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MISSILE AND SPACE DIVISION

GENERAL ELECTRIC

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GASEOUS HYDROGEN DETECTION SYSTEM

FINAL REPORT

Prepared by

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and

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Under

CONTRACT NAS8-24526

for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Huntsville, Alabama 35812

GENERAL ELECTRIC
Apollo Systems
Huntsville Programs
Huntsville, Alabama

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1.0 GENERAL

1.1 PURPOSE

The purpose of this report is to describe the design, fabrication, and test of a gaseous hydrogen detection system furnished on Contract NAS8-24526. The report also includes recommendations for further work in specific areas.

1.2 CONCLUSIONS

The system is an excellent detector of gaseous hydrogen in air. This was emphasized during the development of a suitable testing procedure for inert gas mixtures where initially unexplainable difficulties were finally traced to small amounts of hydrogen gas trapped in the test equipment.

The long time stability of the sensors was not thoroughly investigated because of time limitations. However, based on tests on earlier experimental samples, a long time (approximately one year) slow drift will probably occur under the condition of continuous heater excitation. It is expected that this drift could be accelerated by operating the heaters at a higher temperature for a shorter period of time. However, further work in this area is necessary before definite conclusions can be made.

The sensor also responds to hydrogen and inert gas mixtures. See the appropriate section of this report for a detailed discussion of limitations and recommended further effort.

The complete system was fabricated in accordance with drawings (not included in report) SK56137-6-818,-825,-828,-848,and -858. Figures 1-4 are photographs of the hardware furnished.

The measurement system is basically simple. A fixed resistance of 2.5K ohms, representing the panel meter and recorder shunt resistances, is connected in series with the sensor immersed in a 1 percent hydrogen-air mixture. A variable voltage is applied to the combination to produce a current of 100 microamps (full scale on meter). An additional series resistance rheostat is now introduced and adjusted to reduce the current to 50 microamperes (1 percent hydrogen on meter scale.). Other features in the circuit include an integrity check and a meter relay alarm circuit.

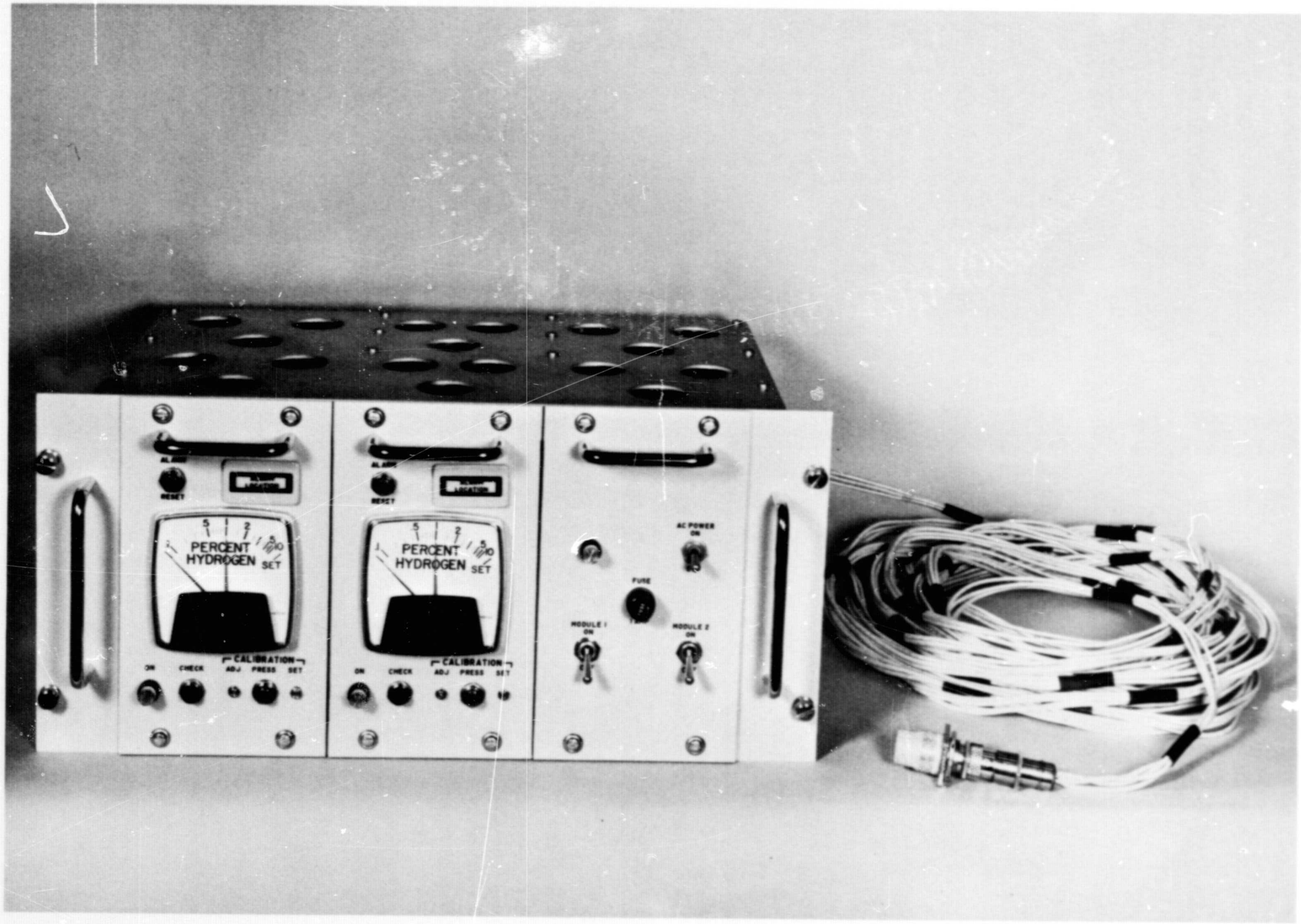


Figure 1. Front View of Hydrogen Detection Rack
Showing Cable and Attached Sensor

Figure 2. Oblique View of Hydrogen Detection Rack Showing Cable and Attached Sensor

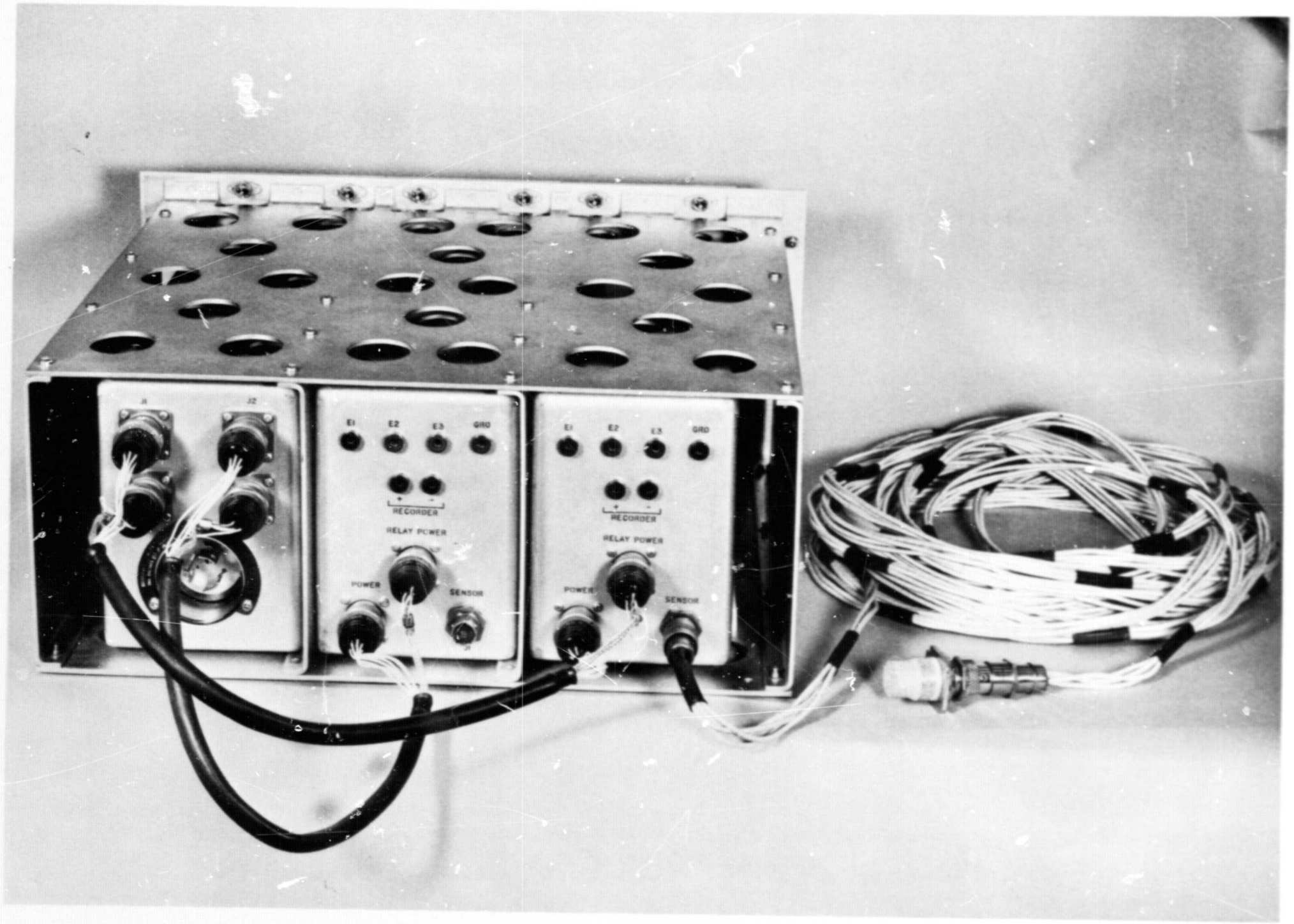


Figure 3. Rear View of Hydrogen Detection Rack Showing Cable and Attached Sensor

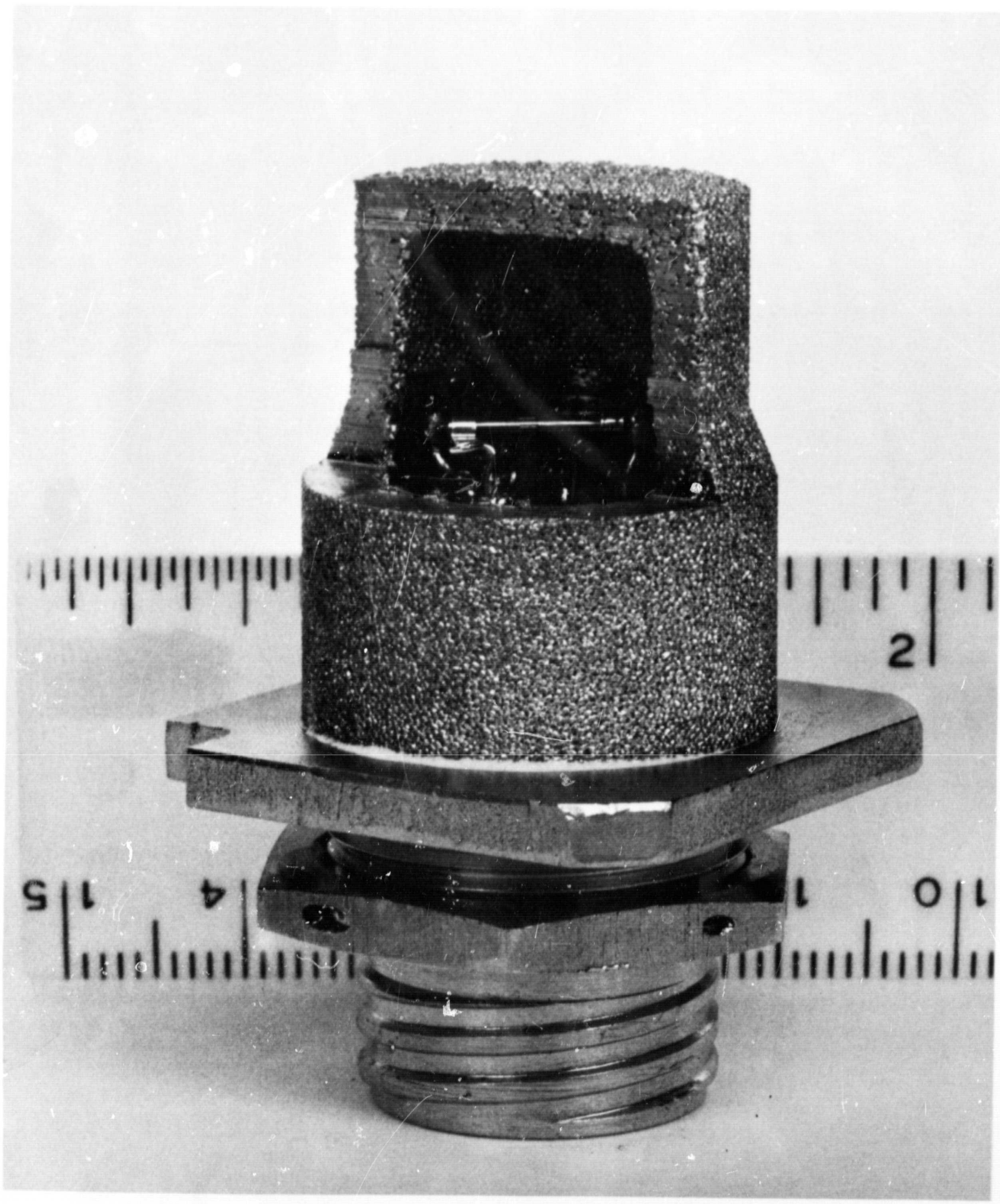


Figure 4. Hydrogen Detector with Sintered Bronze Cover Cut Away to Show Element

Detailed schematics of the power supply and module are shown in the attached drawings SK56137-6-820 and -821.

2.0 TEST PROCEDURES

2.1 GAS MIXTURES

Pre-mixed gases with certified analyses were obtained from the Matheson Company for the 0.1 percent, 0.5 percent, and 1.0 percent tests.

For the 5 percent and 10 percent mixtures, dry air and pre-purified hydrogen were combined. To increase the accuracy of these mixtures, the flow meters were calibrated with air using water displacement methods. Flow meter conversion curves, furnished by the manufacturer, were used for gases other than air.

2.2 TEST CIRCUIT

The circuit used was a duplicate of that in the furnished equipment. A digital ammeter, digital voltmeter, two regulated power supplies and a 0.01 percent decade box simulated the system. See elementary schematic of Figure 5.

One power supply was operated in the current mode and supplied the sensor heater. The other power supply substituted for the SET adjustment on the panel, and the decade box replaced the ADJ control on the panel.

The E and R_c that appear in the tabulations and on the recording Figures are the 1 percent H_2-air mixtures calibration values. They simulate the actual settings of the panel calibration potentiometers.

2.3 GAS ENCLOSURE

The test gas enclosure was designed to provide gas mixing and convenience and may be seen in the photograph of Figure 6.

Volume of the chamber with the sensor in place is 185cc, and the test flow rate used was 700cc/minute. This gives about 3.8 gas changes per minute.

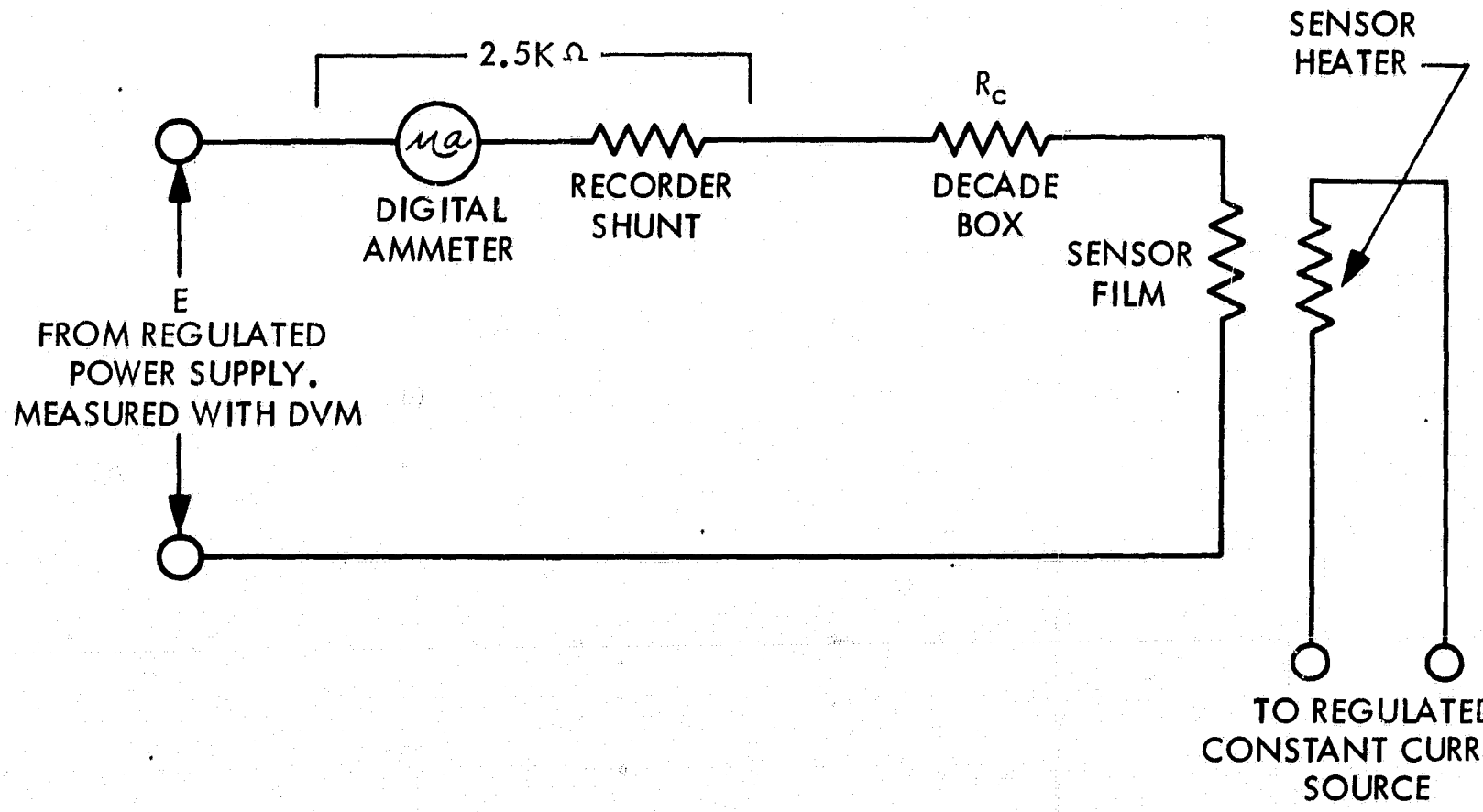


Figure 5. Elementary Schematic

Figure 6. Outdoor Test Setup

2.4 TEST SITES

The 0.1 percent, 0.5 percent and 1 percent testing were conducted in the laboratory. The 5 percent, 10 percent, and inert gas tests were conducted outdoors because of the hazard of explosion (above 4 percent H_2). This outdoor test setup is shown in Figure 6.

2.5 SELECTION OF SENSORS

The ten sensors furnished were selected from a group of fifteen purchased on the contract. The selection was made on the basis of those which best fit the parameters of the measurement circuit, and also provided the optimum calibration match for the percent hydrogen meter scale.

3.0 CALIBRATION TESTS

3.1 ACCEPTANCE TESTS

Sensors as received from another General Electric component (Instrument Department) were immersed in a 1 percent H_2-air mixture and the E and R_c values were determined and recorded.

E volts = [sensor film resistance at 1 percent H_2 + circuit resistance*] x 100 microamps.

R_c = E/50 microamps - [sensor film resistance at 1 percent H_2 + circuit resistance*]

These values of E and R_c were used for comparison after sensor aging.

*2500 ohms.

3.2 AGING

The sensors were all aged at normal heater current for the hours shown in the following tabulation, prior to taking calibration data. The aging hours are all after exposure to 10 percent hydrogen-air mixtures. Prior aging hours are not included. See Section 3.3 for discussion of exposure to 5 percent and 10 percent hydrogen-air mixtures.

SENSOR	HOURS OF AGING
B	330
C	100
E	100
F	100
K	100
M	100
N	70
O	265
P	265
1	330

3.3 CALIBRATION OF SENSORS

The first group of sensors received exhibited a large change in resistance at 1 percent hydrogen-air mixtures after exposure to 5 and 10 percent mixtures of dry air and hydrogen. These sensors were therefore rejected on the supplier as being unsatisfactory.

The cause of the above deficiencies were attributed to contamination from oil trapped in the porous covers and to the catalytic action of the platinum-rhodium heater wire. Six new sensors were constructed with clean covers and Nichrome V heaters. These sensors exhibited no large changes after exposure to 5 and 10 percent hydrogen. Later some sensors constructed in the same manner did exhibit changes as can be seen in Figures 21 to 25 where the current at 1 percent mixtures has changed radically from the original 50 microamp value.

All sensors were exposed up to ten times by the sensor supplier to 10 percent hydrogen-air mixtures without significant changes at 1 percent hydrogen-air mixtures. The air used in these tests was shop air with normal atmospheric moisture present. (Estimated R. H. 70 percent). Some of the sensors when exposed to 10 percent hydrogen-dry air (-75°F dew point) mixtures, exhibited the major changes previously mentioned.

It was also determined that the effected sensors tended to recover their original properties when aged in the laboratory atmosphere with the heater on. A complete check of this aging recovery was not possible in the time available.

The net result of these findings is that exposure to high concentrations (>5 percent) of dry (-75°F dew point) hydrogen-air mixtures can affect the sensors in such a way that hundreds of hours may be required for complete recovery. It should, however, be recognized that the sensors may still be useful during the recovery stage and be capable of holding reasonable calibration for several consecutive days. Also the use of air at this extreme dryness is probably an artificial condition.

All tests to date indicate that normal atmospheric air and high concentrations of hydrogen mixtures do not adversely affect the sensors. Further work in this area is required for complete verification and understanding.

The following tabulations show the 0.1 percent, 0.5 percent, 1.0 percent, 5.0 percent, and 10.0 percent mixture responses.

The tabulation of the calculated data is obtained from the above tabulations in the manner shown.

It should be noted that the data for the 1 percent values used in the 5 percent and 10 percent calibrations was not the radically changed values after exposure, but rather the 1 percent values determined on the previous day before exposure to 5 and 10 percent mixtures. This can be seen by the references to the appropriate figures shown in the tabulations.

CALIBRATION DATA ON H_2 SENSORS (.1% and .5%)

SENSOR	VOLTS E	KΩ R_C	i μa .1%	i μa .5%	i μa 1%
B	9.885	98.8	5.4	36.2	48.4
C	4.429	44.5	10.0	33.6	50.4
E	3.172	31.8	5.8	34.6	48.8
F	3.134	31.4	5.8	34.0	47.0
K	11.510	115.0	4.4	30.0	46.6
M	13.610	135.4	3.4	31.0	45.0
N	6.205	62.0	4.0	26.0	41.8
O	9.231	91.6	6.0	34.0	46.2
P	7.434	74.2	5.4	34.0	47.2
1	7.376	73.8	8.0	36.0	48.0

The above data was extraced from the curves of Figures 7 through 16 at the 3 minute point.

Using the extracted data above, a normalizing process using the indicated calculation was performed.

SENSOR	TOTAL CIRCUIT RESISTANCE E/i = KΩ .1%	.5%	1.0%	SENSOR RESISTANCE E/i - (R_c + 2.5K) .1%	.5%	1.0%
B	1831.0	273.1	204.2	1730.0	171.8	102.9
C	442.9	131.8	87.9	395.9	84.8	40.9
E	546.9	91.7	65.0	512.6	57.4	30.7
F	540.3	92.2	66.7	506.4	58.3	32.8
K	2616.0	383.7	247.0	2499.0	266.2	129.5
M	4003.0	439.0	302.0	3865.0	301.1	164.1
N	1551.0	238.7	148.4	1487.0	174.2	83.9
O	1539.0	271.5	199.8	1445.0	177.4	105.7
P	1377.0	218.6	157.5	1300.0	141.9	80.8
1	922.0	204.9	153.7	845.7	128.6	77.4

Using the preceding sensor resistance values a new R_c (calibration resistance) and a new E were calculated and tabulated as follows:

$$R_c = R_s + 2.5K$$
$$E = (R_s + 2.5K) \times 100\mu a$$
$$E = R_c \times 100\mu a$$

CALCULATED RECALIBRATION

SENSOR	KΩ R_c	VOLTS E	CALCULATED i (μa) .1%	.5%	1.0%
B	105.4	10.54	5.7	37.7	50
C	43.4	4.34	9.8	33.2	50
E	33.2	3.32	6.1	35.7	50
F	35.3	3.53	6.5	36.7	50
K	132.0	13.20	5.0	33.0	50
M	166.6	16.66	4.1	35.5	50
N	86.4	8.64	5.5	32.8	50
O	108.2	10.82	7.0	37.6	50
P	83.3	8.33	6.0	36.5	50
1	79.9	7.99	8.6	37.8	50

CALIBRATION DATA ON H_2 SENSORS (5% and 10%)

SENSOR	VOLTS E	KΩ R_c	i μa 1%*	i μa 5%+	i μa 10%+
B	4.29	43.0	53.6	89.4	92.0
C	2.55	25.6	50.0	82.0	86.6
E	3.16	31.7	48.0	86.6	88.4
F	3.21	32.2	47.2	88.0	89.4
K	4.16	41.5	46.6	90.6	92.2
M	3.79	38.0	44.8	80.0	90.6
N	Not Calibrated				
O	8.38	83.5	44.8	92.4	95.4
P	7.56	75.0	44.0	91.4	94.8
1	11.27	112.0	46.6	91.2	94.2

*From Figures 26 through 34
+From Figures 17 through 25

	TOTAL CIRCUIT RESISTANCE E/i = KΩ			SENSOR RESISTANCE E/i - (R_c + 2.5K)		
	1%	5%	10%	1%	5%	10%
B	79.9	48.0	46.6	34.4	2.5	1.1
C	51.0	31.1	29.4	22.9	3.0	1.3
E	65.8	36.5	35.8	31.6	2.3	1.6
F	68.0	36.5	35.9	33.3	1.8	1.2
K	89.2	45.9	45.1	45.2	1.9	1.1
M	84.5	47.3	41.3	44.0	6.8	0.8
N	Not Calibrated					
O	186.7	90.6	87.8	100.7	4.6	1.8
P	171.8	82.8	79.9	94.3	5.3	2.4
1	242.0	123.6	119.7	127.5	9.1	5.2

CALCULATED RECALIBRATION

SENSOR	VOLTS E	KΩ R_c	i μa 1%	i μa 5%	i μa 10%
B	3.69	36.9	50	88.1	91.0
C	2.54	25.4	50	82.2	87.0
E	3.41	34.1	50	87.7	89.3
F	3.58	35.8	50	89.3	90.7
K	4.77	47.7	50	91.5	93.0
M	4.65	46.5	50	83.4	93.5
N	Not Calibrated				
O	10.32	103.2	50	93.6	96.0
P	9.68	96.8	50	92.5	95.2
1	13.00	130.0	50	91.5	94.5

4.0 INERT GAS TESTS

Two major effects of inert gas (N_2 and He)-hydrogen mixtures on sensor performance were observed. These were a change in sensor operating temperature due to the high thermal conductivity of the helium, and a large change in sensor resistance independent of the concentration of hydrogen in both helium and nitrogen mixtures.

The normal operating temperature, somewhat arbitrarily chosen for these sensors, was approximately 210°C. A measurement of the heater resistance at constant current with the sensor in air compared to the resistance at the same current in helium may be used, in conjunction with the heater temperature coefficient of resistance, to calculate the sensor heater temperature in helium. Figure 35 shows the drop in heater voltage at constant current as the sensor was immersed in helium.

The sensor heater is made of Nichrome V with a temperature coefficient of .00013 ohms per ohm per °C. The air resistance of this heater is 3.409 ohms at .44 amperes. In helium this resistance dropped to 3.364 ohms at this same current. The temperature of the heater in helium may then be determined by calculation to be approximately 110°C. The sensor will not operate at this low temperature, and the helium tests were conducted with increased heater power to attain the normal operating temperature of 210°C. The low temperature coefficient of Nichrome V makes it difficult to deter-

mine the heater temperature with very great accuracy. Therefore, the tests in helium-hydrogen mixtures compared to tests in nitrogen-hydrogen mixtures should be compared on the basis of a possible difference in sensor operating temperature.

Figures 36 through 40 show the response of the sensors to the indicated percentages of hydrogen and the recovery to the indicated percentages of air. The recovery times include the time required to purge the hydrogen from the system. Tests were also conducted with wet gas and showed no significant difference from those using dry gas. The wet gas was obtained by bubbling dry gas through water.

The sensors respond qualitatively to hydrogen-helium and hydrogen-nitrogen mixtures in the same manner as to air mixtures. However, the quantitative properties of the sensor are lost, and all mixtures evidently appear to the sensor as 100 percent hydrogen. The tests also show that air (oxygen) is required for recovery. The response rate appears to be a function of the amount of hydrogen in the mixtures, and the recovery rate, the amount of air (oxygen) in the mixtures. This apparent rate sensitivity offers the possibility of a quantitative operation in inert gases. However, more work is required to confirm this.

5.0 TEMPERATURE EFFECT TESTS

Tests were conducted on one sensor with a 1 percent hydrogen-air mixture at temperatures of 0°F and 130°F. Results are shown in the following table.

Temperature °F	Current μA*
75 (initial)	50.0
0	46.3
130	45.0
75 (final)	44.0

*See Figure 1 E = 18.98 Volts R_c = 190 K ohms

6.0 RESPONSE TO METHANE-AIR MIXTURE

Figure 41 shows the response of the sensor to a 1 percent methane-air mixture as compared to a 1 percent hydrogen-air mixture.

7.0 REFERENCES

1. "Activated Tungsten Oxide Gas Detectors," P. J. Shaver. Applied Physics Letters, 15 October 1967.
2. U. S. Patent 3,479,257.
3. S. Sawada, J. Phys. Soc. Japan, 11, 1237 (1956).

APPENDIX A

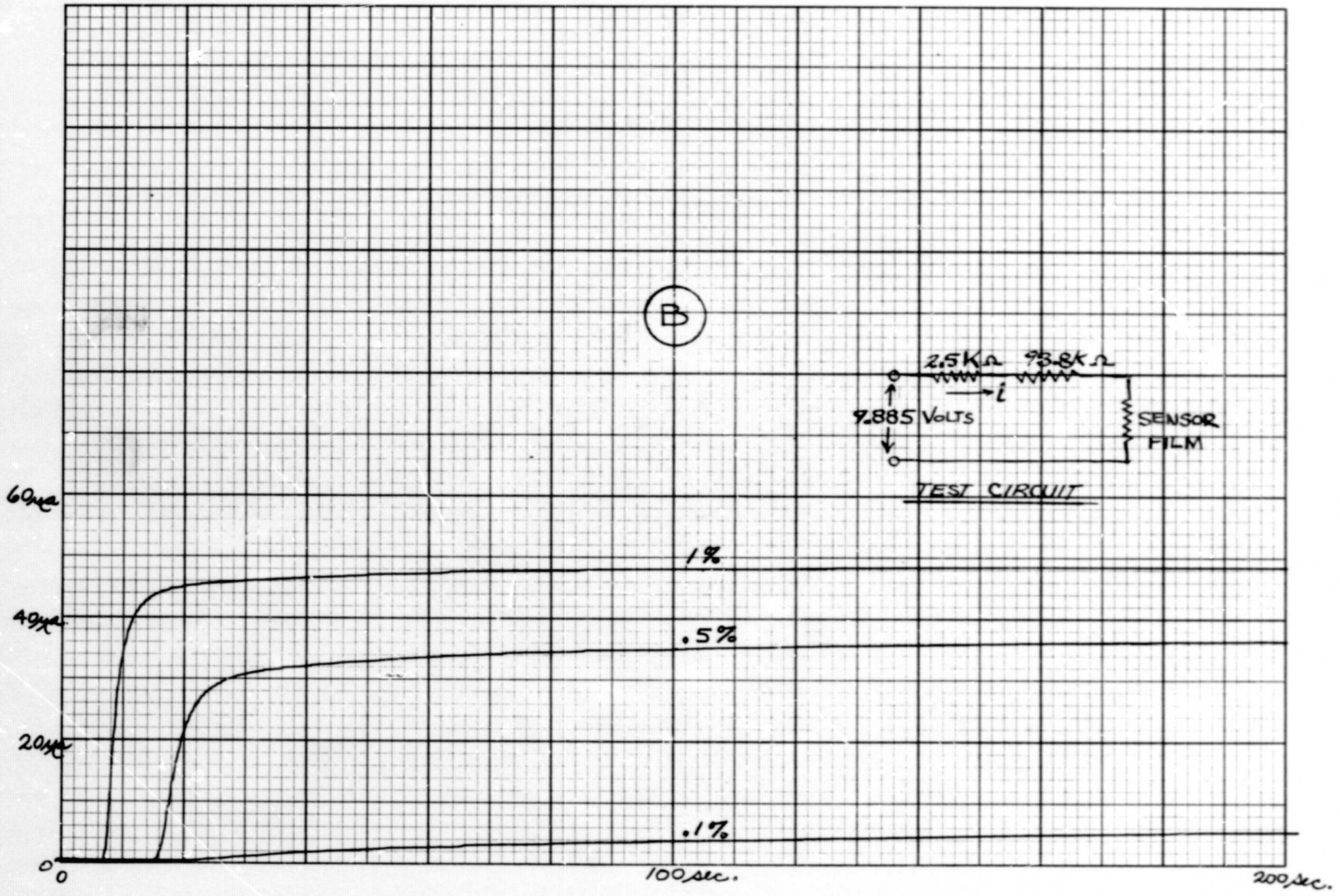


Figure 7. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor B

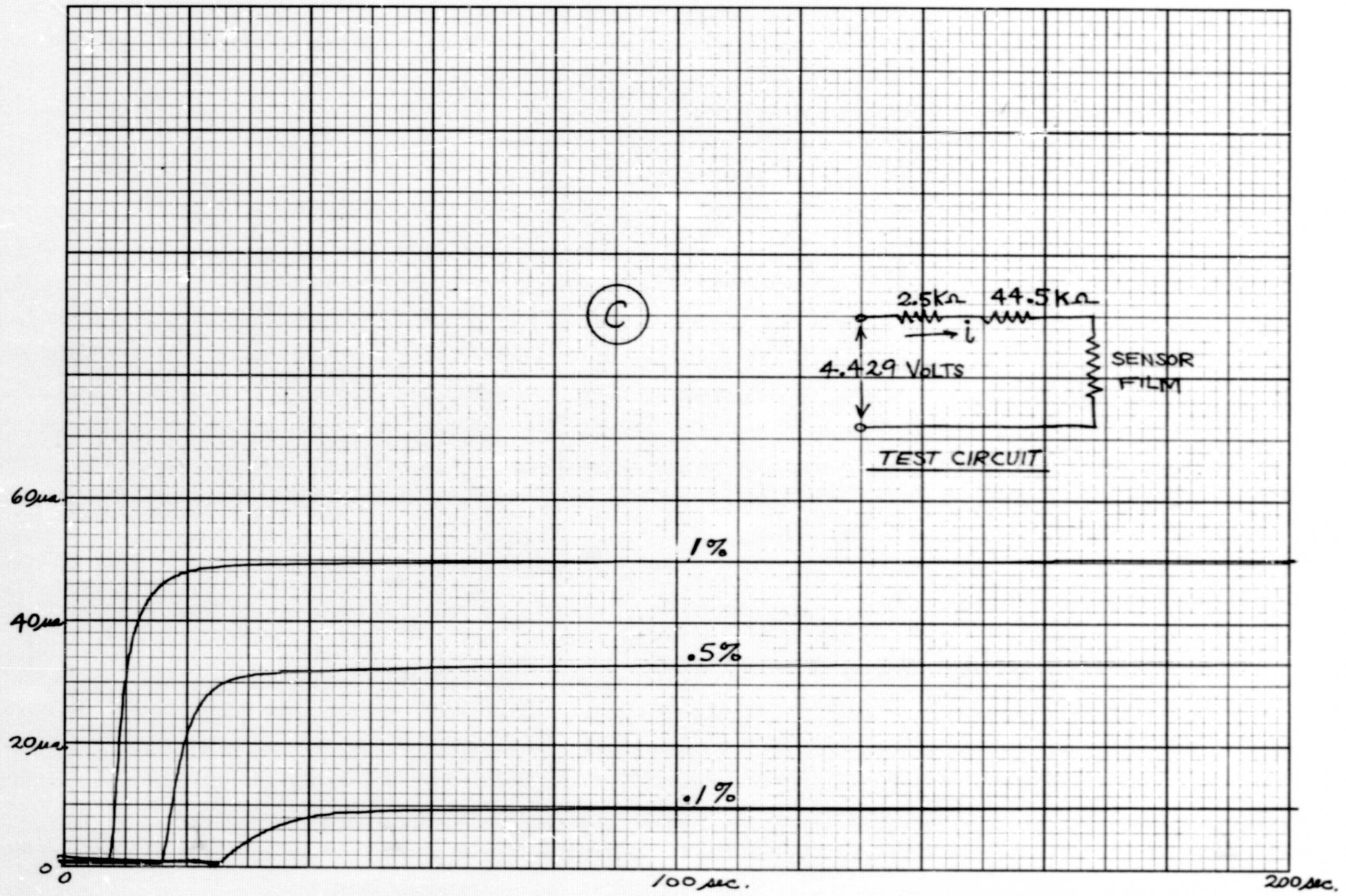


Figure 8. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor C

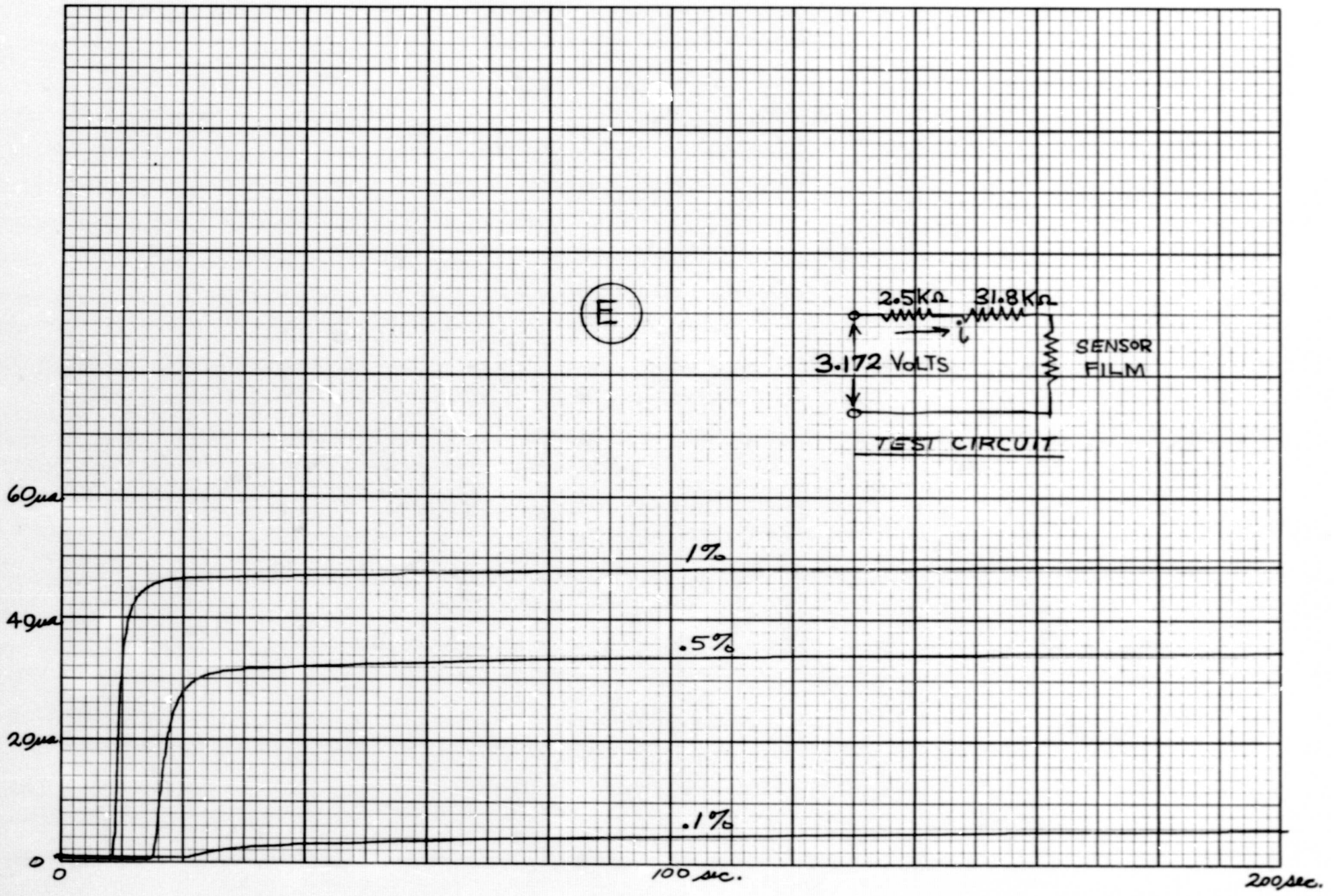


Figure 9. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor E

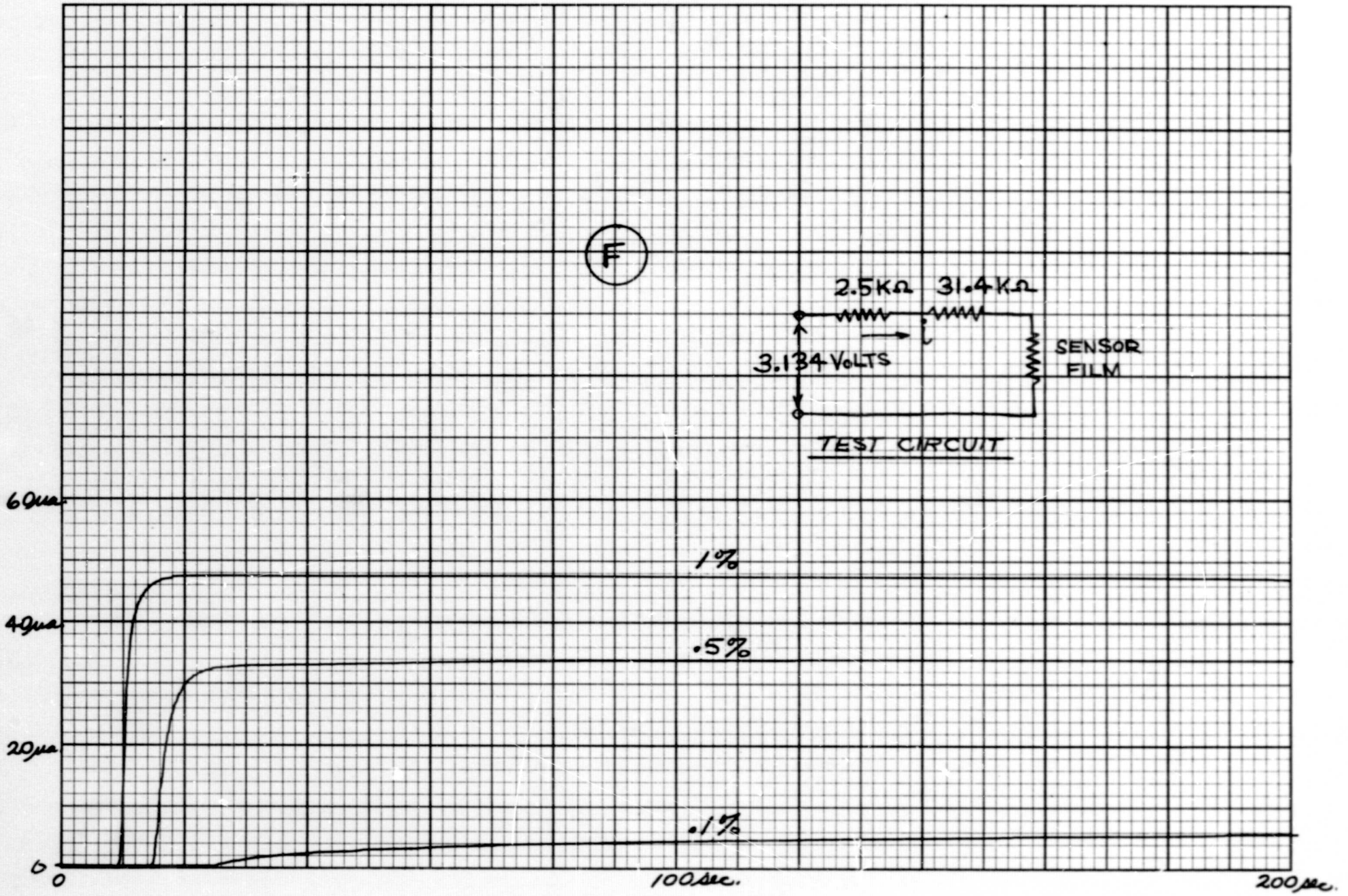


Figure 10. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor F

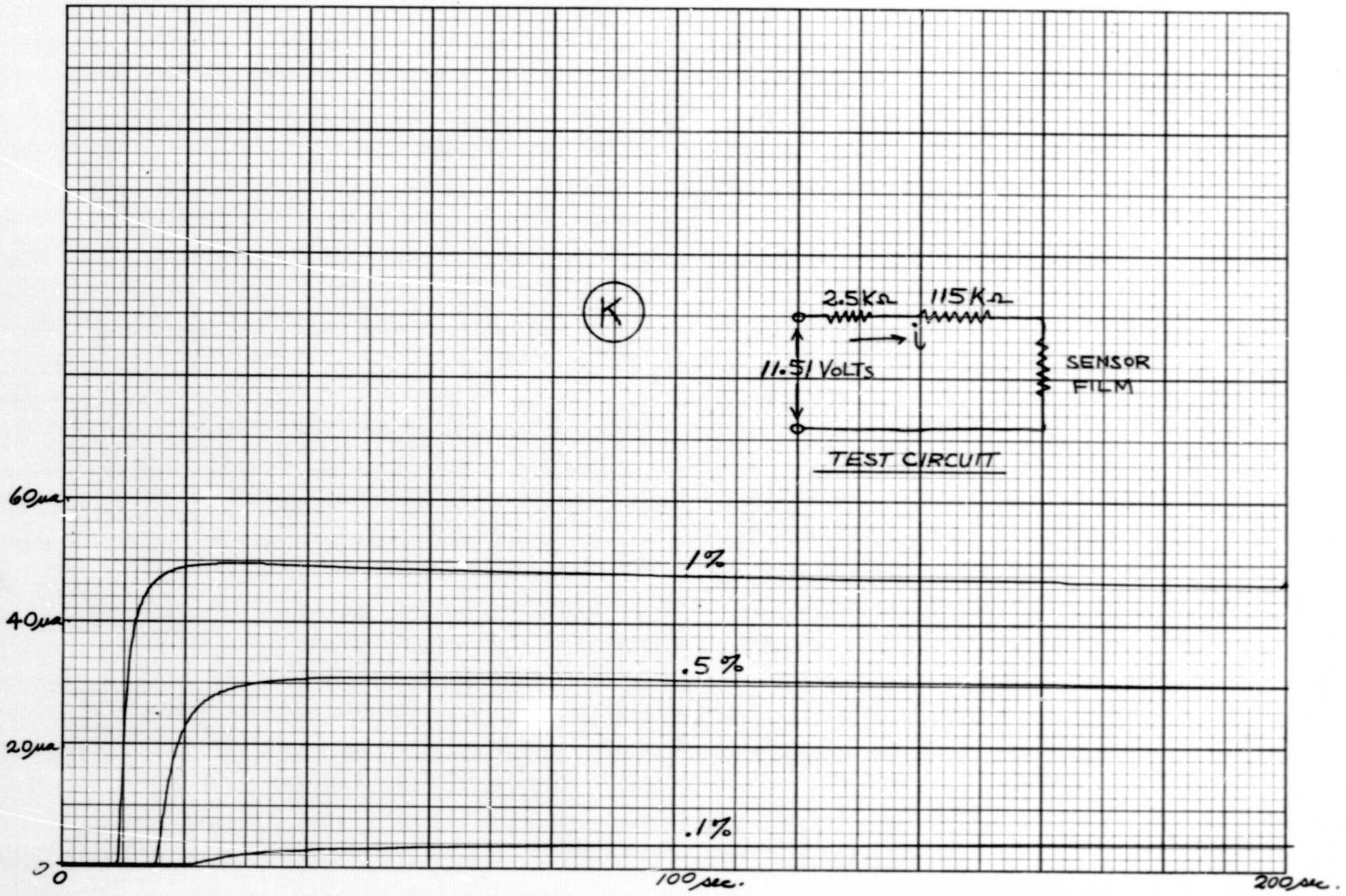


Figure 11. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor K

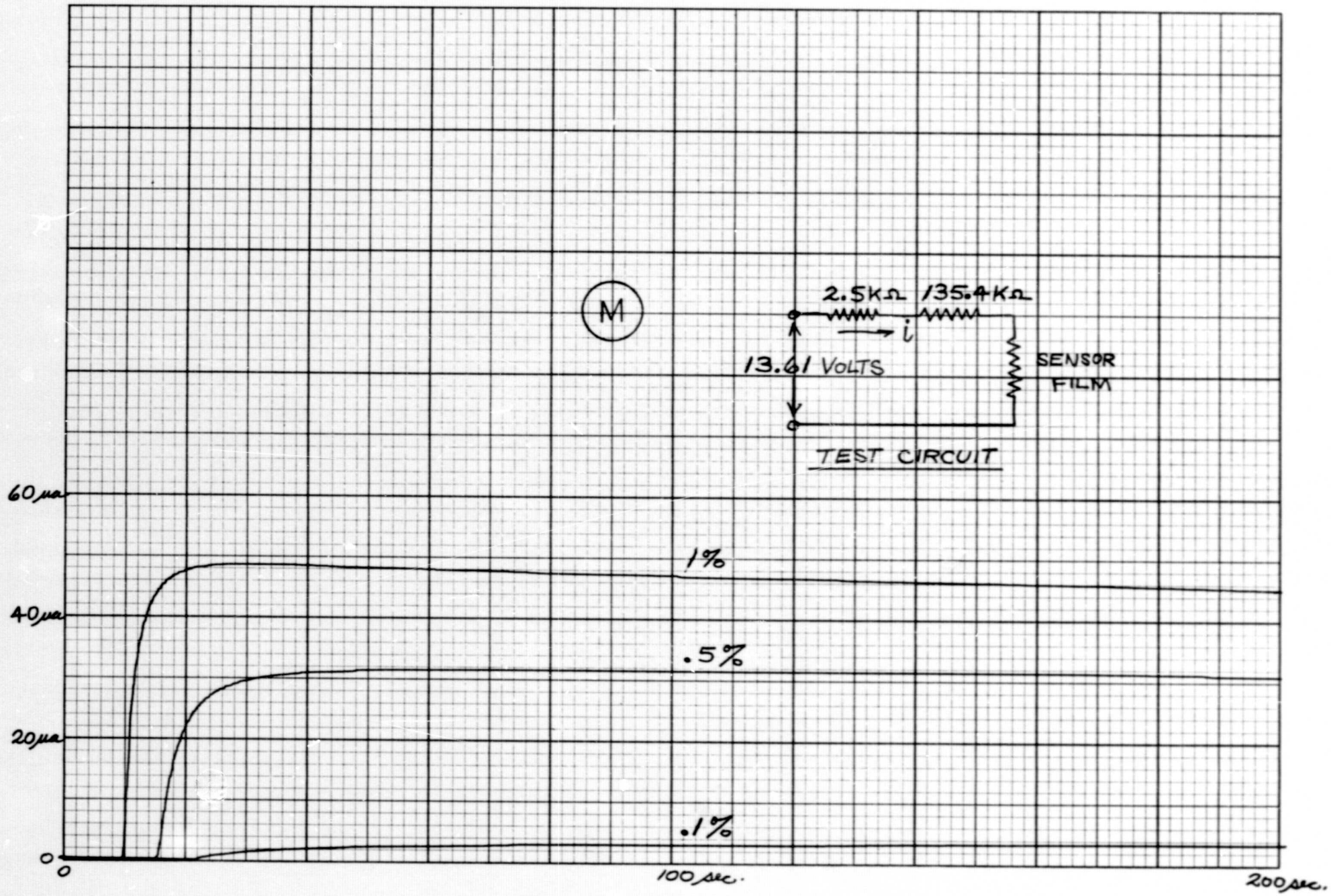


Figure 12. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor M

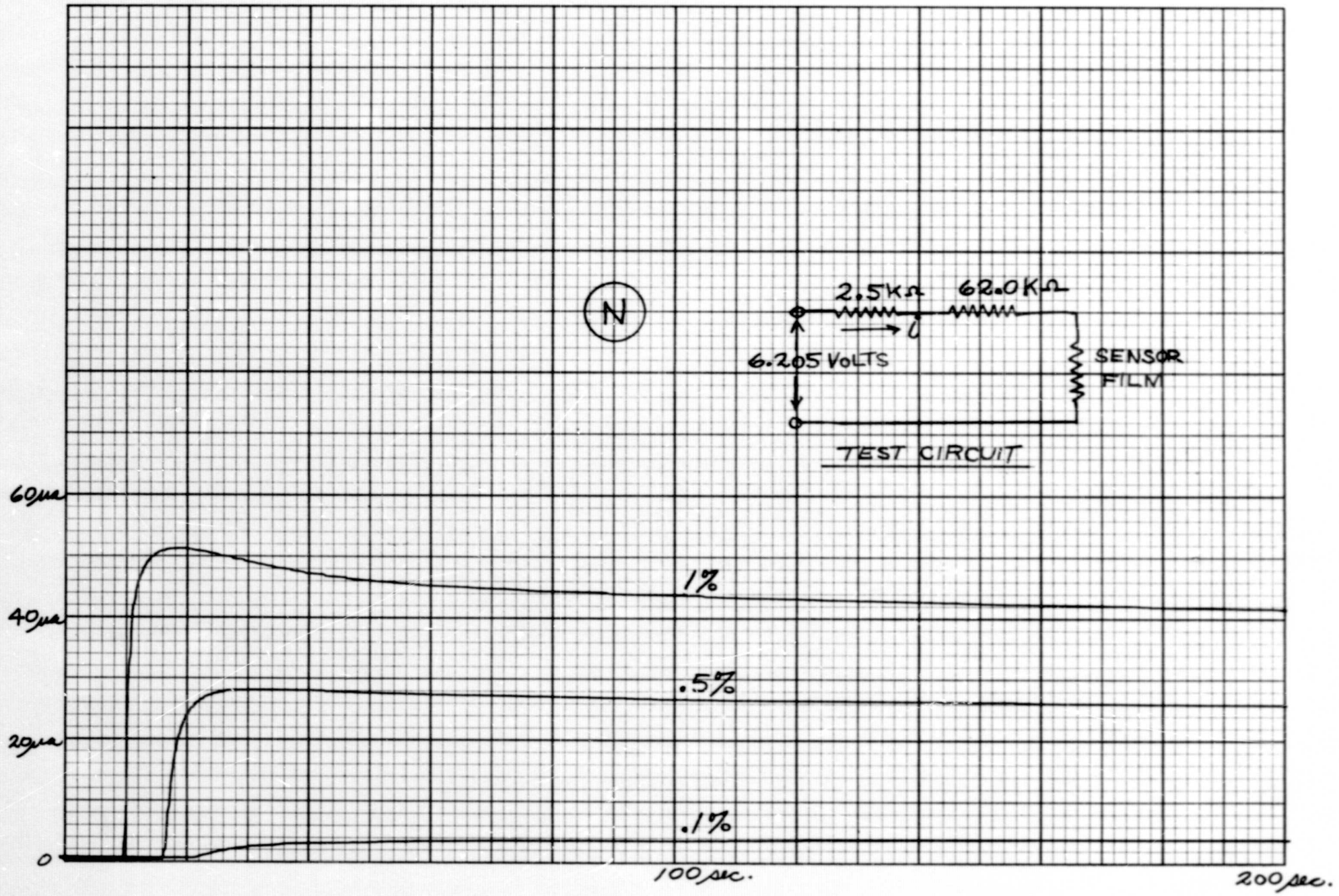


Figure 13. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor N

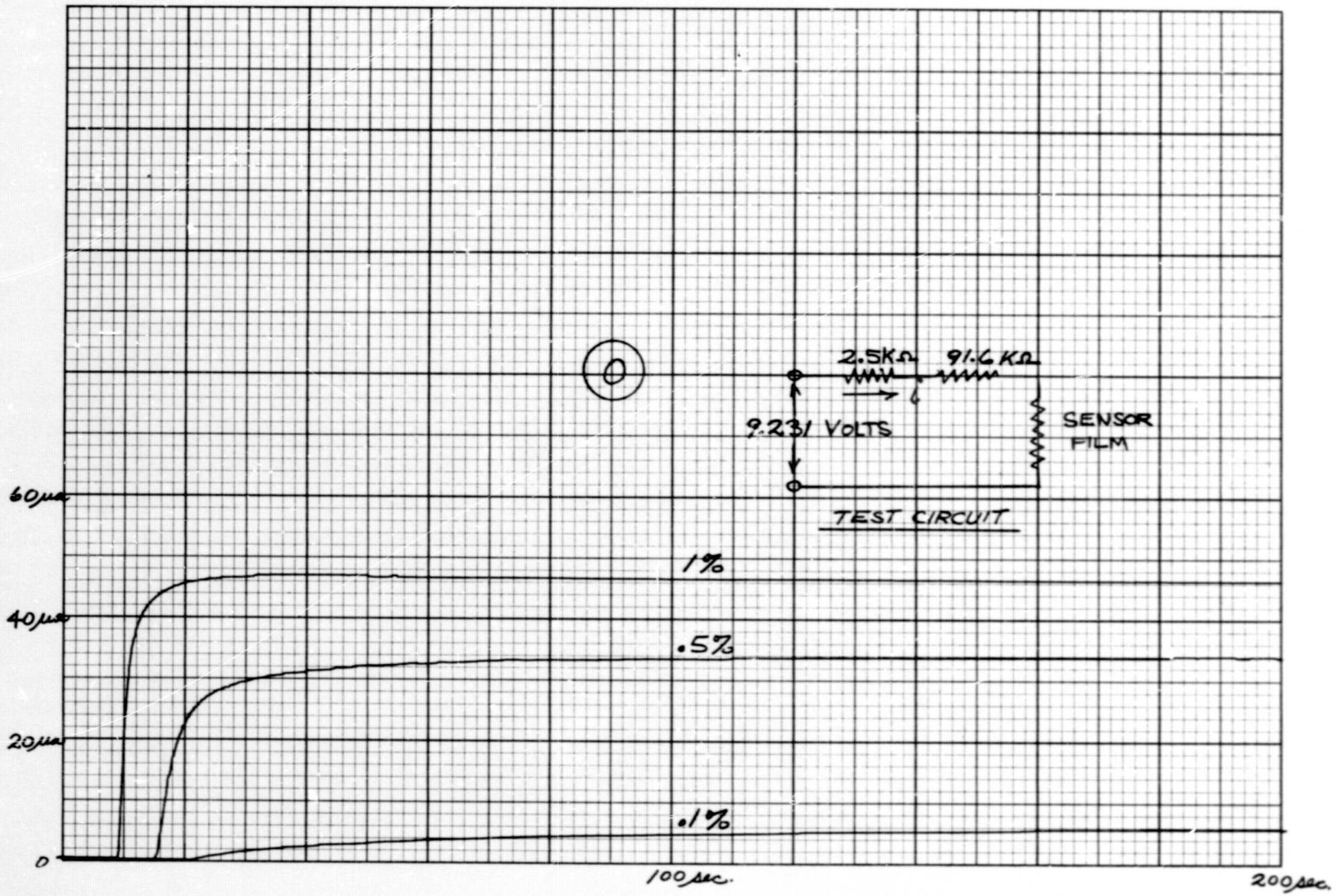


Figure 14. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor 0

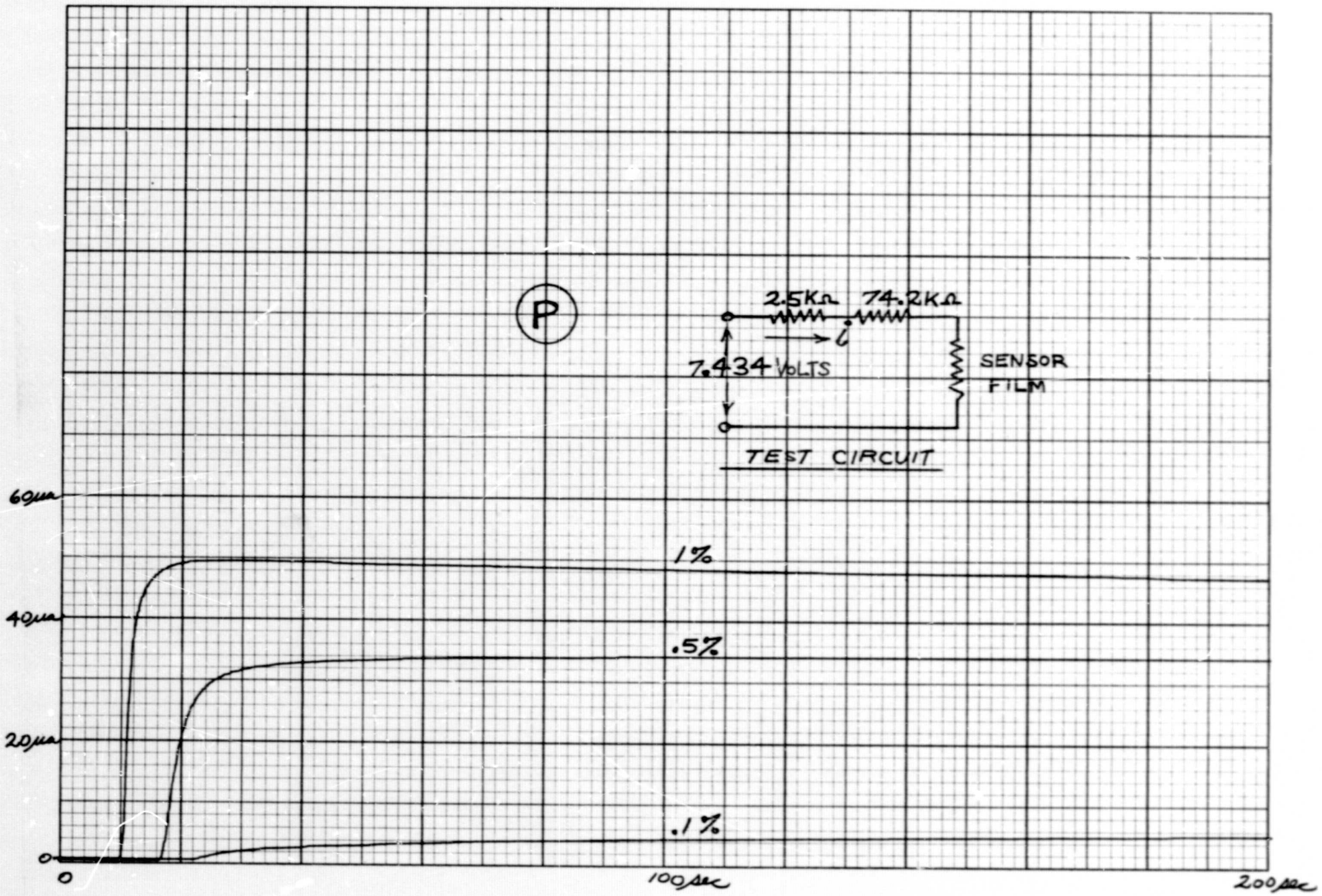


Figure 15. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor P

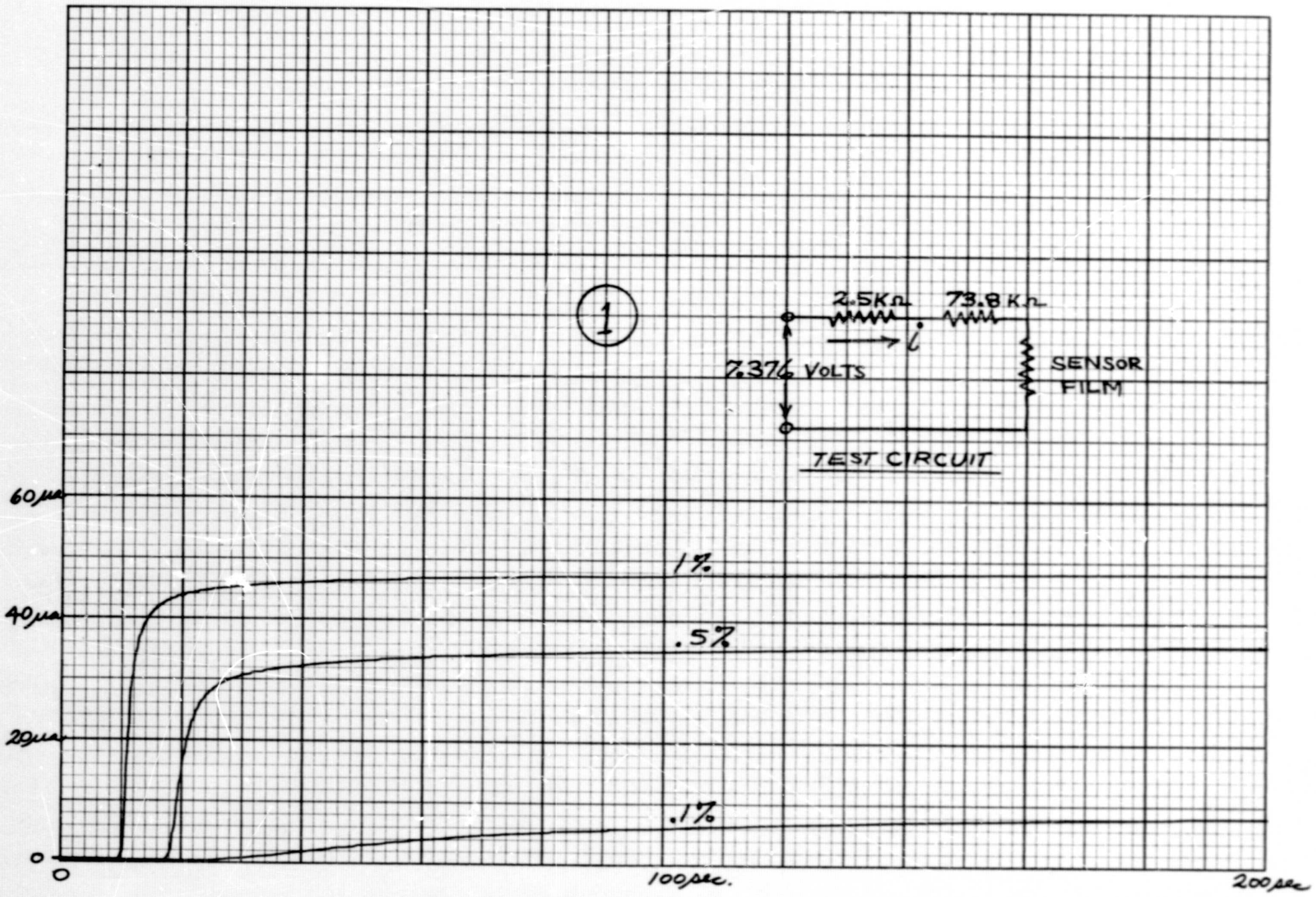


Figure 16. 0.1 Percent, 0.5 Percent, and 1.0 Percent Calibration - Sensor 1

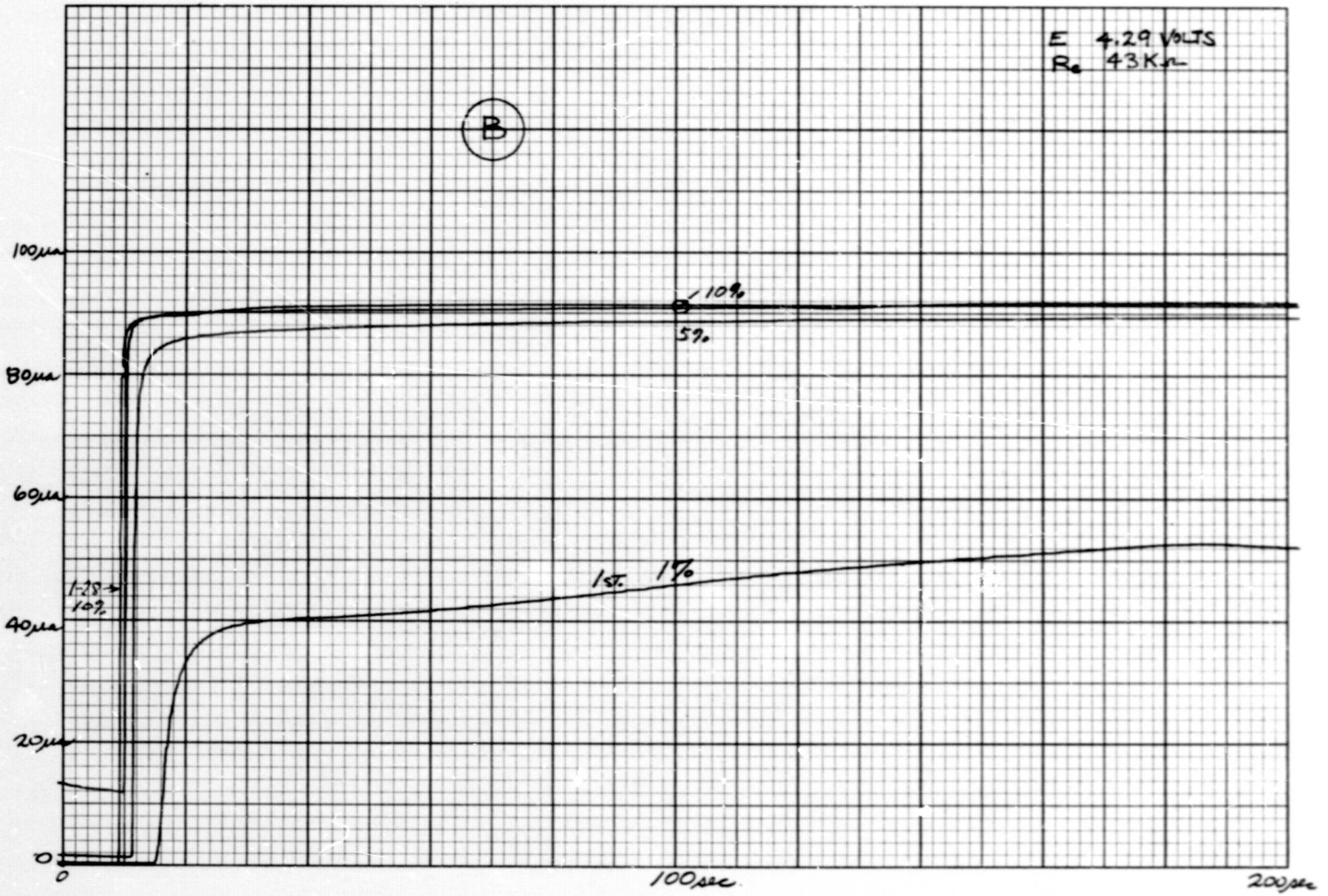


Figure 17. 5 Percent and 10 Percent Calibration - Sensor B

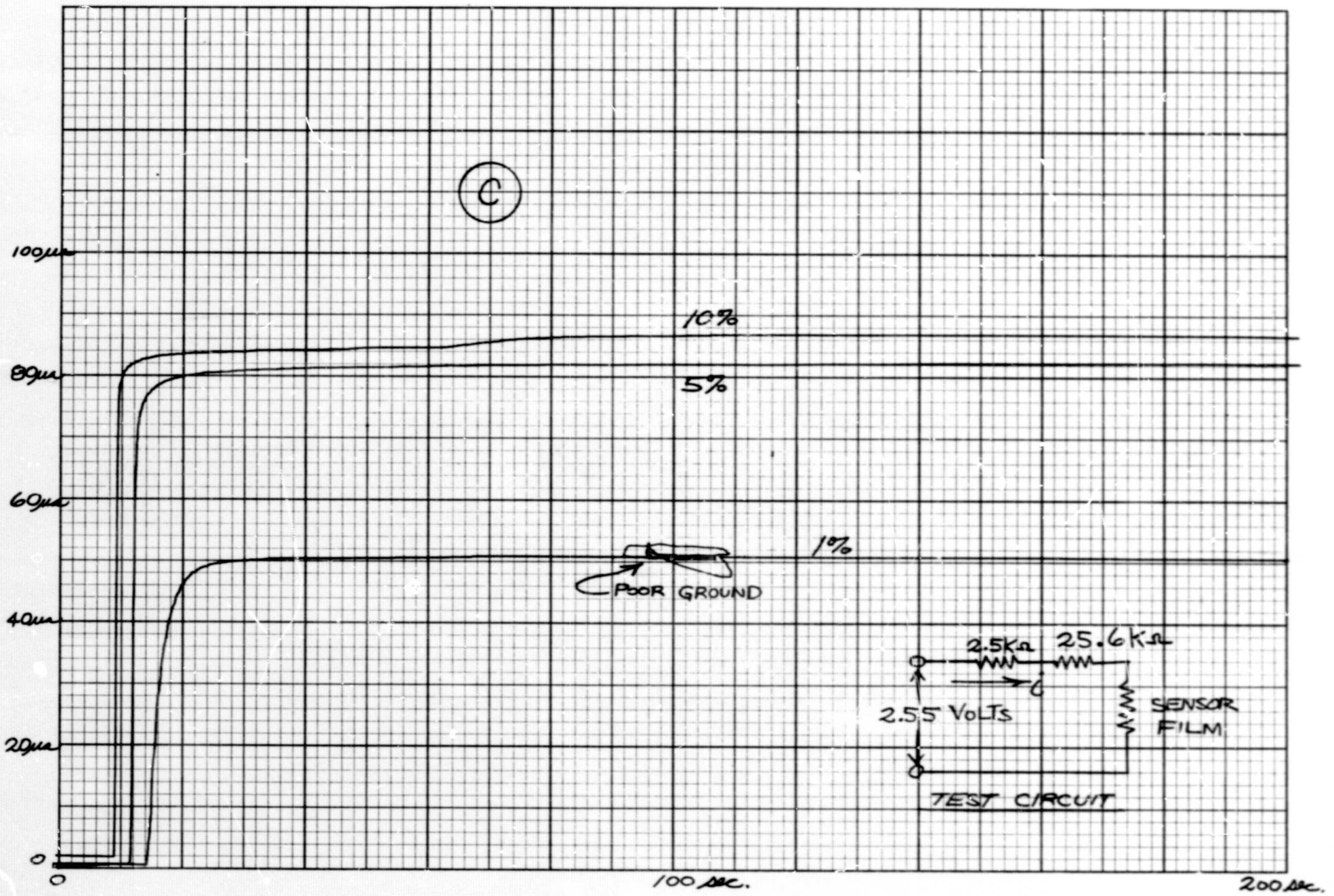


Figure 18. 5 Percent and 10 Percent Calibration - Sensor C

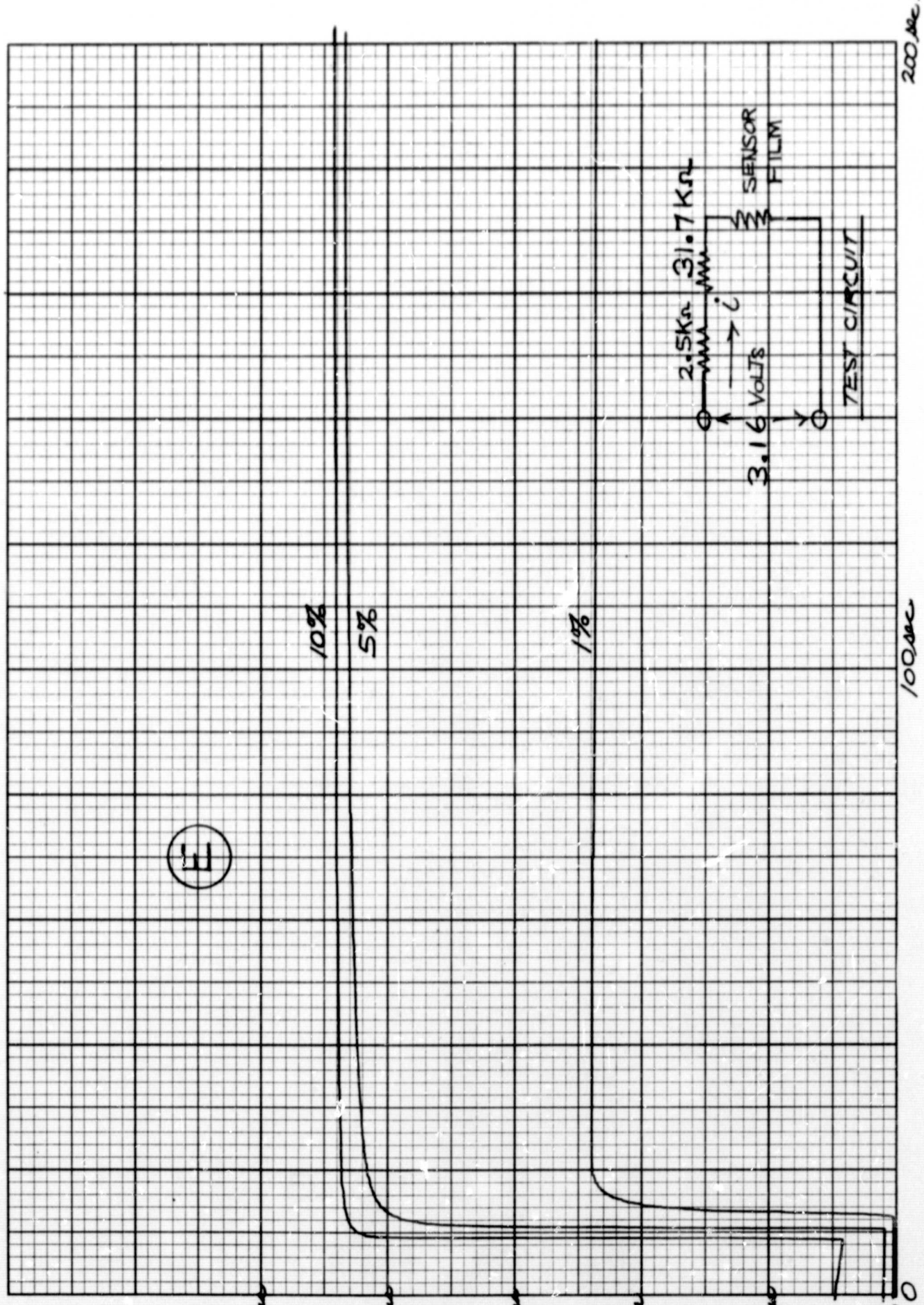


Figure 19. 5 Percent and 10 Percent Calibration - Sensor E

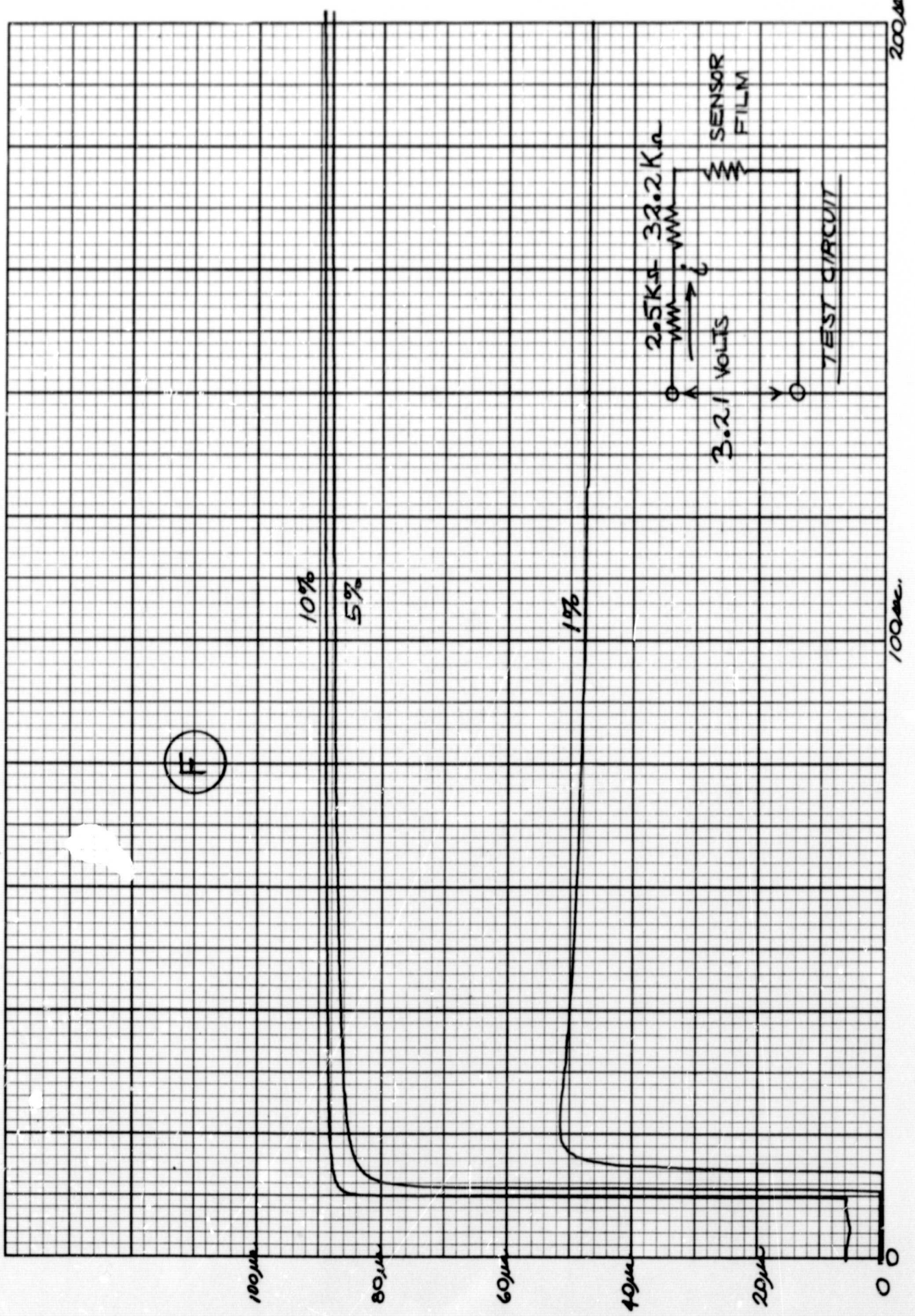


Figure 20. 5 Percent and 10 Percent Calibration - Sensor F

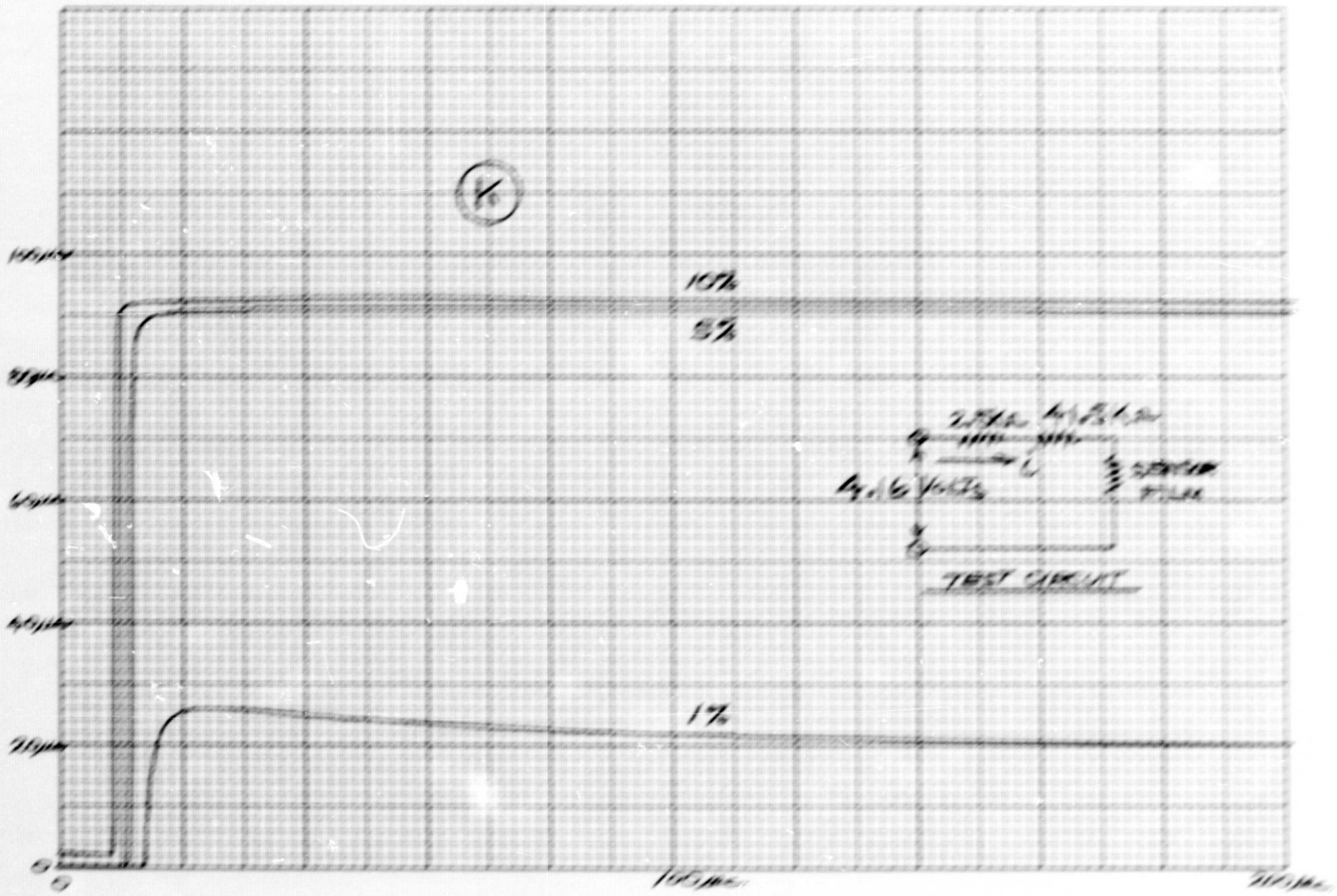


Figure 21. 5 Percent and 10 Percent Calibration - Sensor X

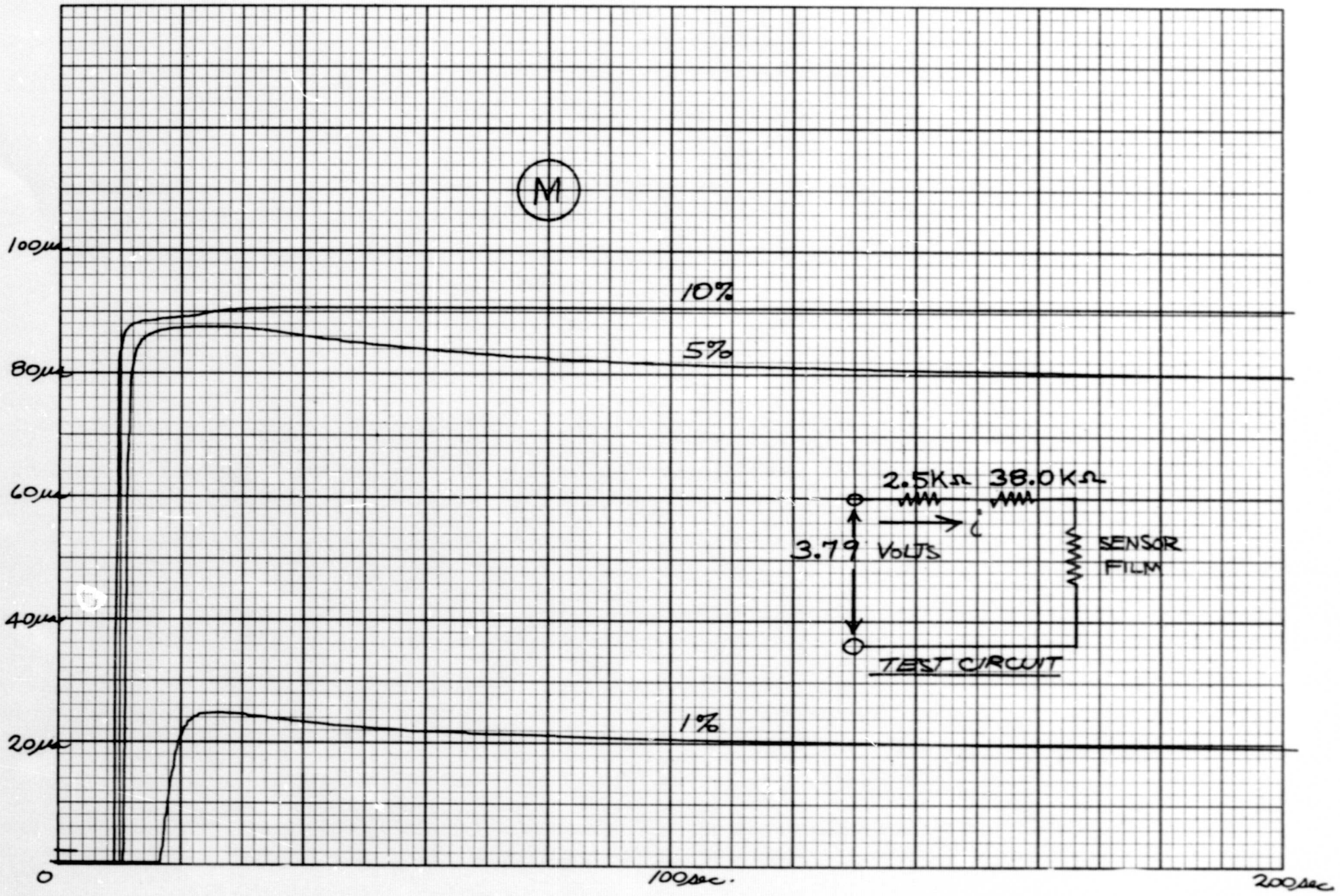


Figure 22. 5 Percent and 10 Percent Calibration - Sensor M

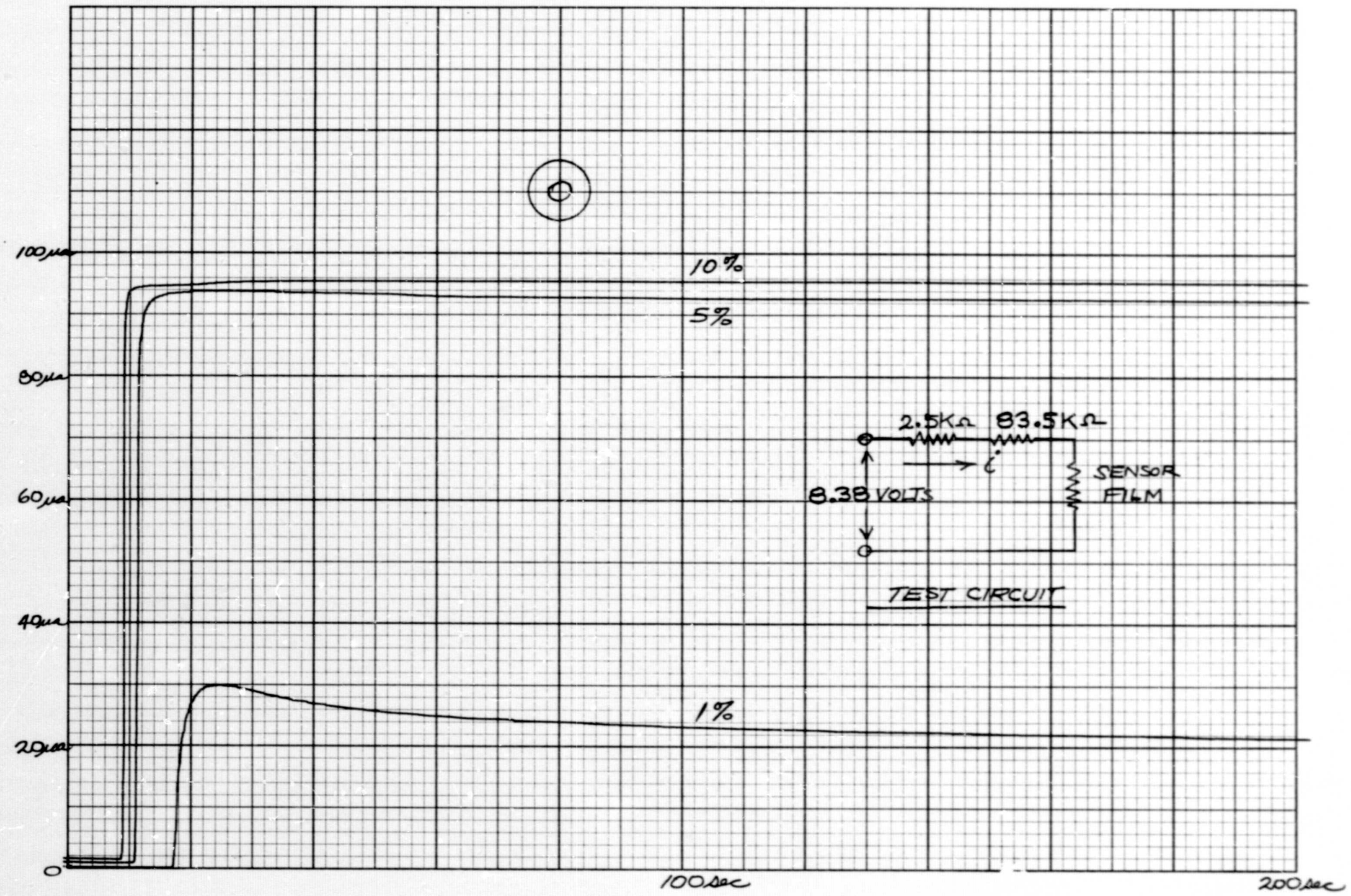


Figure 23. 5 Percent and 10 Percent Calibration - Sensor 0

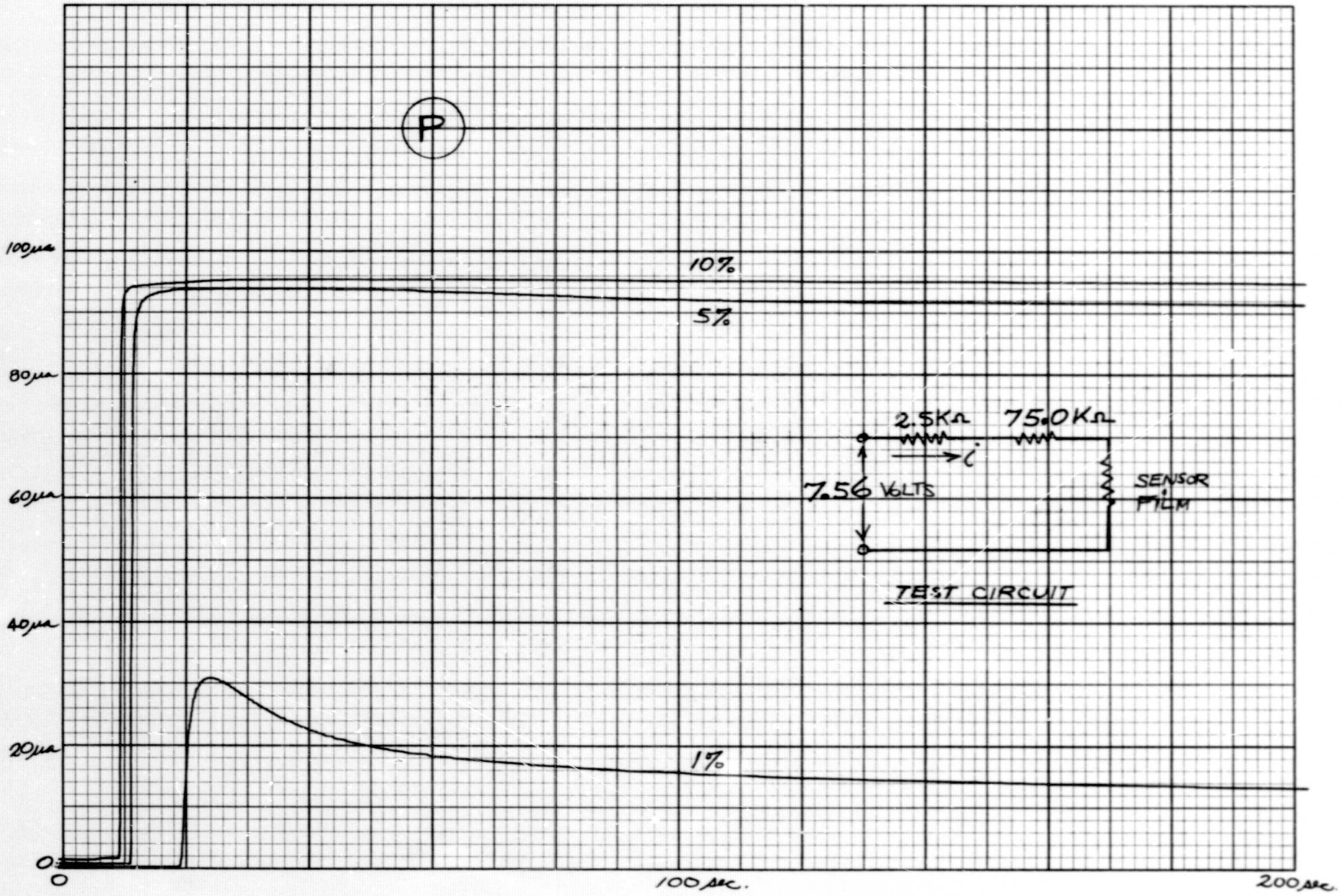


Figure 24. 5 Percent and 10 Percent Calibration - Sensor P

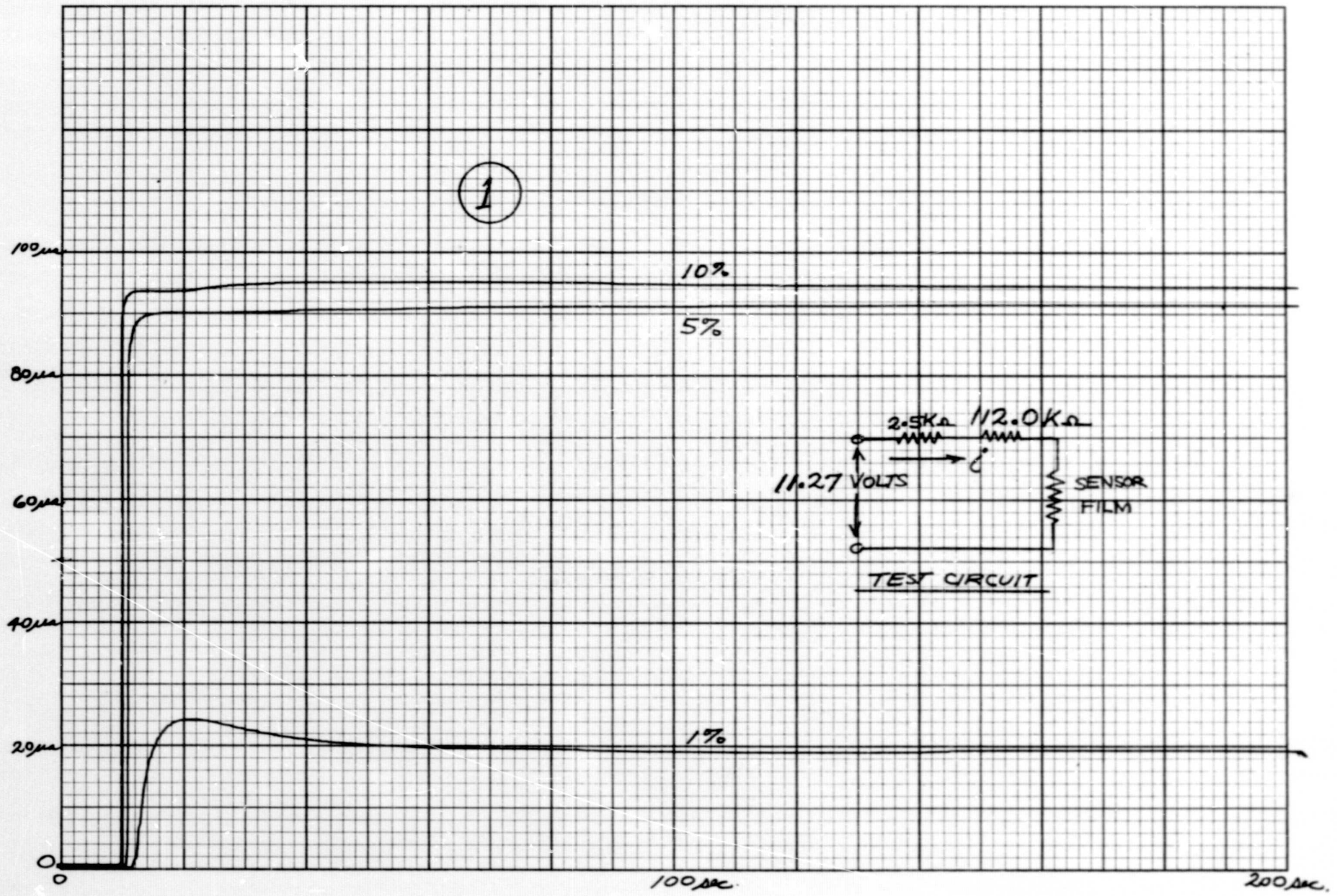


Figure 25. 5 Percent and 10 Percent Calibration - Sensor 1

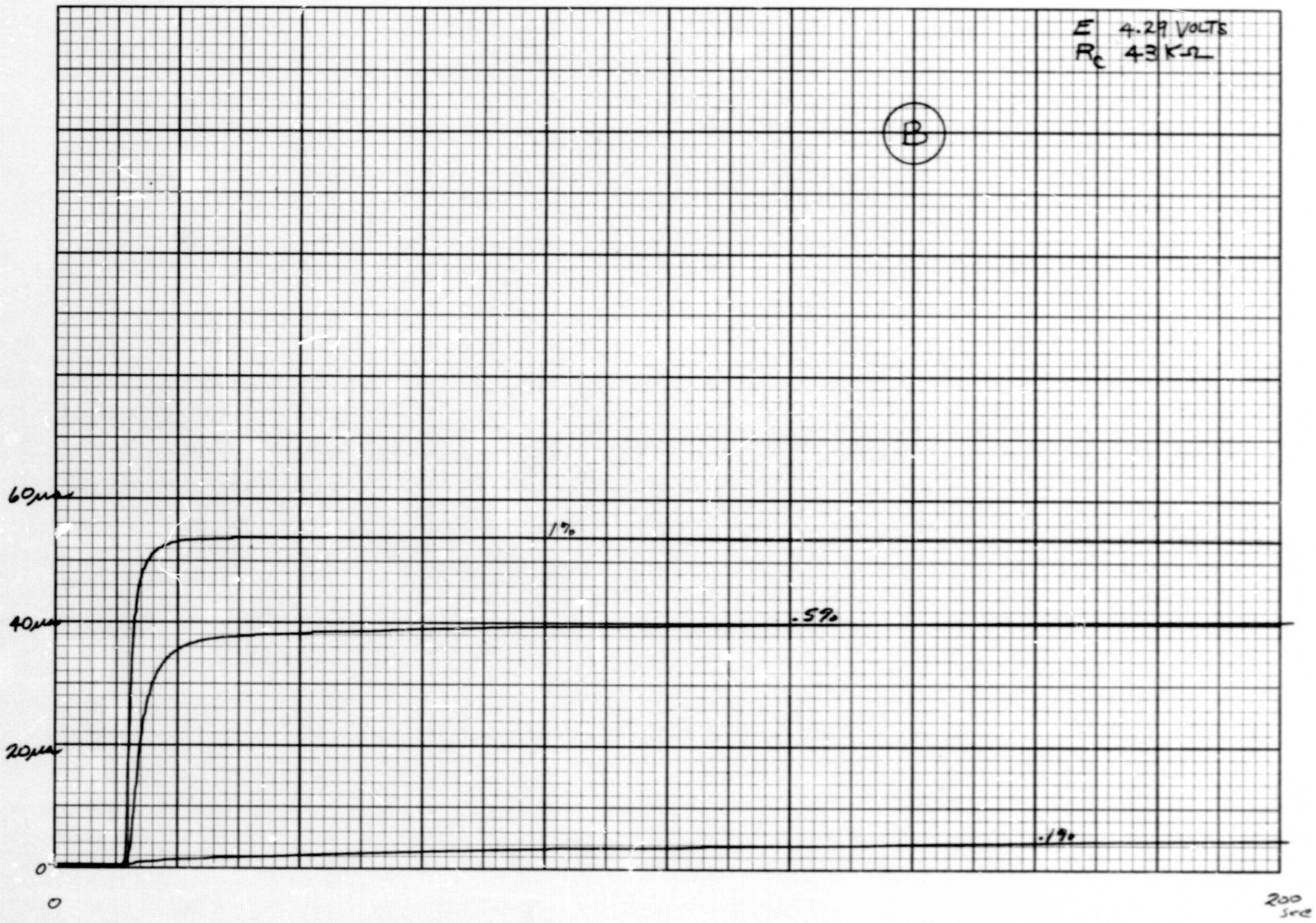
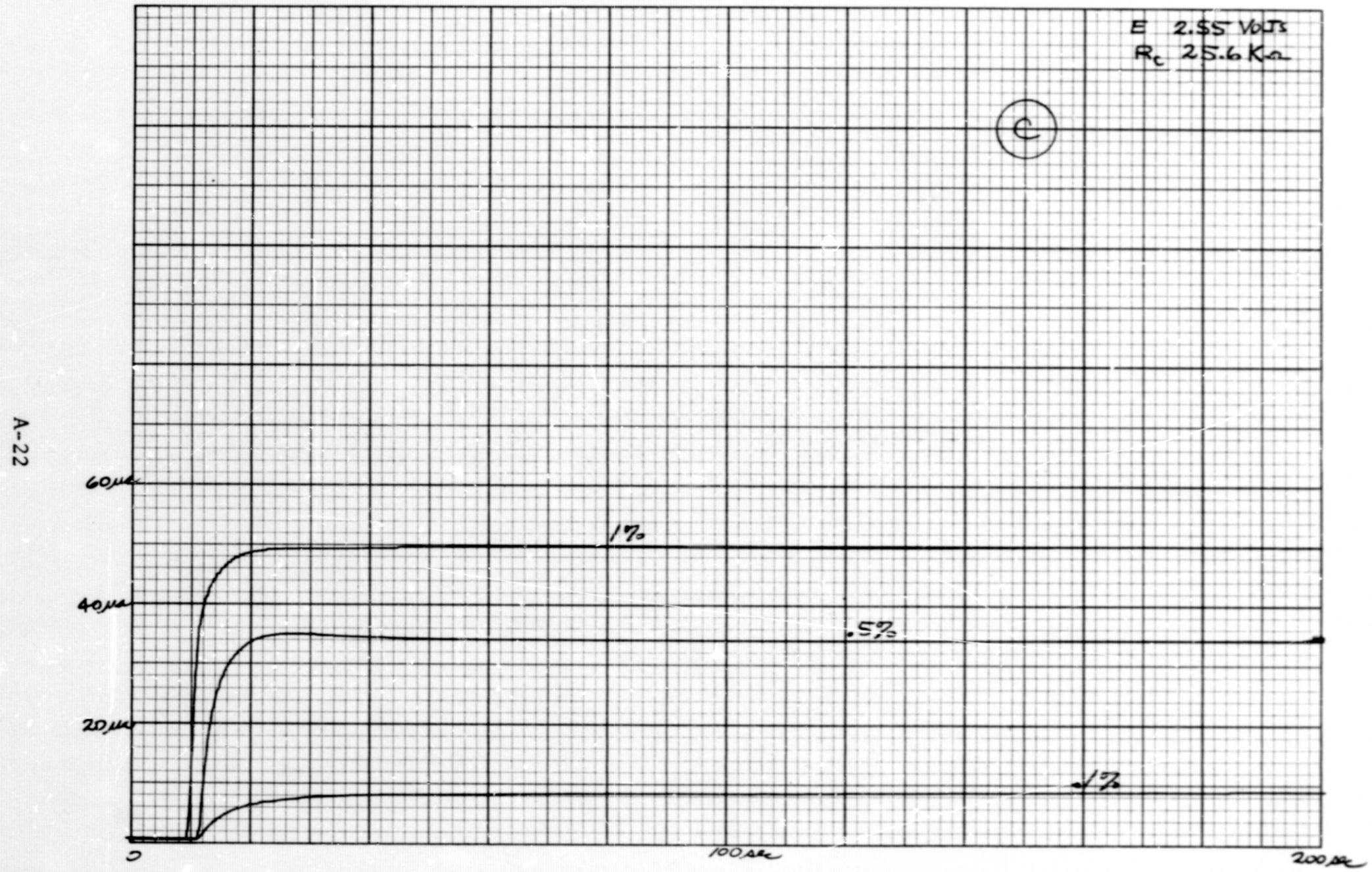


Figure 26. 1 Percent Calibration - Sensor B



A-22

Figure 27. 1 Percent Calibration - Sensor C

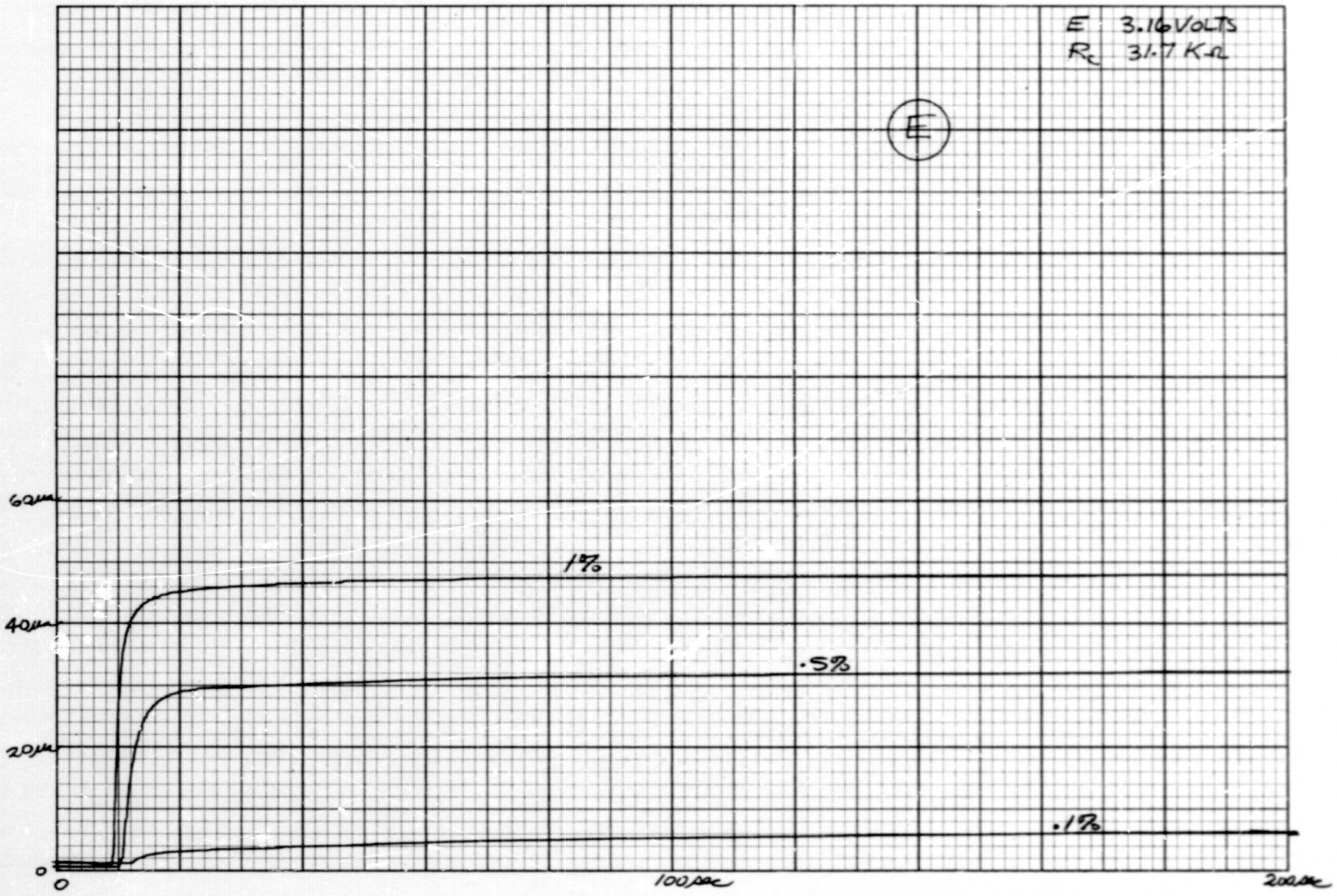


Figure 28. 1 Percent Calibration - Sensor E

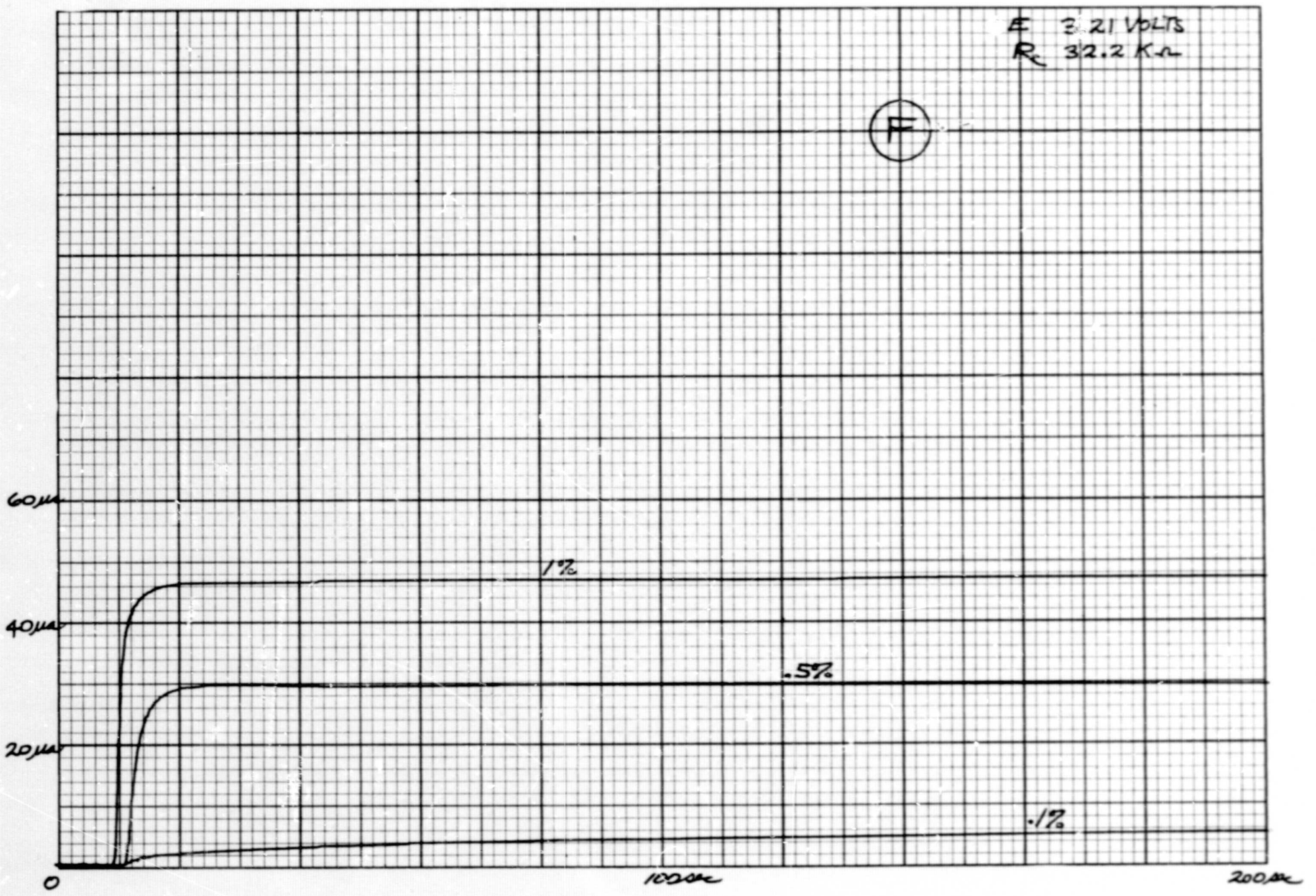


Figure 29. 1 Percent Calibration - Sensor F

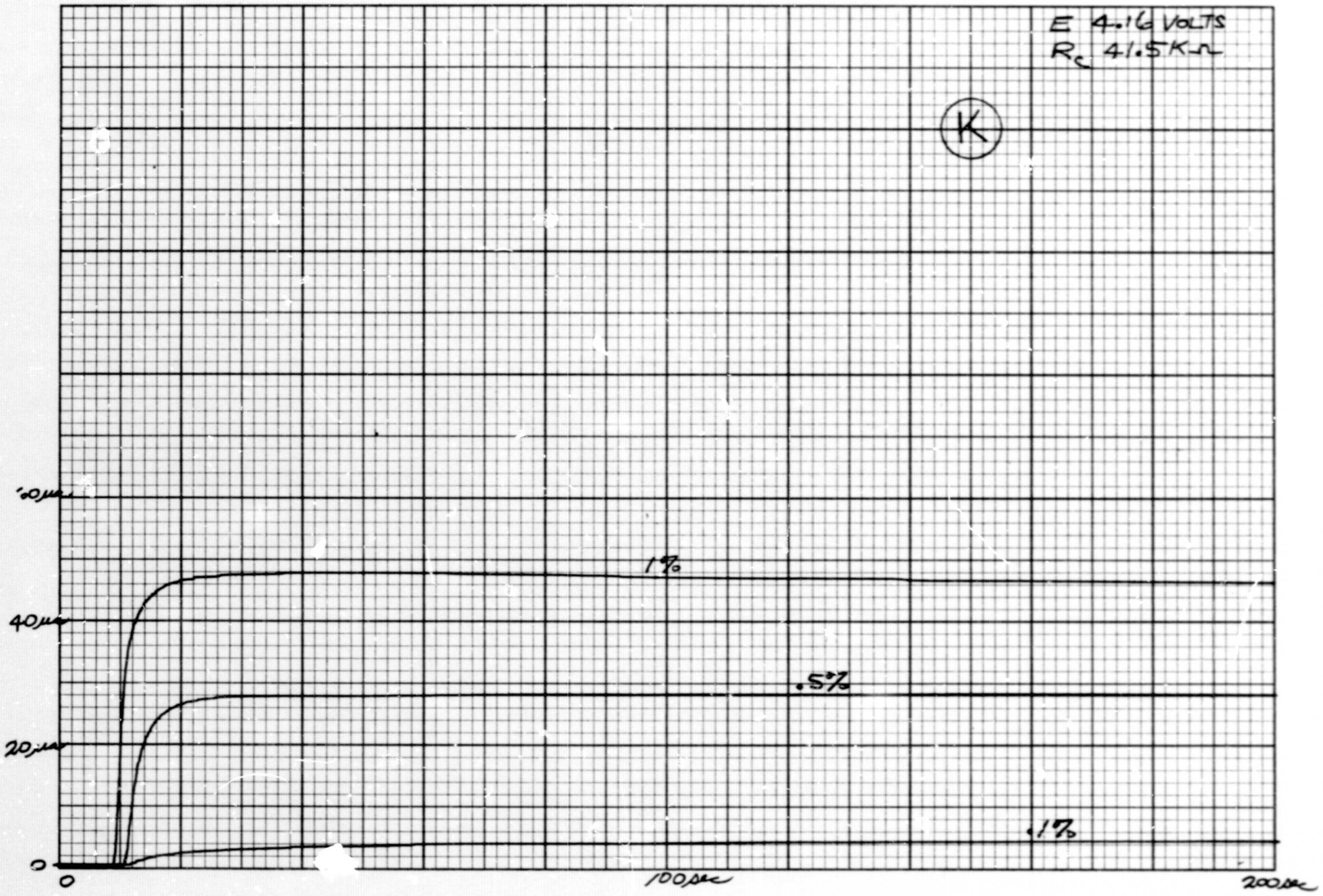


Figure 30. 1 Percent Calibration - Sensor K

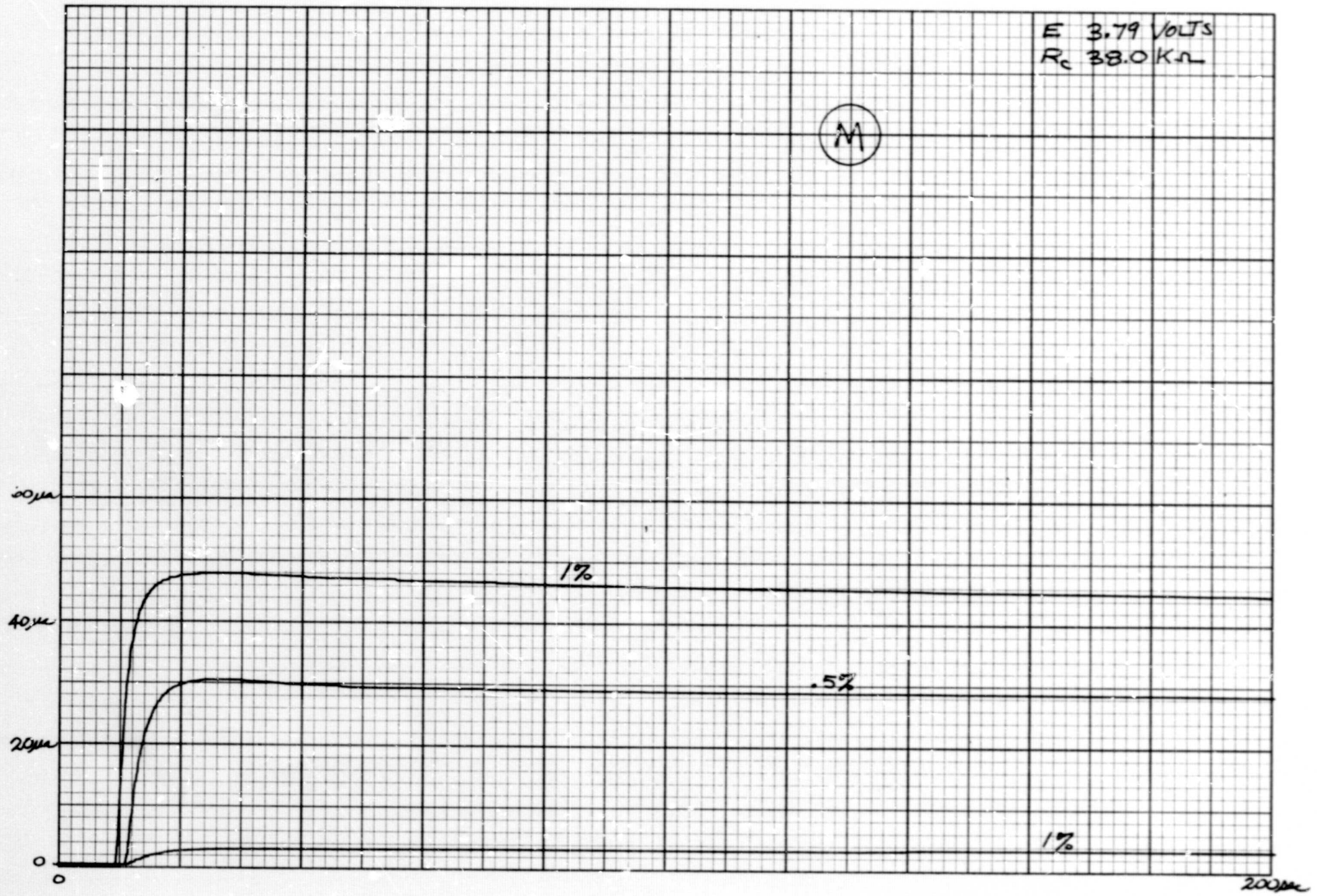


Figure 31. 1 Percent Calibration - Sensor M

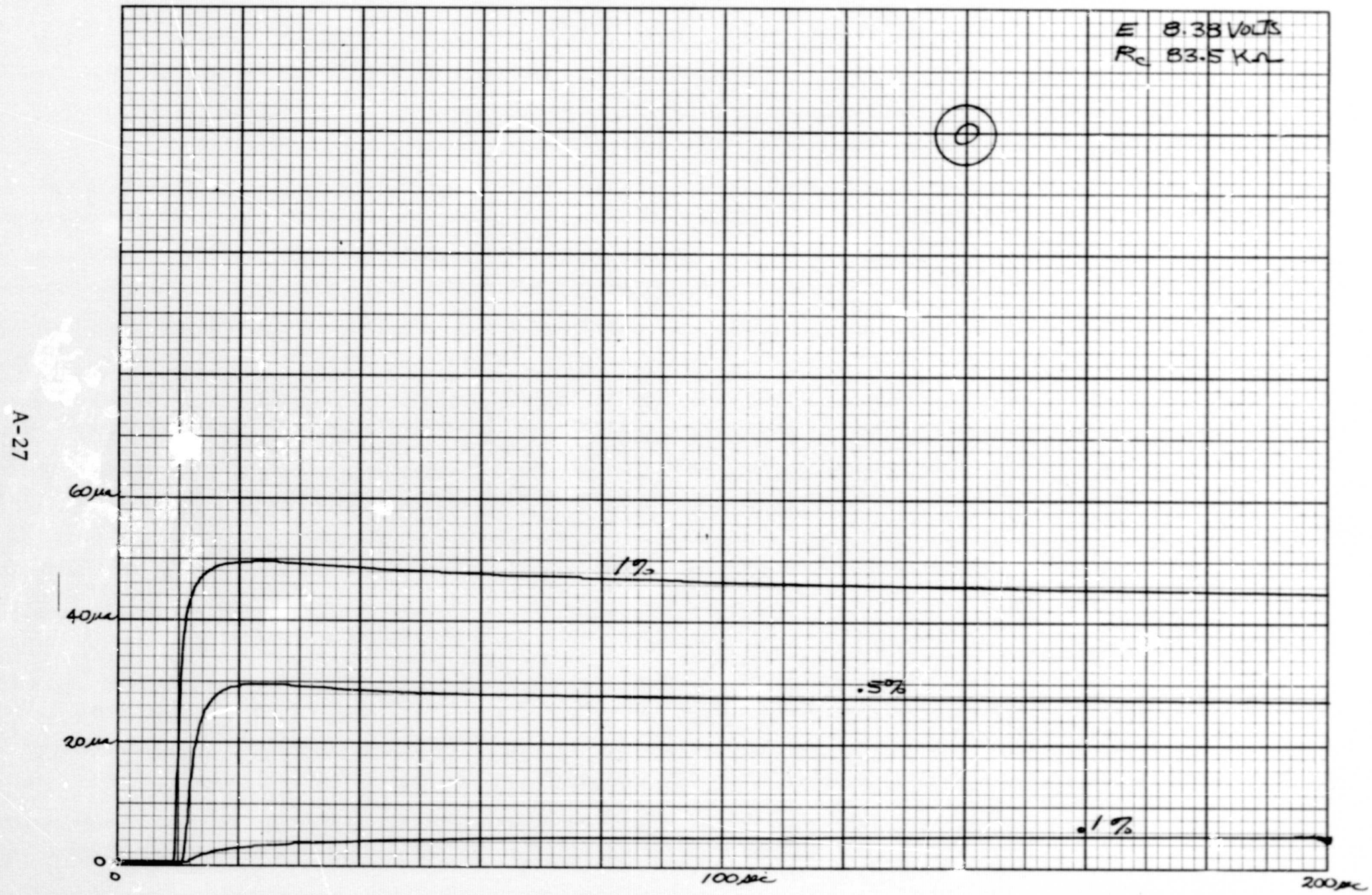


Figure 32. 1 Percent Calibration - Sensor 0

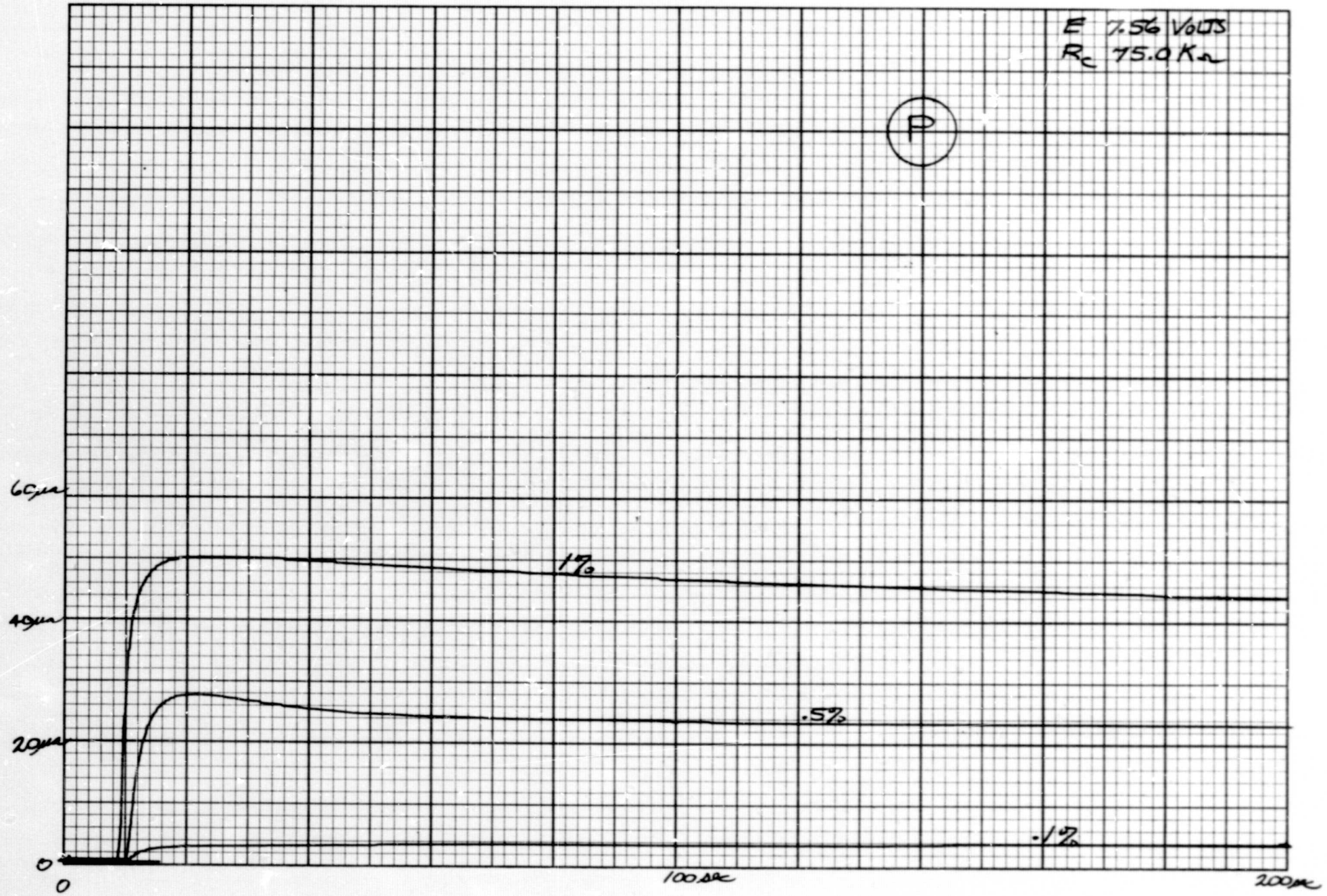


Figure 33. 1 Percent Calibration - Sensor P

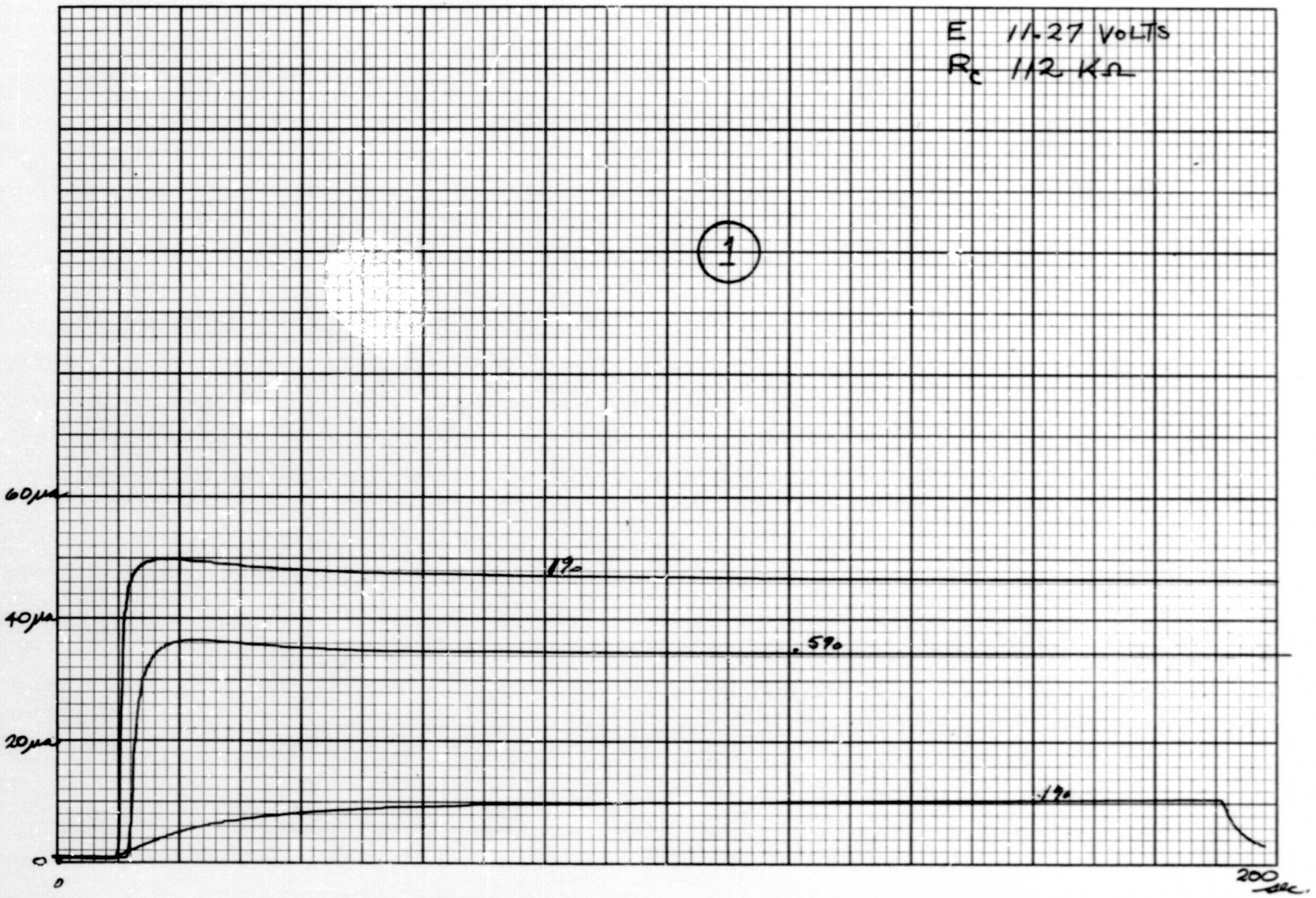


Figure 34. 1 Percent Calibration - Sensor 1

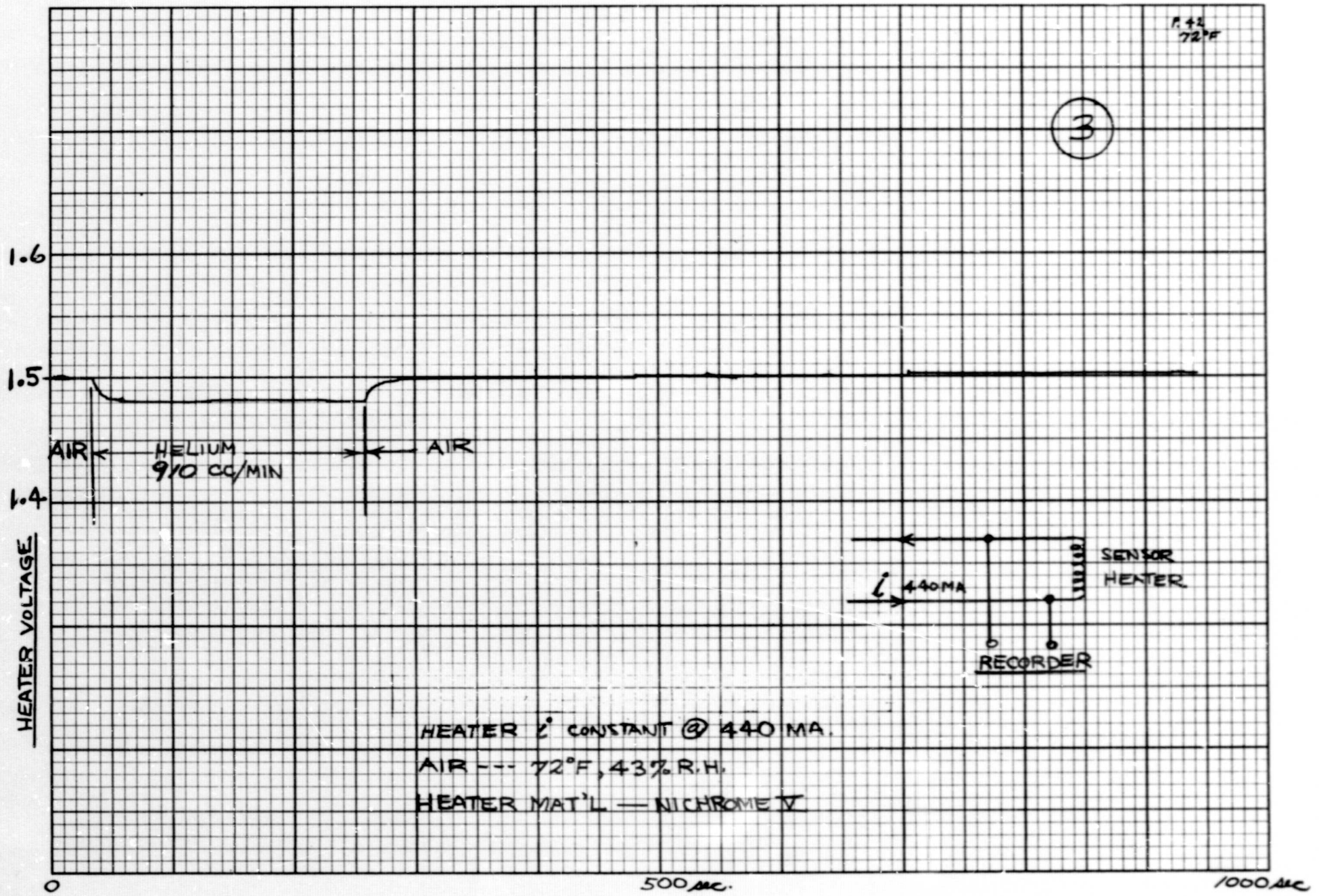


Figure 35. Effect of Helium Ambient on Heater Resistance (Temperature)

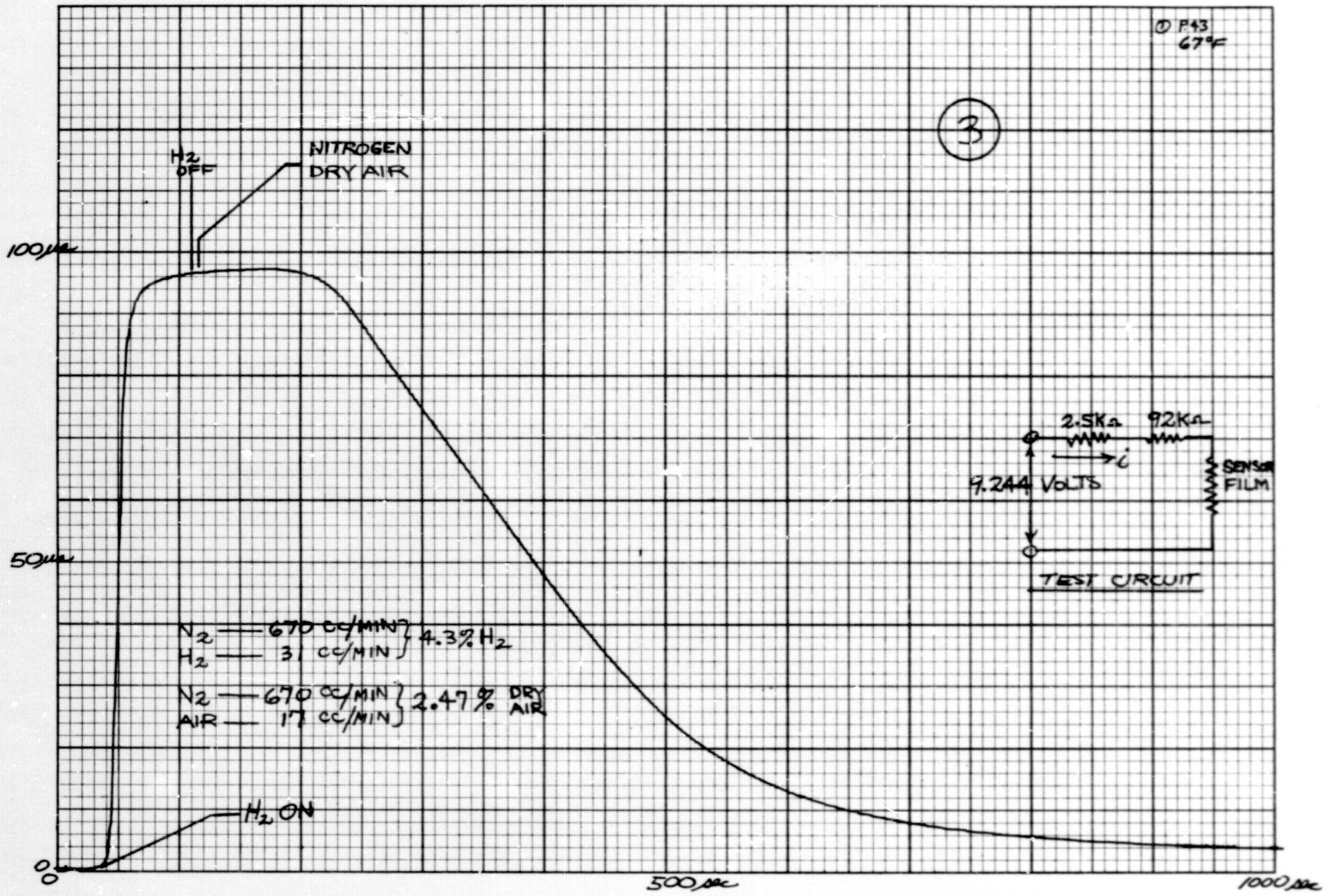


Figure 36. Response to N_2-H_2 Mixture and Recovery to N_2-Dry Air Mixture.

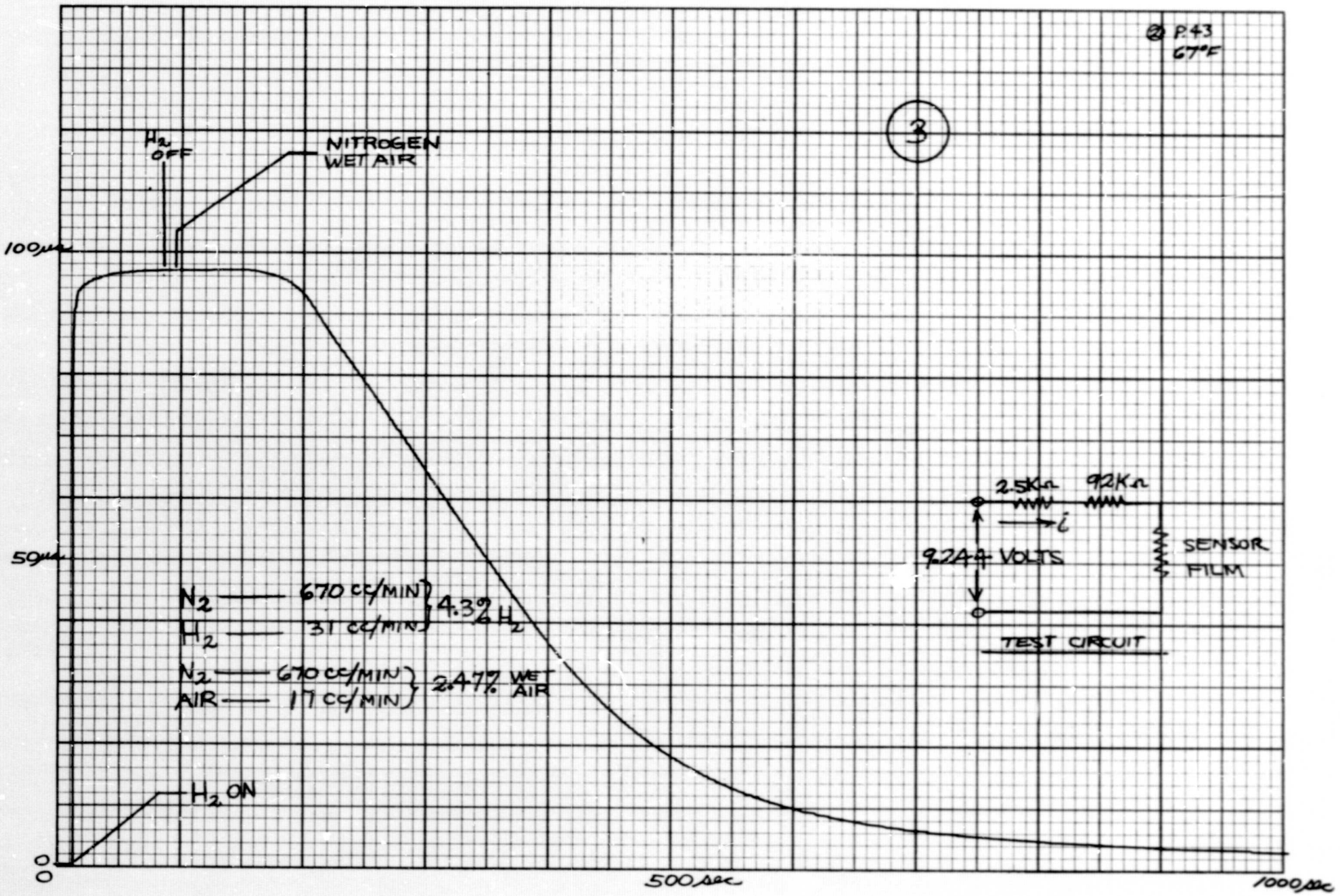


Figure 37. Response to N_2-H_2 Mixture and Recovery to N_2-Wet Air Mixture.

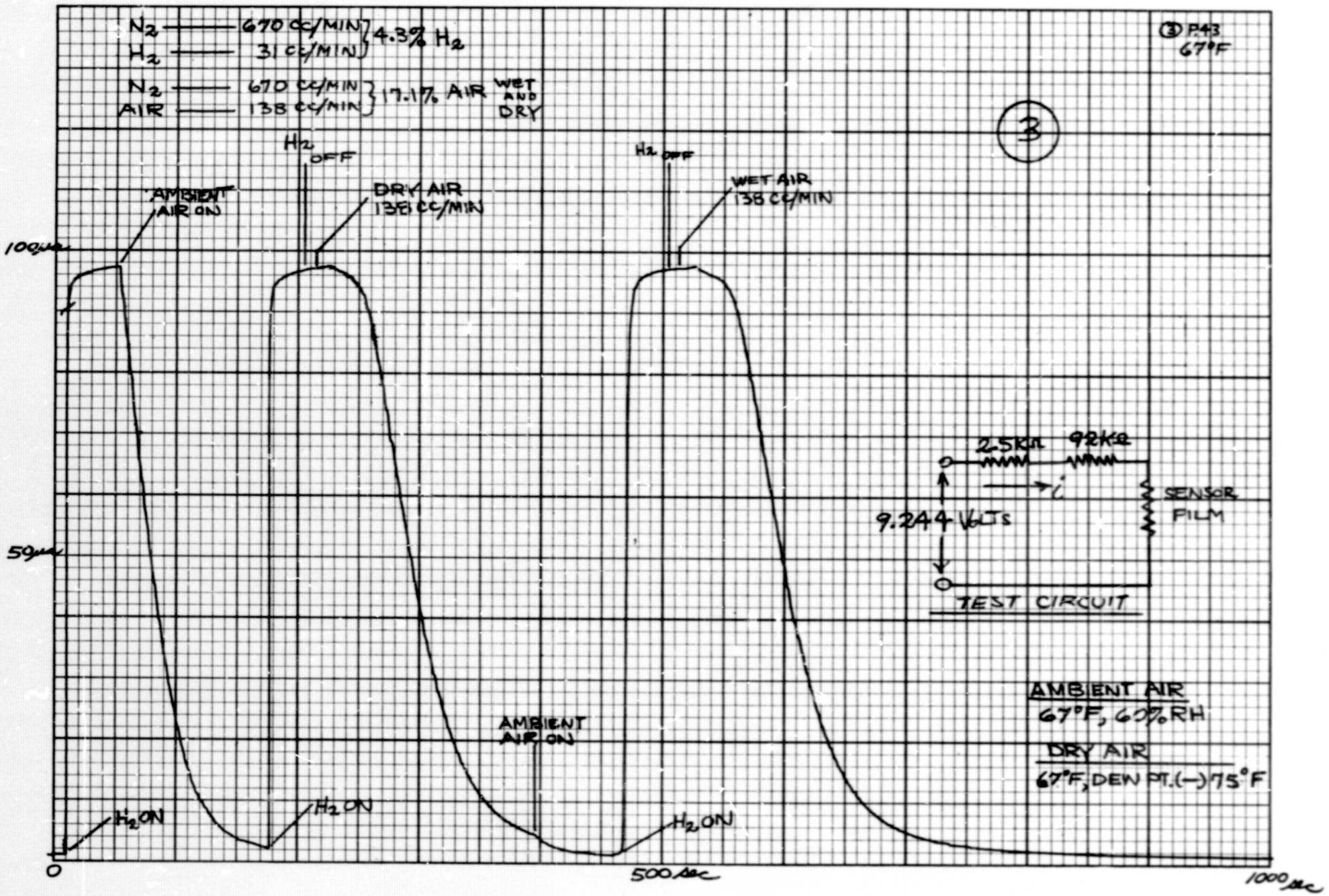


Figure 38. Response to N_2-H_2 Mixture and Recovery to Ambient Air, Dry Air, and Wet Air

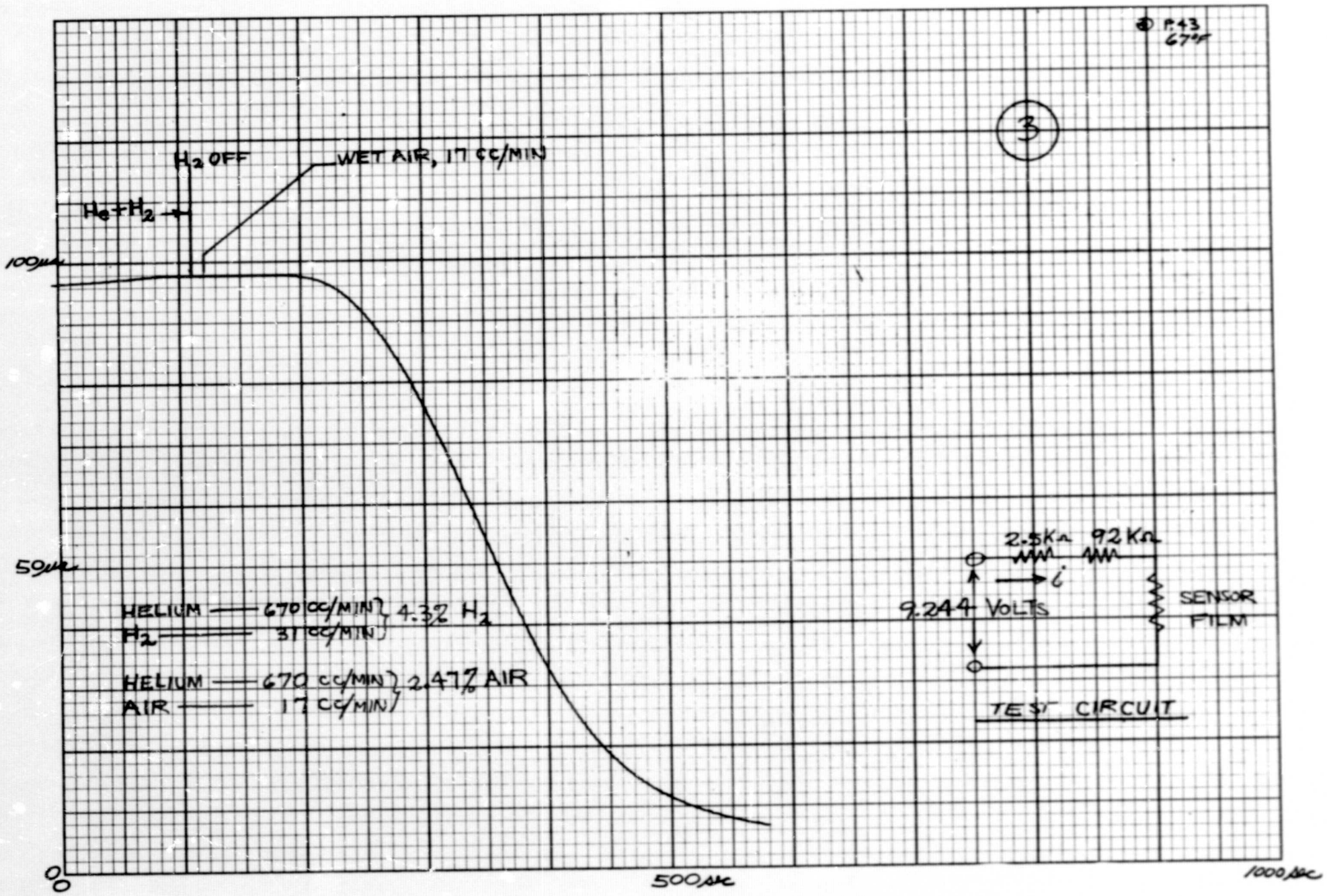


Figure 39. Recovery from H_2-He. Mixture to 2.47 Percent Wet Air-He. Mixture

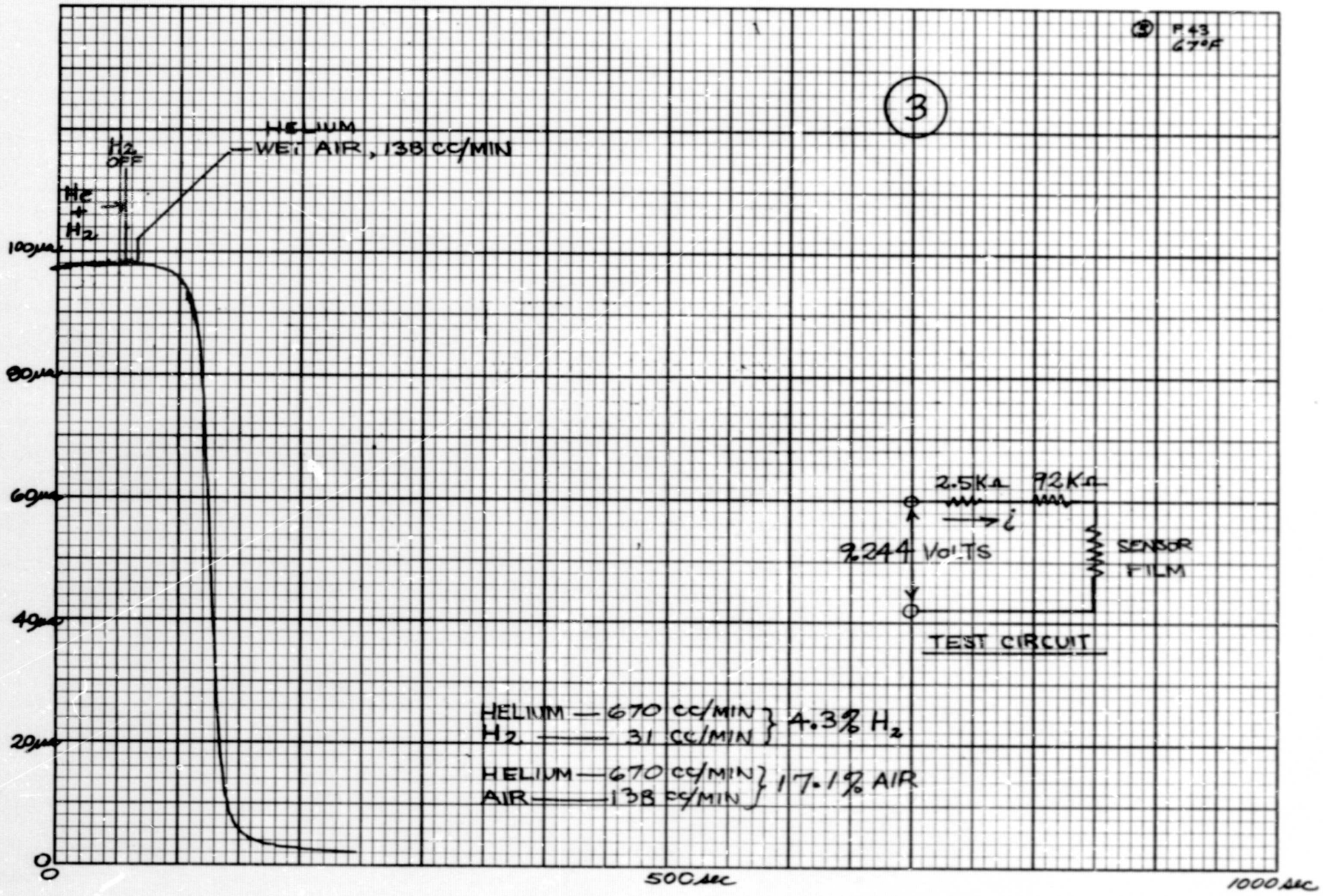


Figure 40. Recovery from H_2-He. Mixture to 17.1 Percent Wet Air-He. Mixture

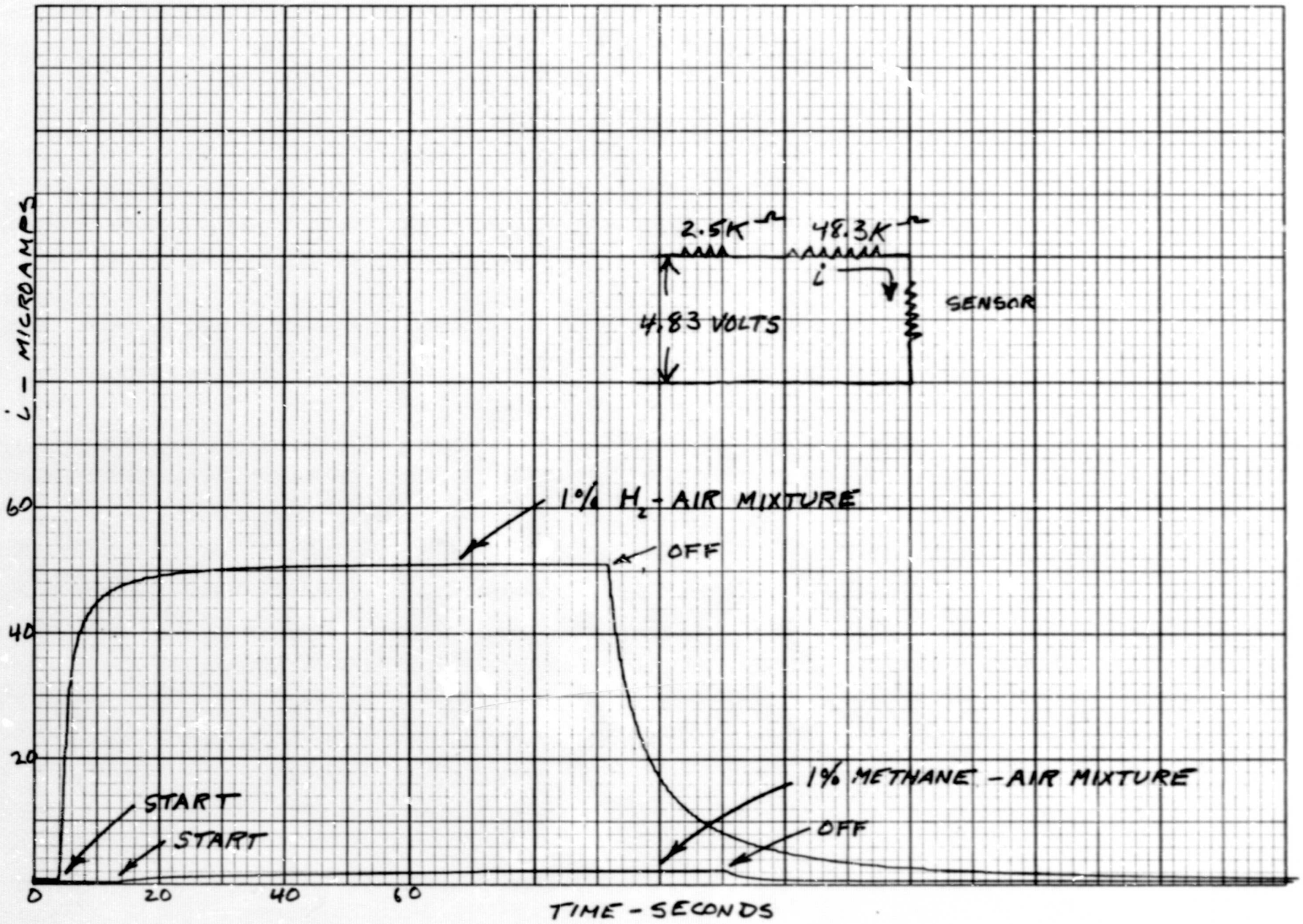
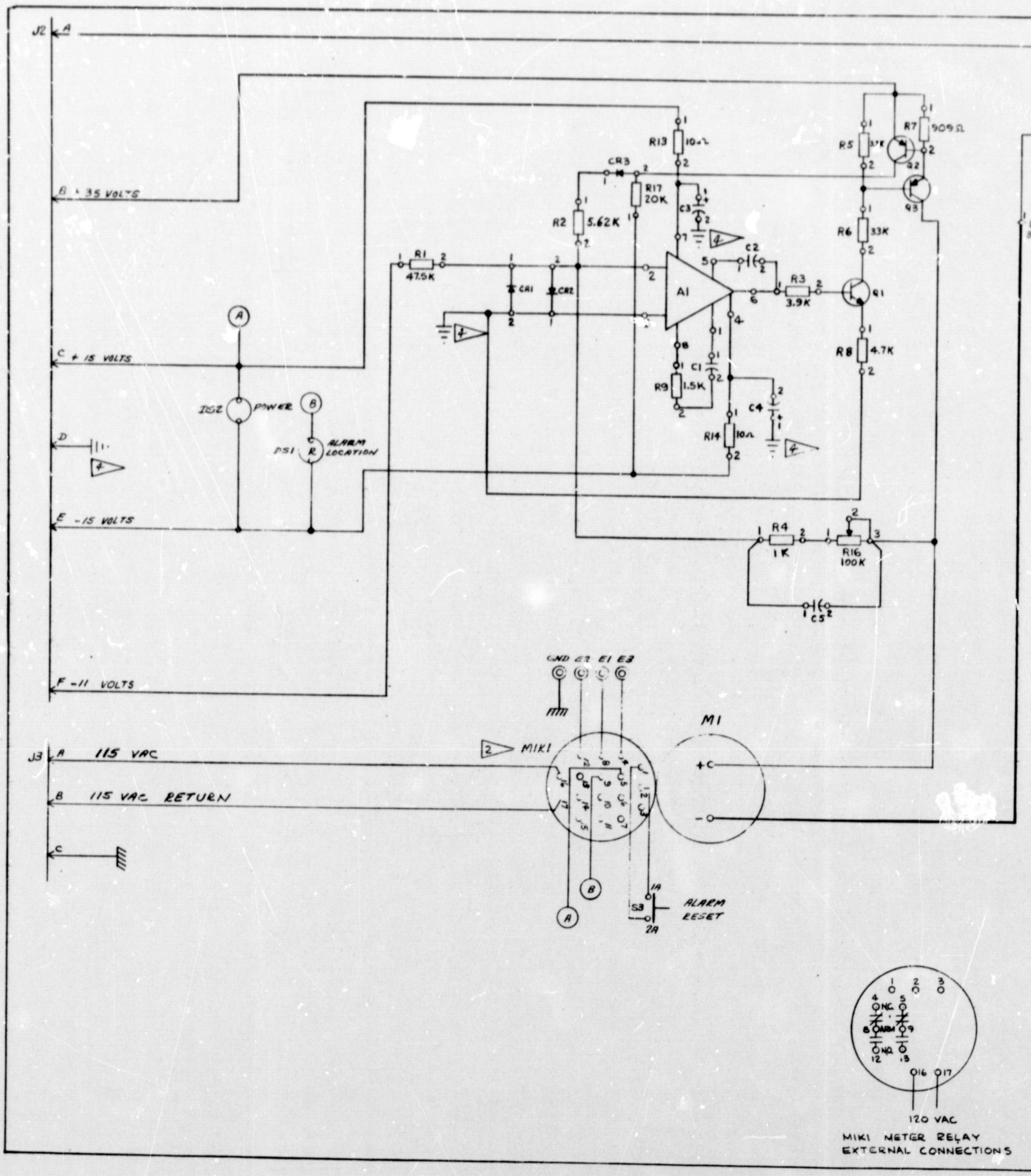


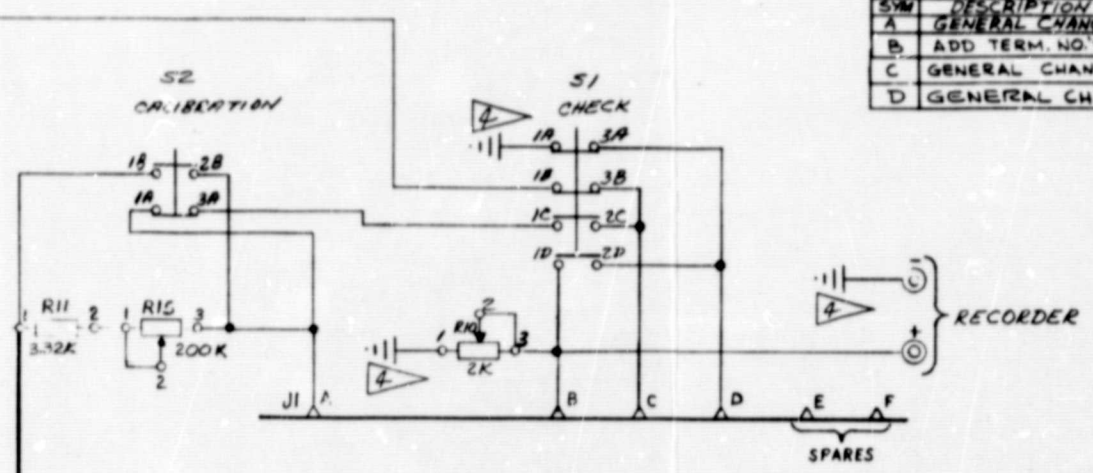
Figure 41. Comparison of Response to 1 Percent Hydrogen-Air Mixture with 1 Percent Methane-Air Mixture



MIKI METER RELAY
EXTERNAL CONNECTIONS

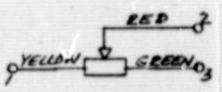
FOLDOUT FRAME

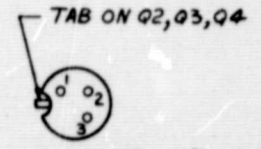
REVISIONS			
SYM	DESCRIPTION	DATE	APPROVAL
A	GENERAL CHANGES	8-2-69	C.B.
B	ADD TERM. NO.'S AT Q1	9-24-69	C.B.
C	GENERAL CHANGES	10-22-69	C.B.
D	GENERAL CHANGES	3-12-70	C.B.

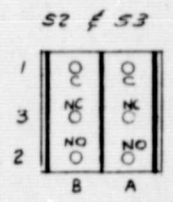


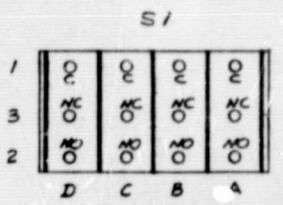
NOTES:

1. ALL WIRE TO BE B20 UNLESS OTHERWISE SPECIFIED.
2. REMOVE JUMPER ON MIKI ASSEMBLY TERMINALS 1, 2, 3 BEFORE INSTILLATION.
3. CHASSIS & AC NETURAL GND.
4. SIGNAL & SINGLE POINT GND. TO BE CONTINOUS WIRE CONNECTED TO PLUG PIN.
5. "R" NUMBERS NOT USED, I.R.
6. ALL WIRE TO TRANSIST. & SOCKETS XQ1, XQ2, XQ3, & XQ4 TO BE B22.









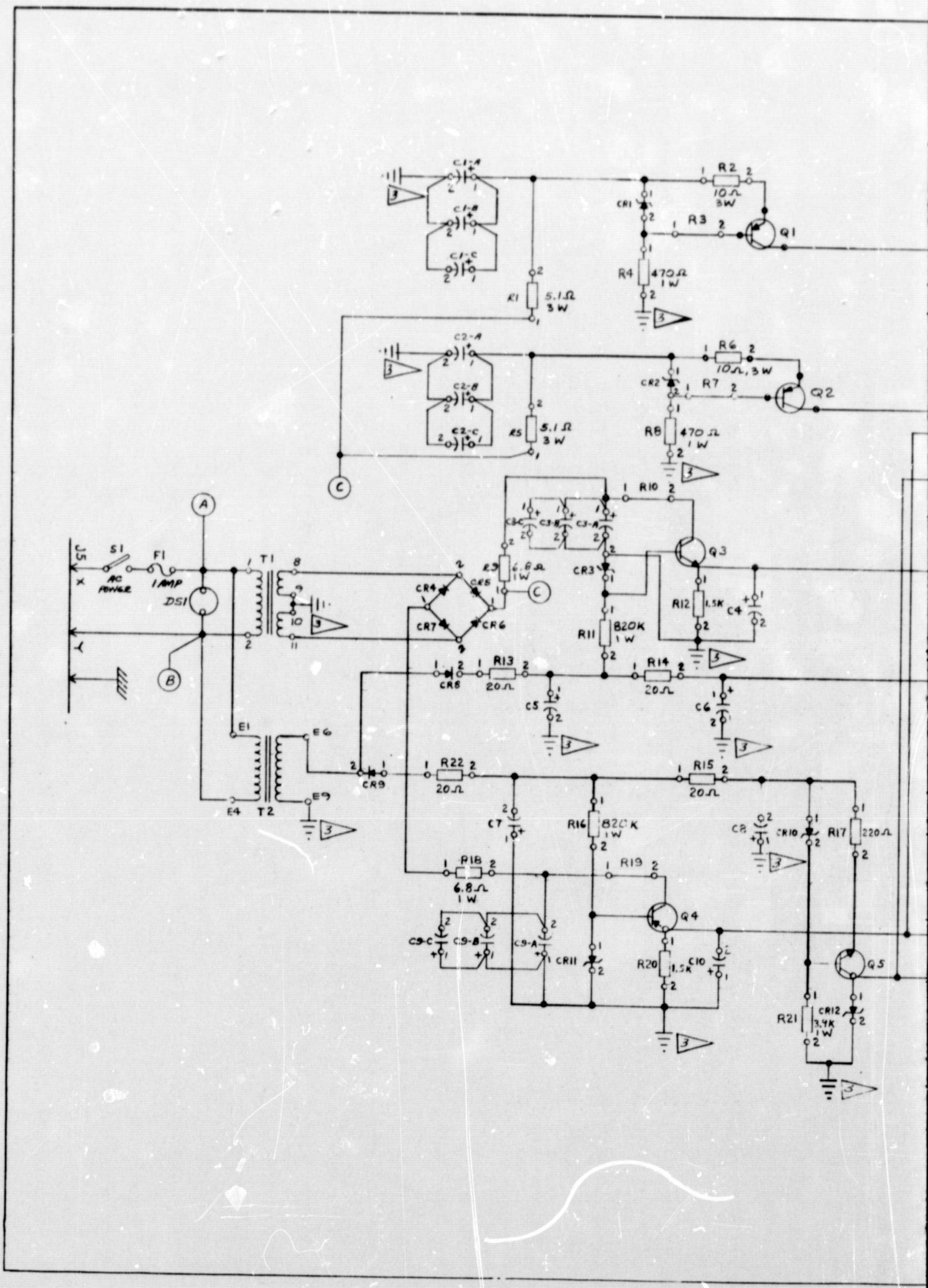
WIRING VIEWS

DRAFTSMAN 7-16-69	SCHEMATIC MODULE, HYDROGEN MEASUREMENT SYSTEM	
APPROVED 7-16-69		
APPROVED 7-18-69		
APPROVED 7-15-69	JOB # F04002	SK56137-6-820

a: 7-25-69

Drawing Number SK56137-6-820

FOLDOUT FRAME 2



FOLDOUT FRAME/

REVISIONS			
SYM	DESCRIPTION	DATE	APPROVAL
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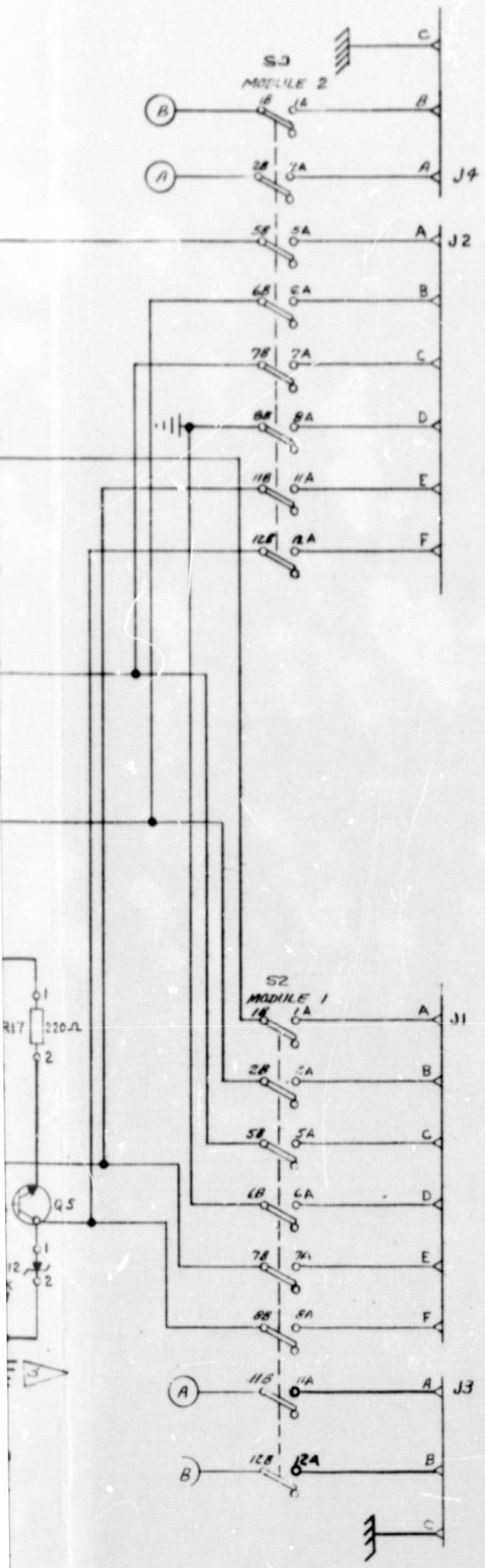
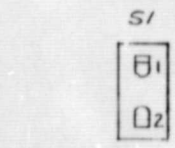
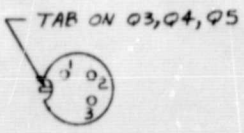
B	REVISE Q1 & Q2	9-28-67	[illegible]
C	GENERAL CHANGES	10-30-68	[illegible]
D	GENERAL CHANGES	3-13-70	C.D.



NOTES:

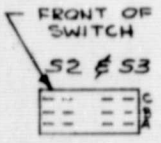
1. ALL WIRE TO BE B20 UNLESS OTHERWISE SPECIFIED.
2. CHASSIS SHIELDS & AC NETURAL GND.
3. SIGNAL AND SINGLE POINT GND TO BE CONTINOUS WIRE CONNECTED TO T1 CENTER TAP
4. ALL WIRE TO TRANSISTOR SOCKETS XQ3, XQ4, & XQ5 TO BE B22

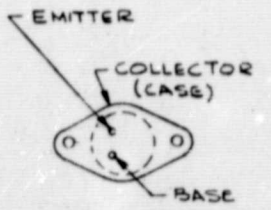




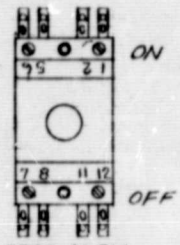
XQ3, XQ4, XQ5 BOTTOM VIEW 4.

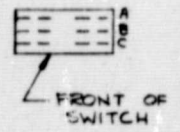
T2

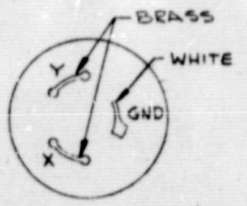




Q1 & Q2







J5 - LOOKING INTO PIN SIDE OF CONNECTOR

WIRING VIEWS

7-1-69 W. Jackson	SCHEMATIC POWER SUPPLY HYDROGEN MEASUREMENT SYSTEM	
7-13-69 [illegible]		
[illegible]		
P.B. 7-15-69	JOB # F04002	SK56137-6-821

7-25-69

Drawing Number SK56137-6-821

FOLDOUT FRAME

APPENDIX B

FN-610-A (12-65)

FOR USE OF G-E EMPLOYEES ONLY

GENERAL ELECTRIC

TECHNICAL INFORMATION SERIES

Title Page

AUTHOR	SUBJECT	NO. DF70MI-04
G.M.Marcotte	Hydrogen Sensors	DATE 1/14/70
TITLE Thin Film Tungsten Oxide Sensors for NASA Hydrogen Detector System		G.E. CLASS 3
		GOVT. CLASS None
REPRODUCIBLE COPY FILED AT Technical Information Unit, W. Lynn, Mass.		NO. PAGES 16

SUMMARY A thin film WO_3 hydrogen sensor, based on earlier ADO and R&DC work, has been successfully designed, packaged and evaluated for NASA on a subcontract from Apollo Systems Department. Fifteen sensors have been delivered and are operating satisfactorily.

The detailed materials and processes used in these development samples are documented.

An exploratory study on the feasibility of age stabilizing the resistance of the sensors by means of a short, high temperature bake showed no significant improvement over control samples.

KEY WORDS Hydrogen Sensor, Tungsten Oxide

INFORMATION PREPARED FOR Apollo Systems Department

TESTS MADE BY George M. Marcotte

AUTHOR George M. Marcotte

COMPONENT Advanced Development Operation

APPROVED A. A. Kessel/R. S. Norman R.S.N. 2/12.

AAK.

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GENERAL ELECTRIC COMPANY

TECHNICAL INFORMATION SERIES

NO. DF70MI-04

INTRODUCTION

The sensor consists of an electrical resistor which is made of a thin film of tungsten oxide - nominally WO_3. In order to detect hydrogen efficiently, this tungsten oxide film must be subjected to a particular activation process described below. When the "activated" tungsten oxide film is heated to 250-400°C, the magnitude of its electrical resistance is inversely proportional to the hydrogen content of the ambient air. This is the basic transducing action. Hydrogen concentrations of from 2 parts per million to 30% have been measured with these thin film detectors.

The activation process involves depositing a small amount of a catalytic element such as platinum on the tungsten oxide film. This activation is thought to produce thin film islands of high catalytic activity on the surface of the tungsten oxide. It is then believed that hydrogen reacts with the tungsten oxide in the localized presence of the catalytic centers to produce a change in the electrical resistance of the films. Continuous activation is needed to produce the desired short response and recovery times since the resistance of the tungsten oxide thin film changes with the ambient concentration of hydrogen.

A simple schematic representation of the hydrogen detector is shown in Fig. 1. Currently, detectors are heated by means of fine nichrome wires instead of the thin film heater as indicated in Fig. 1.

A detailed discussion of the theory of hydrogen gas detection with the tungsten oxide (WO_3) sensor will be found in Report 67-C-293, Activated Tungsten Oxide and Other Activated Oxide Gas Detectors, by P.J. Shaver, August 1967.

In 1968, this laboratory received an IR-100 award for a a battery operated portable hydrogen detector using this technology.

Based on the early development work by R&DC, ADO and Apollo Systems Dept., a contract was issued to ASD by NASA for the development and design of a hydrogen detector system.

The design and fabrication of the sensor itself was to be done by ADO and all environmental testing of the complete sensor system was to be done by ASD.

OBJECTIVE

This report describes the development, design and fabrication of the hydrogen sensors and exploratory work on the feasibility of stabilizing the sensor output by baking at elevated temperatures.

DESIGN

Two items of the first ADO development samples were modified to comply with NASA requirements. First, the header to which the sensor is mounted was changed to a special stainless steel receptable per NASA Specification TEC-1064. The other change was the use of an explosion-proof cover instead of the aluminum cover and was accomplished by means of a sintered porous brass part. See Fig.2.

CONSTRUCTION

Preparation of WO_3 on Quartz

Quartz tubes, see Materials List, were cut to 6" lengths and cleaned by immersing in acetone and air dried. A very thin layer of platinum paint was then applied to the quartz per Fig. 3. The platinum paint was dried at 105°C for two hours. The pieces of quartz were mounted 1/16 of an inch above the surface of a hot plate whose temperature was raised to 550°C. After 3-4 hours, the paint changed from black to a metallic platinum. This process must be carefully controlled, e.g., if the paint is too thick, it will blister off the quartz - too thin, and it will disappear. Too rapid elevation of the temperature can also cause blistering.

The quartz rods were cut into two sensor lengths and these pieces were laid side by side on a flat plate. This holding fixture held 15 pieces or 30 sensor films; but could easily be expanded to hold more if this became necessary.

A WO_3 film of about 1000 Å was evaporated on the quartz in an NRC 3116 Vacuum Coater and a Sloan DTM3 Deposit Thickness Monitor was used to check the film. The evaporated quartz tubes were then cut into sensor lengths as indicated in Fig. 3.

Heater

Twenty turns of .004" nichrome V wire were wound on a .006 mandrel. These turns should be tight and evenly spaced. After removal of the mandrel, the coil of wire was stretched so that the distance from the first to the twentieth turn was 1/4". See Fig. 4 for details.

Final Assembly

Leads of .020 platinum wire were welded to the appropriate pins in header, TS07-12-8P-F2, as detailed in Fig. 5. The platinum clamps were formed around the quartz as shown in Fig. 4 and Fig. 5, and then welded to the proper leads already on the header. The heater coil was inserted in the quartz tube and its ends wrapped around the proper lead and welded. The quartz tube was oriented so that the WO_3 surface faced up. The platinum leads were adjusted to make the quartz stay level and square in the header.

Sensitizing

This was accomplished by passing the WO_3 sensor film near, approximately 2-3 millimeters, a platinum wire maintained at orange-white heat, or about 1200°C. Platinum atoms evaporated from the hot platinum are deposited on the WO3 in the 1/32" wide area on the quartz. This is the catalyzed sensor area which was described earlier. The sensor was energized by applying 1.5 volts a-c on the nichrome V heater and exposed to a gas mixture of 1% hydrogen in air. If the electrical resistance didn't change from the megohm range down to 100K ohms, the sensitizing process was repeated. Some sensors required 2 or 3 passes before giving the proper response. Table 1 gives a summary of the behavior of 9 sensors on exposure to both 1% and 10% hydrogen.

Explosion-Proof Cover

The explosion-proof cover was manufactured by Sintered Metals Corporation, Boston, Mass., as shown in Fig. 6. The 11/16" x 24" thread and counterbore were provided for assembly to the header with particular attention being paid to the exact fit of the cover against the header flange.

As it was intended to cement the explosion-proof cover to the header with "Armstrong" A-12 epoxy cement in the threads, a working sensor was sealed in this manner. The response of this sensor taken before and after sealing with A-12 showed no variation beyond that which was normally expected.

Sensor Film Temperature

The film temperature was measured on two samples by means of a thermocouple in contact with the outer surface. The center reading was taken on the WO_3 film sensing area; and the off center reading was taken near one of the platinum clamps. The two sensors used in this test had platinum 20% rhodium heaters. Fig. 7 compares the sensor surface temperature versus voltage applied to the heater. Sensor No. 7 produced 210°C at .9 volts; Sensor No. 8 showed 190°C at .9 volts.

Heat Stabilization Study

Observations by other workers have suggested that the output of the WO_3 sensor to hydrogen falls off with time. To determine if a short bake at an elevated temperature would stabilize the output, five sensors were selected and baked as follows:

Sensor	Hours at Temperature
a	CONTROL
b	2 hours at 300°C
c	2 hours at 350°C
d	1 hour at 400°C
e	1 hour at 450°C

These sensors were then allowed to age in the energized condition and the resistance of each with 1% hydrogen in air at 2 scfh was measured weekly. Table 2 shows the results obtained.

RESULTS

1. The original sensors sent to ASD had to be reworked because of erratic behavior after exposure to 10% hydrogen. Two factors were involved:

a) residual cutting oil in the explosion-proof covers contaminated the WO_3 film.

b) abnormally high film temperatures due to the reaction of the hydrogen (at high concnetrations) with the platinum wire.

2. New sensors were made with nichrome V heaters and rigidly cleaned covers; these sensors operated satisfactorily.

3. Materials and processes have been documented in detail for the fabrication of the WO_3 hydrogen sensor. See attached Materials List.

4. The cover of a sensor cemented with "Armstrong A-12" resin has not affected the response to hydrogen.

5. A heat stabilization study was performed on five sensors. After three months, the response of these sensors showed no significant difference from the control.

SUMMARY

Fifteen development thin film WO_3 hydrogen sensors have been successfully fabricated and delivered to ASD under a NASA contract. Long term evaluations and studies are being performed on these development units by ASD.

A thin film WO_3 hydrogen sensor, based on the earlier RDC invention, has been successfully designed, packaged and evaluated for NASA on a subcontract from Apollo Systems Department. Fifteen

sensors have been delivered and are operating satisfactorily.

The detailed materials and processes used in these development samples are documented.

An exploratory study on the feasibility of age stabilizing the resistance of the sensors by means of a short, high temperature bake showed no significant improvement over control samples.

ACKNOWLEDGEMENT

Consulting advice on theory and experience was supplied by P.J. Shaver (R&DC), J.C. Loh (ADO), and J.R. Macintyre (ASD).

TABLE I

H_2 GAS SENSOR (NICHROME V HEATER)

SUMMARY

Sample	Hours of Aging	Times Activated	Response to H_2 in K Ohms 1%	10%	1%	Heater E	I	No. Test Cycles
G	38	2	170	0.6	220	1.5	.43	10
H	38	2	170	0.9	400	1.5	.43	10
J	38	2	110	1.2	440	1.5	.41	10
K	38	2	50	0.5	65	1.5	.41	10
L	20	1	55	0.5	61	1.5	.42	4
M	20	1	110	0.6	130	1.5	.42	3
O	37	3	160	0.6	170	1.5	.43	5
P	18	3	180	0.2	280	1.5	.46	3
#1	18	2	200	0.9	180	1.5	.41	3

TABLE II

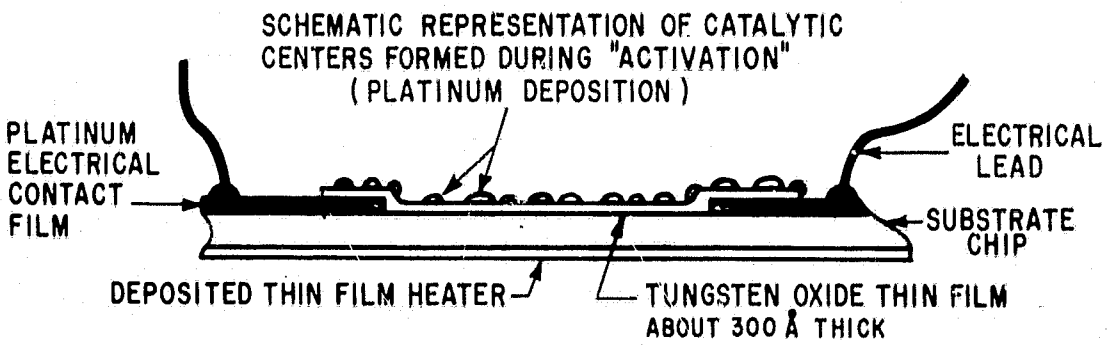
SENSOR RESISTANCE IN K OHMS WITH 1% HYDROGEN VERSUS DAYS OF AGING AT .9V

Days	a	b	c	d	e
INITIAL	41	50	130	11	54
AFTER BAKE	28	1	300	35	150
6	40	9	175	11	21
10	13	4	175	18	30
20	25	1.5	65	2.5	8
27	15	1.5	50	3	11
34	20	1.4	100	2.2	7.5
42	21	2	35	2.4	11
50	10	1	9	2	7.5
64	28	1.7	6.5	2	8
80	10	.8	5.9	1.5	6.5
99	7.2	.68	8	3.3	8.7

MATERIALS LIST

1.	Quartz tubing	1.5 mm OD x 0.5 mm bore type 204 from G.E. Lamp Glass Department
2.	Platinum point	Liquid Bright Platinum Engelhard, Hanovia Liquid Gold Division, E. Newark, New Jersey.
3.	Tungsten oxide (WO_3)	
4.	Platinum sheet stock	.003" thick
5.	Platinum wire	.020" diameter
6.	Nichrome V wire	.004" diameter
7.	Header	Shell Receptacle TS07-12-8P-F2 Environmental Components Inc.
8.	Cover	Sintered Bronze, Grade AB, 45 micron pore size, Sintered Metals Corp.

ACTIVATED OXIDE THIN FILM GAS DETECTOR
BASIC PHYSICAL GEOMETRY



A SCHEMATIC REPRESENTATION

EQUIVALENT ELECTRICAL CIRCUIT DIAGRAM

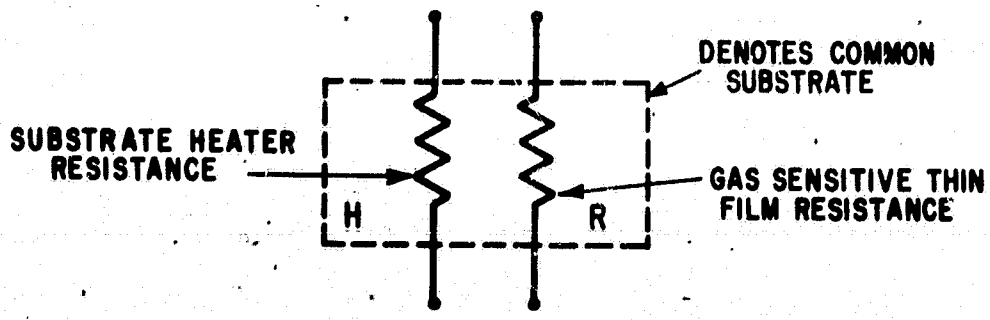
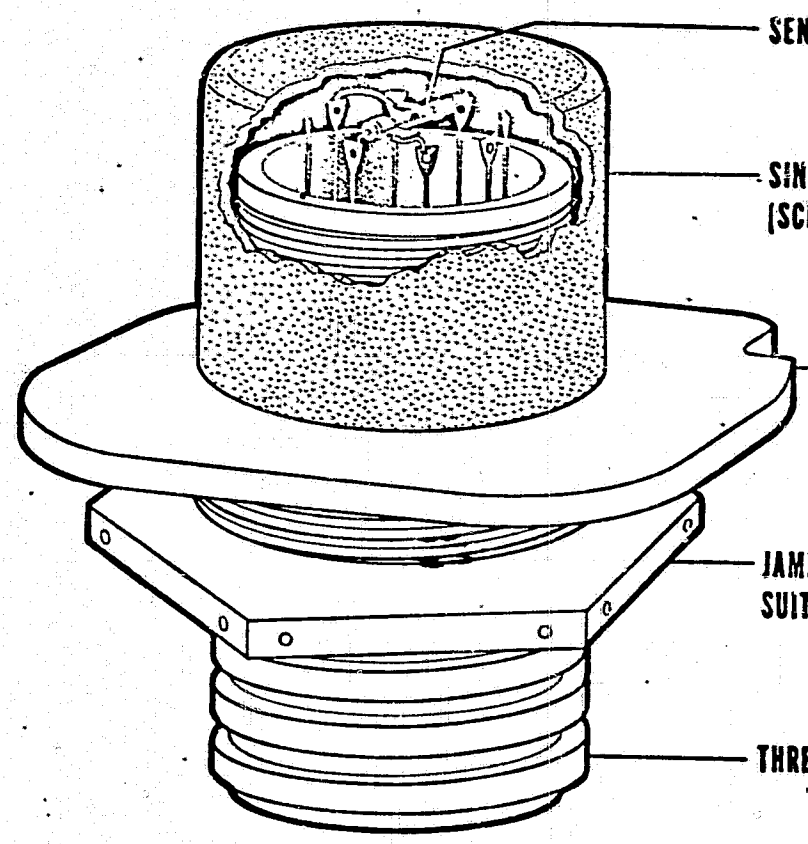


Figure 1

THIN-FILM HYDROGEN DETECTOR



*MATING PLUG TS06-12-8S-F2

Figure 2

GENERAL ELECTRIC COMPANY

TECHNICAL INFORMATION SERIES

NO. DF70MI-04

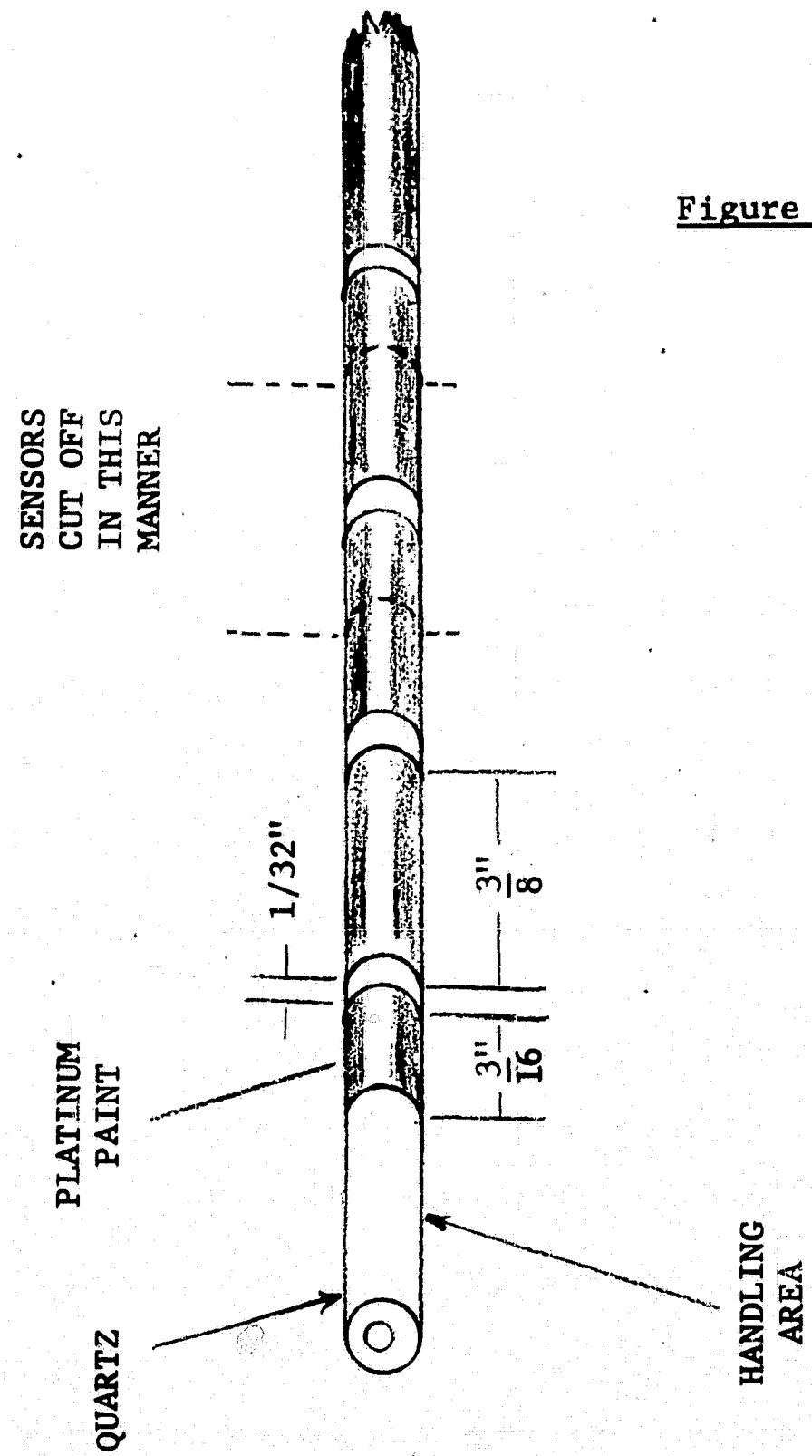
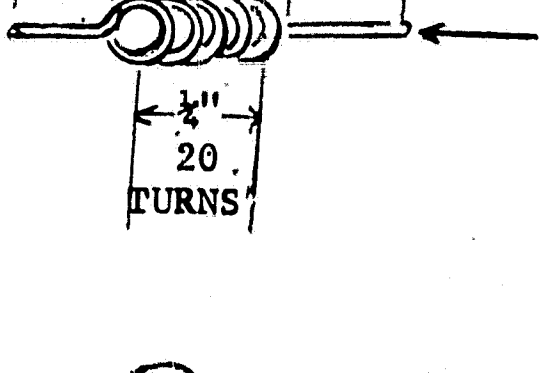


Figure 3

GENERAL ELECTRIC COMPANY

TECHNICAL INFORMATION SERIES

NO. DF70MI-04

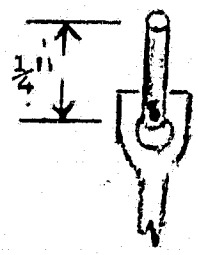


HEATER COIL - .004" NI

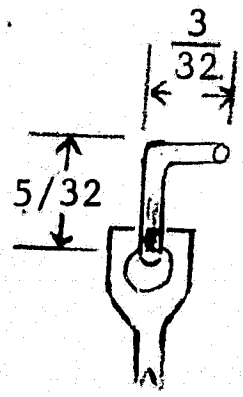
CHROME V, COIL I.D. = .008"

PLATINUM CLAMPS, 2 NEEDED

FORMED FROM 3/8 X 1/16 X .003" BLANKS



PINS E&A .020" PT. WIRE



PINS F & B .020" PT. WIRE

Figure 4

GENERAL ELECTRIC COMPANY

TECHNICAL INFORMATION SERIES

NO. DF70MI-04

WO_3 SENSOR ASSEMBLY

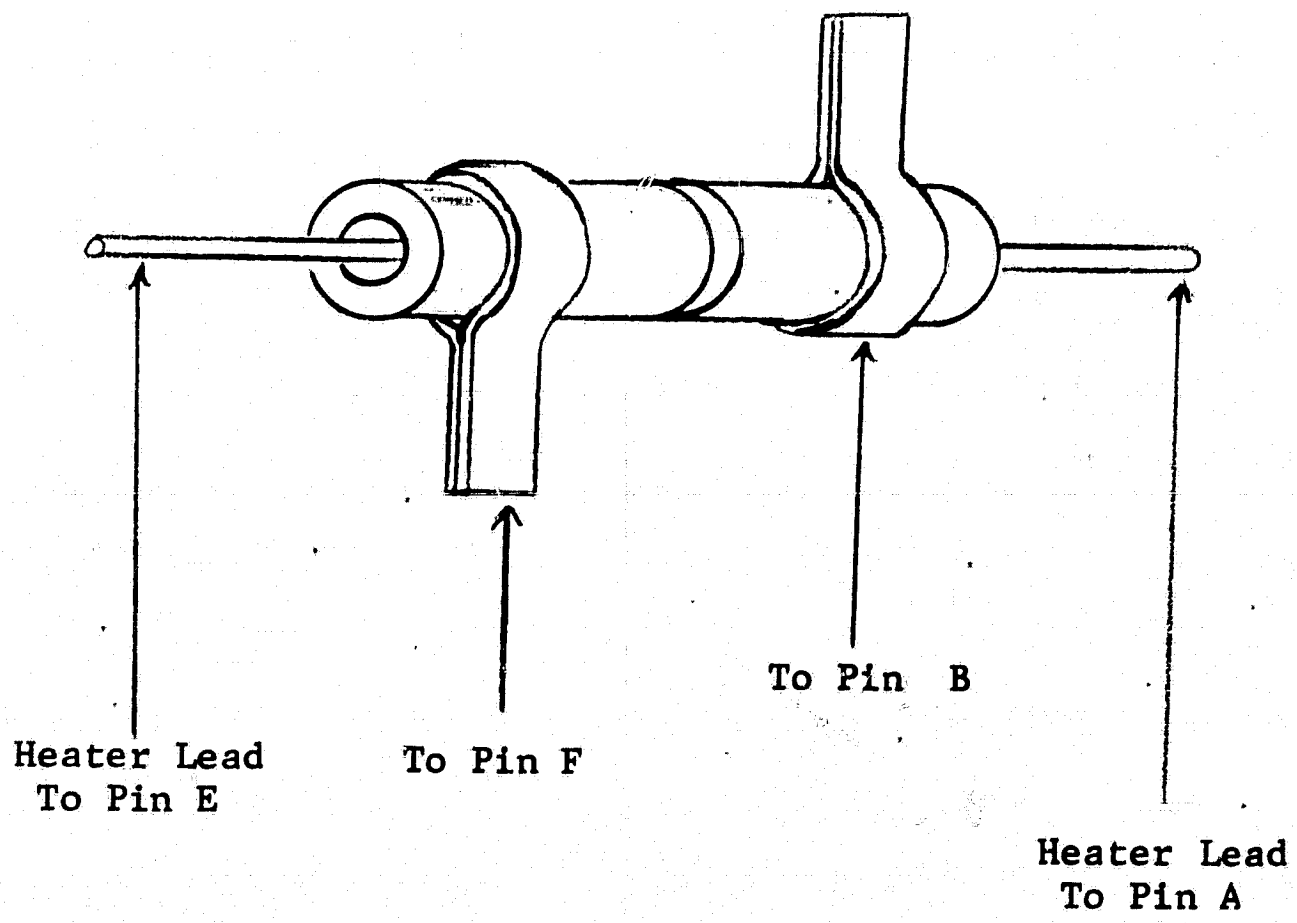


Figure 5

GENERAL ELECTRIC COMPANY

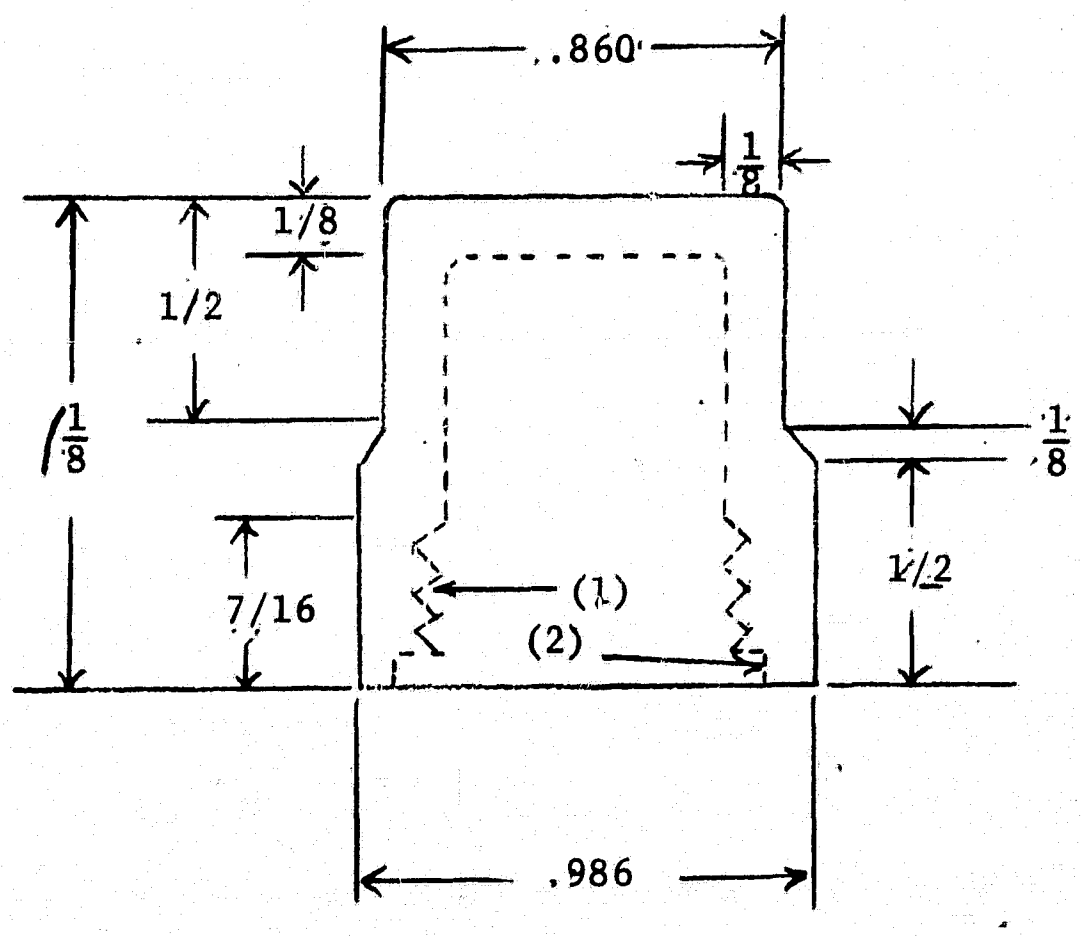
TECHNICAL INFORMATION SERIES

NO. DF70MI-04

Figure 6

H_2 GAS SENSOR
EXPLOSION PROOF COVER

Material - Grade AB Bronze, Sintered (45 micron)



(1) 11/16 X 24 THREAD

(2) 3/4 X 1/8 COUNTERBORE

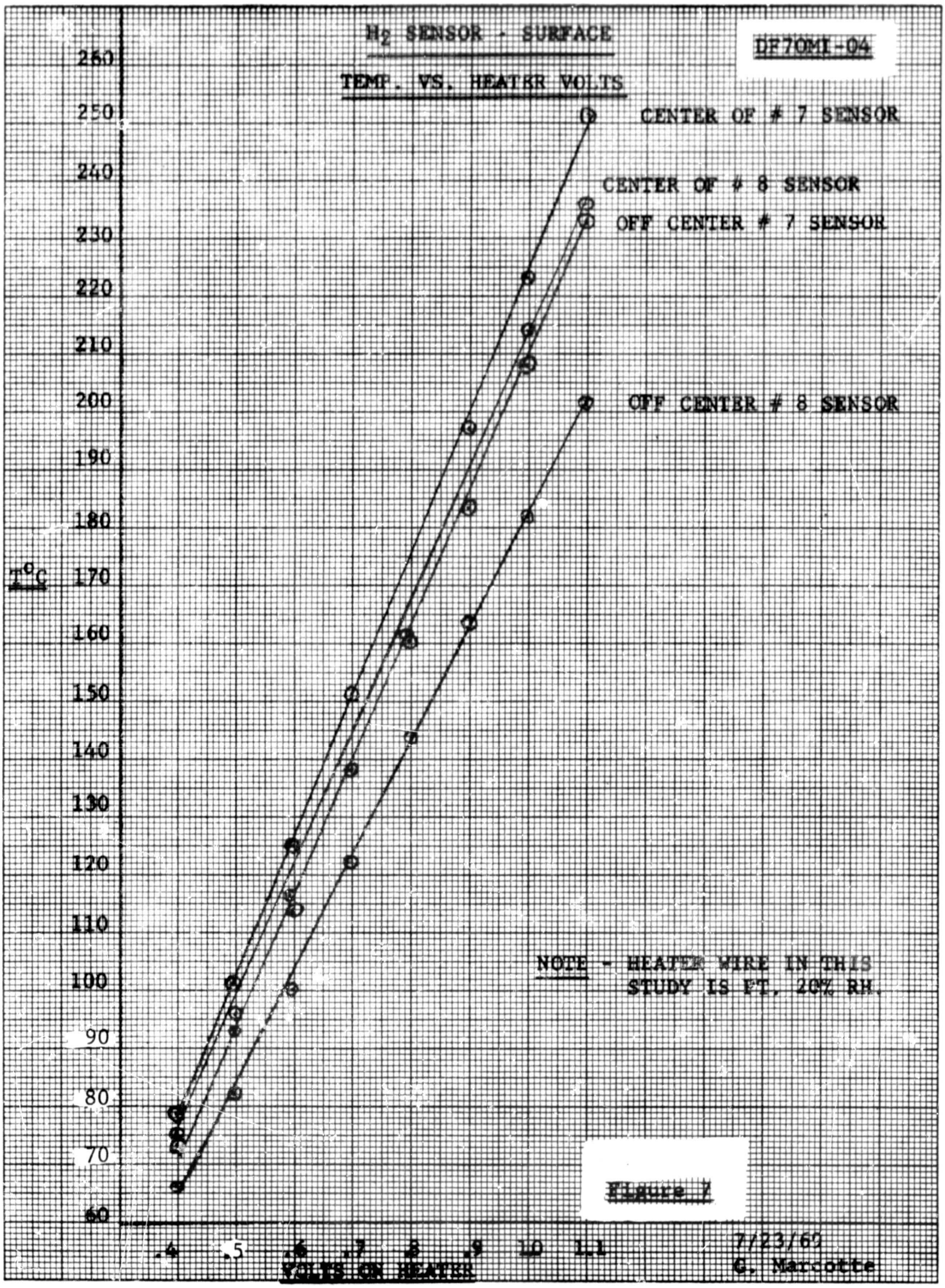


Figure 7