DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

I. INTRODUCTION, ABSTRACT AND SUMMARY

This report will cover the work performed from 1 January 1970 through 30 June 1970 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 systems for control and separation of gases.

Results 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, 12). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor 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 (Publication 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 nonreflective 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.

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. Efforts are directed towards gaining an understanding of the physics involved and developing a practical CO detector for The United States Public Health Service.

II. SUMMARY OF WORK IN THE PAST SIX MONTHS

A. CO or H_2 Reactions with Hot Palladium

Studies of the reaction of CO or H_2 with hot palladium indicate that the change in positive ion emission, that occurs when these gases contact the metal, seems to be dependent on a number of reactions. There is evidence that the gas enters the lattice and speeds diffusion of sodium and potassium impurities to the surface. At the same time sulfur and carbon impurities, on the surface, react with the CO and are removed as gases.

When positive ion emission occurs there is also a release of non-thermal exo-electrons. In view of the complexities involved we have split the effort into two parts. The first is a continuation of the basic research with hope that certain new instrumentation will allow us to understand the physics of the process. The second is an effort to apply what we know about the CO/Pd phenomina to construct a sensitive CO detector. This latter work is being funded by the Environmental Control Administration (the old USPHS) under Grant 1R01EC-00467-01.

The two studies are very different in nature but both will be discussed in one section of this project report. At this point we shall only comment that there has been significant progress in understanding the physics of the CO/Pd reaction. The work on the CO detector indicates it will be possible to observe CO in air at the 100 PPM level.

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 is being repackaged and tested for use in field studies. The effects of temperature are the major object of our work at this moment.

C. Electroadsorption of O_2 on ZnO

A new system has been designed and built to make use of the gas chromatograph. We have finally (after 12 months) found a satisfactory way to hold the ZnO, pass gas mixture through it, and apply ultraviolet light while changing the ambient electric field. We are studying the adsorption--desorption reactions of ZnO with oxygen and carbon monoxide.

D. Electron Emission from Thoriated Tungsten as a Detector for Trace Quantities of Water Vapor

This investigation of a possible water detector system, for use in Mars Lander vehicle, has been abandoned. The interference of CO_2, at 5 torr partial pressure, was too great.

E. Surface Catalysis and Exo-Electron Emission

This is a very new program that is an outgrowth of our earlier studies of gas-surface interactions with the mass spectrometer. There are definite indications that when catalysis of the $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ reaction begins (on 700°C platinum) there is emission of nonthermal exo-electrons. We are just starting this investigation, so only limited data is available, but the phenomena exists and is repeatable. The possible implications, in terms of an understanding of catalysis, are great.

F. Other Activities in the Laboratory

The ARPA-sonsored 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. A talk on this new technique for non-destructive testing will be given at UCLA on September 2, 1970. A copy of the manuscript is attached as Appendix A, the work was done by Mr. Ott as part of his studies for the MSEE degree.

The program has been extended to 1971 and we have expanded the effort to include a study of exo-electron emission from thin films in which current induced mass migration is occurring.

Mr. Michael Pomeroy is working on a wireless device to encourage student response in class. This work is supported by University of Arizona funds and will be used by Mr. Pomeroy as an undergraduate thesis project. The mode of operation and objectives are described in Appendix B of this report.

Mr. Leland Payne is using the laboratory for developing the various components of a State-wide Medical Telemetry System that will connect the various outlying community hospitals to the University of Arizona Medical School. This project will be used by Mr. Payne for His Ph.D. (EE) dissertation.

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. The University of Arizona Medical School feels that future physicians *must* see and learn about modern scientific apparatus from mass spectrometers to gas chromatographs. This would be impossible without the long term support that we have received from NASA.

In connection with these courses a textbook entitled *Electronics Without Pain* is being prepared by Hoenig and Payne. It is our hope that one or more sequences of this type will be a definite part of the Medical School curriculum.

The laboratory is still used regularly 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.

III. INDIVIDUAL PROJECT REPORTS

A. CO or H_2 Reactions with Palladium

Robert Goetz and Freedoon Tamjidi

Mr. Richard Pope has finished his MSEE work on the interactions of CO, H_2, N_2, and O_2 with hot palladium. The phenomena involved are complex; we have observed changes in positive ion current when any of the above gases contact hot palladium. At the same time there is evidence that surface impurities are reacting with ambient CO or H_2 and releasing the products of reaction into the gas phase. This is further complicated by an apparent release of exo-electrons, from Pd during the reaction.

The change in positive ion emission is thought to depend upon the gas entering the metal lattice and increasing the rate or diffusion of sodium or potassium along grain boundaries. A recent report from the USSR gives convincing evidence that this is in fact the case, Reference 1. The USSR data was obtained with O_2 on Pt but the similarities to our own results are so great that one simple experiment with a Pd will settle the question.

In essence Reference 1 showed that plastic deformation of a Pt foil stops all effect of O_2 on positive ion emission--until the dislocations due to the deformation are annealed out. This then ascribes the effect of stress on positive ion emission to dislocations moving through grain boundaries and interferring with diffusion of sodium and potassium. A test of this mechanism will be run in the next six-month period.

With respect to the exo-electron emission, observed when CO or H_2 contacts Pd, we have no suggestions as to the mechanism. The problem seems quite complex and because of this we have chosen to take two seperate courses; Mr. Robert Goetz is working on our PHS contract to develop a detector for CO at the 30 PPM level. Here we are looking at the reaction from a pure engineering point of view to build a CO detector that works without worrying about how it works. To attain this objective we have looked at the ion and electron emission to determine which type of emission would yield the highest signal to noise ratio with dilute CO/air or CO/N_2 mixtures. A typical result is shown in Figure 1, by using two collecting and recording systems the electron and ion currents at the same time.

Mr. Goetz has decided to use the positive ion current as a measure of the CO/air ratio. To improve the sensitivity and signal to noise ratio he has investigated various "treatments" of the palladium filament. This idea of "treating" or "promoting" the filament is a purely empirical technique based on the fact that Pd is improved as a catalyst by certain "treatments". (We believe that a connection *must* exist between the response of Pd to H_2 or CO and its effectiveness as a catalyst for the oxidation of these gases.)

The promotion techniques have involved the use of palladium black, NaOH deposited from a water solution and the natural oxide that develops when Pd is heated in oxygen. The results are shown in Figure 2. The Pd/Pd black filament gave no exo-electron emission and an erratic positive ion emission. The Pd/NaOH filament yielded an intense exo-electron emission and no ion emission. The Pd/oxidised in O_2 filament produced an intense and stable ion emission but no exo-electron current. The data was quite repeatable but for obvious reasons we will not try to discuss the physics of the various phenomena. Mr. Goetz has looked at the signal to noise ratio, for detection of CO, of these treated filaments and he has chosen the Pd heated in oxygen for further study. This filament treatment can be expected to remain unchanged by continued operation in air.

The work to date has involved development of an accurate filament temperature control system. Precision flowmeters have been installed and calibrated to provide controlled CO/air ratios down to 30 PPM (0.003%). At the moment CO/air ratios of 400 PPM can be easily observed, extension to 100 PPM will be accomplished in the next six months.

Another part of the PHS program involves a survey of the existing commercial detectors for CO. This work is being done by Miss Beverly Martin, she will compile this data into a bibliography that covers every CO detector that has been reported in open literature.

The first basic research work in this area will be the O_2, CO, Pd dislocation study discussed above. We are considering the construction of a soft X-ray spectrometer for analysis of surface impurities. This instrument is quite sensitive to the carbon and sulfur impurities that have plagued researchers working with palladium. It is also much simpler to build than the conventional Auger or LEED systems.

This technique was developed by Park and Houston at Sandia Base in Albuquerque, New Mexico. We are trying to set up a two week visit for Professor Hoenig at Sandia in August. This would facilitate seeing the device in action and permit us to make a decision about building one for the laboratory.

B. Corona Discharge Humidity Detector

Mark Carnes and Steven Bird

In our last report we discussed the repackaging of this detector in a sturdy metal container and presented a typical calibration curve for the 10% - 70% R.H. range. In the last six months we have built a heater system so that we could investigate the effects, if any, of high ambient temperatures. Summer temperatures over 115°F are not uncommon in Arizona deserts.

We have also obtained an Alnor Dew Pointer* to calibrate the system. There has been a long standing problem with the wet and dry bulb hygrometer in that its accuracy diminishes at high R.H. where the wet and dry bulb temperatures differ by only a few degrees.

Preliminary results with the air heater indicate that the Corona Discharge is not seriously affected by high temperature ambients. The Alnor Dew Pointer may have solved the somewhat puzzling change in slope that we have observed above 70% R.H. This change in slope was the reason that we had limited the proposed applications of the detector to

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*The assistance of Mr. Christian Savitz and his former associates at North American Rockwell Corporation (Air Maze Division), Cleveland, Ohio is gratefully acknowledged.

70% R.H. or less. Apparently the problem was more in the wet-and-dry bulb than in the corona device itself. This is encouraging and we are proceeding with calibration up to 90% R.H.

We are hoping to design apparatus for calibration below 10% R.H. but this will require at least another six months. This is an undergraduate project and the pace is somewhat slower than a typical graduate research program. Mark Carnes is no longer working on the program, Mr. Bird will continue the studies as part of his EE undergraduate program.

C. Elecroadsorption of O_2 on ZnO

Brad Frazier

In our earlier reports we discussed the electroadsorption of oxygen type gases on ZnO. It was demonstrated that ZnO could serve as a controlled and specific adsorbent but the application of this effect required more study and development. To further this work, we purchased a Hewlett-Packard Model 700 gas chromatograph. This instrument and the ancillary gas handling apparatus was described in our last report.

During this period we have built a ZnO experimental column which appears to satisfy the complex requirements of this experiment. The column is shown schematically in Figure 3. The inner tube is a G. E. quartz tube mercury lamp. This is wrapped with fine brass screen which serves as the inner electrode. There is a space of some 5 mm to the counterelectrode (a film of stannous oxide on the inside of the outer pyrex tube. The ZnO is in the 5 mm space between the electrodes. We have found that it is necessary to mix a separation material with the

ZnO to prevent excessive pressure drop in the gas flow system. The present experiment makes use of 0.5 mm quartz sand material. The sand and ZnO (N. J. Zinc Company, USP-12) are mixed in the ratio of 3 sand to 1 ZnO by volume and packed into the column with a vibratory feeder.

The experiments to date have been devoted to studying the adsorption of oxygen and carbon monoxide on the ZnO in the presence of UV light. Typically the O_2 or CO is pushed through the system by a carrier gas (He or N_2), and the column inlet and outlet are monitored by the gas chromatograph. Typical results of this experiment are shown in Figure 4. With the ultraviolet light off the oxygen passes through the ZnO column without noticeable adsorption. With the UV light on the oxygen is strongly adsorbed for several minutes until the ZnO is saturated with oxygen. At the same time a release of CO_2 is observed which we suggest is partially due to a reaction between residual carbon in the ZnO and the O_2 passing through the system. The remainder of the CO_2 is thought to be due to displacement of CO_2 by oxygen on ZnO.

These replacement reactions have been observed by Saltsburg [2]. It is most interesting to observe that in this case the presence of UV *induces* O_2 adsorption. Exactly the *opposite* effect was observed with the ZnO thin films used for our earlier experiments. At the moment we have no explanation for this phenomena but we suspect that it is due to impurities in the ZnO. Bulk ZnO is difficult to manufacture at high purity levels (the A. R. grade is only 99.0%)

We have not run electric field experiments on this material because the strange O_2 adsorption reaction makes it very difficult to know what to expect. There is also a question about the heating effect of the quartz UV source. At present the ZnO is in direct contact with the quartz tube and the tube does get hot from the discharge. However we do not feel that effects reported above are due to thermal heating, because of the similarity to the work of Reference 2 where thermal effects were excluded. To remove any thermal heating effects except those due to the UV light itself, we are designing a reaction system which allows for a flow of cooling air over the quartz tube UV source.

With respect to the CO_2 desorption we have suggested that a reaction of the form $C + O_2 \rightarrow CO_2$ is responsible. This seems reasonable in view of the well known activity of ZnO as a catalyst for the $CO + \frac{1}{2}$ $\rightarrow CO_2$ reaction. We have studied the response of the ZnO system to CO but the data is not yet complete because of leak problems in the CO handling apparatus.

D. Surface Catalysis and Exo-Electron Emission

Freedoon Tamjidi

In our earlier reports we discussed certain experiments that indicated a connection existed between chemisorption and exo-electron emission. Further evidence of this effect is given in Section III-A of this report.

Surface catalytic phenomena is known to depend upon chemisorption and for this reason we decided to see if a correlation existed between catalysis and exo-electron emission. If such a correlation did exist it might be an opening to understanding the phenomena we call catalysis. There is some evidence for the above ideas from the work of Lee [3] who showed that electrostatic fields did have an effect on the catalysis of oxidation of CO over Ni. We chose to look at a simple reaction first studied by Faraday and then by Langmuir [4]. It is interesting to note that this $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ reaction on hot platinum was studied by Langmuir in 1922. He commented that very little progress had been made in this area since Faraday's work in the era about 1850. This comment might well be repeated to describe the situation in 1970.

The University of Arizona's experiments have made use of the EAI Quad 250 mass spectrometer and associated apparatus used by Mr. Richard Pope for his MSEE thesis. The catalyst is a platinum wire, the reaction is $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ with an excess of O_2. We follow the rate of reaction, at a total pressure of 10^{-5} torr, by monitoring the H_2O (MN - 18) peak. The exo-electron emission is observed with a + 10 volt collector and a Keithley picoammeter. The Pt filament is operated at about 700°C to induce the catalytic reaction. At this temperature there is no thermal electron emission.

We have observed emission of electrons from the Pt during the catalytic process and a plot of emission current and catalytic rate versus time is shown in Figure 5. There is a *direct* correlation between the gross exo-electron current level and the rate of catalysis. It is important to note the drop in electron current that occurs after 480 seconds of operation. This drop *always* occurs if operation continues long enough and may be due to the conclusion of some surface distortion or diffusion phenomena. The time from the start of catalysis until the current drop occurs is dependent upon the filament temperature. At

800°C the time involved is in the order of minutes, at 600°C, hours are required. This suggests that during the start-up phase some surface rearrangement is occurring (catalysts are known to become "grooved" and distorted in service). A most puzzling fact is the speed with which the current drops, this seems very strange and inexplicable at the moment.

A few preliminary experiments with the $CO + \frac{1}{2} O_2 \rightarrow CO_2$ reaction indicate that the same sort of exo-electron phenomena exists but the time scale is entirely different.

We have suggested that this exo-electron emission is due to surface rearrangement that occurs when the filament is heated. This modified surface is somehow more suitable for catalysis of the reaction than the surface state which exists at room temperature. Interestingly enough another very short burst of exo-electrons is observed when the filament heating current is turned off. This may represent the relaxation of the surface structure to its equilibrium configuration. The rate of catalysis does begin to decrease as the wire cools indicating that a less favorable catalytic situation is developing.

It is most interesting to speculate on the questions:

1. What is the significance of the fine structure in the exo-electron current shown in Figure 5?
2. Can we use exo-electron emission to investigate the induction period when a catalyst first begins to act? (Many catalysts are inefficient until they have been in use for some time--this is called the "induction" phase.)

3. If the exo-electron emission is retarded or enhanced by applying electric fields, will this affect the rate of catalysis?

These topics will be investigated by Mr. Tamjidi for his MSEE thesis.

IV. 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 Rozgonyi, 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. Associate Professor, University of California, Santa Barbara.
6. John Lane, M.S., 1968. Philco Ford Company, Tucson.
7. William Ott, M.S., 1970. Burr-Brown Research Company, Tucson. (Partial NASA support.)

V. PUBLICATIONS GENERATED TO DATE BY RESEARCH ON THIS GRANT

S. A. Hoenig and Others

1. "Chemisorption Detector for Oxygen," *Rev. Sci. Instr.*, *35*, 15 (1964), with D. Collins.
2. "Protection of Copper in High Temperature Air," *Rev. Sci. Instr.*, *35*, 904 (1964).
3. "Chemisorption Detector for Hydrogen," *Rev. Sci. Instr.*, *36*, No. 1, 66 (1965), with M. Eisenstadt.

4. "Change in the Thermionic Emission Current of Palladium Due to Chemisorption of Atomic and Molecular Hydrogen," *J. Chem. Phys., 45,* No. 1, 127-132 (July 1966), with M. Eisenstadt.

5. "Beam Source for Molecular and Atomic Hydrogen," *Rev. Sci. Instr., 36,* No. 12, 1878-1879 (1965), by M. Eisenstadt.

6. "Use of Liquid Nitrogen Cooled Shield to Protect Proton Accelerator Against Oil Vapor Contamination," *Rev. Sci. Instr., 37,* No. 7, 977 (1966).

7. "A Low Cost, High Temperature (1300°C) Vacuum Furnace," *J. Vacuum Sci. & Technology, 3,* No. 6, 351 (1966).

8. "Detection of Hydrogen in Air by Means of Alkali Ion Current from Hot Palladium," *Rev. Sci. Instr., 38,* No. 1, 92-94 (Jan. 1967), with C. W. Carlson and J. Abramowitz.

9. "Contamination of MOS Field Effect Transistors by Alkali Ions Emitted from Hot Tungsten or Molybdenum Filaments--Removal by Electric Fields," *Elec. Communicator,* 16-17 (Nov./Dec. 1967).

10. "Polarization Sensitivity of the RCA 6903 Photocathode Tube," *Applied Optics, 5,* No. 6, 1091-1092 (1966), with A. Cutler.

11. "Chemisorption of Oxygen on Zinc Oxide--Effect of a DC Electric Field," *Surface Sci., 11,* 2 (1968), with J. Lane.

12. "The Electronic 'Sponge'--Selective Gas Adsorber," *Indus. Research,* (May 1968).

13. "Replication Versus Metallization for Interference Microscopy of Thin Films," *J. Vacuum Sci. & Technology, 5,* 125-126 (July/Aug. 1968), with J. Lane.

14. "Ion and Electron Currents from Hot Filaments: Effects of Alloying on Electron Emission," *Solid State Tech., 11,* No. 12, 53 (Dec. 1968), with R. Pope.

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.

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1. L. P. Rekova, Va. M. Fogel, L. V. Nesterov. Soviet Physics - Solid State II, No. 7, January 1970, 1524-6.

2. H. Saltsburg. Studies in Zinc Oxide Photoconductivity, A.D. 673836, August 1968.

3. V. Jang Lee. Science, Vol. 152, No. 3721, 22 April 1966.

4. I. Langmuir. *The Collected Works of Irving Langmuire*, ed., G. Suits, Vol. 1, p. 295, Pergamon Press, New York, 1960.

LIST OF FIGURES

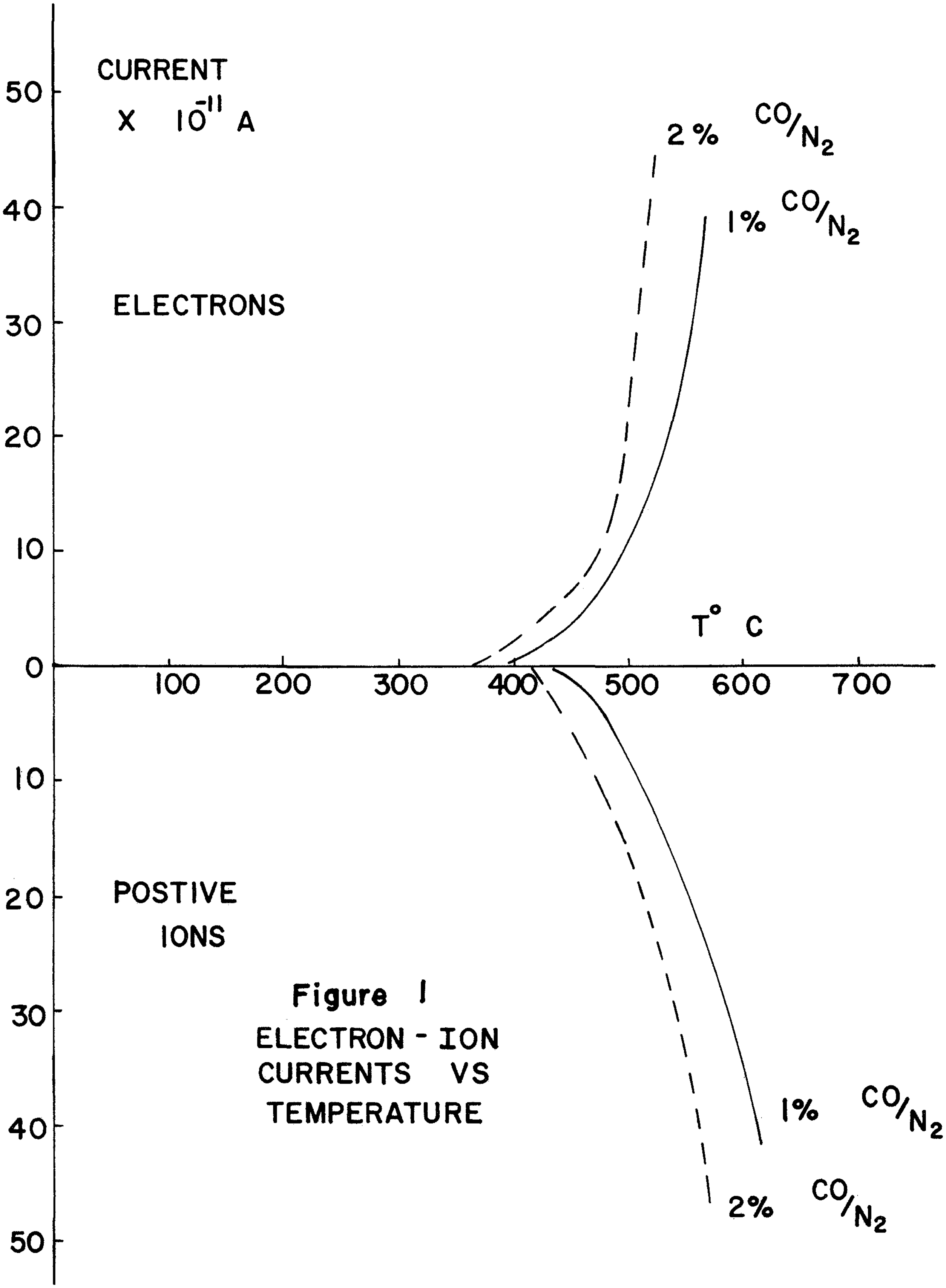

Figure 1

ELECTRON - ION
CURRENTS VS
TEMPERATURE

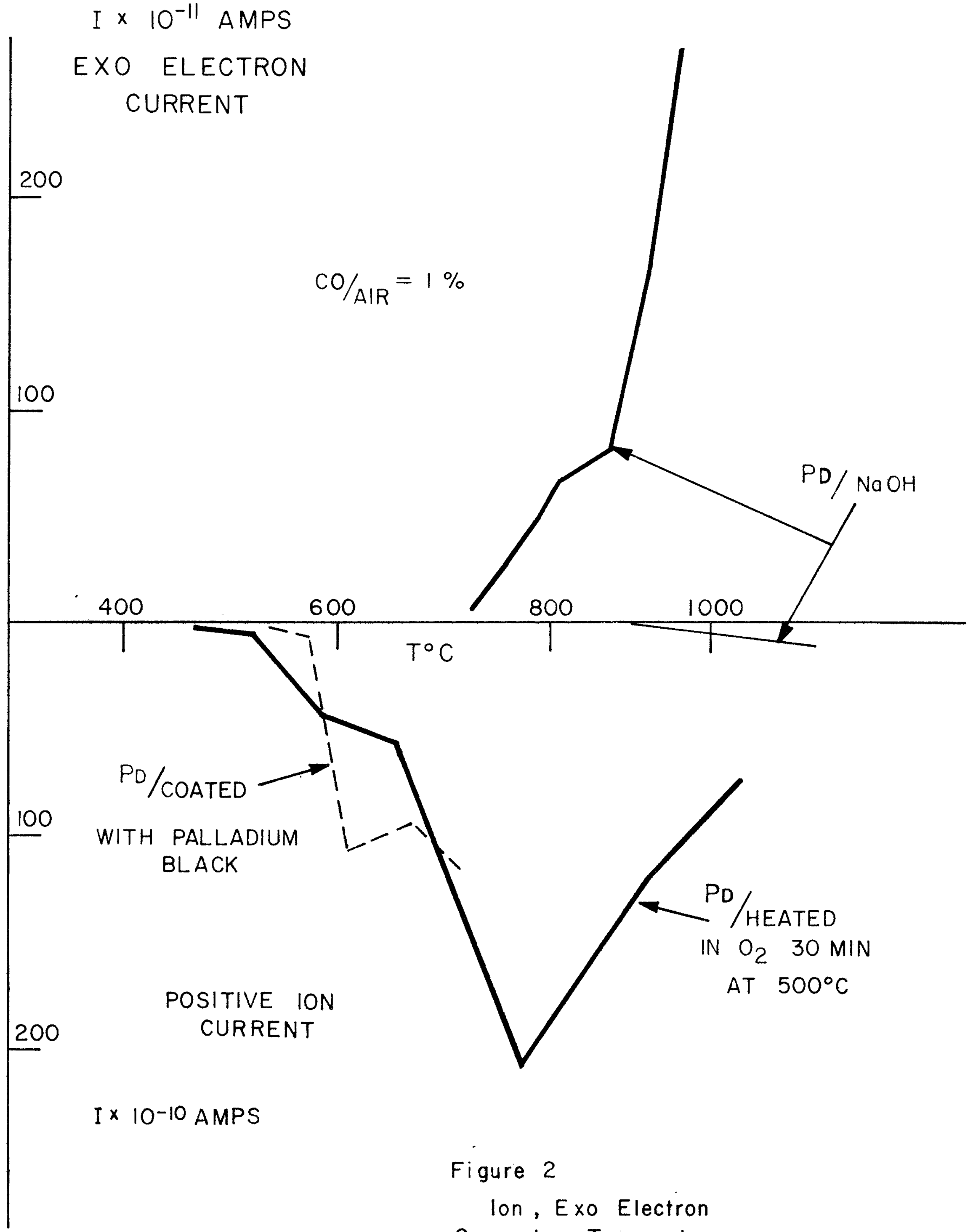

Figure 2

Ion, Exo Electron Current vs. Temperature

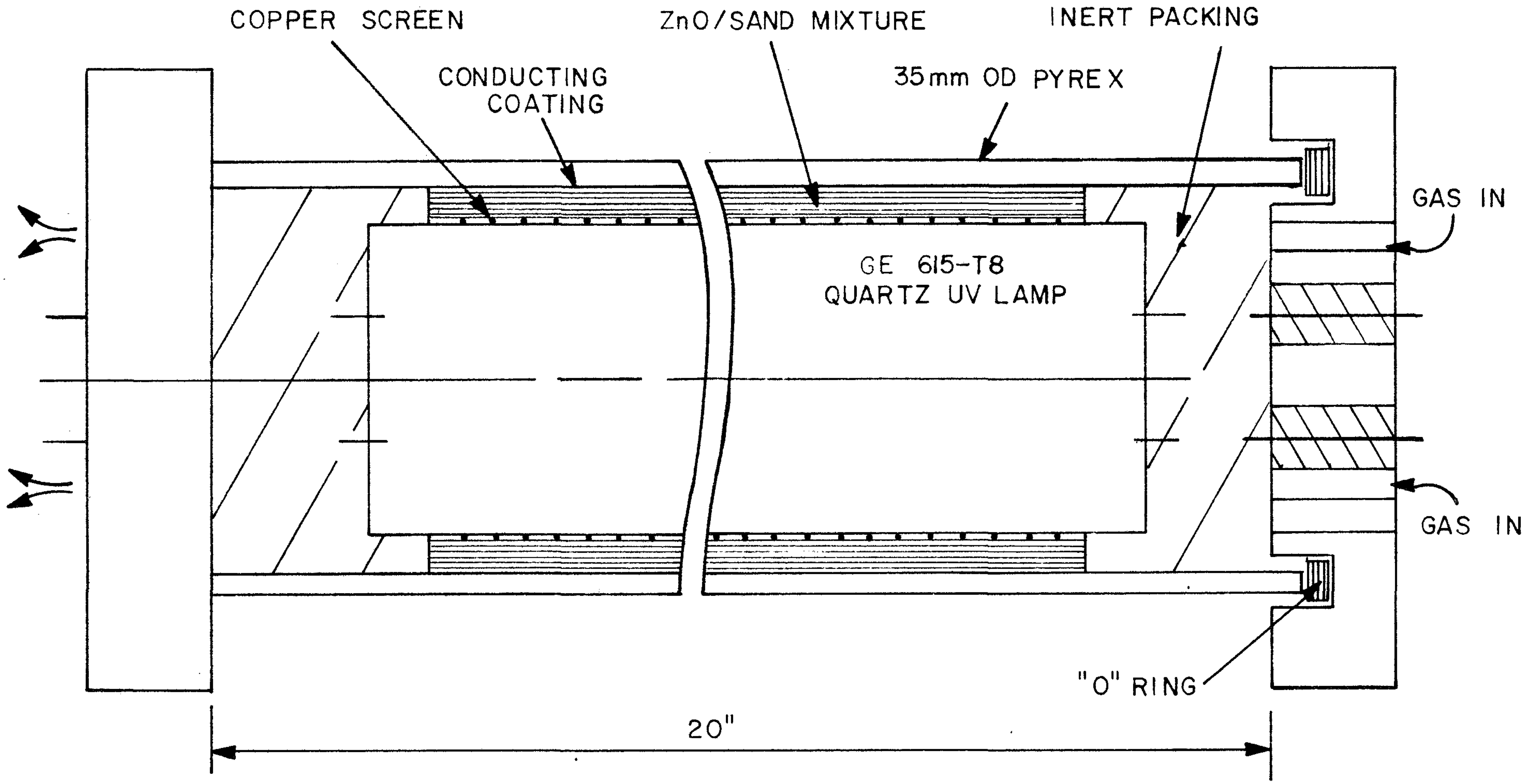

Figure 3 ZnO Adsorption System

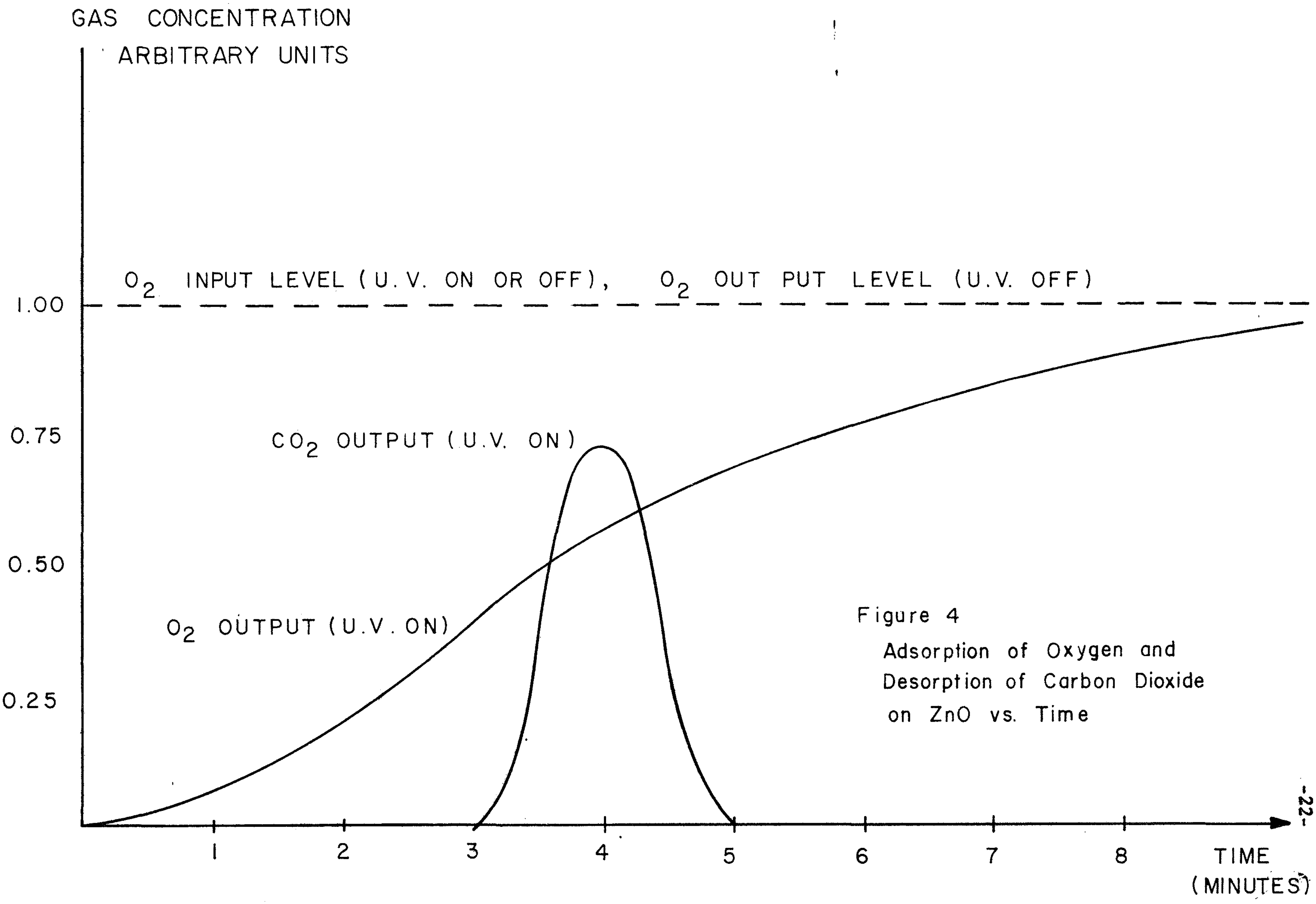

Figure 4
Adsorption of Oxygen and Desorption of Carbon Dioxide on ZnO vs. Time

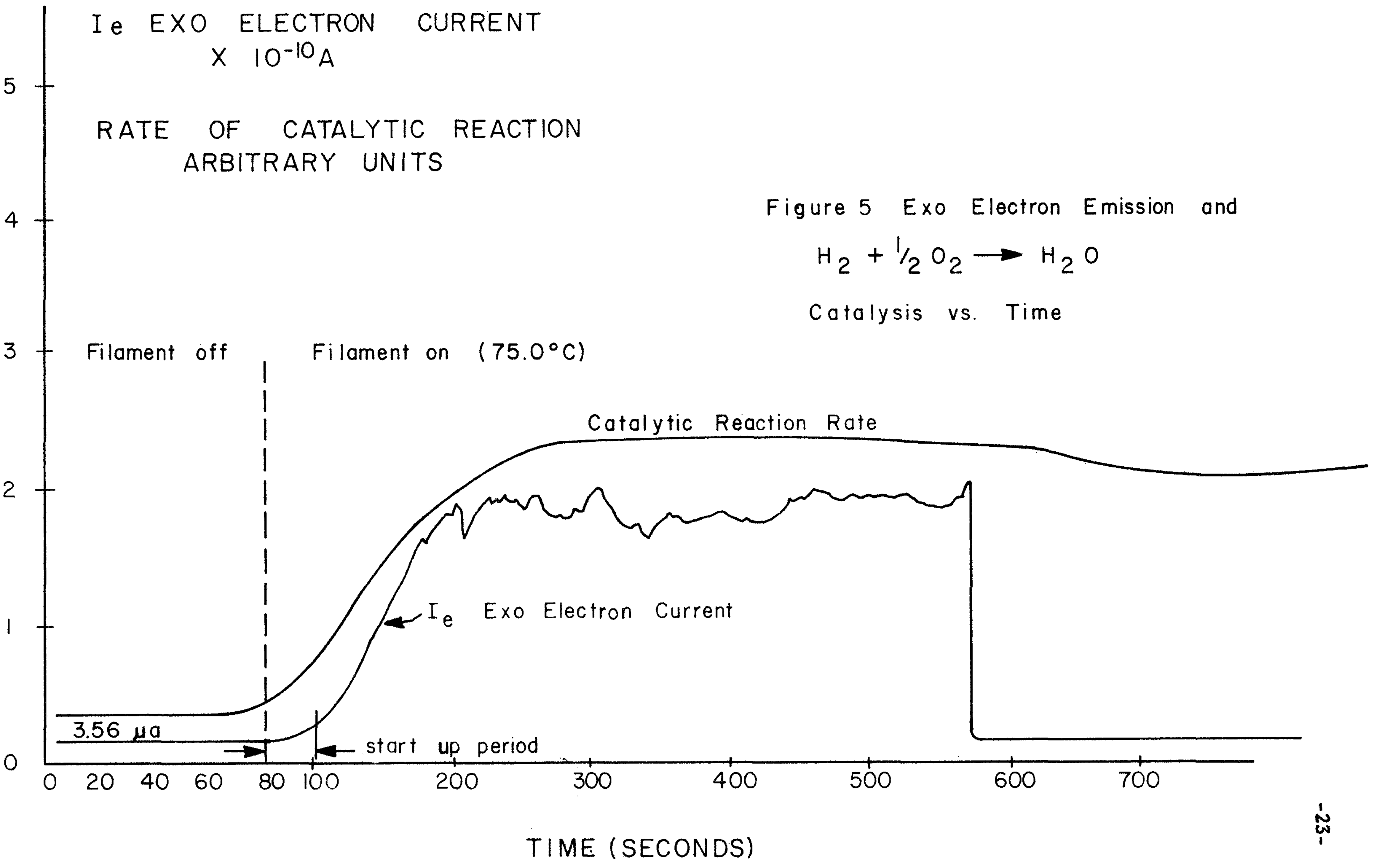

Figure 5 Exo Electron Emission and $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ Catalysis vs. Time

APPENDIX A

APPLICATIONS OF EXO-ELECTRON EMISSION TO NON DESTRUCTIVE TESTING

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The phenomena we call exo-electron emission (EEE) was first reported over 130 years ago by Moser, Reference 1. Unfortunately there is still a general lack of understanding of the physical causes of EEE. However, we do have enough knowledge of cause and effect relationships to consider applying EEE to specific types of NDT.

We suggest that whenever the surface of a liquid or a solid is disturbed, there is a tendency for electrons to escape into the vacuum phase. In the case of insulators or semiconductors, these electrons may come from F centers near the surface. In metals one might invoke the presence of F centers in surface oxides, but a vacancy mechanism is a more reasonable explanation of the existing experiments, It is this proposed connection between vacancies and EEE that permits application of EEE to NDT.

A number of reviews of EEE have been given recently, References 2, 3 and 4. At this point we need only mention that any process which disturbs a solid surface results in EEE. Experiments discussed in References 2, 3 and 4 include wire brushing, phase changes, tensile stress, annealing , sintering, alloying, X-Ray excitation, ball milling and grinding. The major problem in studying EEE has been the fact that the currents involved are small ($\sim 10^{-10}$A) and the electrons have a relatively low energy ($\sim$ 1 ev). This forced investigators to use Gieger tubes with all the attendant problems of gas surface interactions and non-uniform field distributions. More recently investigators have tried to use electron multipliers for detecting exo-electrons, but low energy electrons are not efficient in inducing secondary emission.

The advent of the field effect transistor and the operational amplifier has made it possible to measure currents of 10^{-15}A without difficulty. This capability is a major factor in the application of EEE to practical NDT.

Turning now to actual EEE experiments, it is convenient to mention the use of EEE to detect alloying reactions. This work was done under our NASA grant and concerned the emission of electrons and ions, from hot tungsten, during evaporation processes for deposition of Au, Ag, Al etc. The details were reported in Reference 5. Effectively we observed that when an alloying reaction occured between the tungsten or molybdenum substrate and the metal being evaporated, a substantial current of exo-electrons was observed. In the case of an exo-thermic reaction (Al/W) the electron energy was as high as 5 ev. The number of electrons emitted during evaporation was a sensitive measure of the alloying reaction. Even weak alloys such as Cu/W could be distinguished from a no-alloy case like Ag/W.

This phenomena can be understood in terms of the disturbance of the surface that occurs during the alloying process. It would be most interesting to investigate the relations between exo-electron emission and certain possible alloys predicted by the Engel Theory, Reference 6.

The application of exo-electron emission to NDT really began in 1963 before we knew that exo-electrons existed. In 1963 we began looking at the application of field emission techniques to observation of surface microcracks. Using 0.020" diameter wires and a cylindrical field emission microscope (FEM) it was possible to detect microcracks as small as 4 microns (10^{-4} inches). The field emission microscope is particularly suited for finding microcracks because there is no need to scan the entire surface as in optical microscopy. Only cracks and other sharp edge defects emit electrons and are imaged, Reference 7. The FEM is shown in Slide 1. Slide

In 1967 the FEM was used to study stress corrosion cracking of uranium-molybdenum alloys. With the FEM it was possible to follow the various steps in the SCC process, Reference 8.

During these studies we often pulled specimen wires to failure at high (600°C) temperatures and low electric fields so that the electrons were emitted by a combined field-thermal process. The electron images were observed with a Bolex camera at 64 fps and we noticed that emission did not cease immediately when the wire broke. The post-fracture emission came primarily from the broken ends of the wire with intense emission from the cup and cone areas. Typical single frames are shown in the next two slides, the material was titanium at an initial temperature of 660°C. One of the frames shows what might be exo-electron emission from a Luders band structure on the cone. We felt that this emission was due to exo-electrons escaping from the metal as the disturbed fracture area relaxed to its equilibrium shape.

Slide

Slide

In 1969 we began studies of the application of exo-electron emission to NDT of metal fatigue. Our program had two objectives:

1) Gain an understanding of the exo-electron phenomena particularly the driving potential for emission.
2) Develop a technique for application of exo-electron emission to NDT.

We will discuss the results of objective 2) first. In this case we felt sure that exo-electron emission occured during the fatigue process, but it seemed more important to develop a system for measuring the fatigue damage *after* rather than *during* the fatigue cycle. In aircraft applications it is difficult to observe and record events during flight. In any case it is most important to be able to fatigue test a critical structure *before* the next flight to be sure that catastrophic failure will not occur after takeoff.

We proposed that during fatigue a complex structure of vacancies and dislocations developed near the specimen surface. Most of these "defects" would be sessile at room temperature but upon heating a significant fraction of these defects might be expected to diffuse to the surface. This vacancy diffusion would in turn induce EEE, which would then be used as a measure of the fatigue level of the specimen. This application is contingent upon; first, having a large enough current to measure and second, not heating the structure to the point where fundamental metallurgical changes occur.

The specimens for this study were aluminum (1100-0 and 7075-T6), steel (D6AC) and titanium (Ti - 6Al - 4V). The specimen shape is shown in the next slide. Specimens were 0.090" thick, and were chemically polished to a 40 microinch finish. The specimens were fully annealed to remove fabrication stresses and then heat treated to the proper temper.

Slide

Fatiguing of the aluminum specimens was done in a vibratory machine designed and built by Mr. Christian Savitz. The machine is shown in Slide 5. The steel and titanium specimens were sent out for fatiguing and our data on those materials is incomplete. The discussion will be limited to our work with aluminum. To test the aluminum a group of 10 specimens was run at 3450 cpm to failure to establish a mean lifetime. The scatter in this life test was about ± (5 - 10%). The next set of specimens were run to some fraction, 0%, 20%, 40%, 60%, 80% of their expected life and tested for exo-electron emission.

Slide

The test apparatus is shown in the next slide (6) and a circuit diagram is shown in Slide 7. The specimens were heated

Slid

Sli

electrically by passing some 280A of current for 8 minutes. The temperature after 8 minutes was 90°C, far below the temperature where metallurgical changes would occur. The ultraviolet source was added to the apparatus to increase the exo-electron signal to noise ratio. A number of investigators have reported that light increases the observed EEE. We have no theory for this at the moment, there may be some complex photon-vacancy interaction.

The data obtained with this system are shown in the next three slides. We wish to emphasize that these fatiguing and exo-electron emission studies were done in ambient air. Slides 8 and 9 show exo-electron current as a function of time for 1100-0 specimens at various fatigue levels. There is a clear, distinct relation between fatigue and exo-electron emission (at least in 1100-0 aluminum).

The experiments with 7075-T6 have been delayed by heat treatment problems. We did get some data that indicates EEE may be used to measure the manufacturing stresses in a fabricated part. In Slide 10 we show the exo-electron current versus time for four 7075-T6 specimens that had no fatigue or heat treatment after fabrication. The specimens were run to failure after the exo-electron test. Except in one case, No. 49, there was a direct relation between EEE and time to failure. This suggests that exo-electron emission can be used for evaluating the fatigue or cold work that a specimen has been exposed to before it is put into service.

Our other area of investigation has been directed toward gaining an understanding of the exo-electron phenomena. Here we have followed the work of Reference 9 where aluminum was strained in tension and the EEE was followed both during and after straining. Once again the mechanism involves the generation of vacancies during plastic deformation. Subsequent vacancy diffusion releases exo-electrons. Exo-electron emission persists for some time after straining ceases and this is taken as a measure of the rate at which mobile vacancies are exhausted.

Van Voss and Brotzen investigated the effect of ambient UV light on exo-electron emission. They tenatively adopted an F center model involving a surface oxide as part of the photon-electron interaction. We suggest that when a vacancy arrives at the surface, the normal barrier potential is disturbed and high energy electrons can "leak out". If photons are present the number of electrons which "leak out" is correspondingly greater.

Our first experiments in this area were done by Mr. William Ott for his MSEE thesis. The specimens were nickel wires 0.032" in diameter, necked down to a gauge section in an electropolishing machine. The specimens were mounted in the vacuum fatigue machine shown in the next slide. This system can provide either a direct tensile or an oscillating torsional stress while maintaining a vacuum of 10^{-8} torr. Slide 1

The specimens were annealed at 1000°C for 24 hours (in vacuum) and then either strained or fatigued in vacuum at room temperature. The experiments included

1) Exo-electron emission under tensile stress
2) Exo-electron emission under torsional fatigue
3) Exo-electron emission after tensile stress or fatigue

The results for experiment (1) above were in agreement with those of Reference 9. Exo-electron emission was observed during tensile testing without any added UV source. The current increased more slowly than the tensile stress. When the load was removed the current died away over a 30 second interval. When the stress was reapplied the exo-electron current rose rapidly until fracture then decreased slowly after the wire broke.

In experiment (2) exo-electron emission on at the 10^{-13} amp level was observed. The pressure during fatigue was 10^{-8} torr. Each time the wire was twisted a burst of electrons was recorded. The currents were small and the interference from electrons emitted by the mechanical gearing made it difficult to follow changes in current level. Other inestigators (Reference 10) have observed exo-electron emission during fatigue. The current first increases with each cycle and then decreases again. This may be due to work hardening making it more difficult for dislocations to move. We do not feel that measurements of exo-electron emission during fatigue are as useful as post-fatigue studies.

The studies of EEE after fatigue (3) involved heating the specimen to some fixed temperature in the vacuum system (at 10^{-8} torr) and following the EEE. The results of a typical run on three specimens fatigued to various levels are shown in Slides 12-13. Again there is a clear relation between fatigue and post fatigue EEE. This data was obtained without any UV light and the temperatures required for significant exo-electron emission are quite high (800°- 1000°C).

<u>Slide</u>
<u>Slide</u>

In view of the placket detector that will be discussed in the next section we began integrating the observed exo-electron current and looking at the graph of $\int$ Idt versus the fatigue level of the specimen. Typical results are shown in Slide 14 for our nickel specimens. The correlation is quite good up to about the 55% level where the exo-electron current begins to decay. We suggest that this represents the level at which the vacancies and dislocations begin to pin one another and diffusion is impeded. This suggests that further heating, to above 1000°C, would induce exo-electron emission at high fatigue levels. There is some evidence for this but it is not practical to heat nickel above about 1000°C with our present apparatus.

<u>Slide</u>

The experiments suggest that vacancy motion rather than oxide vacancies is the parameter that controls EEE. Future experiments will make use of U-H-V apparatus and sputtering equipment to produce reproducible and completely "clean" surfaces. This will permit us to settle the vacancy versus oxide question once and for ever.

Application of this post-fatigue technique to NDT requires a system for heating the structure and collecting the emitted electrons. It is impractical to use resistive heating on something as complex as an airplane and optical sources are limited by the high reflectivity of aluminum. We have designed a device we call a placket detector, consisting of a squib heat source, a Glaubers Salt heat buffer, a battery driven UV source and a self developing electron sensitive film. The system is shown in the next slide. The diameter of the placket is about 2", to permit its application in restricted areas. The operational sequence would involve:

Slide 15

1) Fastening the placket to a fatigued structure, turning on the UV light and hooking up the 45 volt battery.
2) Firing the squib. This releases a very short but intense thermal pulse which lasts only a few seconds. The Glaubers Salt dissociates according to the formula

$$Na_2SO_4 \cdot 10H_2O \leftrightarrow Na_2SO_4 + 10H_2O$$

and the resultant steam circulates in the sealed placket. As the placket cools below $100^{\circ}C$ the reaction goes backwards releasing the heat previously adsorbed. The effect of this buffer reaction keeps the structure from being heated above about $100^{\circ}C$ and spreads the heating cycle over about 8 minutes.
3) Exo-electrons are collected on the film, which is of the Polaroid self-developing variety. The blackening of the film provides a direct read-out of the fatigue

of the structure. The structure has only been heated to some 90°C so no major metallurgical changes have occured.

The next question is, where are we in the development of the placket detector?

1) The squib, UV light, Glaubers Salt components are off-the-shelf items. The Glaubers Salt heat buffer is under test at the moment, in another organization.
2) The Kodak Co. has indicated that electron sensitive films for low energy (10 ev) electrons are practial. No work has been done to date on a self developing film for 10 ev electrons but self developing films are well known in nuclear safety programs. The Kodak Co. has suggested that a Xerox type system might be equally practical for this application. The exo-electrons would be collected on an insulating plate and then "developed" by depositing colored, insulating powder. The quantity of powder deposited would be a measure of the total number of exo-electrons collected. The final development of the placket detector will be a function of the support and assistance available from industry and government agencies.

Other NDT work at the University of Arizona has involved the application of EEE to observation of grinding and milling processes. This was first suggested by Kramer (Reference 11) who used a modified Gieger counter to examine samples of ZnS, K_2SO_4, NaCl or Gypsum after grinding. Exo-electrons were indeed observed and there was some evidence that exo-electron emission could be correlated with the grinding process. This would follow from the mechanism proposed earlier where disturbing the surface permits electrons to escape.

It seemed possible that this process might be an explanation of the fires and explosions that have occured during grinding inflammable materials i.e. flour, paint, magnesium. We also hoped that it would be possible to follow ore crushing processes which are of interest to Arizona's copper industry.

To test this latter suggestion we used a ball mill borrowed from the Anaconda Co. Laboratories in Tucson. The ball mill and the associated electronics are shown in the next slide. The contact to the drum was made with brass scrubbing brushes, the center electrode was a stainless steel rod. Test batches of copper ore were run with iron balls and the iron balls were run alone for a blank experiment. The ore was milled without water, experiments with wet grinding yielded confusing results because of deposits of mud on the insulators. <u>Slide</u>

Typical data is shown in the next slide. The observed current rises and then falls. We suggest that the time at which the current begins to drop is the point where the ore has been ground as finely as it can be with the large balls that we used. From that time on we are only grinding the iron balls, which pro- <u>Slide</u>

duces a small but significant residual current.

The grinding experiments at the University of Arizona have stopped (by general demand of everyone within the sound range of our laboratory). The work is continuing at another laboratory under the auspices of Battelle Development Corp.

The last and latest experiment involving EEE at the University of Arizona is a study of electron migration in thin films. This is a problem in the electronic industry, when large (10^6A/cm^2) currents go thru thin films of Ag or Al the film moves by a vacancy diffusion mechanism and eventually the film becomes an open circuit. A review of this phenomena has been given by Black in Reference 12. We have begun looking for exo-electrons, from thin films of aluminum, under high current conditions. We think that this emission process was that first observed by Shenstone, Reference 13. To date no other possible explanation has been given for the Shenstone Effect. Our ultimate objective is the development of a test technique for use during the burn-in period when integrated circuits are under load. A metal film with an excess number of vacancies would be expected to "stand out" because of its intense exo-electron emission. This would permit a manufacturer to discard or rework semiconductor chips that would otherwise be "early failures".

This work has just been started but the indications are that the phenomena is indeed as we have suggested.

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12) Black, J.R.,Trans. IEEE 57, No. 9, Sept. 1969 Pg. 1587-98

13) Shenstone, A.G. Phil. Mag. 41, Pg. 916 (1921)
Phil. Mag. 42, Pg. 596 (1921)
Phil. Mag. 45, Pg. 916 (1923)

LIST OF FIGURES

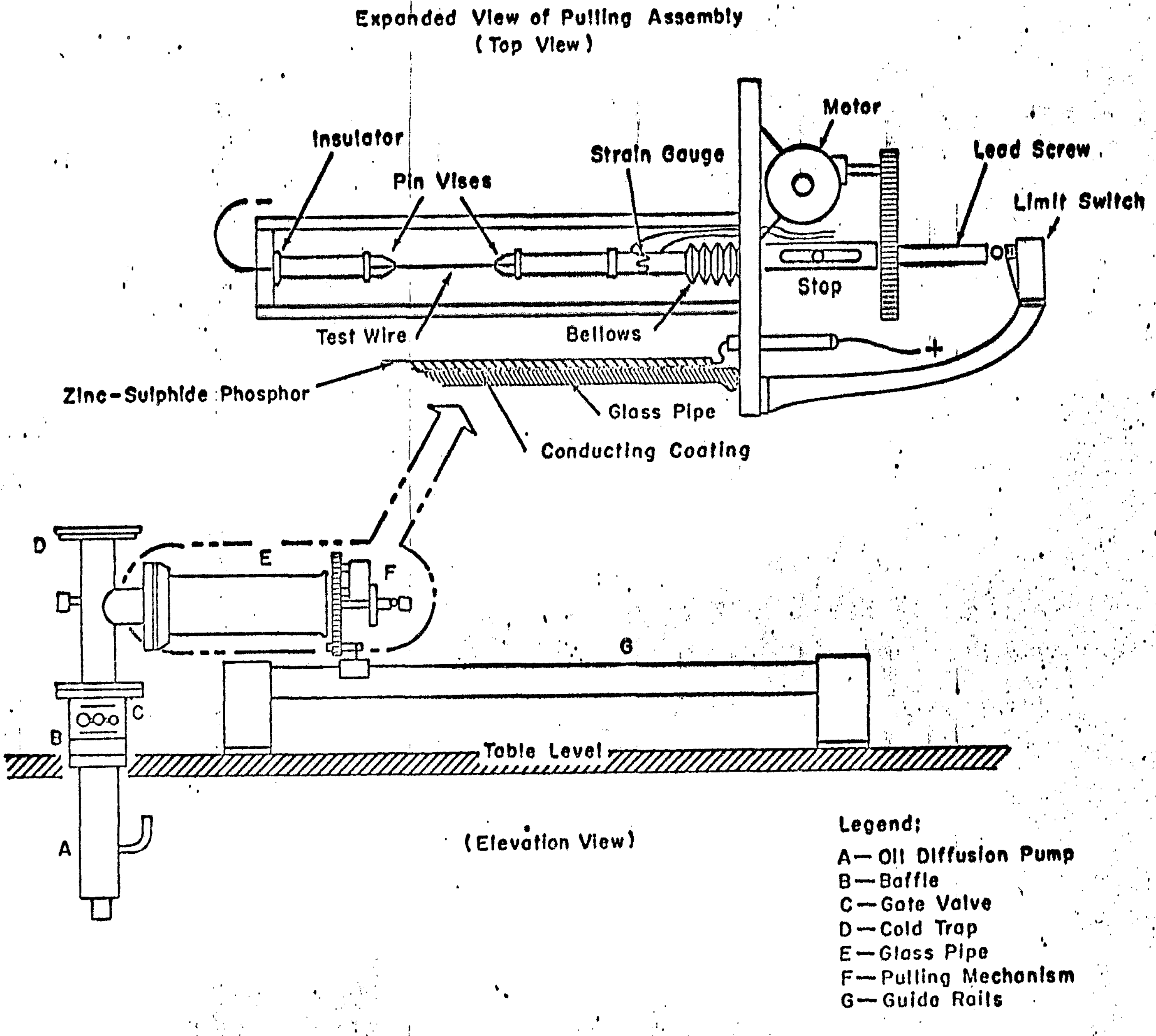


FIG.1 CYLINDRICAL FIELD EMISSION MICROSCOPE FOR WIRE STUDIES

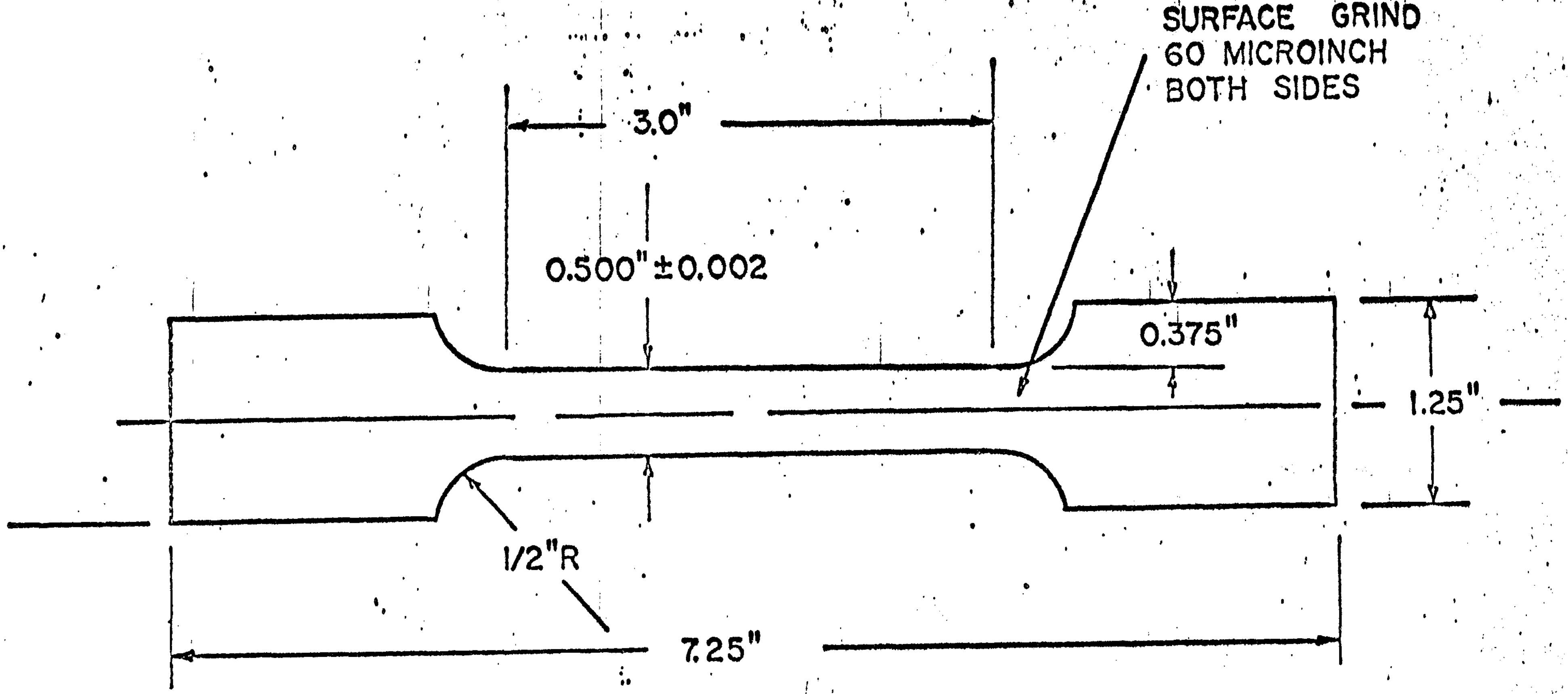


FIGURE 4
EXO ELECTRON—FATIGUE TEST SPECIMEN
SCALE — FULL

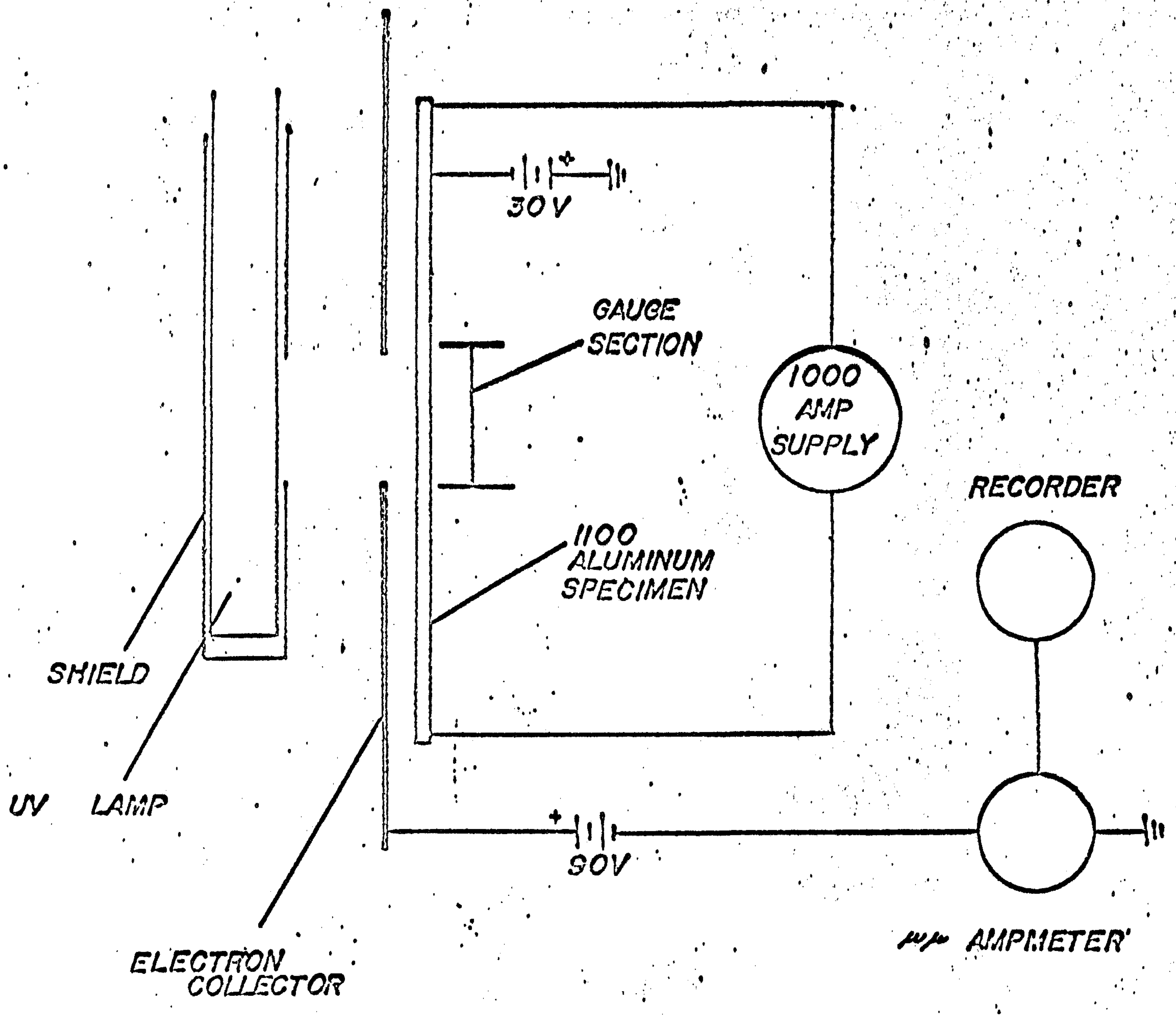
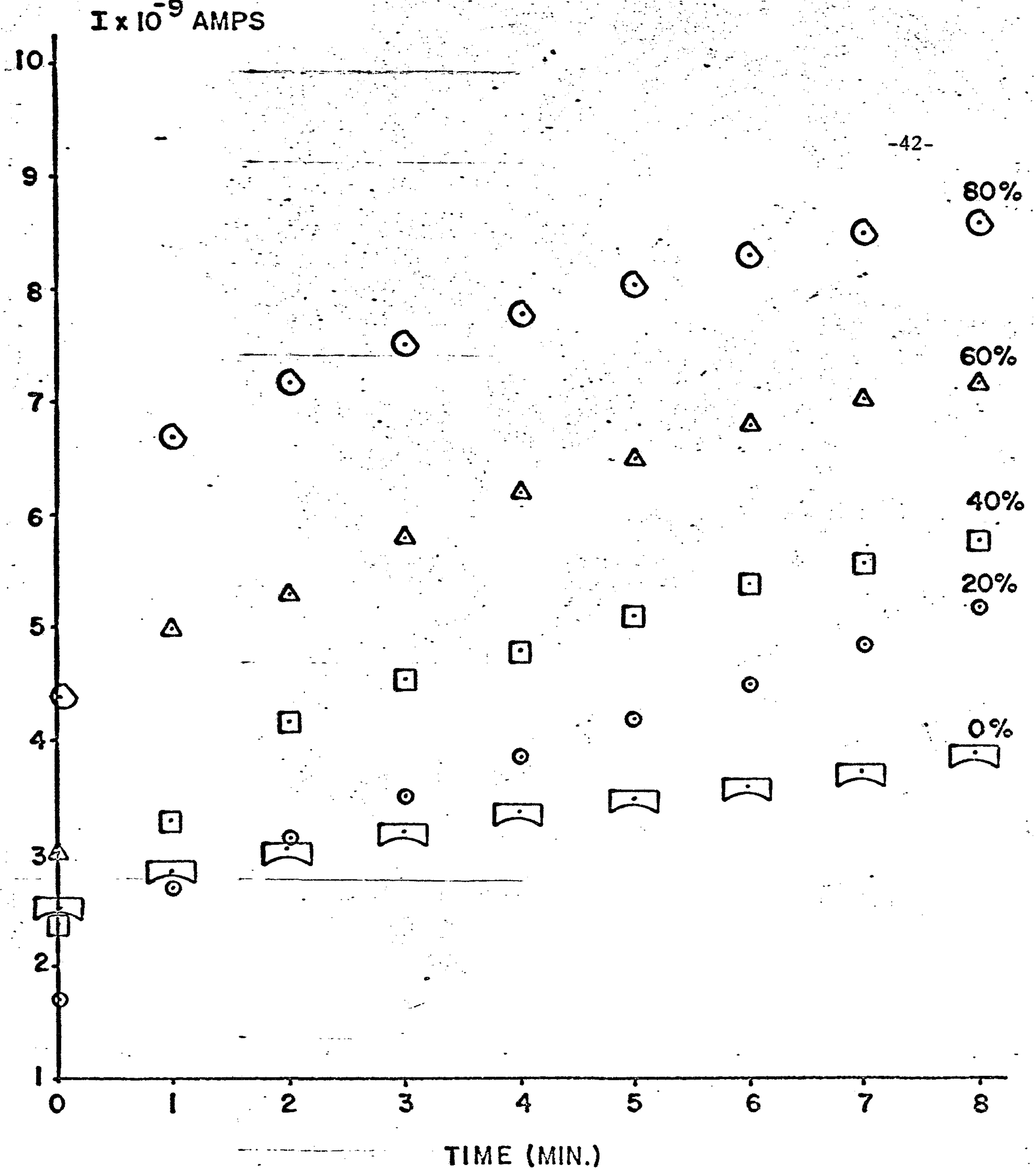
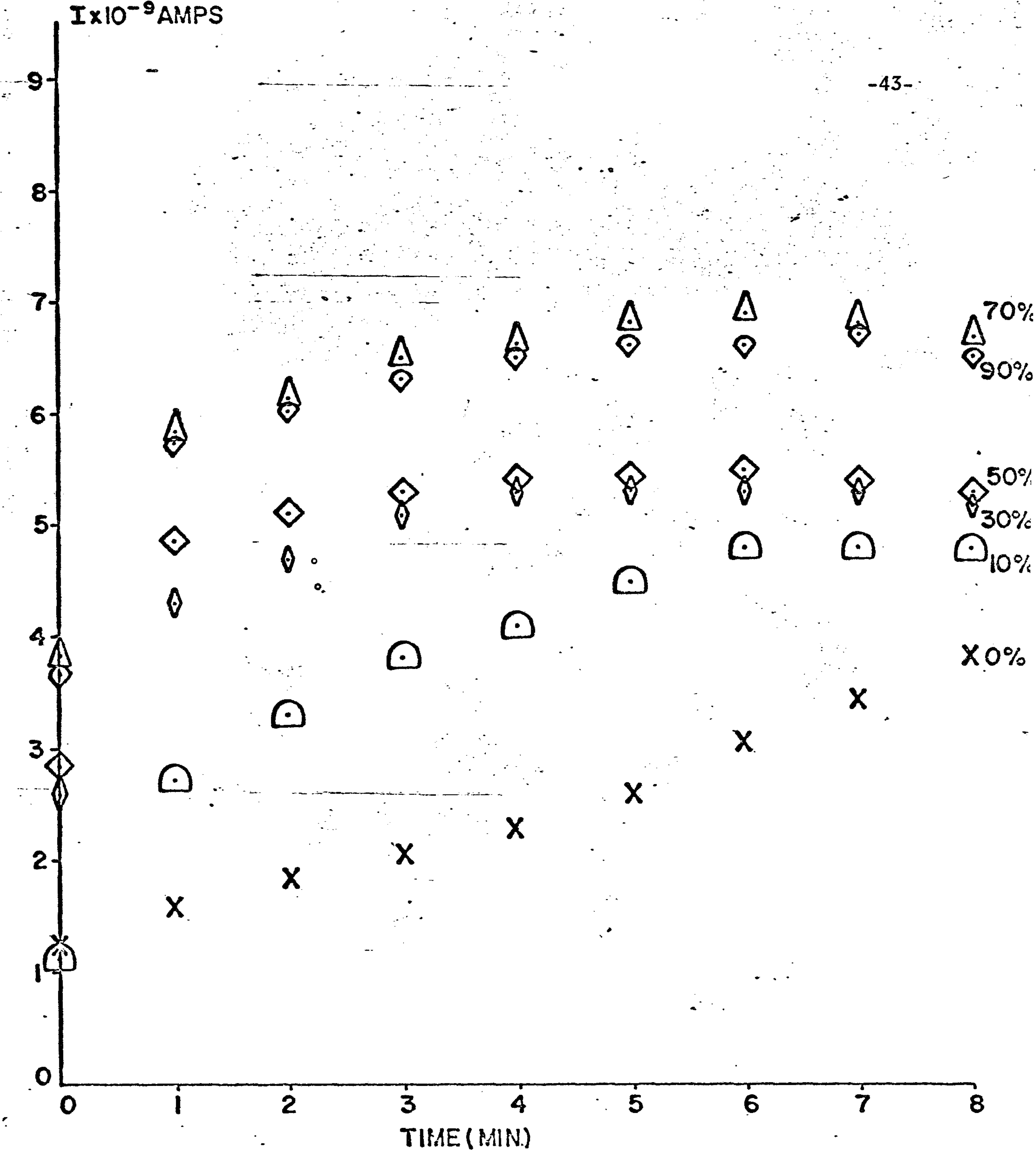


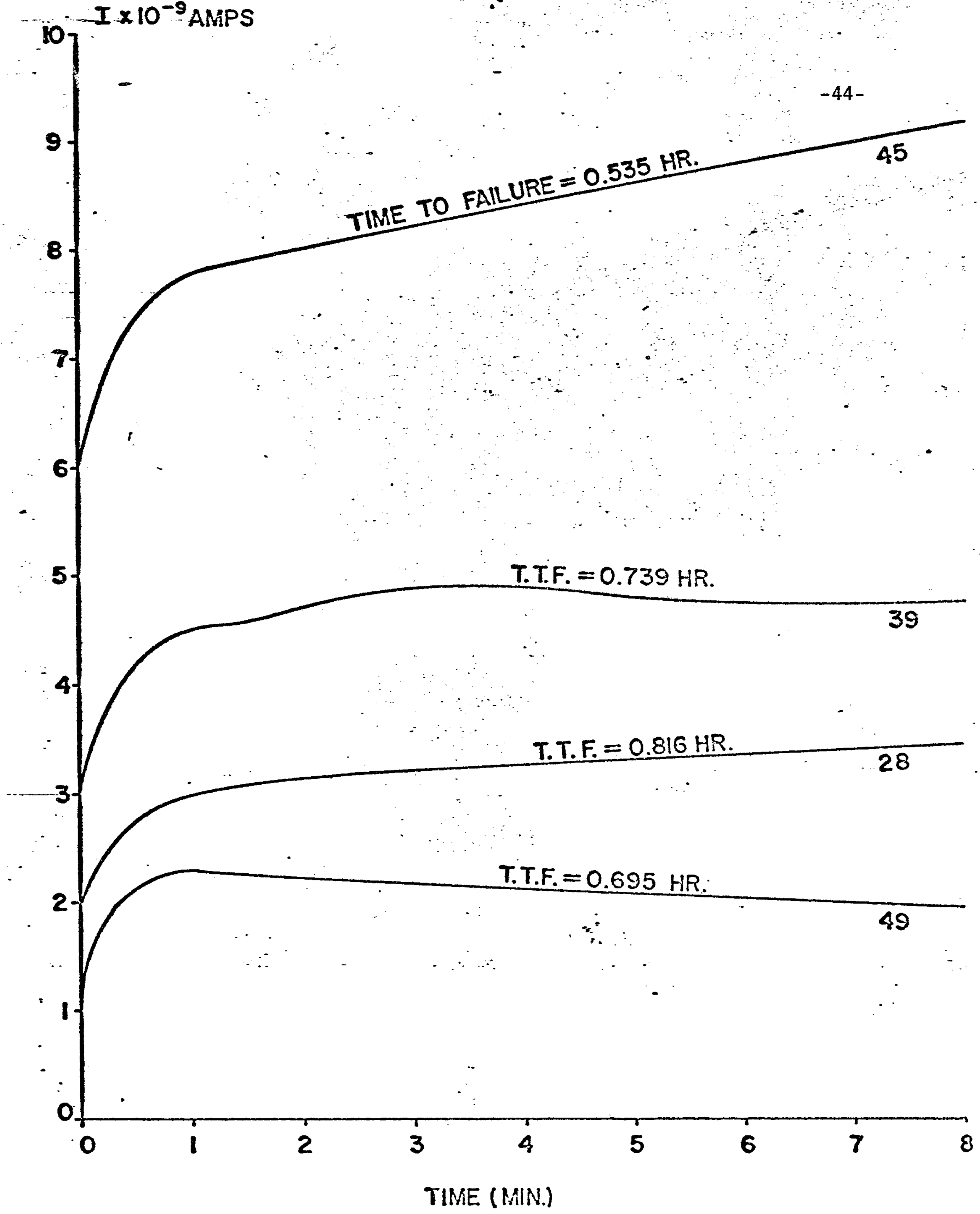
FIGURE 7 EXO-ELECTRON APPARATUS



8 EXO-ELECTRON CURRENT VS TIME AND FATIGUE LEVEL



9 EXO-ELECTRON CURRENT VS TIME AND FATIGUE LEVEL
1100—0 ALUMINUM


I x 10⁻⁹ AMPS
10
9
8
7
6
5
4
3
2
1
0
TIME TO FAILURE = 0.535 HR.
45
T.T.F. = 0.739 HR.
39
T.T.F. = 0.816 HR.
28
T.T.F. = 0.695 HR.
49
0
1
2
3
4
5
6
7
8
TIME (MIN.)

10

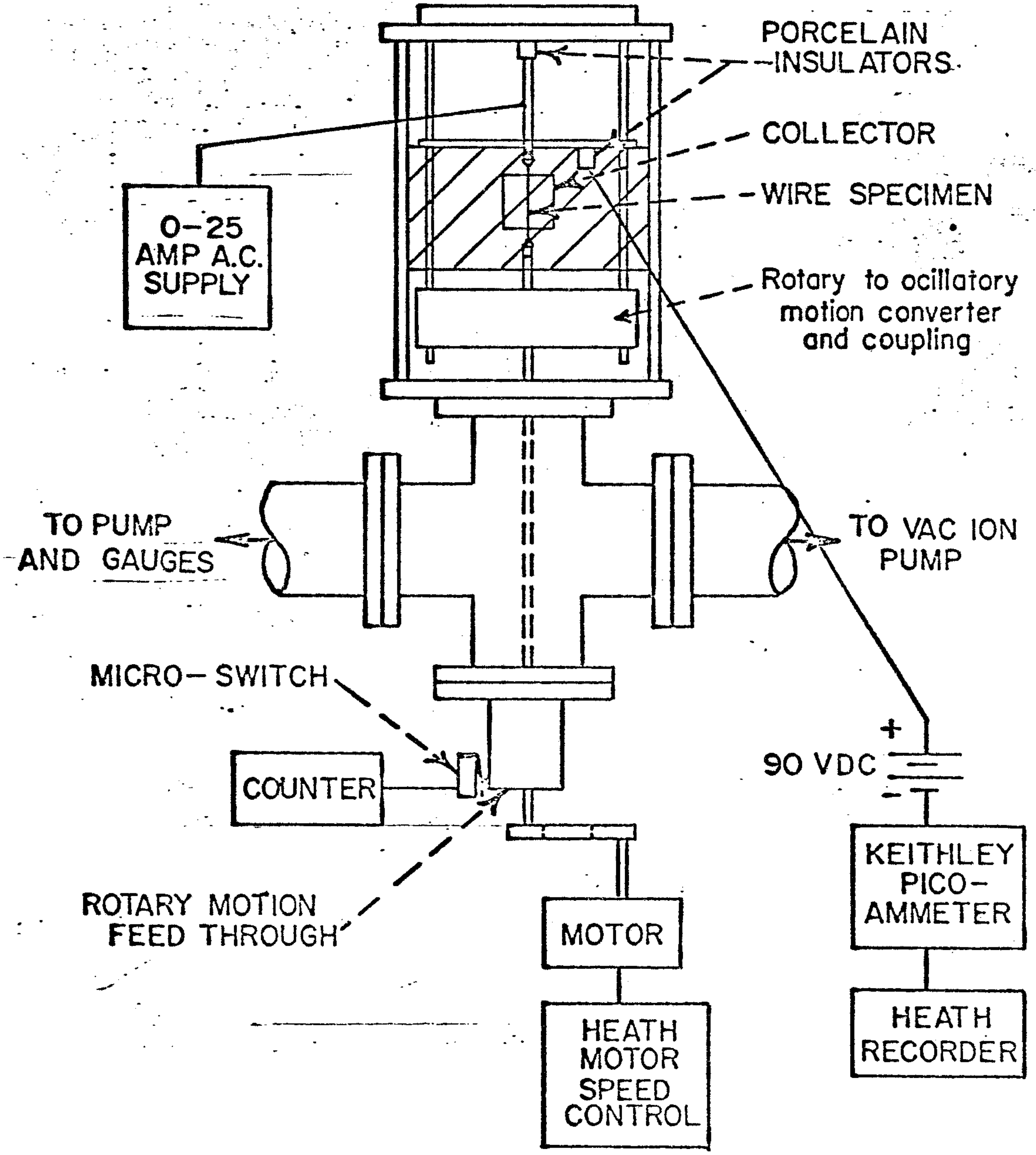
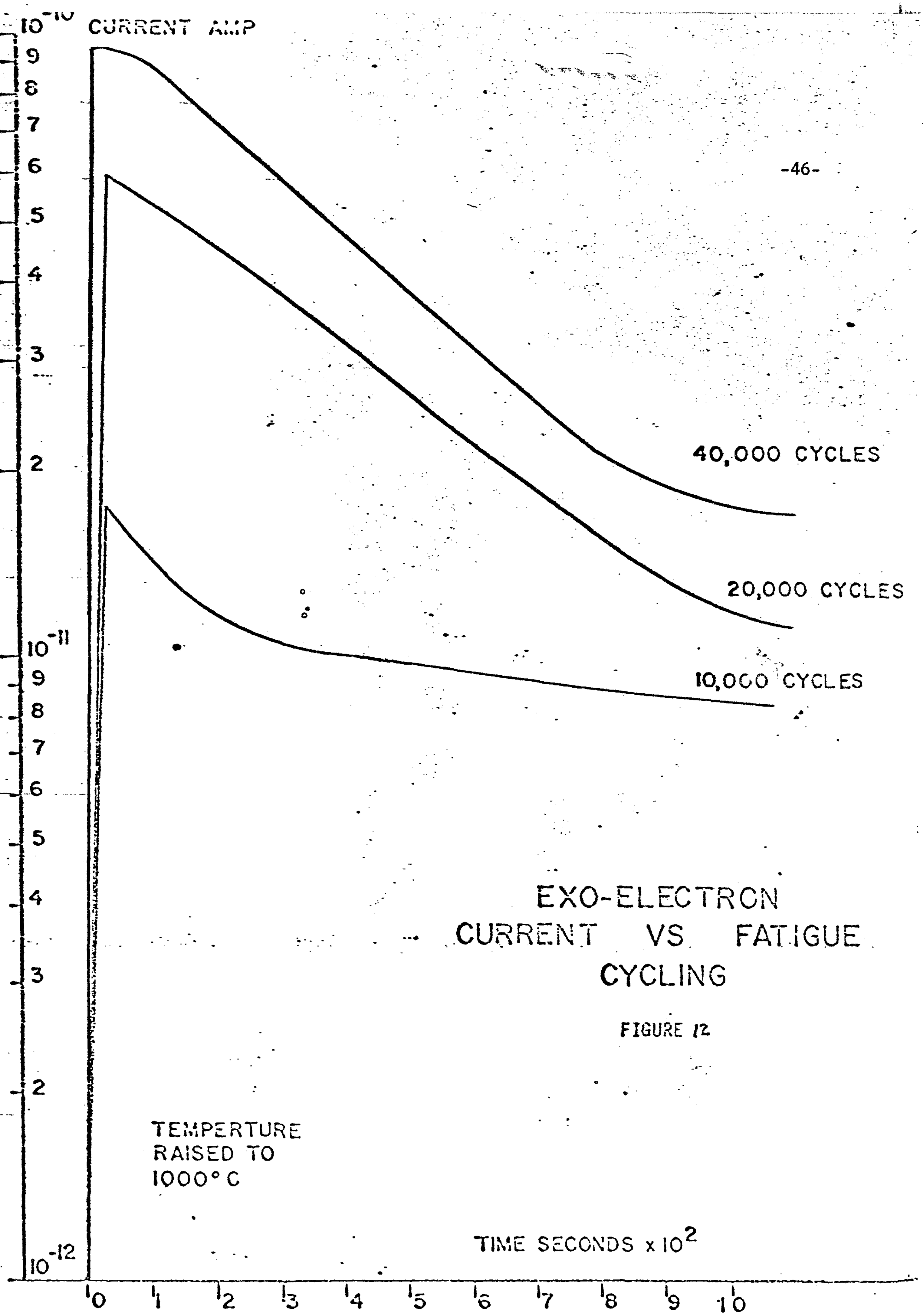


Figure 11. Vacuum Fatiguing Assembly and Associated Electronics



EXO-ELECTRON CURRENT VS FATIGUE CYCLING

FIGURE 12

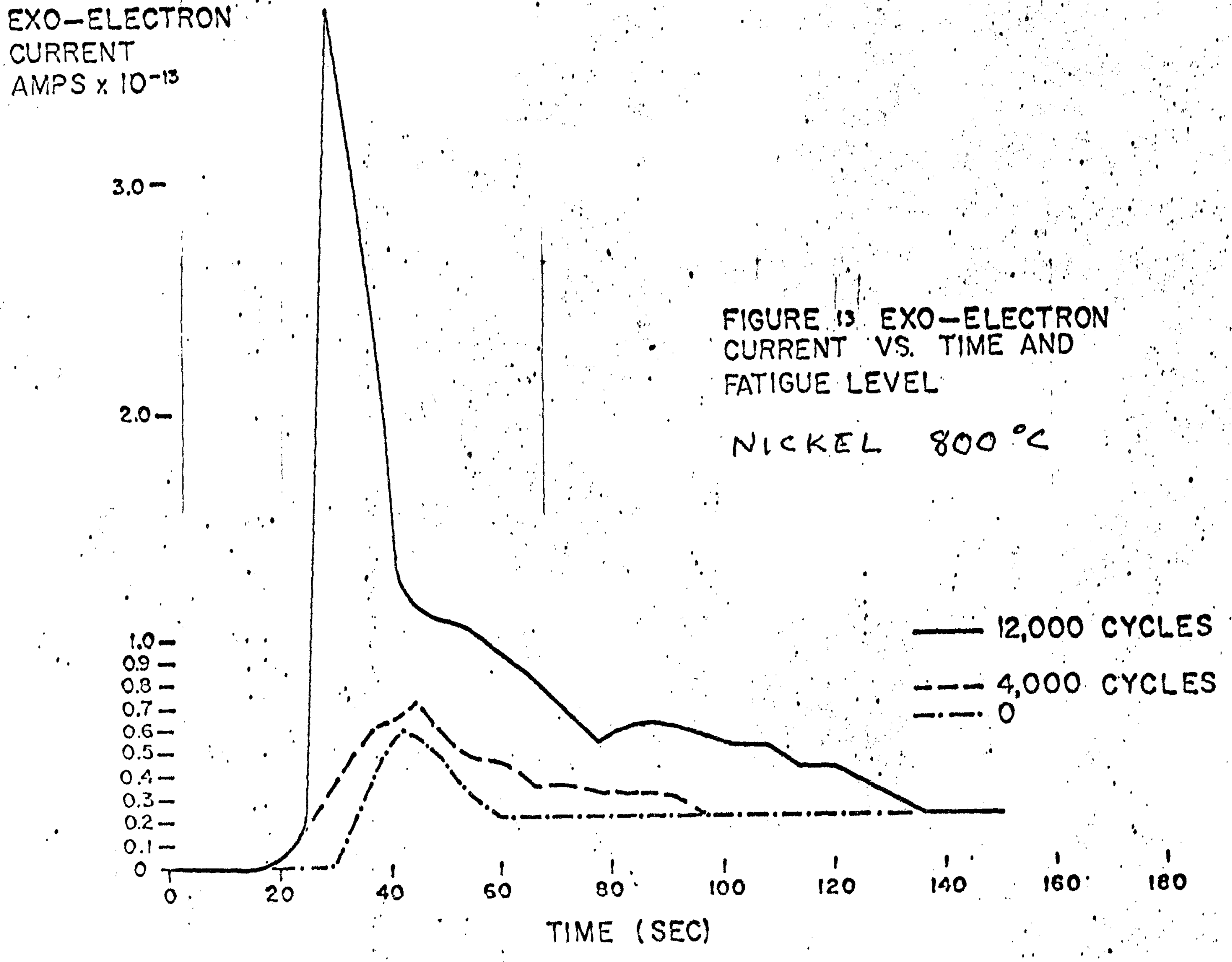


FIGURE 13 EXO-ELECTRON CURRENT VS. TIME AND FATIGUE LEVEL

NICKEL 800 °C

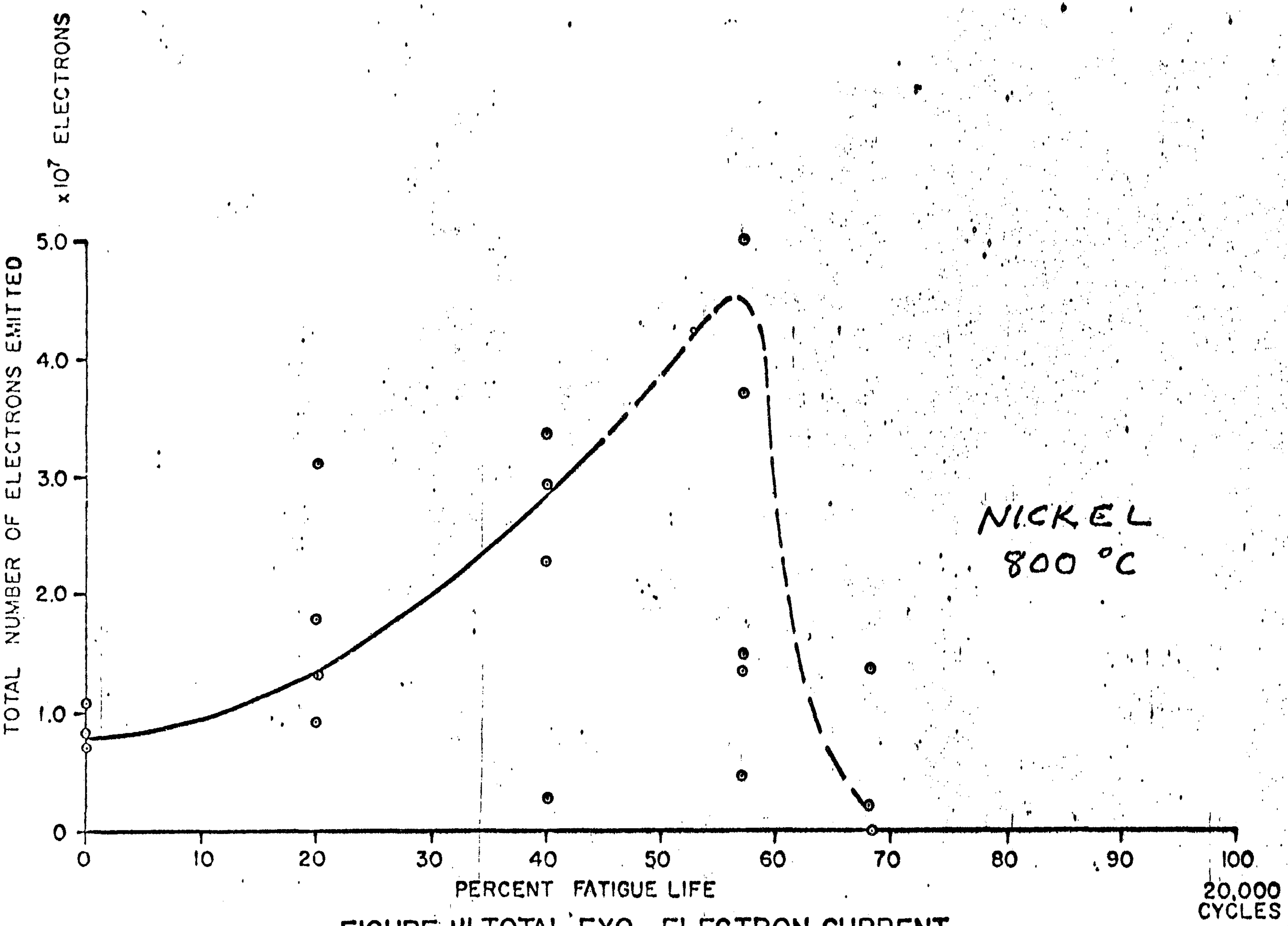
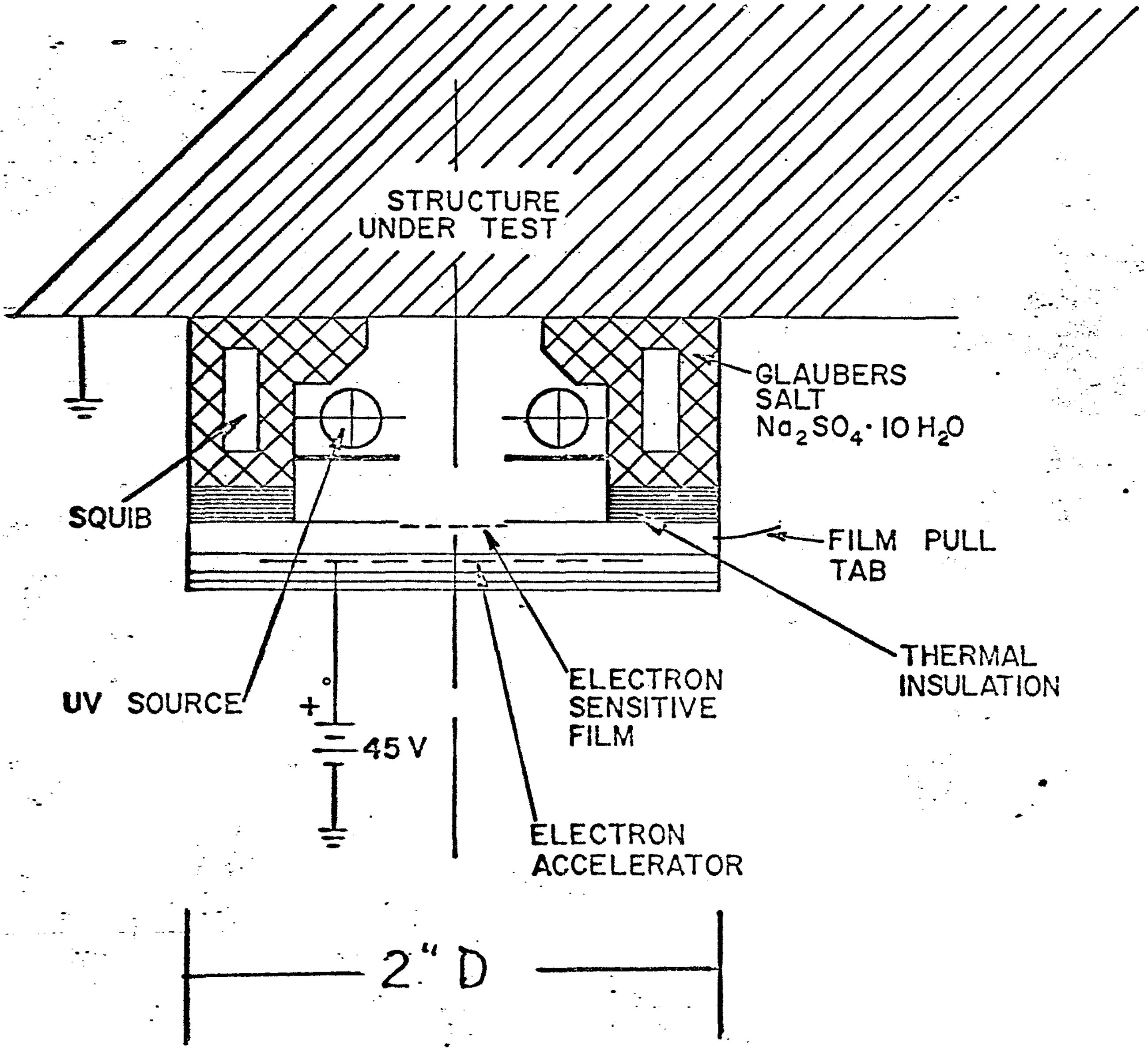


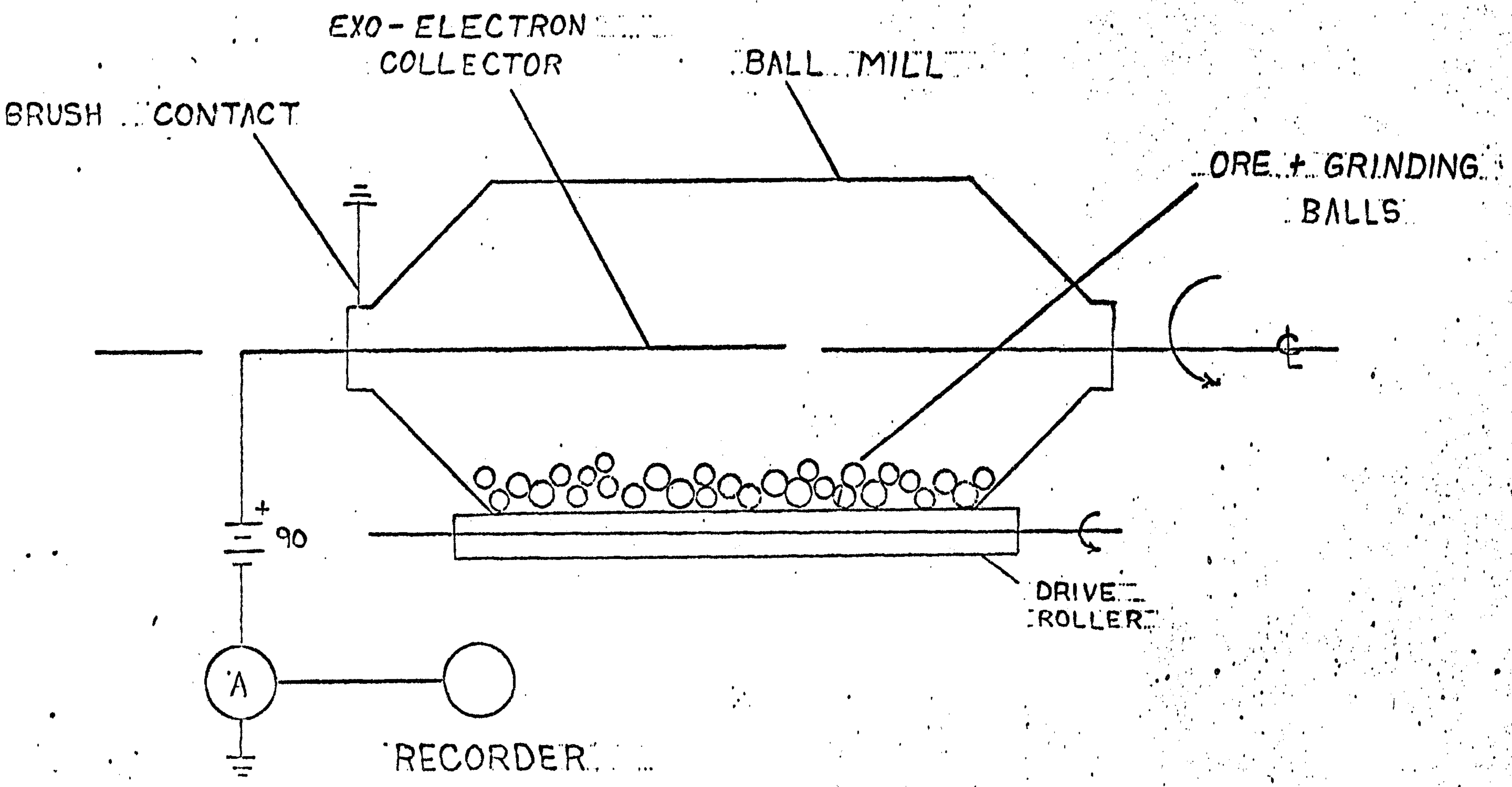
FIGURE 14 TOTAL EXO—ELECTRON CURRENT VS. PERCENT OF FATIGUE LIFE



15

PLACKET DETECTOR

SCALE FULL



EXO - ELECTRON SYSTEM

FIG. 16

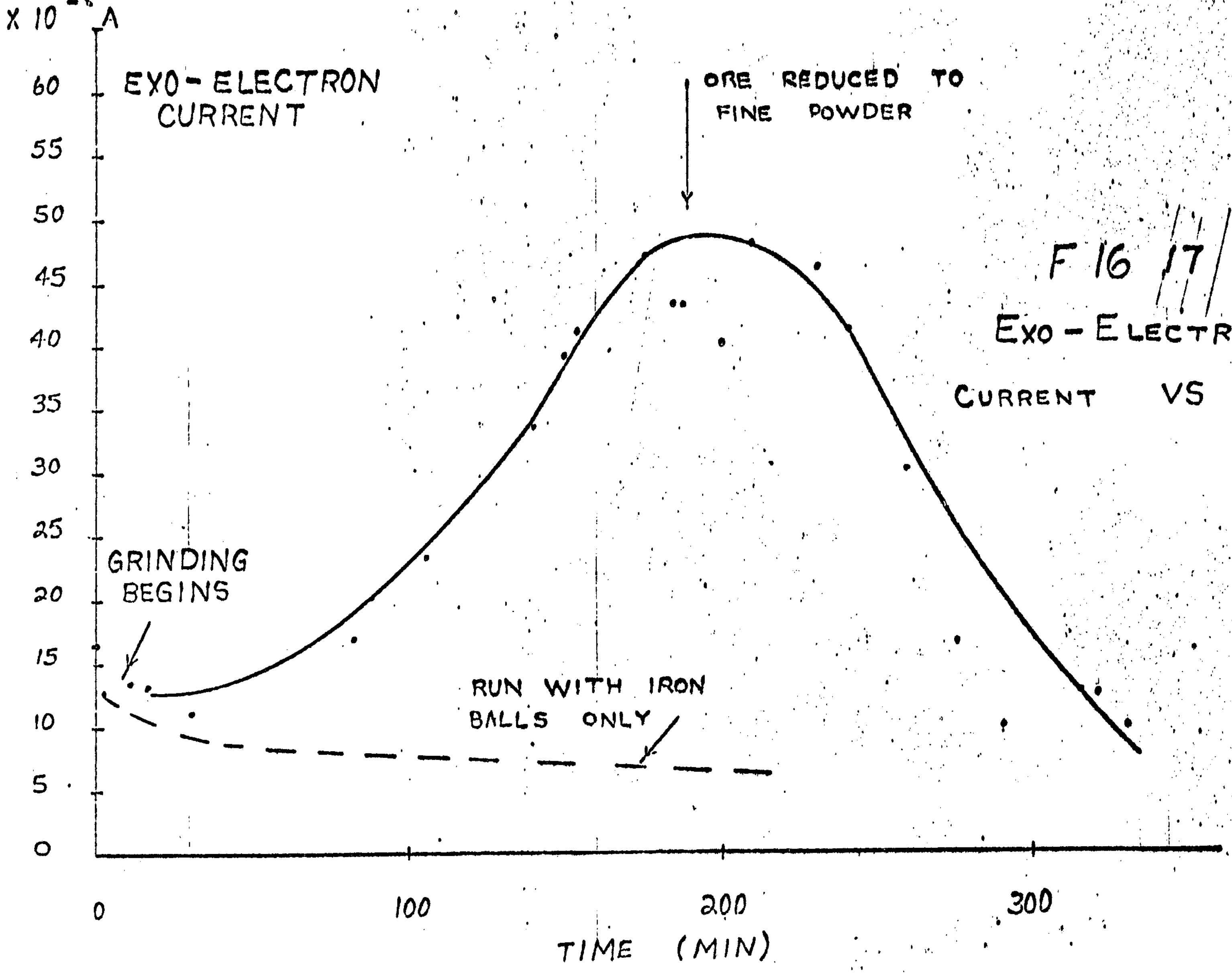


FIG 17

EXO-ELECTRON CURRENT VS TIME

APPENDIX B

A WIRELESS STUDENT RESPONSE SYSTEM

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University of Arizona
Tucson, Arizona

I. Introduction

A system for measuring student response during lectures is badly needed in the universities. This is particularly true in Engineering, where the second part of a course may depend very strongly on what is taught early in the semester. However, it is often difficult to get students to ask questions and to indicate when they are confused because they don't want to look stupid in class. This problem is intensified by the trend to large classes where a close student-teacher relationship cannot exist.

What is needed is a system where the instructor can say "is that a second order non linear differential equation?" "If you think it is, push - your - button." The signals from the student buttons would be added up on the instructors receiver and he would know immediately what fraction of the class was with him. If over 50% of the class is lost he can say so, and the questions will come when each student realizes that he isn't the only one that is confused!

A hard-wire system for this purpose was developed by the author in 1967 (1) and proved practical and easy to use. However the installation costs were too high for general application.

II. The Wireless System

The functional diagram is shown in the attached figure 1. In practice the instructor asks a question, then each student answers "yes" or "no" by pushing or not pushing his button. Each button generates a single microsecond pulse, the receiver totals the pulses for say 10 seconds and then presents the total as a fraction (0 - 100%) of the total number of students in class. No student can vote more than once because of a transmitter lock-out system. The receiver can be reset automatically by a timer or held until the instructor clears it manually. When the receiver clears the student transmitters are ready to go again.

The receiver can be adjusted by the instructor to read 100% for classes from 5 to 200 students. Since about 5 seconds are required for the entire class to respond the probability of an overlap, with 1 microsecond pulses is negligible for 200 students.

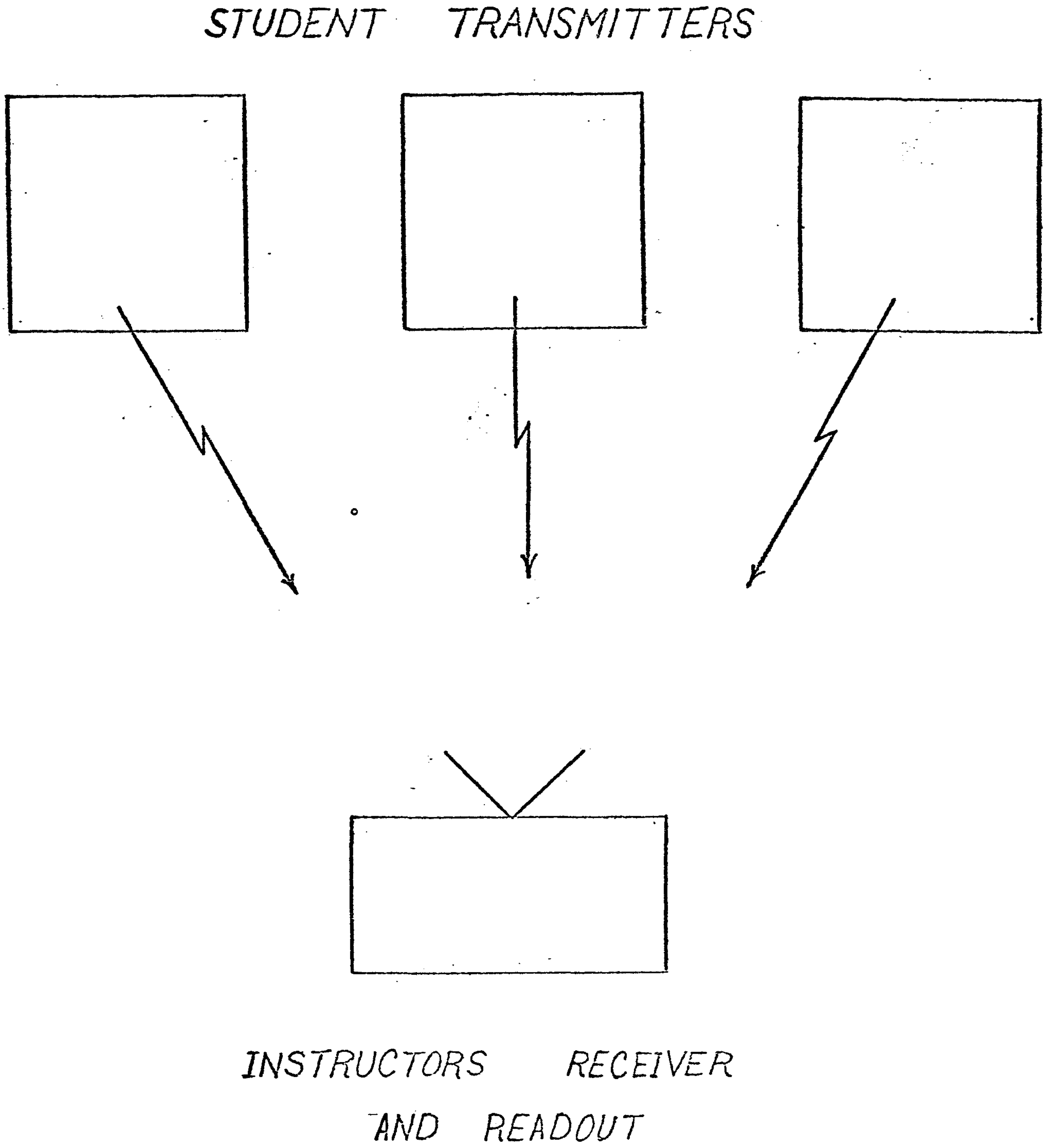
$$P \approx \frac{200 \cdot 10^{-6}}{5} = 4 \cdot 10^{-5}$$

The transmitters will be the size of a ball point pen, transmitters and receiver will fit in a small attache case. The system will be portable so that an instructor can check it out for a particular class application.

A system diagram is shown in figure 1. A functional diagram is shown in figure 2.

Reference

(1) Engineering Education
April 1967 Pg. 588



WIRELESS STUDENT RESPONSE SYSTEM

FIGURE 1

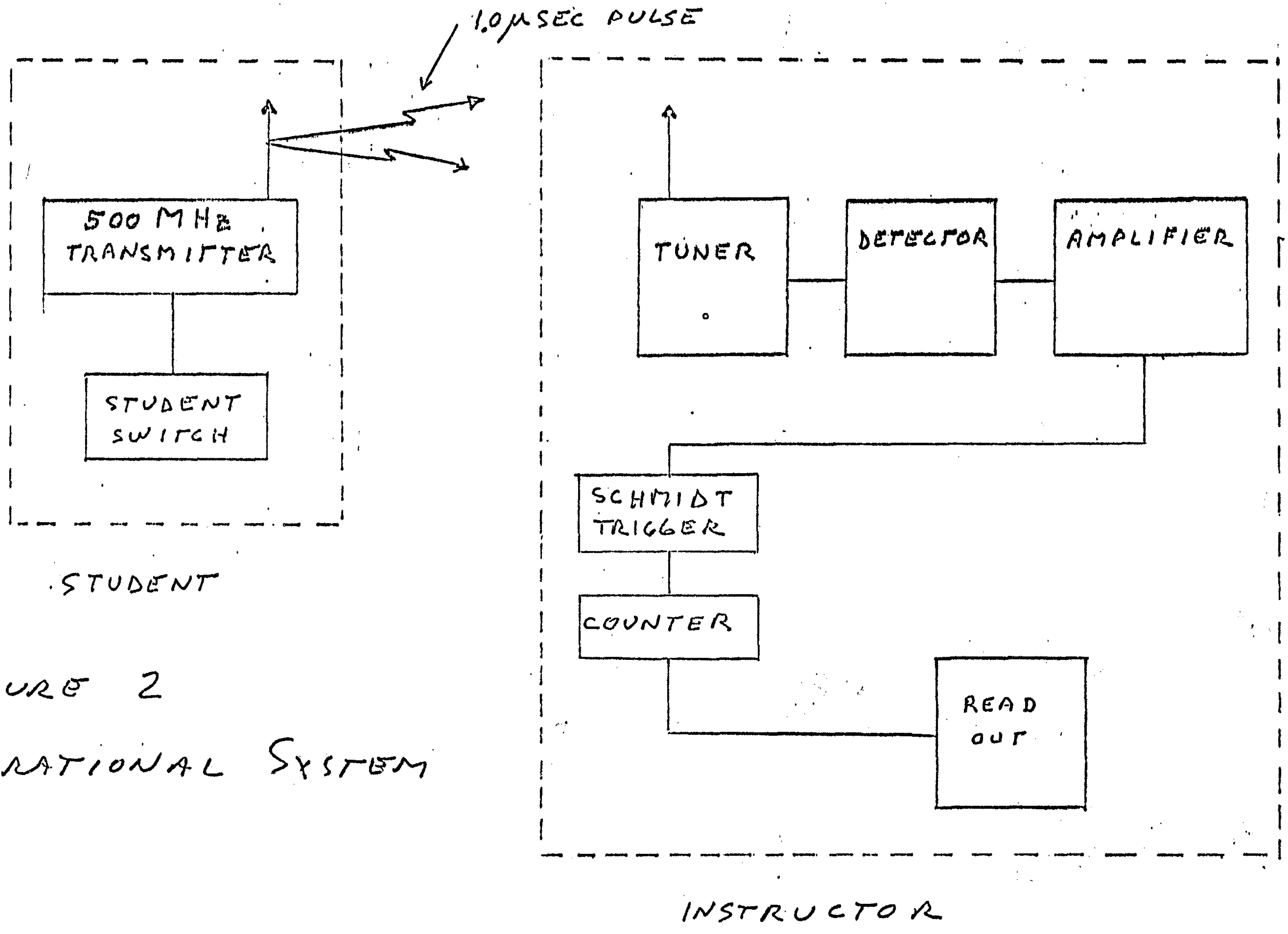


FIGURE 2

OPERATIONAL SYSTEM