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Twenty-Ninth Six-Month Report

DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES.

For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
NGL-03-002-019

By

Stuart A. Hoenig

January 1978



ENGINEERING EXPERIMENT STATION
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THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

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INTRODUCTION, ABSTRACT AND SUMMARY

This report will cover the work performed from 1 July 1977 through 31 December 1977 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 high 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 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 (Publications 11, 12).

In 1968 a new technique for dry replications and measurement of 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).

During the period from 1968 through 1971 the Carbon Monoxide Detector, first demonstrated on the NASA program (Publication 8), was refined and improved for use by the Department of Health, Education and Welfare.

In 1969 studies began on a Corona Discharge Detector for water vapor. This system was shown to be rapid in response, suitable for continuous operation, and reasonably linear in output (on a logarithmic plot) from 10 percent relative humidity to 95 percent relative humidity. A program to develop this detector for hydrological applications began in 1970 but was temporarily dropped because of limited user interest.

In 1970 we began an investigation of the catalytic oxidation of various gasses, i.e., CO, NH₃ and H₂ over metallic catalysts. We demonstrated that the rate of reaction could be observed and controlled in terms of the exoelectron emission from the catalysts (Publication 16). In 1971 this study was directed to the expanded monel metal catalysts used for auto exhaust emission control and for spacecraft atmospheric purification (Publication 19).

This investigation has been extended to catalysts operating at ambient (one atmosphere) pressure (Publication 22) and to the dispersed metal-ceramic catalysts used in the chemical industry. There seems to be no question that the exoelectron effect can be used to monitor catalyst operation.

The capability of monitoring the actual rate of catalysis is important in many industrial operations where a slight change in rate-of-reaction can have a significant effect on the safety or economics of the processes. The conventional techniques, which involved analysis of the reactant or temperature control of the catalyst, are frequently too slow to permit accurate control. Commercial applications of this control technique has been discussed

with the Dow Chemical Company (Texas Division). Another application of the exoelectron effect exists in the area of catalyst research. An understanding of the mechanism relating catalysis to electron emission will help in obtaining a better explanation of the catalytic process itself.

In 1971 we began the study of a new technique for analysis of solid materials. This system involved heating or grinding the substance and observing the induced exoelectron emission. The effect is known as Temperature Stimulated Exoelectron Emission (TSEE). One application of this phenomenon to observation of grinding processes has been published (Publication 18).

In 1973-74 we began investigating the electrostatic charging phenomena that are associated with the generation of dust particles. These charge effects may be an important factor in the atmospheric suspension of particulates during dust storms. This may be particularly significant in the Martian dust storms where the irregular Martian surface would almost preclude the usual wind-dust mechanism.

We have demonstrated that naturally occurring dusts acquire electrostatic charges when agitated. These charged particles are "levitated" by the planetary electrostatic field and become "permanent atmospheric impurities". If similar conditions exist on Mars the electrostatic effects might be the mechanism for suspension of vast quantities of dust in the "thin" Martian atmosphere.

Other aspects of this dust investigation relate to an understanding of dust levitation on the moon. Recent lunar observations suggest that a significant amount of moving dust is associated with the solar terminator.

This dust suspension can only be understood in terms of electrostatic phenomena. An additional problem in understanding the lunar dust studies is the obvious lack of any "wind" to raise the dust. It has been suggested that sand slides or thermally induced rock splitting might provide enough electrostatic charging to induce dust levitation. To investigate this question we began, in 1975, a study of electrostatic charging of minerals under stress. Another facet of this study was aimed at an analysis of the charging of sand as sliding occurred. This work is continuing; partial support for the rock studies has been obtained from the National Science Foundation. The NSF interest relates to the pre-failure detection of underground rock bursts.

Another application of the dust charging studies is aimed at the control of respirable industrial dust by exposure to oppositely charged water fog (Publications 20 and 21). This system is being tested at several industrial plants and the indications are that it is a practical dust control technique. Other applications to the control of coke oven emissions and power plant fly ash/SO₂ are under investigation. We feel that these applications are an important demonstration of useful fallout from the Space Program.

The commercial aspects of this work are being developed by the Ransburg Company of Indianapolis, Indiana. Support for these applied studies is provided by the Ransburg Company and a number of Federal Agencies.

SUMMARY OF WORK IN THE PAST SIX MONTHS AND STUDIES
PLANNED FOR THE NEXT REPORTING PERIOD

Electrostatic Charging of Dust and Its Effect
On Planetary Atmospheres

Experimental Studies at the University of Arizona

As part of this work we reviewed the dust charging work of a number of authors and concluded that the best possible simulation of conditions at the surface of Mars would involve elimination of all external contamination. Another requirement would be a vacuum system to provide the appropriate pressure and gas composition.

The experimental setup for these experiments was shown in our last report (1). In this unit the sand is agitated by a magnetic spinner* driven from outside the vacuum system. The atmosphere in the Pyrex cylinder is monitored by a MKS Corporation diaphragm pressure gauge and dust samples can be taken by flowing dry air or CO₂ into the cylinder and exhausting through an Anderson 2000 impaction sampler. The sampler allows a measure of the particle spectrum from 10 micrometers to 0.6 micrometers.

In another mode the charge of the various dust fractions can be measured, we feel that this information will be of great importance in understanding the dust levitation phenomena.

An important feature of this "spinner system" is its action in throwing the sand up against the walls of the container so that sand sliding is an important factor in sand--sand contact and in generation of fine particulates.

*The magnetic spinner is sealed in Teflon to avoid any chance of contaminating the system with metal.

Studies of the Charging of Ultra Pure Silica Samples

In earlier reports (1) we discussed that charging behavior of typical desert sands and "boom sand" from Fallon, Nevada. In all cases significant negative charging was observed and levitation was demonstrated by observation of charged particulates above the sand bed.

In the present period these studies were extended to ultra-pure silica supplied by the International Minerals and Chemical Corporation of Libertyville, Illinois 60048. This material is particularly free of the heavy metal contamination that has been suspected as a cause of the negative charging observed with other sand samples. An analysis provided by the supplier is given below in Table I.

TABLE I

IOTA Quartz Sample

Chemical Analysis (PPM)	
Fe = 0.5	Cr 0.1
Na = 1.3	A typical initial size analysis
Ca = 1.0	indicated that the particles ranged
K = 0.7	from 0.30 mm to 0.104 mm in
Al = 16.7	diameter

The entire series of experiments is not yet complete but the results to date suggest that the "pure silica" material acquires a significant

charge but that the charge changes sign (from negative to positive) as a function of the altitude above the sand. Typical examples of this data are shown in Figures 1 and 2. In Figure 1 we show the charge in volts at an altitude of 25mm above the sands as a function of time after the spinner is stopped. The voltage is negative and some 3.3 times larger than the voltage measured in essentially the same position with boom sand from Fallon, Nevada (1).

Other data of this type at altitudes of 50, 75 and 100mm above the sand are shown in Figures 2, 3 and 4. It is interesting to note that the initially high negative voltage seems to decrease with altitude and finally becomes almost zero (if we take the average of the data presented in Figure 4). We have no explanation for this at present but it may well be due to the significant "sticking" of the sand after spinning. It should be noted that the ambient pressure for these tests was 50 microns (measured by a Pirani Gauge) rather than the 5 Torr typical of Mars. This was done deliberately in an attempt to reduce the "sticking problem" discussed below. A few runs at higher pressure (5 Torr) showed no significant difference from those discussed above.

The sticking seems to be an electrostatic phenomena in that it is always observed after spinning in vacuum. In some cases it has been so severe that the magnetic spinner was actually brought to a halt. If air was admitted to the system the "sticking" decreased suggesting that an electrostatic effect is involved. We plan to repeat these experiments with pure quartz that has been heated to drive off water vapor. Another question of interest is the effect (if any) of solar ultraviolet in the

charging of dust. Data from the Viking Landers indicates that significant amounts of dust are present at high altitudes where we can expect intense solar ultraviolet radiation.

To evaluate this ultraviolet effect we took samples of "boom sand" and ultra-pure quartz. The materials were "ground" with a mortar and pestle and then drawn into the Anderson sampler for charge analysis. The process was repeated with material that had been exposed for some fifteen minutes to intense ultraviolet from a Ultra Violet Products Company (San Gabriel, California) model 11 SC-1 quartz lamp. These units produce some 2.4 mW/cm^2 of 2537 Angstrom radiation at a distance of 25 mm. The results are given in tabular form below. It appears that both the boom sand and the pure quartz acquire a significant negative charge when agitated. After exposure to the Ultraviolet the boom sand lost quite a bit of charge. We suggest that this was due to emission of photoelectrons from the metallic contamination (iron) that is a naturally occurring component in most desert sands. In contrast the ultra pure quartz lost little or no charge suggesting that there was no significant photoelectron emission.

TABLE II
EFFECTS OF GRINDING AND ULTRAVIOLET EXPOSURE ON DUST CHARGING

Dust Charge (Arbitrary Units)	Average Diameter (Microns)			
	11	5.8	2.7	0.88
Boom Sand Ground	-40	-15	-4	-1
Boom Sand Ground & UV Exposure	-10	-4	-1	-0.4
Ultra Pure Sand Ground	-80	-16	-3	-1
Ground + UV Exposure	-80	-11	-3.7	-1.5

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These results are highly preliminary but they suggest that the naturally occurring charge on high altitude dust particles might be modified by exposure to solar ultraviolet. This may, in turn, be a factor in the long term suspension of such particulates in the Martian atmosphere.

Studies of Adsorption-Desorption Charging of Desert Sand

One question about Martian dust storms that has not been resolved concerns the initiating factor; "what lifts the sand or dust in the first place?" One suggestion has been made by Johnson, et al, (2) that thermally induced adsorption-desorption of CO_2 might result in charging and levitation of fine particles. On Mars one would expect that CO_2 would occur during the night followed by desorption during the day. To investigate this phenomena a test tube was set up so that it could be cooled by a mixture of dry ice and alcohol or heated by water at room temperature. The tube was partially filled with desert sand and a thermocouple was used to monitor the sand temperature. To observe any emission of electrons during desorption a probe was placed some 25 mm above the sand. The probe was biased at +90 volts and connected to a Keithly 610 electrometer to measure the currents if any.

The results with this system were erratic for reasons which are not clear at this time. In a number of cases significant (10^{-10} amp) currents were observed during desorption while occasional hopping of sand grains was noticed. Unfortunately this data was not consistent from run to run and at the moment we cannot draw any conclusions about this aspect of the problem.

We have been discussing this work with a research group at NASA Ames Laboratory that has been doing some work on saltation of sand grains with

applications to Martian dust storms. We anticipate further work with this group and possibly some tests at the Ames facility.

Development of Specialized Apparatus for Dust Measurements on a Planetary Lander

In our first evaluation of apparatus that might be used from a lander vehicle we rejected the impaction sampler because of its requirement for a vacuum pump to pull the gas through the system. Another problem with impaction samplers is their aerodynamic operation that depends directly upon the atmospheric density, temperature and viscosity. Conditions on the Martian surface do not lend themselves to the accurate prediction of the effects of these parameters.

We felt it most important to provide a system that could be used for measurement of ambient dust density, as a function of particle size. Another part of the system would be used for observation of the charge, if any, of the collected dust. In our last report (1) we discussed the charge measurement system* but at the time we indicated that the proposed "pressure drop" method for measuring the quantity of dust deposited was fraught with difficulty. In the last period we have made significant progress with an optical system for evaluation of filter dust loading.

The present system is a portable, battery powered, version of the tape samplers used for industrial smoke evaluation.

*The initial studies of this system were done under a grant from the Ransburg Corporation of Indianapolis, Indiana and are the subject of a patent application by that company.

To test the optical evaluation technique a series of dust samples were collected on the filter by means of a small pump. The weight of the collected material was determined and the change in optical density was evaluated using the system discussed above. This was done for a series of filter loadings and for some different types of dust, the results are shown in Figure 5. We note that the curves are essentially linear in that the optical density decreases linearly as the filter loading increases. This is encouraging and suggests that an evaluation method of this type can be used over a wide range of dust loadings. The curves vary in slope depending upon the material involved. This was expected because of the great difference in reflectivity between various dusts.

In this study the filter opening was 8 micrometers to catch all particulates above that size. The application of filters in series, i.e., 10, 8, 6, 4, etc., micrometers would allow the dust to be separated by size with a small, low power blower rather than a high current vacuum pump.

This variation in slope from dust to dust should be no obstacle to the use of the system in a planetary lander. The dust picked up by a lander system will be of a single kind and we are concerned primarily with the quantity of dust in each size range rather than particular type of dust (which might well be measured by other techniques). The optical system requires only low power to operate and that on an intermittent basis. No radioactive source or delicate detection equipment is needed as would be the case with beta ray dust measurement systems. We suggest that a portable optical system is most suitable for planetary dust evaluations. A system for in-situ evaluation of the filter dust loading is under consideration.

Monitoring of Catalyst Operation by Means of Exoelectron Emission

The catalysis investigations have continued the work reported six months ago. During the present period we have been working with dispersed catalysts to determine if it is possible to control the rate of reaction by changing the rate of exoelectron emission associated with the catalytic reaction.

The investigation is directed at the reaction between ethylene and oxygen and we have demonstrated that the product material is definitely ethylene oxide rather than carbon dioxide. In our report of one year ago we suggested that this was the case, but the fact that both product materials have the same M/e value of 44 made it difficult to prove that ethylene oxide was being formed. In the last twelve months we have made use of a gas chromatograph to demonstrate that the reaction of ethylene and oxygen, over heated sheet silver, produces ethylene oxide rather than carbon monoxide.

In the last six months we have made use of a dispersed silver catalyst on a ceramic tube that can be heated by an internal element. This is the same system used in our earlier studies except that provision has been made to hold the conductive silver catalyst at a chosen voltage to enhance or retard the exoelectron emission. In an earlier publication (number 16) we indicated that controlling the exoelectron emission will affect the rate of reaction. In that case the reaction used a palladium wire catalyst and no attempt was made to use alternating voltages to control the exoelectron emission. We hope to show the frequency dependence of the exoelectron/reaction rate effect and to demonstrate that this control technique can be used on dispersed catalyst materials.

Typical first results in this test series are shown in Figure 6. Here the catalyst was brought to operating temperature in the ethylene plus oxygen environment. At this point an AC voltage (10^VRMS) was applied to the catalyst and we observed the exoelectron emission I_A and the rate of reaction (K) as a function of frequency.

Looking at Figure 6 we note a small peak in I_A at about 20 Hz and a much larger rise beginning at 150 Hz. At 220 Hz there was a reversal in current sign with a sudden increase at 250 Hz. This portion of the curve was traced several times with increasing and decreasing frequency signals. No hysteresis was observed.

The plot of (K) is also shown in Figure 6, no sudden changes in (K) were observed but there was an increase in the 150-250 Hz range that can be correlated with the I_A data.

We suggest that this frequency dependence is a most important effect that will be investigated in more detail in the next six months.

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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, September 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 NASA support)
4. Col. C. W. Carlson, M.S., 1965; Active Duty, U. S. Army.
5. Melvin Eisenstadt, Ph.D., 1965; Soltrax Inc., Albuquerque, N. M.
6. John Lane, M.S., 1968; Philco Ford Company, Tucson.
7. William Ott, M.S., 1970; Burr-Brown Research, Tucson. (Partial NASA support).
8. Richard Pope, M.S., 1972; Hewlett-Packard Corp., Palo Alto, California.
9. Robert Goetz, M.S., 1972; North American Rockwell Corp., Los Angeles, California.
10. Freedon Tamjidi, M.S., 1972; Field Engineer, Westinghouse Corporation.
11. Douglas K. Darlington, B.S., 1977; Graduate School, University of Arizona.

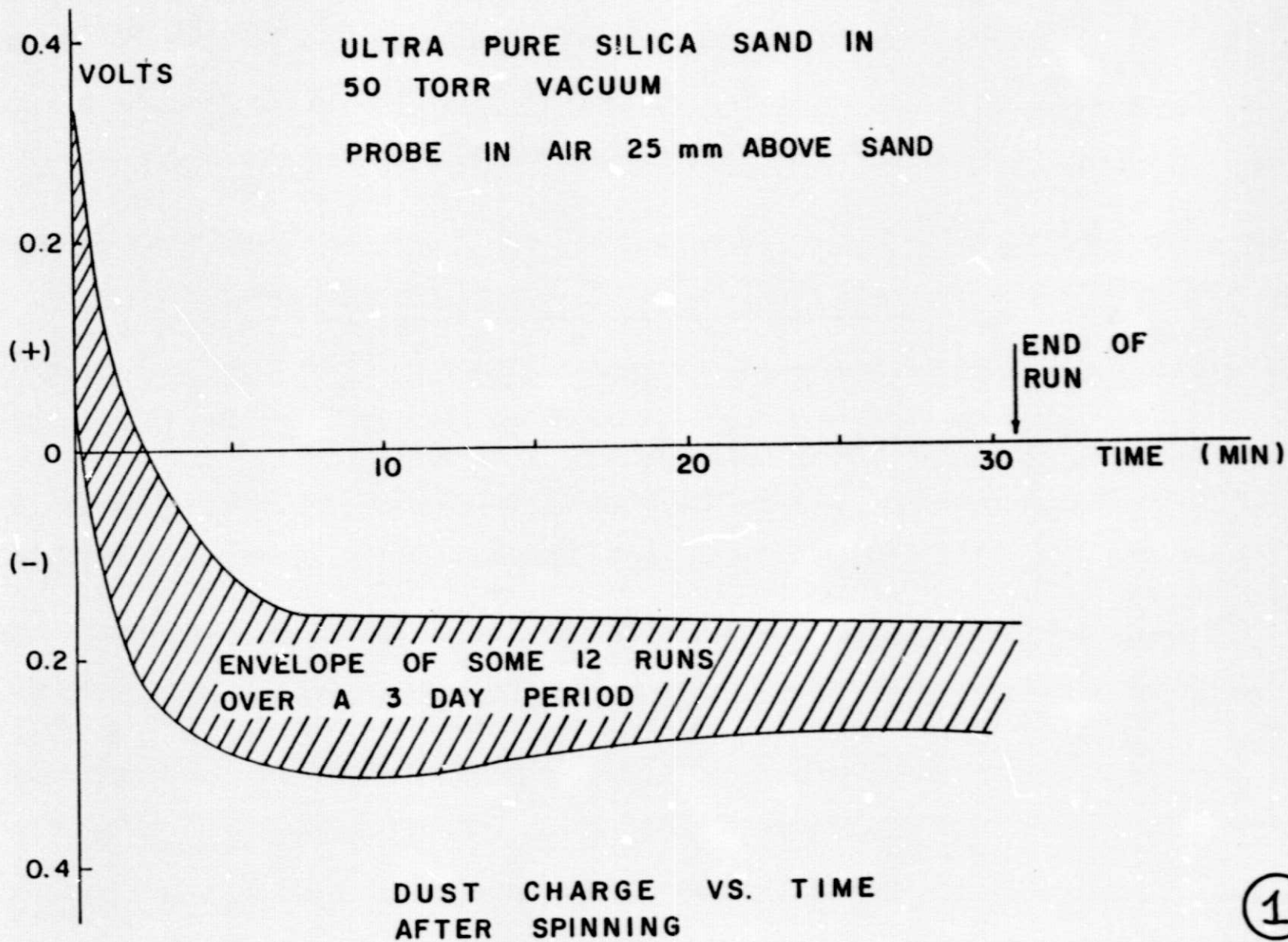
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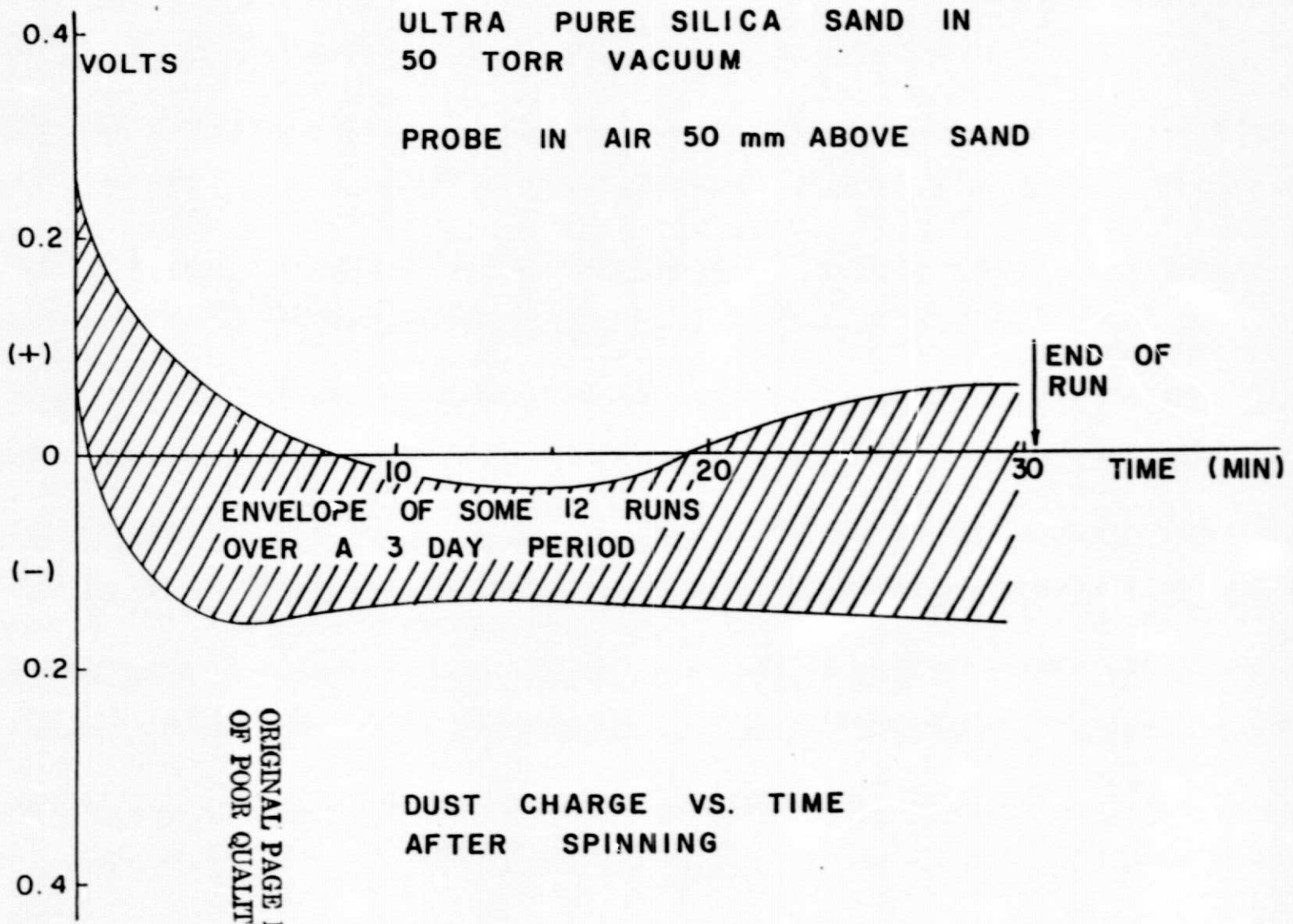
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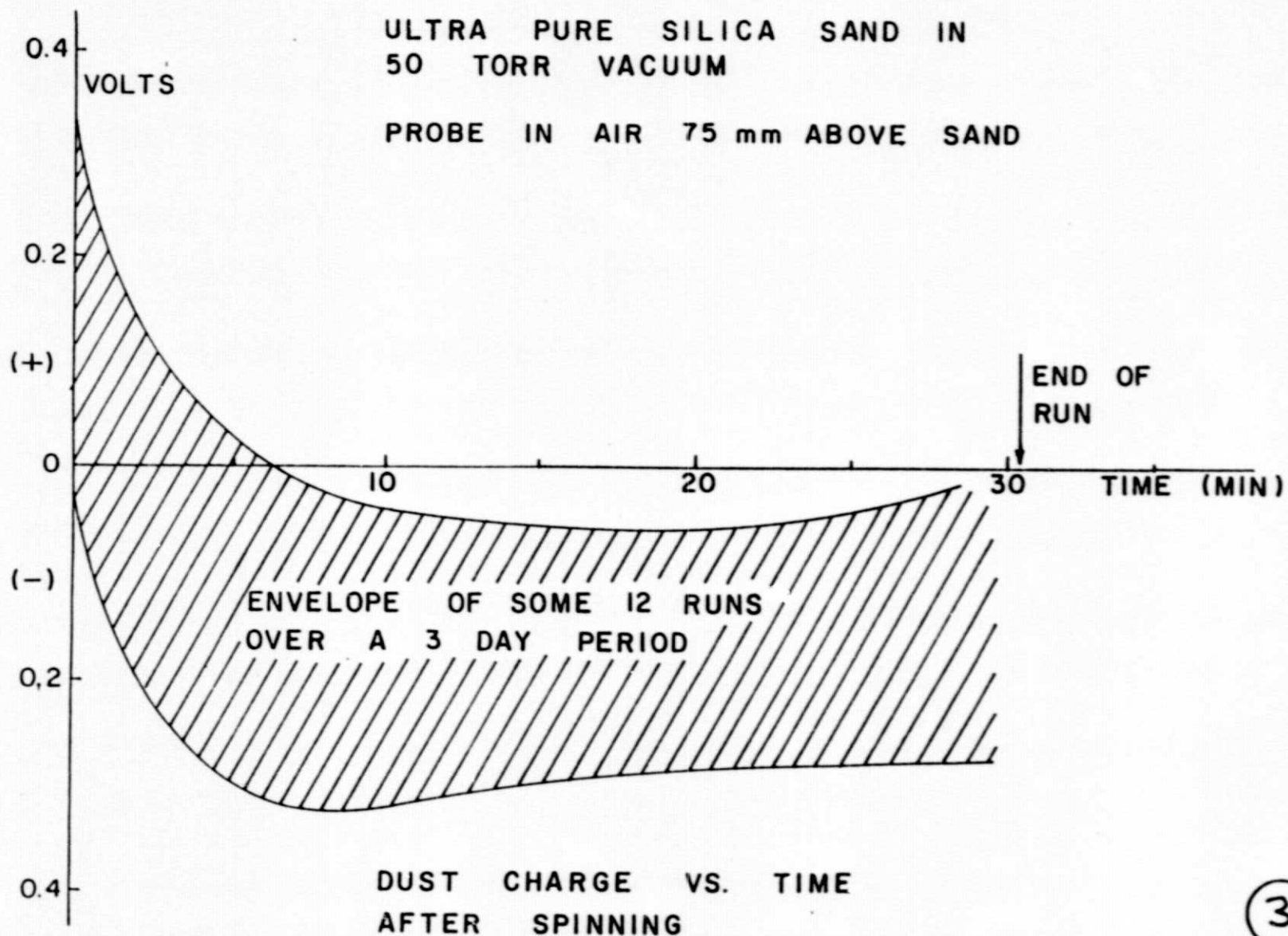
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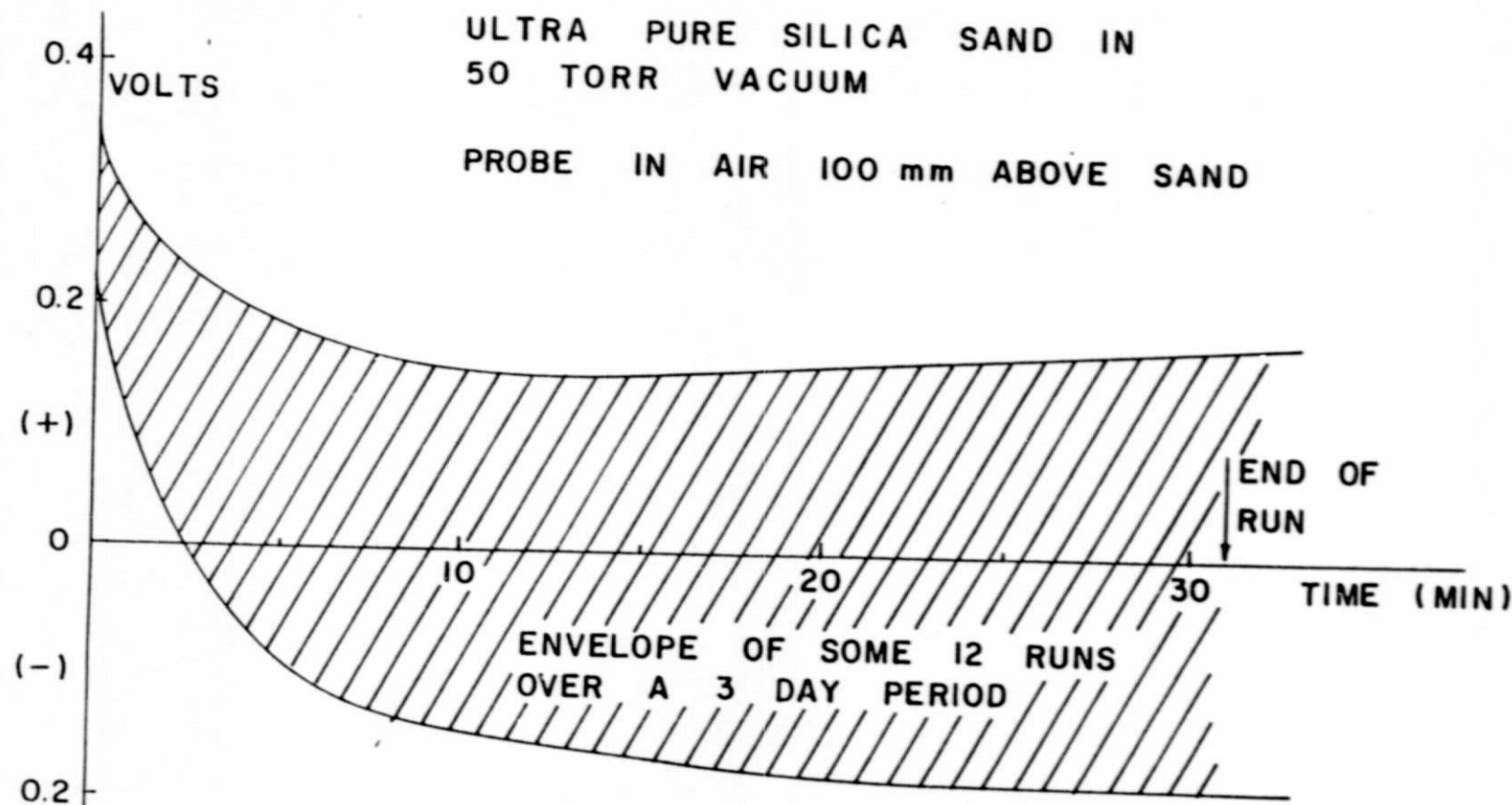
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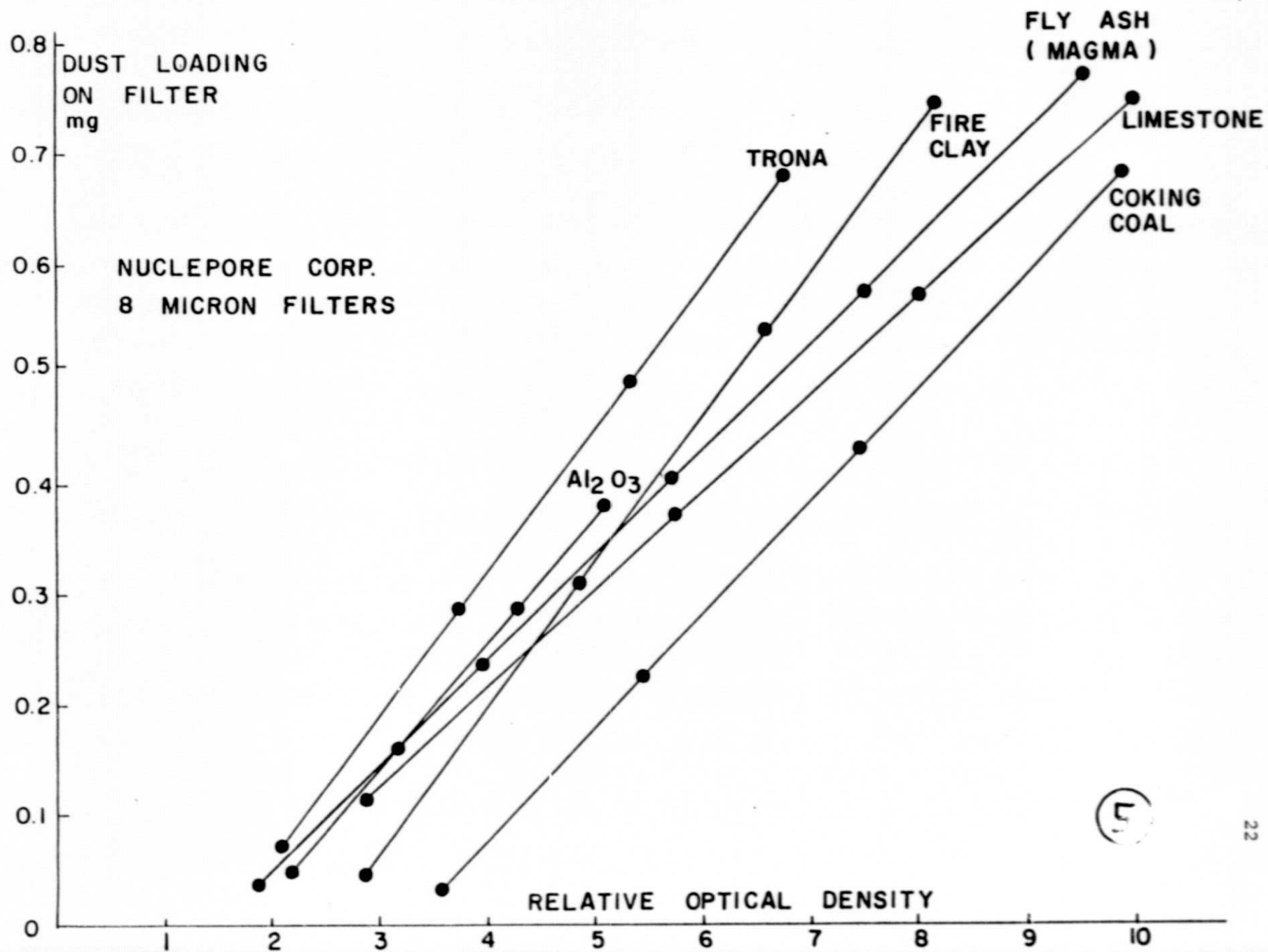
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DUST CHARGE VS. TIME
AFTER SPINNING

4



EXOELECTRON CURRENT AND REACTION RATE VERSUS FREQUENCY

(APPLIED VOLTAGE 10 VRMS)

