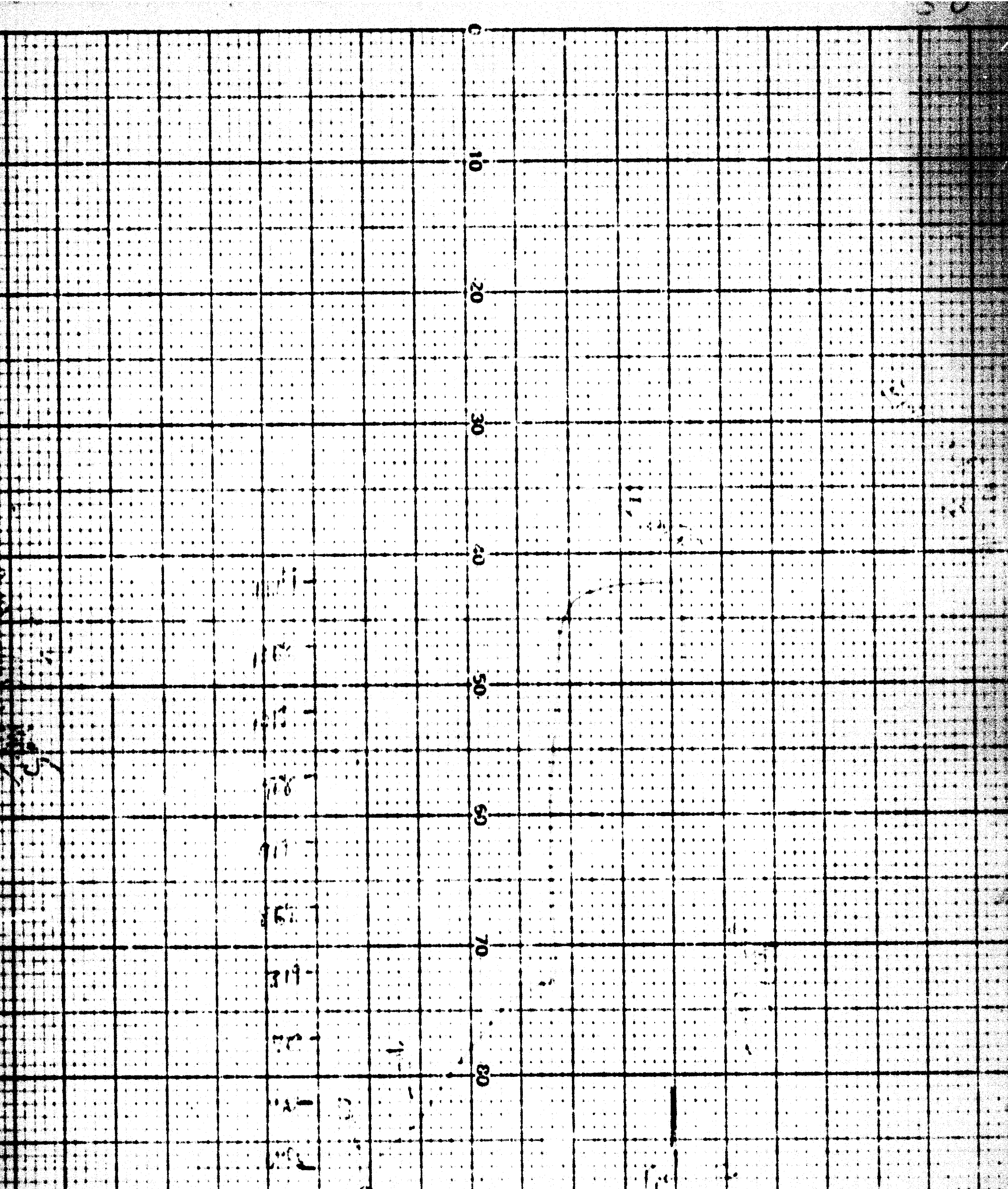
47



KURVE II - CATHODES

PROC. III - 1st EXP


END OF RUN #13
1200 –
O2 off
1130 – O2 increase
100
90
80
70
60
50
40
30
20
0
– 811
–775
785 –
O2 on
920
O2 off



CONTROLS CORPORATION BUFFALO NEW YORK

No. LNR 0100-0025

100

90

80

70

60

50

40

30

20

10

RUN #5 - [illegible]

[illegible] III - 1st EXP

RUN #6 - CATALYST

[illegible] - 2MR [illegible]

[illegible]

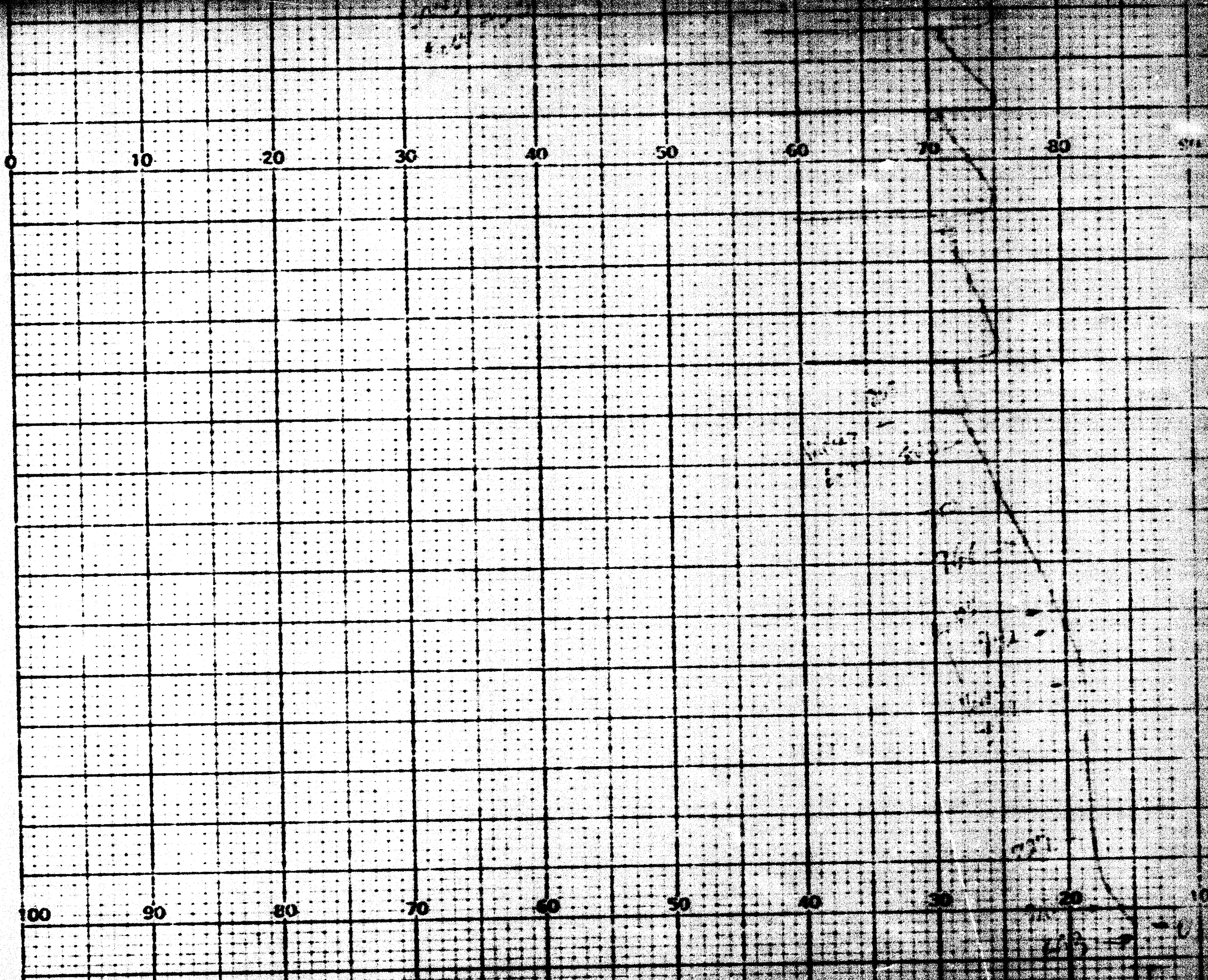
PROBE 12 - [illegible]

Run 1 - Christi[illegible]

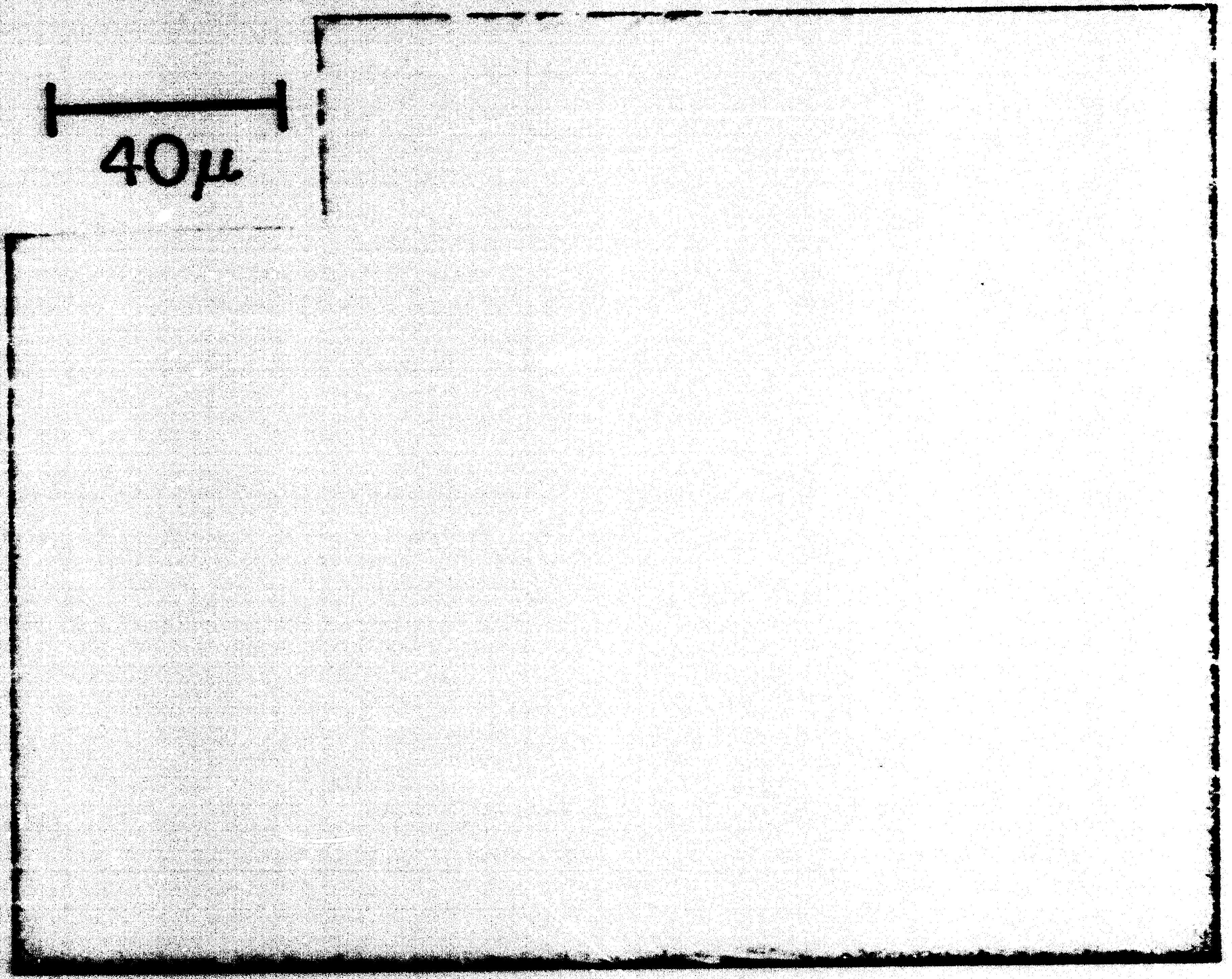
PAGE I

No. [illegible] 0100 0025

5.5

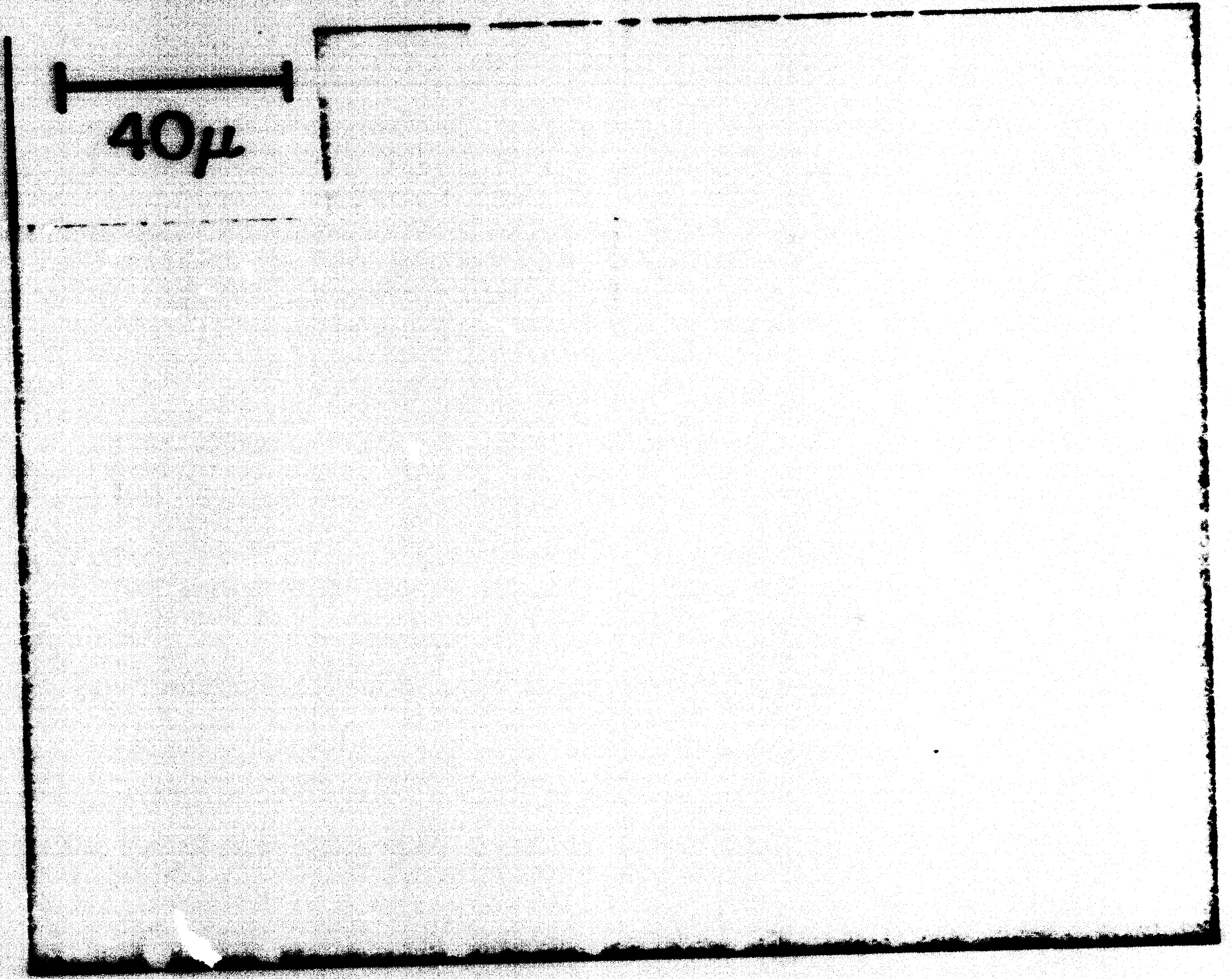


APPENDIX B: ADDITIONAL AUGER PICTURES

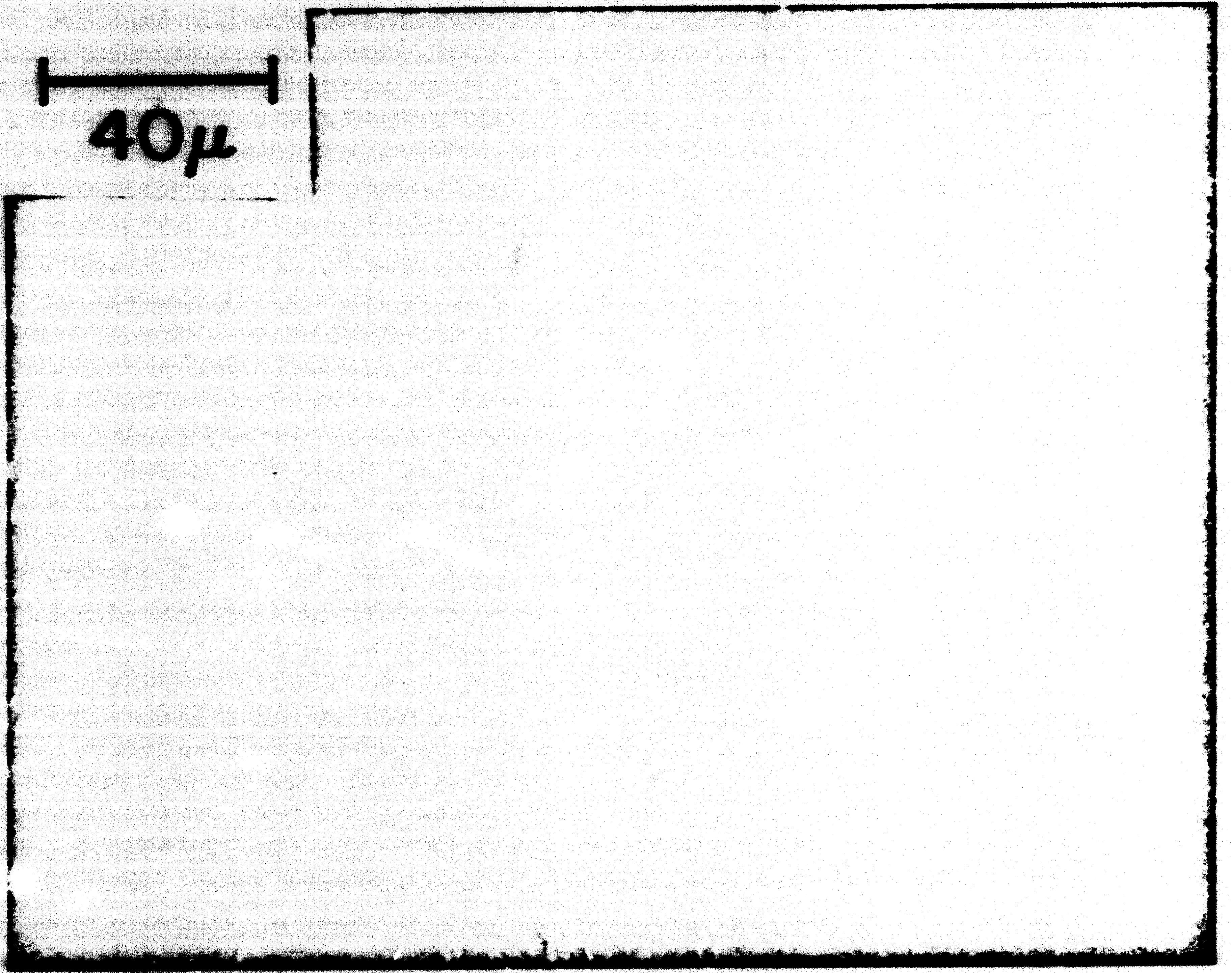


CATALYST AFTER LONG EXPOSURE
TO HIGH TEMPERATURE STATE

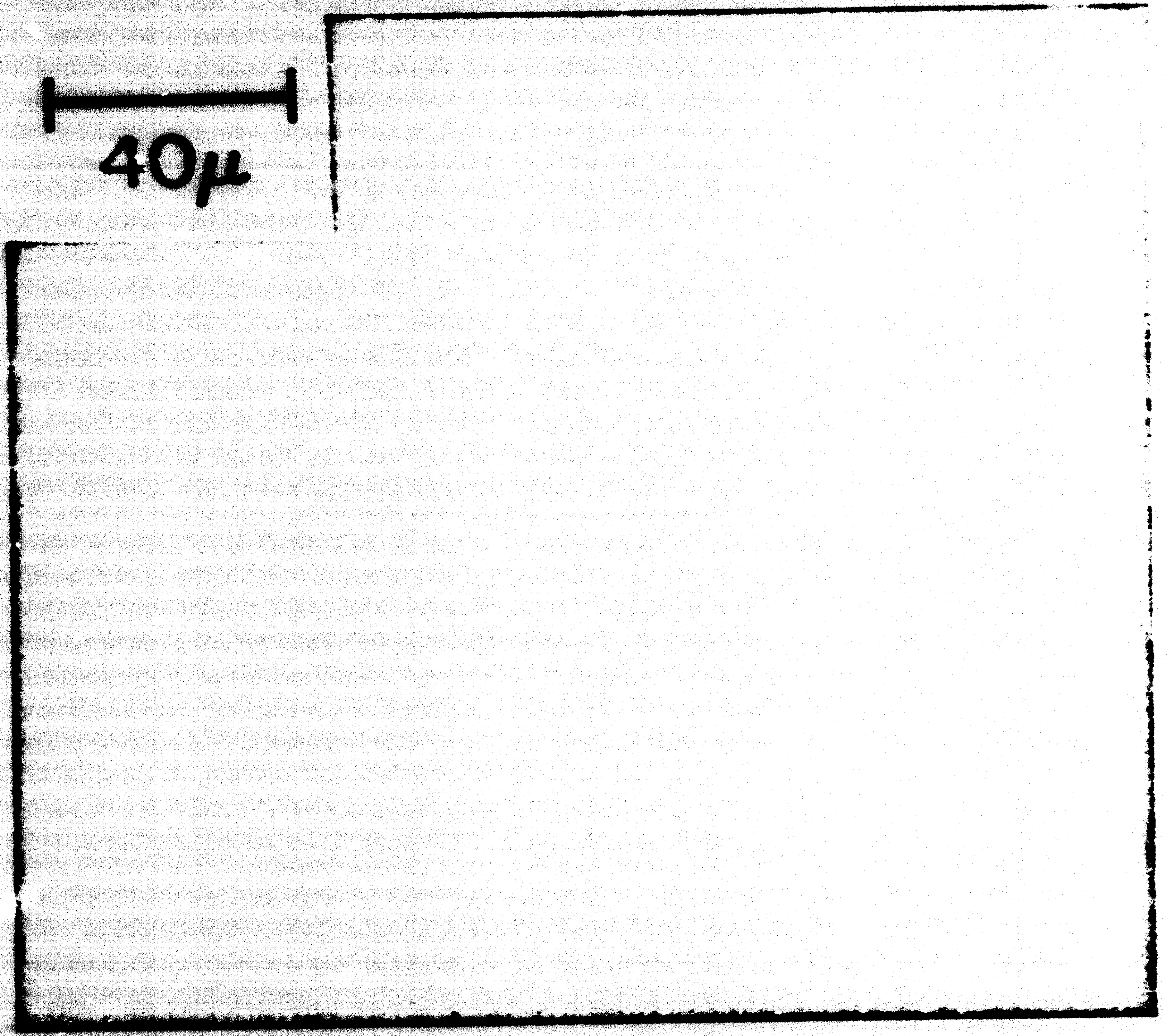
RUN #9 CATALYST 3



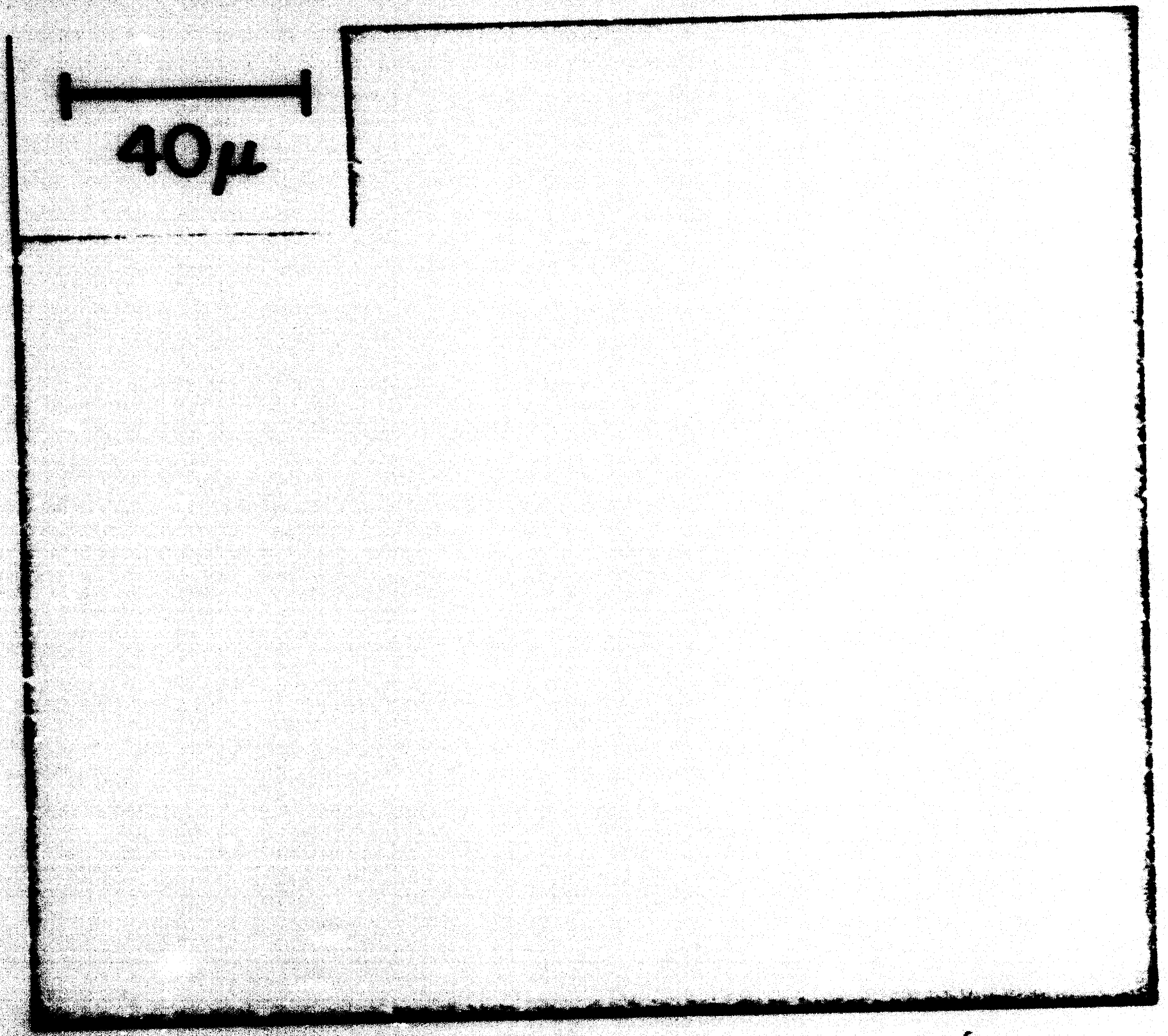
CATALYST PREPARED BY PROCEDURE III
1ST EXPERIMENT RUN #11 CATALYSTS



CATALYST PREPARED BY PROCEDURE III
2ND EXPERIMENT RUN # 13 CATALYST 5



CATALYST PREPARED BY PROCEDURE III
RUN #18 CATALYST 7



CATALYST PREPARED BY PROCEDURE II
RUN #A CATALYST 8

APPENDIX C DETAILS OF EXPERIMENTAL PROCEDURE

1. Turn on oxygen, and increase the flowrate until the float disappears at the top

2. Set Variacs to 105 volts (Adjust if necessary to keep temperature between 550°F and 450°F) Turn O_2 off after one hour

3. After one hour purge with reasonable N_2 flow for five minutes. Set Variacs to 95 volts.

4. Turn off N_2, and turn on hydrogen. Raise H_2 flowrate slowly to a reading of 41 on the flowmeter

5. Place Shield in front of reactor (Hold in place with duct tape)

6. After ½ hour, turn on O_2 again and adjust to a reading of 38 on the flowmeter

7. After run, turn off variacs and oxygen flows. Cool to ~300°F in hydrogen before removing samples