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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Sixteenth Six-Month Report
for the period
1 January 1971 to 30 June 1971

For the
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Grant NGL-03-002-019

CASE FILE
COPY

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I. INTRODUCTION, ABSTRACT AND SUMMARY

This report will cover the work performed from 1 January 1971 through 31 June 1971 on Grant NGL 03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption system for control and separation of gases.

Result to date have included detectors for O_2 and H_2 under partial vacuum conditions (publications 1, 3, 4). Experiments on detectors for use at higher pressures began in 1966, and systems for CO, H_2, and O_2, were reported in 1967 and 1968 (publications 8, 11). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semi-conductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (publications 11, 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of the film (publication 13).

In 1969 studies began on a corona discharge detector for water vapor. This system was shown to be rapid in response, suitable for continuous low power operation and reasonably linear in output (on a logarithmic plot) from 10% R.H. to 75% R.H. A Program to develop this detector for hydrological applications began in 1970. A field usable system was developed for the Hydrology Department and finished in 1971. A unique feature of this system was the fact that no fan was needed. Airflow through the system was induced by the corona discharge itself, (this is often called the Electric Wind Effect).

The electroadsorption phenomena reported in 1968 (publication 12) was extended to bulk ZnO samples by using a gas chromatograph. The objective of developing a controllable electroadsorbent is slowly being realized.

Studies of the reaction between carbon monoxide and palladium have been under way since 1966. In 1970 this work was split into two separate programs; the first one is a study of gas-metal interactions with emphasis on catalysis. The second is a development of the CO/Pd system into a practical system for use by public health groups.

II. SUMMARY OF WORK IN THE PAST SIX MONTHS

A. Carbon Monoxide Detector

This program is now supported by the Environmental Control Administration rather than NASA and will therefore be discussed in Section E (Other Activities in the Laboratory) of this report. Here we shall only comment that the detector operates at CO levels below 50 PPM. A final model of this system is being prepared for delivery to the ECA.

B. Corona Discharge Humidity Detector

The current generated in a point-to-plane corona discharge has been shown to be dependent on the ambient water vapor pressure. The use of a multipoint brush and an ultraviolet source stabilizes the system and maintains sensitivity over a wide range of R.H. The system has been repackaged and tested for use in field studies where only 12 VDC power is available. We have demonstrated that high ambient temperatures ($50^{\circ}C$) do not affect the operation of the device. The field useable system operates without a fan, air is pushed through the system by means of the Electric Wind Effect induced by the corona discharge.

C. Surface Catalysis and Exo-Electron Emission

This program that is an outgrowth of our earlier studies of gas-surface interactions with the mass spectrometer. We have shown that when catalytic oxidation of CO, H_2, or NH_3 begins (on hot platinum) there is emission of nonthermal exo-electrons. This "exo-electron" emission can be used to monitor the progress of catalysis. This exo-electron emission is directly related to the rate of reaction itself. Suppression or enhancement of this exo-electron emission results in an increase or decrease of the rate of catalysis itself.

D. Analysis of Soil Samples by Means of Exo-Electron Emission

One of the major objectives of the planetary landing experiments has been the analysis of rock and gravel type materials. Many techniques have been investigated, but a need for new instruments, of a simple type, still exists. In view of this interest in soil analysis we have been investigating the possibilities of analysing soil samples for their silica content by heating the sample and observing the exo-electron emission. There is definite evidence that the silica content of various materials can be evaluated by exo-electron emission techniques.

E. Thermoelectric Power Supplies for Venus Lander Missions

The planet Venus has a very high temperature and high pressure atmosphere. Typical conditions at the surface are 100 Atm at 750°K. The possibility of a Venus Lander Mission that would transmit data after a soft landing is very attractive from a scientific viewpoint. However, problems of supplying electrical power and operating electronic gear under Venusian surface conditions have held back the development of a Venus Lander Mission.

We have begun investigating the application of a thermocouple power generator for a Venus Lander. The generator would operate between the surface temperature of 750°K and a boiling ammonia sink at 400°K. A single thermocouple with a total cross-sectional are of 3 cm^2 would produce a current of some 13.5 amps at about 1.5 volts, as long as the ammonia lasted.

The Venus surface temperature makes it impractical to use any conventional semiconductor electronics without a severe thermal insulation penalty. However, a corporation recently formed in Tucson is manufacturing a line of new vacuum tubes with indirectly heated cathodes. These tubes, if attached to the inner skin of the Venus Lander would operate when heated to 700°K without <u>any</u> need for electrical heating of the cathode. The application of a thermocouple power generator and a directly heated vacuum tube system to a Venus Lander is certainly deserving of the most careful consideration.

E. Other Activities in the Laboratory

The ARPA-sponsored studies on the relationships between fatigue and subsequent exo-electron emission are continuing. We have shown that if a metal is fatigued to some fraction of its total life and then heated gently, it will emit exo-electrons. This electron current can then be related to the fatigue history of the specimen. We have developed an exo-electron system for monitoring aircraft structures for development of cracks and crack growth during flight. This system will be evaluated by the Air Force and NASA (Langley) during the summer of 1971.

Mr. Michael Pomeroy has finished a wireless device to encourage student response in class. This work was supported by University of Arizona funds and used by Mr. Pomeroy as an undergraduate thesis project. A patent application on this device has been filed by the Battelle Development Corporation in the name of the University of Arizona. At the moment Mr. Pomeroy is working at the University of Arizona Medical College to develop a urine velocity monitor. This work is supported by College of Engineering funds.

Another use of laboratory facilities occurs in connection with two courses taught by Professor Hoenig in Electronics and Instrumentation for graduate students in the Zoological, Geological and Medical

Sciences. These students use the laboratory and its apparatus for demonstration and simple projects. This would be impossible without the long term support that we have received from NASA.

The laboratory is still used occasionally by members of the University of Arizona Lunar and Planetary Laboratory. We feel that this use of NASA supported facilities by another NASA funded project is an important example of how research funds can be conserved by joint use of facilities. Mr. Godfrey Sill of LPL is assisting with the Venus Lander power supply evaluation.

Mr. Robert Goetz has been working with the CO detection system. This carbon monoxide detection makes use of a palladium coil which is exposed to the radiation from a quartz ultraviolet lamp. The Pd wire is heated by DC current to about 200°C, this induces emission of positive ions (Na^+,K^+). The ion current is a function of the partial pressure of CO. The reaction is quite specific, only H_2 or $C\,C\ell_4$ have a similar effect.

A recent calibration curve for this detector is shown in Figure 1. The system is being packaged for delivery to the Environmental Control Administration.

III. DETAILED PROJECT REPORTS

A. Corona Discharge Humidity Detector

Two versions of the system are now operating in the laboratory. The laboratory system has been calibrated again with a substantial improvement in terms of linearity and reduction of scatter. A typical recent calibration curve is shown in Figure 2. We are ready to write up this system for submission to The Review of Scientific Instruments.

The Field-usable Corona Discharge System has been finished and is shown in Figure 3. The system is unique in that no fan is needed to push the air through the detector. The corona discharge induces its own flow by means of the Electric Wind Effect. This has been a severe problem in field applications because fans require low voltage, high current power supplies. This is difficult to do in the field where only a few lead-acid batteries may be available.

The field-useable system obtains the necessary + 3000 VDC from a solid state DC to DC converter operating from a 12 VDC lead-acid battery. The resultant ± 5 volt signal is ready for recording or telemetry. The ultimate plan calls for telemetry of the data to a satellite as it passes over the area.

This system is calibrated by wetting the cloth pad shown in Figure 3 or by passing humid air into the 5 gallon drum. A sample of the air that flows into the corona discharge is picked up by a tube and drawn through a Cambridge Systems Model 880 Dewpointer. A typical calibration system is shown in Figure 4. The output is much larger than that of the laboratory device but begins to drop off drastically below 25% R.H. We are working on this problem and expect to clear it up within the next six months.

B. Monitoring and Control of Surface Catalysis by Means of Exo-Electron Emission

Freedoon Tamjiri

In our last six month report we discussed the experimental system and indicated that the catalytic oxidation of CO or H_2 could be monitored by observing the exo-electron emission from the catalyst during the reaction. We further suggested that the rate of catalysis itself could be changed by enhancing or reducing the exo-electron emission. This has important applications in the control of industrial catalytic processes.

In the last six months we have repeated this work and expanded the study to the oxidation of NH_3. Typical results are shown in Figure 5. The exo-electron current follows the rate of catalysis, if the filament is biased negatively to enhance the electron emission the rate of catalysis also increases. The converse effect, with positive bias, can also be observed but the effect is small. The observations with NH_3 suggest that this effect is a common one and our technique may have wide application in the study of catalytic reactions.

One immediate area of application is the control of hydrazine dissociation ($3N_2H_4 \rightarrow 4\ NH_3 + N_2$). This reaction is used by NASA for spacecraft orientation control. Normally the NH_3 is flow controlled over the catalyst but if the reaction fails to start immediately the fuel can accumulate. Then when the reaction does start an explosion may occur. We are planning to investigate the reaction of N_2H_4 over hot platinum with the hope of demonstrating that the process can be observed and controlled by means of exo-electron emission. If this turns out to be the case, it should be of direct use to NASA. Other investigations of the physical phenomina involved will continue as part of the program.

C. Analysis of Soil Samples by Means of Exo-Electron Emission

William Duffy

When rock-like materials are heated they emit exo-electrons. This so-called temperature-stimulated-exo-electron-emission (TSEE) is characteristic of the material involved and has been used for analysis of lunar material [Ref. 1]. In conversations with the Environmental Control Administration it appeared that TSEE might be a way to analyse ground materials for silica and that excess exo-electron emission from silica might be related to the occurrence of silicosis [Ref. 2].

In view of these two applications we have begun a study of the TSEE from various ground materials supplied by the ECA or available in the laboratory. The apparatus is shown in Figure 6, for a test the specimen is loaded into the holder and heated to 400°C over a 16 minute period. Typical exo-electron current versus time data is shown in Figure 7. In Figure 8 we show the silica content versus the steady state current observed after ten minutes. There appears to be a relationship between the silica content and the exo-electron current.

We are continuing this study with two objectives, first developing TSEE as a possible technique for planetary soil analysis. The other objective will be the demonstration that TSEE can be used for measuring the amount of silica in industrial dusts.

E. Thermoelectric Power Supplies for the Venus Lander Missions

The feasability of a Venus Lander System will depend upon the availability of electronic systems which can withstand the extreme conditions of this mission. This would be very difficult to accomplish with conventional semiconductor devices. However, there is a company in Tucson manufacturing a new type of two-dimensional vacuum tube device. This system was developed at Stanford Research Institute under Air Force and NASA sponsorship. The inventors have established a facility in Tucson called Electron Emission Systems to manufacture these devices under various patents.

A typical system is shown in Figure 9. Electrons are emitted by the indirectly heated cathode, controlled by the grid and collected at the plate. The system is compatable with integrated circuits, very rugged and highly resistant to radiation. The most important characteristic for the Venus Mission is the capability or operation between 450°C and 650°C. This means that the devices should be placed directly inside the skin of the lander, exposure to the 500°C Venus temperature would induce cathode operation. The voltage provided by the thermocouple generator would be sufficient for control and amplification. The complete system could provide adequate power for telemetry from the Venus surface to an orbiting bus vehicle.

A small scale study of this system will continue for the next six months, if it appears that there is interest at NASA a proposal will be prepared by Electron Emission Systems with S. A. Hoenig as a consultant. The details of the thermocouple system are discussed below.

A thermocouple power supply would operate between the surface of the package (assumed to be at the Venus ambient of 750°C or about 500°C) and a boiling liquid stored inside the package. The power output would continue until all the liquid had been consumed. The total power-time integral would be dependent upon the quantity of liquid and its heat of vaporization. The voltage generated by a single thermocouple would be a direct function of the temperature difference.

The cold junction coolant liquid must meet several requirements:

1. It must have a vapor pressure above 100 Atm at some temperature much below 500°C.
2. It must have a critical pressure and temperature which allow it to remain a liquid during the transportation and the Venus-boil-off process.

Very few liquids meet this requirement, for example water has a vapor pressure of 100 Atm at 314°C. We note that the critical temperature for water is 374°C so water is a potential material except that the temperature difference between 500°C and 374°C is relatively small. Ammonia on the other hand has a critical temperature of 132°C and a vapor pressure of 100 Atm at about 127°C. It may be a more practical coolant for our purposes. NH_3 has a very large heat of vaporization (Lv), it is exceeded in this property only by water. However, there is still a substantial difference, Lv for water at 314°C (100 Atm) is 305 $\frac{\text{cal}}{\text{g}}$. For ammonia at 127°C we estimate the value of Lv from the Clapeyron equation

$$Lv = \frac{RT^2}{P} (\frac{dp}{dt})$$

Evaluating $(\frac{dp}{dt})$ from the vapor pressure curve for ammonia (at 127°C) using

$$P = 1500 \text{ psia } (\frac{76}{14.7}) = 7760 \text{ cm Hg}$$

$$T = 400^\circ K$$

$$R = 2 \text{ cal}/^\circ K \text{ mole}$$

$$Lv = \frac{(200 \text{ psia})\ 76 \text{ cm Hg } ^\circ F}{(24^\circ F)\ 14.7 \text{ psia } (0.56)^\circ C}$$

$$Lv = 3180 \text{ cal/mole } ^\circ C \quad \text{or}$$

$$Lv = 187 \text{ cal/g.}$$

This indicates that Lv for NH_3 is about 61% of that for water. The ΔT using water would be 286°C, with ammonia it would be 373°C an advantage of about 30% in favor of NH_3.

Having chosen the collant liquid the next thing is to design the thermocouple power system. We should note that the design of systems of this type is both an art and a science requiring much experience. The design shown below should be considered a first approximation to show that a system of this type can be built. A final design would require many man hours and the services of an organization devoted to this type of work.

Assuming that the landing vehicle can be erected, we show in Figure 10 a proposed design. The vehicle is assumed to be spherical with an outer diameter of about 2 feet. The ammonia container, boil off tube, thermocouple supply and electronics package are shown schematically in Figure 10. After landing, the electronics package would warm up, the thermocouples would provide power while dumping heat to the liquid ammonia. As the liquid vaporized, the vapor pressure would open the dump valve to vent NH_3 vapor as necessary. The system would operate until the ammonia ran out.

The problem of vented ammonia contaminating the local area might be a serious one; however, the reaction $2NH_3 + CO_2 \rightarrow NH_4COONH_2$ may produce a fine powder which will fall rapidly to earth. If necessary the gaseous NH_3 could be contained by a bladder which would inflate outside the lander as the gaseous NH_3 was generated.

To design the thermocouple generator we followed the procedures of Reference 3, (most of the analysis and computations were done by Mr. Steven Bird).

The thermocouple generator design assumes a hot junction temperature of $500^\circ C$ and a cold junction of $127^\circ C$. The TC System is shown in Figure 10, typical element length is assumed to be 1 cm with a total element crossectional area of 3 cm^2. The n type element is 75% $Bi_2\ Te_3$

plus 25% $Bi_2 Se_3$, the p type element is an alloy with composition Ag Sb Te. The open circuit voltage developed by the system depends upon the Seebeck coefficient (α) and ΔT, as $Voc = \alpha \Delta T$. The current is set by $I = \frac{Voc}{R+Ro}$ where R is the source resistance and Ro the load resistance.

Evaluating the coefficients for the temperatures involved indicates that the open circuit voltage would be about 0.148 volts. The current, into a low impedance ($7 \cdot 10^{-3}$ ohm) load would be about 13.5 amps for a power output of some 1.33 watts.

These generators can be operated in series to obtain more voltage or in parallel for more current. In terms of the power to operate the electronics package the 1.33 watts looks quite adequate. The need for a low impedance load can be satisfied by an electronic circuit with a low input impedance and a high output impedance. This circuit would provide the high voltage at low current needed for telemetry.

The rate at which liquid NH_3 would be consumed is a function of heat leakage through the thermocouples and power dissapated at the cold junction. The total heat input at full power output would be about 8.33 watts. This is equivalent to 34.8 calories per second which would be absorbed by the vaporization of 0.186 g of NH_3 per second. This suggests that 1 liter of NH_3 loaded into the vehicle at 20°C and 8.5 Atm, ($\rho = 0.61$ g/cm^3) would weigh 610 grams and operate the thermocouple system at full power for 3280 sec (54.7 min). This should be adequate for the telemetry of data to a bus vehicle.

It would seem that the system is feasible for a Venus Lander. We emphasize that this is a very preliminary estimate of the various parameters. If a system of this type is to be deployed, a much more detailed analysis would have to be performed.

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   TM - 3131 (1970)

2. Chr. Boose et. al
   Naturwissenschaften
   78 (1964) 388

3. S. Angrist
   Direct Energy Conversion, 2 ed.
   Allyn and Bacon, Boston 1971

PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M.S., 1963, Ph.D., California Institute of Technology, Sept. 1969. Presently Research Associate, CIT.
2. George Rozgoni, Ph.D., 1963. Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964. Professor, University of Missouri, Rolla.(Partial NsG-458 support).
4. Maj. C. W. Carlson, M.S., 1965. Active duty, U.S. Army.
5. Melvin Eisenstadt, Ph.D., 1965. Professor of M.E., University of Puerto Rico, Mayaguez, P.R.
6. John Lane, M.S., 1968. Philco Ford Company, Tucson.
7. William Ott, M.S., 1970. Burr-Brown Research Company, Tucson. (Partial NASA support).
8. Richard Pope, M.S. 1970. Hewlett Packard Corporation, Palo Alto, California.

PUBLICATIONS GENERATED TO DATE BY RESEARCH ON THIS GRANT

S. A. Hoenig and Others

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2. "Protection of Copper in High Temperature Air," Rev. Sci. Instr., 35, 904 (1964).

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15. "A Study of Stress Corrosion Cracking of U-10% Mo Wires," in Applications of Field-Ion Microscopy in Physical Metallurgy and Corrosion, Edited by R. F. Hochman, et al., Geo. Inst. of Tech., Atlanta, (Dec. 1969) with H. Sulsona.

LIST OF FIGURES

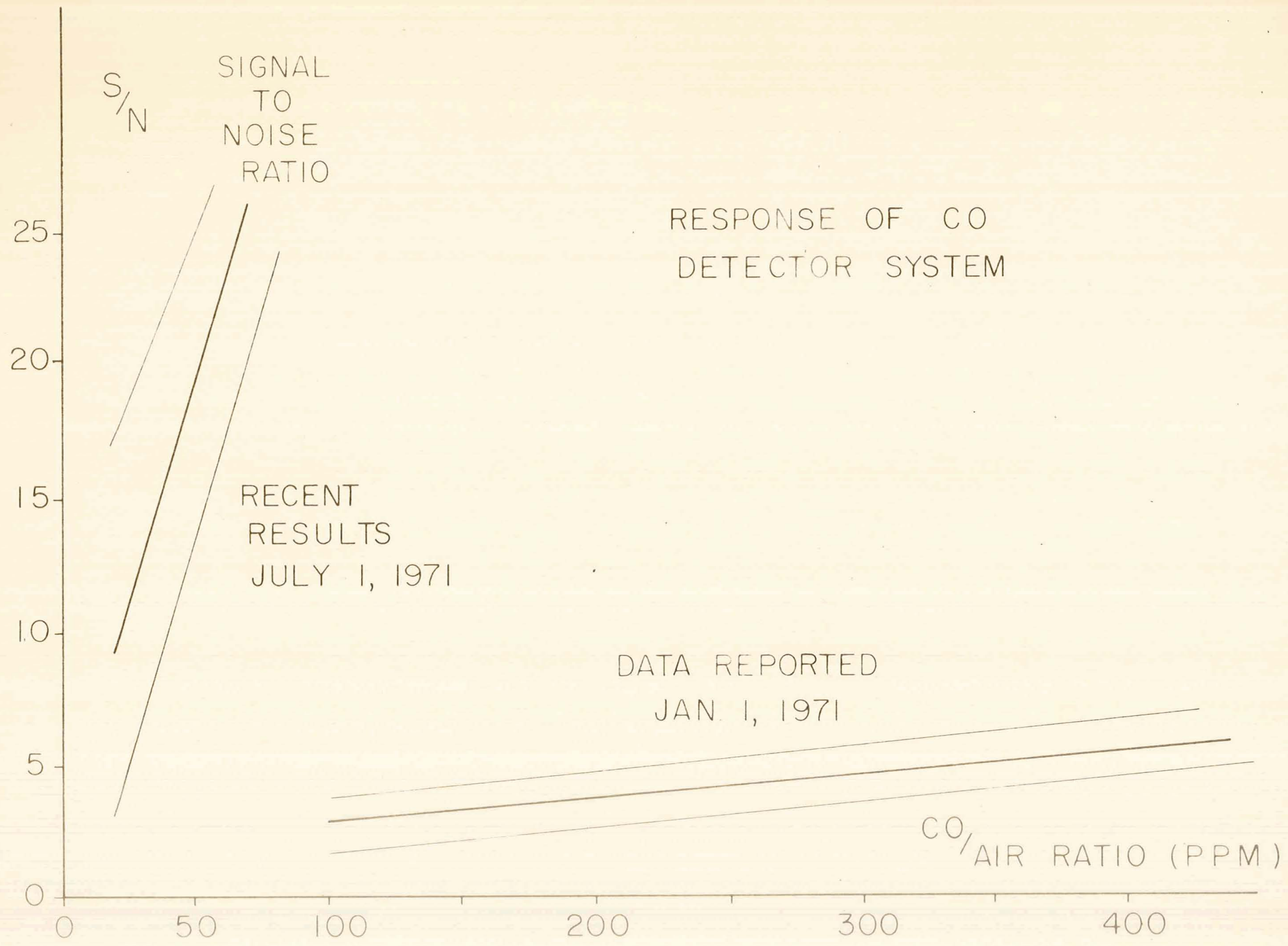

S/N
SIGNAL TO NOISE RATIO
RESPONSE OF CO DETECTOR SYSTEM
RECENT RESULTS JULY 1, 1971
DATA REPORTED JAN. 1, 1971
CO/AIR RATIO (PPM)
25
20
15
1.0
5
0
0
50
100
200
300
400

Figure 1.

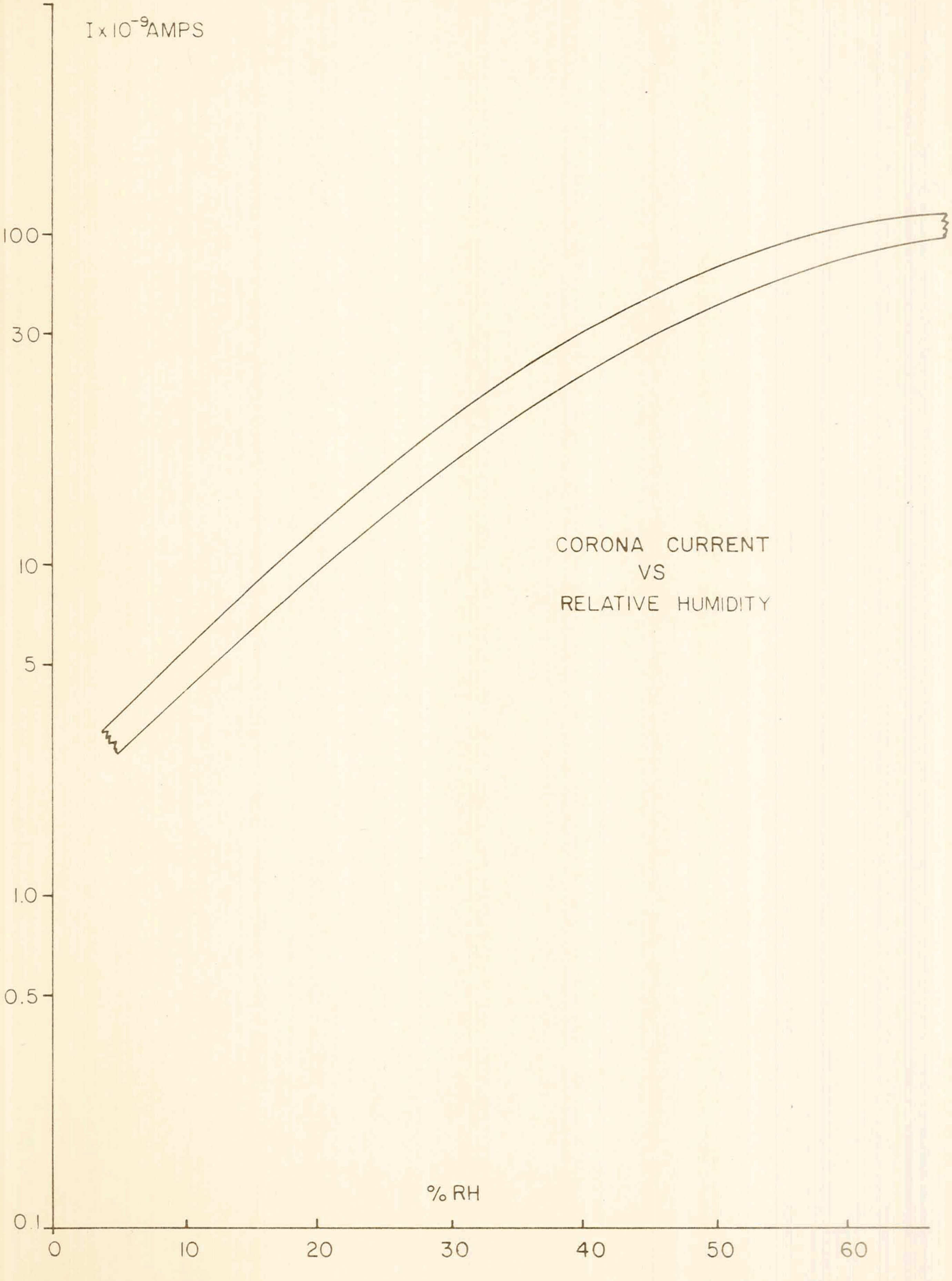
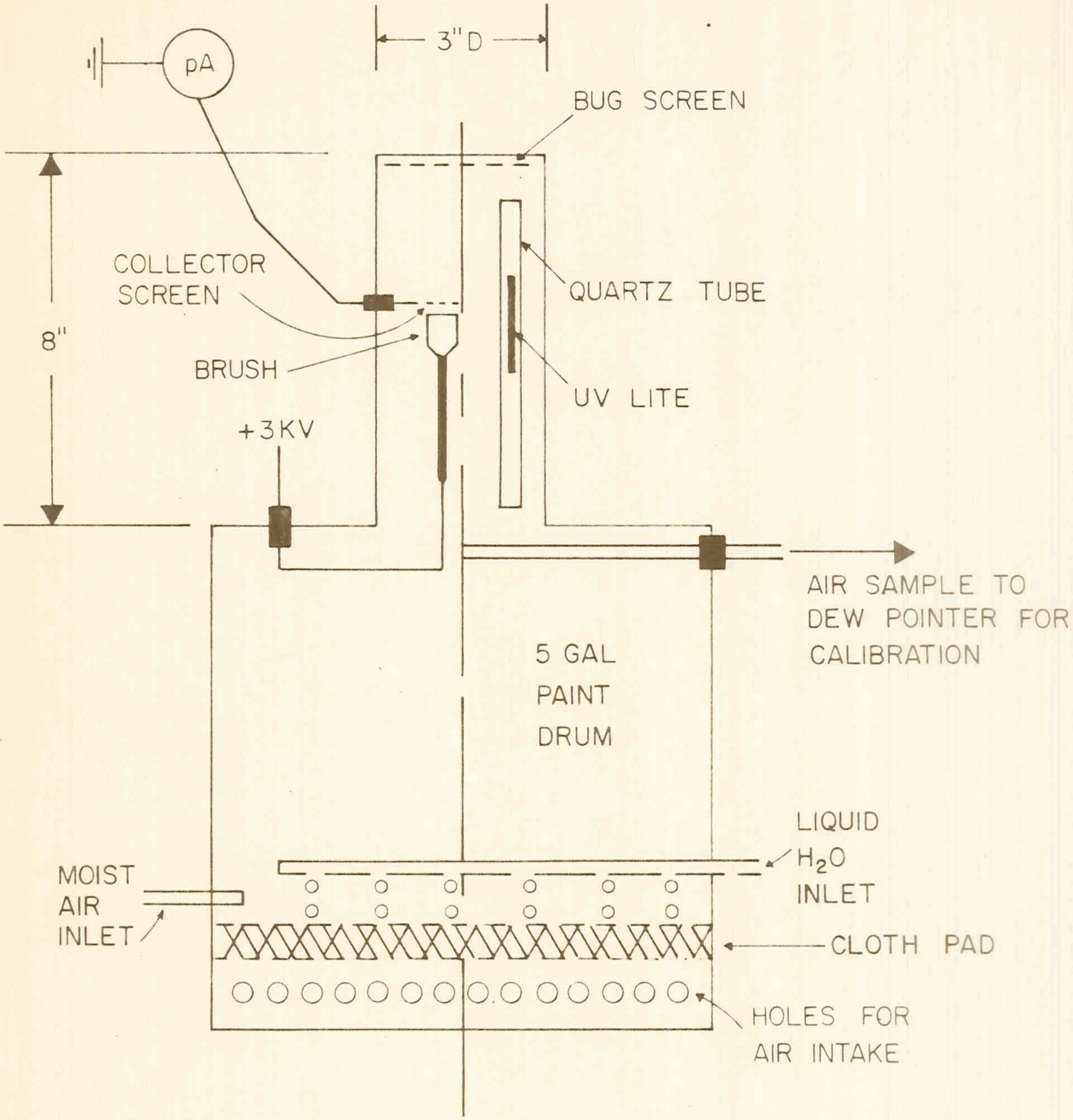
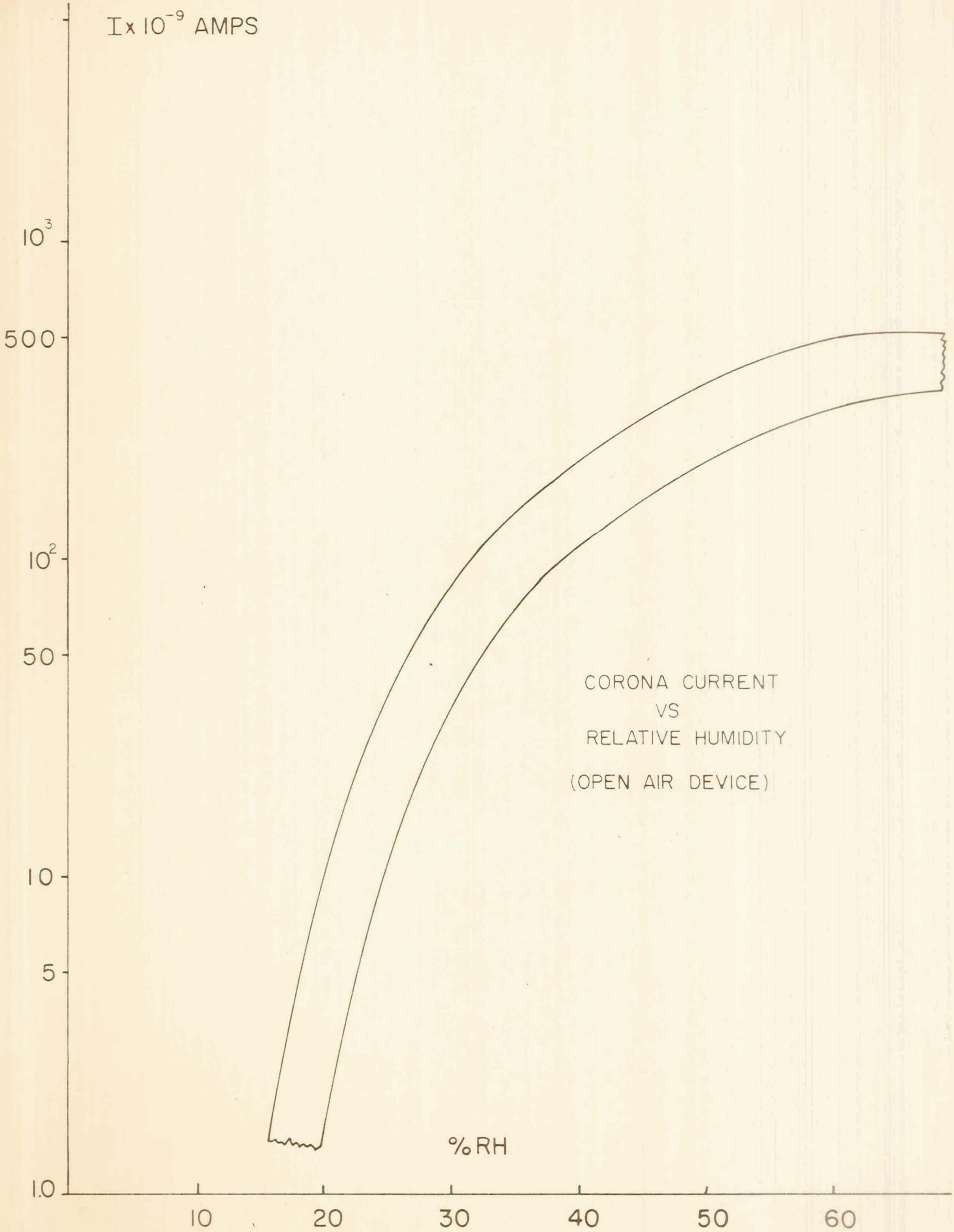

I x 10^{-9} AMPS
100
30
10
5
1.0
0.5
0.1
CORONA CURRENT
VS
RELATIVE HUMIDITY
% RH
0
10
20
30
40
50
60

Figure 2.



CORONA DISCHARGE
HUMIDITY SYSTEM
FOR FIELD USE

Figure 3.



CORONA CURRENT
VS
RELATIVE HUMIDITY

(OPEN AIR DEVICE)

Figure 4.

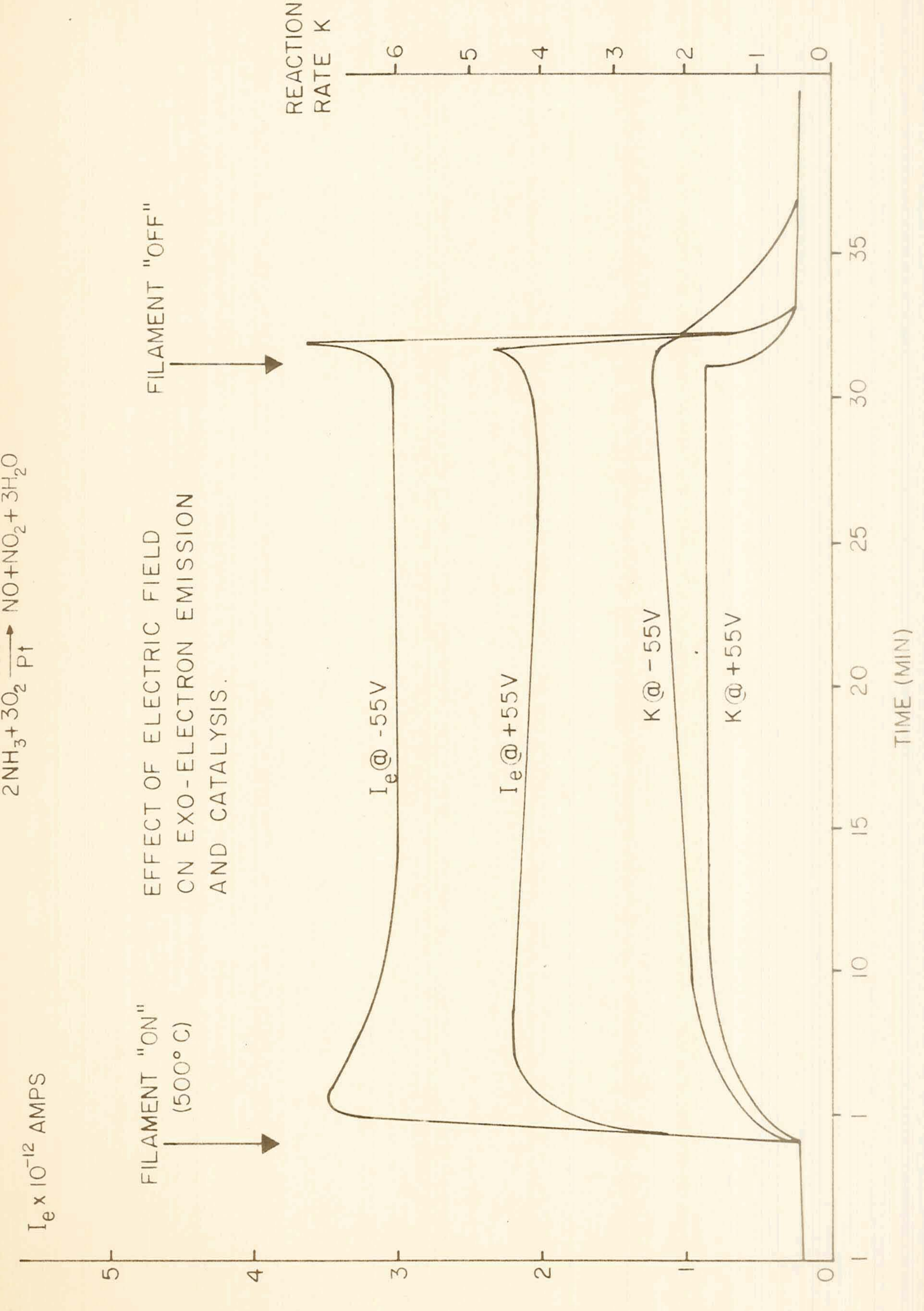
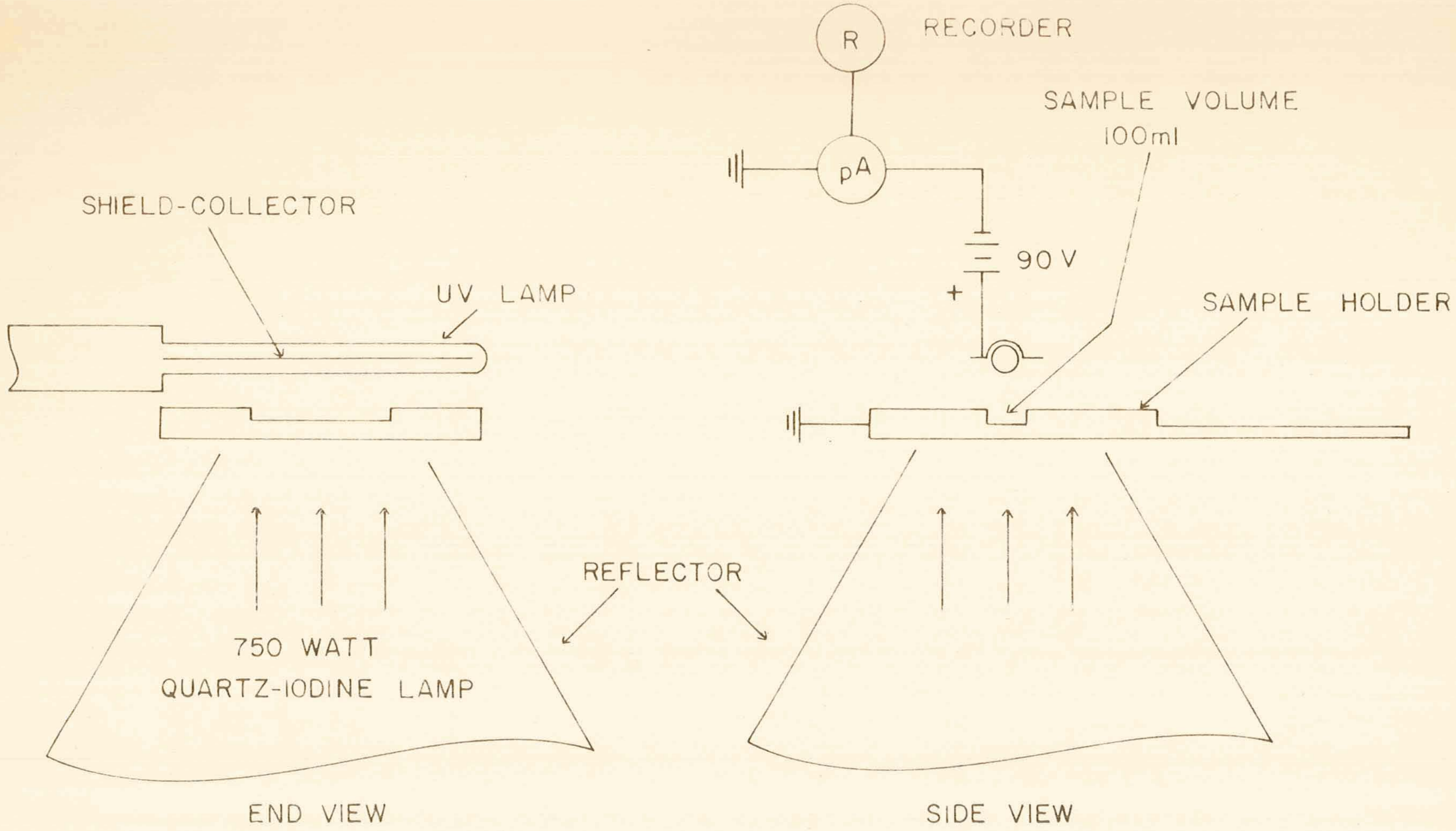

$2NH_3 + 3O_2 \xrightarrow[Pt]{500°C} NO + NO_2 + 3H_2O$
EFFECT OF ELECTRIC FIELD
ON EXO-ELECTRON EMISSION
AND CATALYSIS.
I_e x 10^{-12} AMPS
REACTION RATE K
FILAMENT "ON" (500° C)
FILAMENT "OFF"
I_e @ -55V
I_e @ +55V
K @ -55V
K @ +55V
TIME (MIN)
0
1
2
3
4
5
6
10
15
20
25
30
35

Figure 5.



EXO-ELECTRON POWDER TEST SYSTEM (SCALE NONE)

Figure 6.

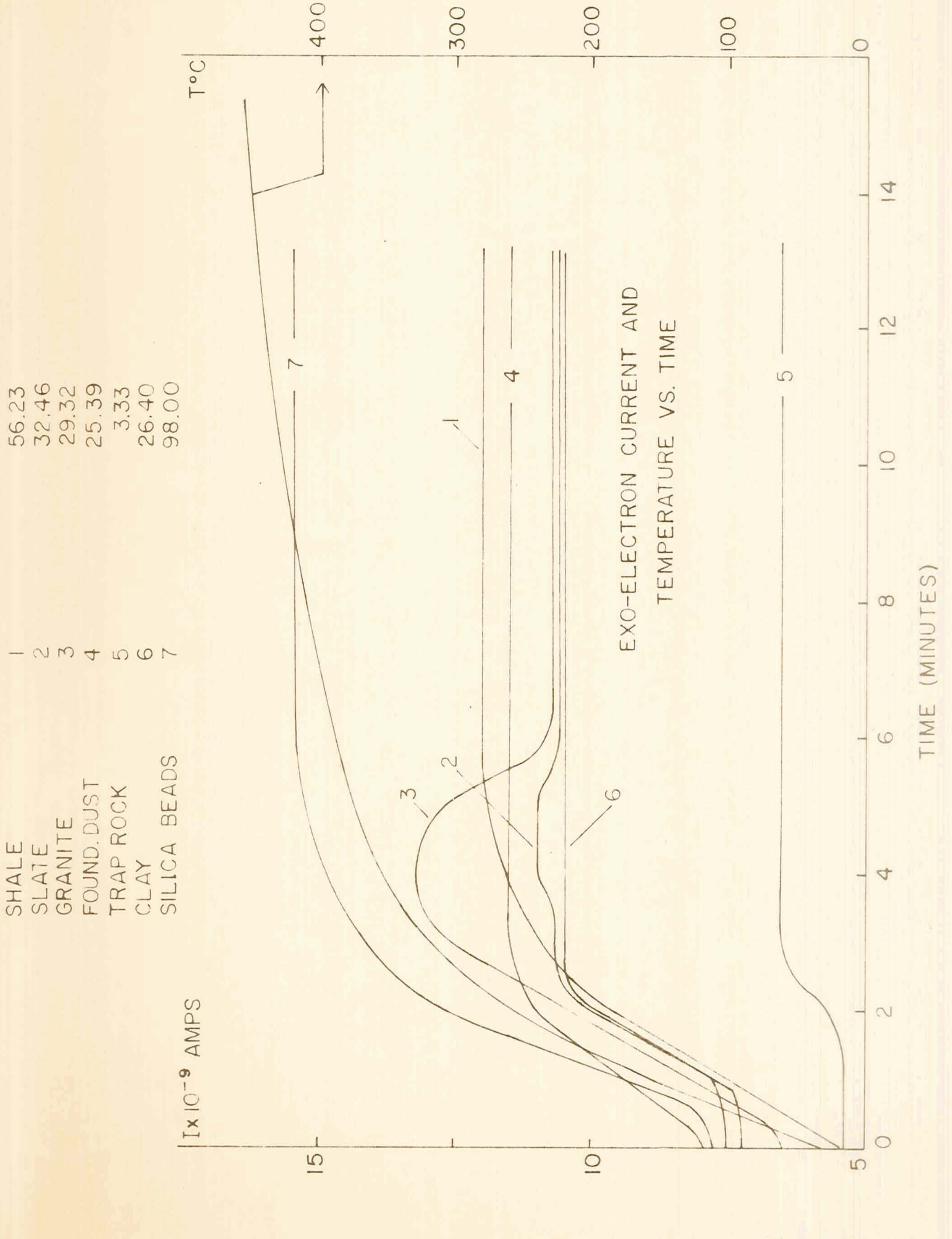
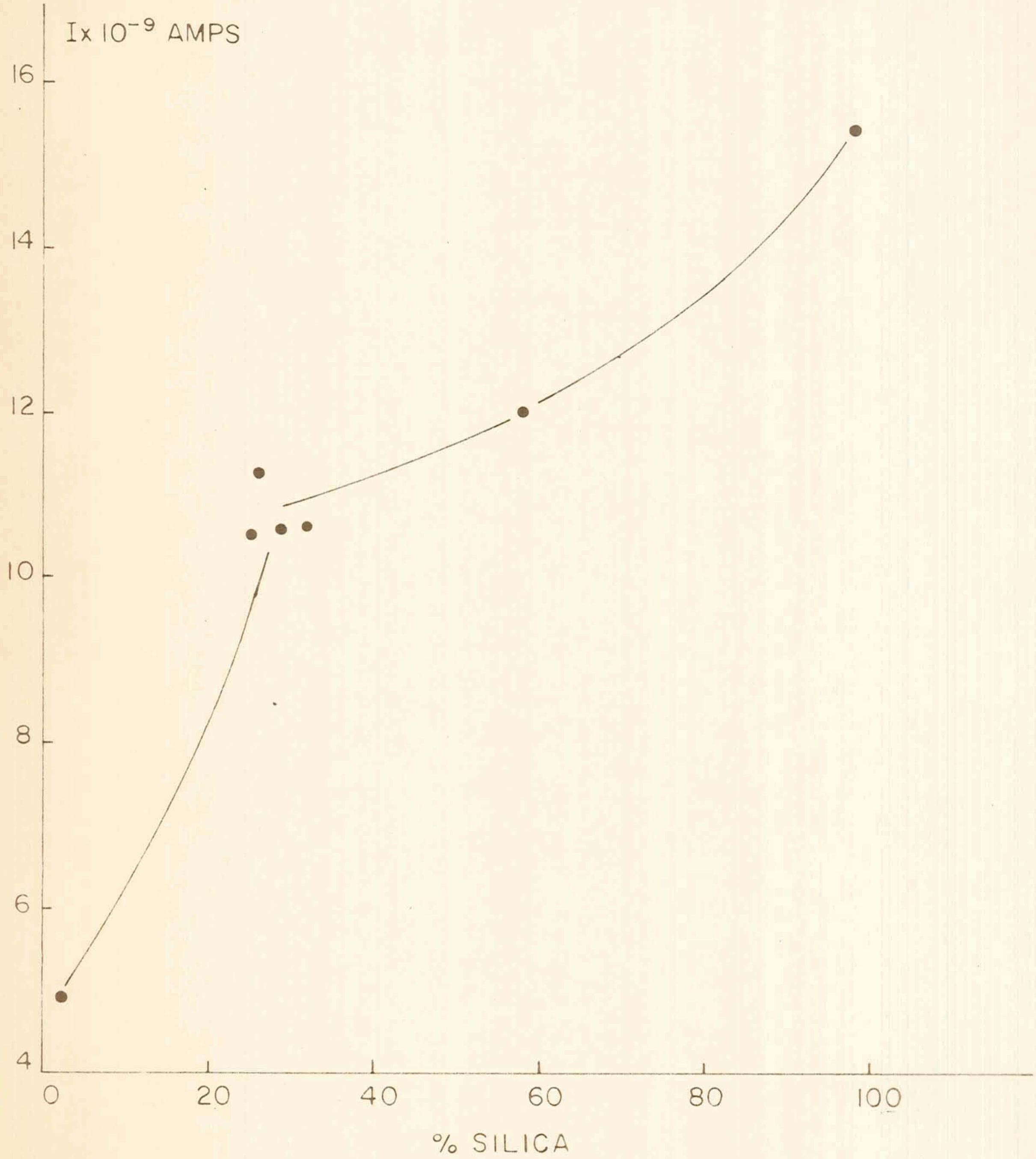
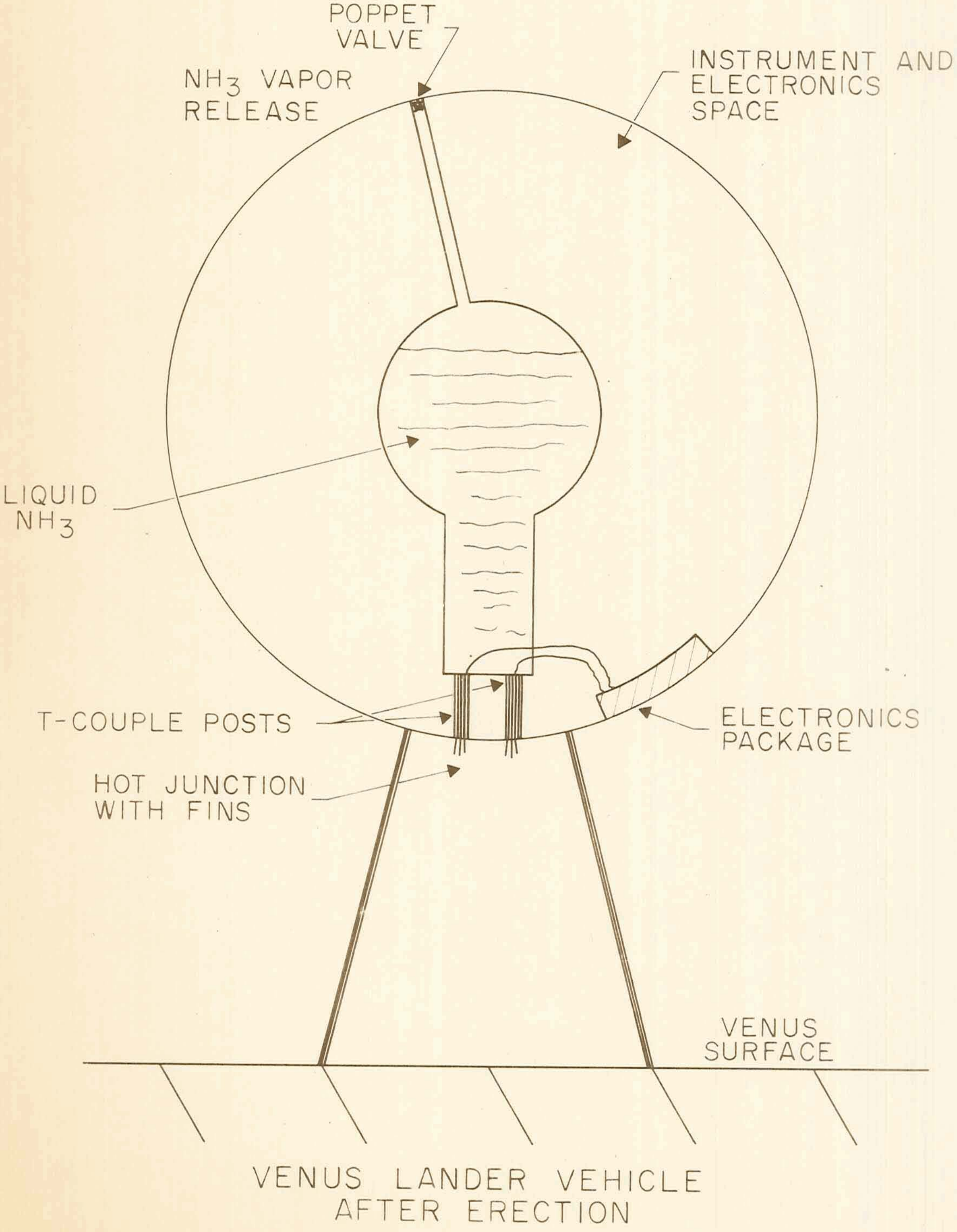

SPECIMEN
% FREE SILICA
SHALE 1 56.23
SLATE 2 32.46
GRANITE 3 29.32
FOUND. DUST 4 25.39
TRAP ROCK 5 3.33
CLAY 6 26.40
SILICA BEADS 7 98.00
I x 10⁻⁹ AMPS
T°C
EXO-ELECTRON CURRENT AND TEMPERATURE VS. TIME
TIME (MINUTES)
0
2
4
6
8
10
12
14
5
10
15
0
100
200
300
400
1
2
3
4
5
6
7

Figure 7.



EXO-ELECTRON CURRENT LEVEL AFTER 8 MINUTES
VS. SILICA CONTENT

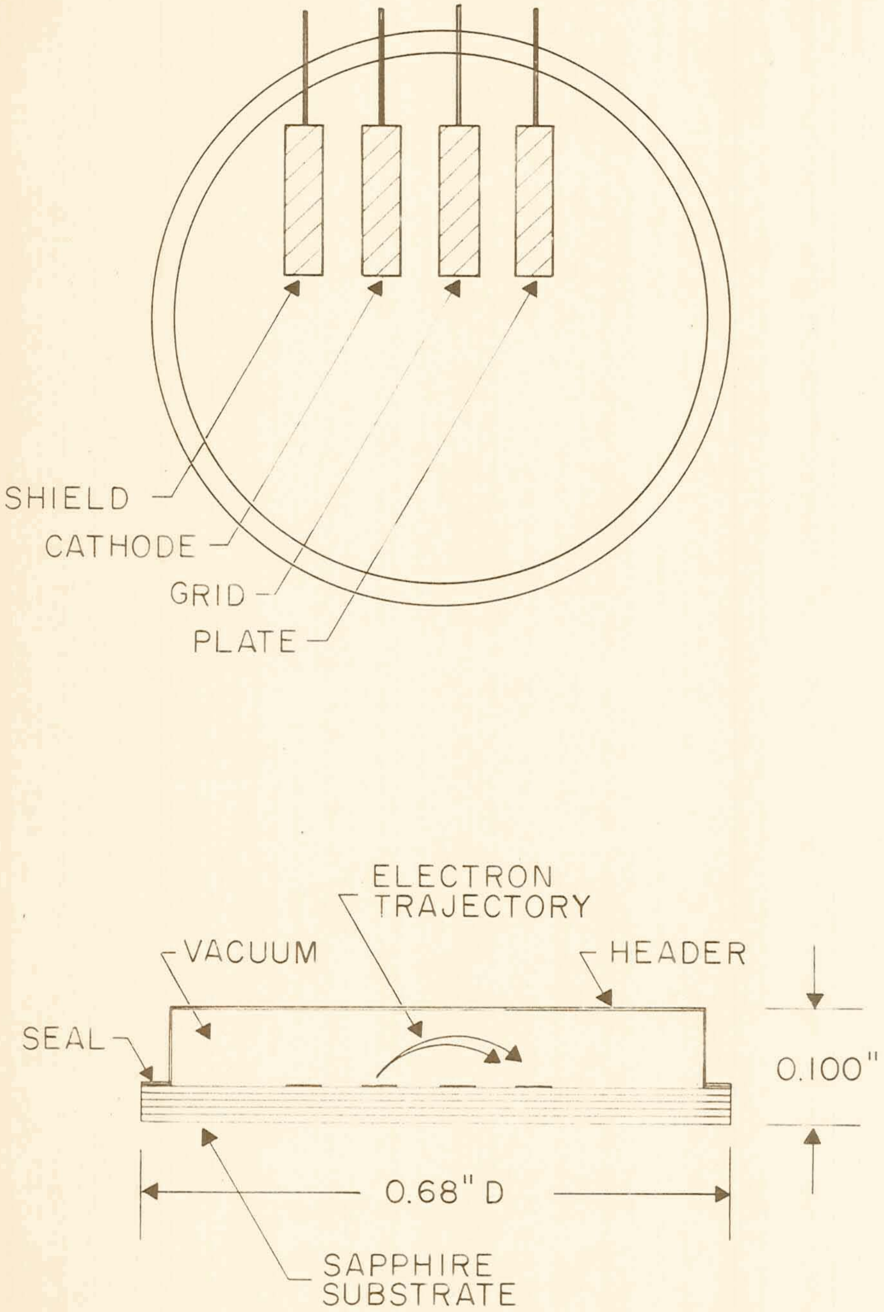
Figure 8.



VENUS LANDER VEHICLE
AFTER ERECTION

SCALE - NONE

Figure 9.



ELECTRON EMISSION SYSTEMS PACKAGE

SCALE - NONE FOR SCHEMATIC PURPOSES ONLY

Figure 10.