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Interim Report

MEASUREMENT OF NITRIC OXIDE IN THE EARTH'S ATMOSPHERE

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INTRODUCTION

The role of nitric oxide (NO) in the lower ionosphere continues to be controversial. Nicolet and Aikin (1960) prepared a D-region model based primarily on the photoionization of NO by solar Lyman- α radiation. Recently Aikin, Kane, and Troim (1964) reported D-region electron concentration profiles that confirmed the NO mechanism according to their interpretation. Poppoff and Whitten (1962) and Poppoff, Whitten, and Edmonds (1964) have shown that currently accepted values of NO concentration, photoionization cross-section, and ion-electron recombination coefficients can provide the basis for a D-region model only during solar sunspot minima. The bases for all current models and interpretations have been NO profiles on the order of 10^{-10} to 10^{-9} of the total concentration of ionospheric species in the D-region (Nicolet, 1955; Barth, 1961).

During the past year Barth (1964) has reported measurements of NO (the first ever made) in the D-region that have caused considerable confusion and consternation among aeronomists concerned with physical and chemical processes in the lower ionosphere. The reported concentrations, derived by analysis of NO resonance scattering observations, were from one to three orders of magnitude greater than previous theoretical estimates. The implications of these measurements, if correct, are profound and will require a complete overhaul of D-region models, mainly because of the exceedingly high electron densities that should result from photoionization of such large concentrations of NO. In order to provide reasonable electron concentrations, either the ionization cross section must be reduced or the recombination rate must be increased (or, perhaps, both). Neither possibility appears reasonable at this time. Another problem that must be resolved is the identification of the mechanism for NO production that would provide these large concentrations. A recent attempt by Nicolet (1964) to provide such a mechanism for the D-region requires that the ion-interchange reaction, $O_2^+ + N_2 \rightarrow NO^+ + NO$, assume an important role. Unfortunately, the cross section for this reaction is not known and the validity of this theory cannot be properly assessed.

The present quandary, however, underscores the urgent necessity for another, independent means of measuring NO in the ionosphere. Whether the values reported by Barth are correct or not, they must be checked because of their great importance in assessing the various ionization processes in the ionosphere.

Nicolet's hypothesis based on the above mentioned ion-interchange reaction has a special significance to the ionization interests of DASA. Nicolet's suggestion implies that any excess nuclear burst ionization (which results in increased formation of C_2^+) will result in the production of large concentrations of NO^+ (both directly through the ion-interchange reaction and through the photoionization of neutral NO produced in that reaction). If true, it would follow that NO ion-electron recombination is undoubtedly the controlling reaction for electron removal.

The nitric oxide detector now being developed at SRI with DASA support promises to be an excellent instrument for checking the controversial measurements made by Barth as well as providing the means of investigating the importance of changes in NO concentrations produced by high altitude nuclear tests.

The theory of operation of this unique instrument was described in the original proposal (SRI No. PAU 63-146 Rev.) and will not, therefore, be discussed further. The feasibility of the technique was demonstrated by an earlier project for DASA (Young, et al, 1963). During the past year a D-region simulator has been constructed for the purpose of testing both laboratory models and prototypes of the NO detector with special emphasis on the assessment of possible interference by excited states of O_2 , N_2 , and NO. Although only limited testing has been possible, the concept of selectively measuring NO by photoionization appears sound. The D-region simulator and current activities are described in this interim report.

OBJECTIVES

The objectives of the work performed under this contract were

1. To develop a testing facility capable of evaluating a nitric oxide measuring device
2. To develop, individually, the components of the NO measuring device to a degree adequate for D-region measurement.

METHOD OF APPROACH

The current model of the D-region nitric oxide measuring device is shown in Figs. 1 and 2. An intense beam of krypton resonance radiation (1236 Å) is projected between parallel electrodes. The outer electrodes sweep the ambient gas free of ions as it enters and the central region collects the ions formed by the Kr resonance radiation. Modulation of the ionizing radiation permits unique identification of its effects.

This method of measuring nitric oxide is feasible. It will be initially assumed that primarily NO is ionized by photons of approximately 10 eV energy. The ionization cross section of NO is accurately known (Watanabe, 1958), and detection of the ions produced is simple and extremely sensitive. Consider a parallel-plate ion collection system 10 cm long. If a 1 cm^2 photon beam of 10^{16} photons/sec is projected between the plates, the number of ions produced per second per cc will be $[\text{NO}] \times (2 \times 10^{-18}) \times (10^{16}) = 0.02 [\text{NO}]$; roughly 2% of the NO present will be ionized in one second. The current collected from the 10 cc that are irradiated will be $\approx [\text{NO}] \times 10^{-20}$ amps. If $[\text{NO}] = 10^4/\text{cc}$, the collected current will be $\approx 10^{-16}$ amps, which is presently detectable in a measuring time of 1 sec. Removal of NO by local photoionization will be negligible for any reasonable atmospheric sampling flow through the detector. Other losses of the ions created by photoionization, such as recombination, will also be negligible under the conditions existing in the upper atmosphere and in the time available between creation and collection.

Though the method is specific and feasible -- even for such minute amounts of NO as $10^4/\text{cc}$ -- it is not without its drawbacks. The ions

normally present in the ionosphere and swept between the collecting electrodes by the motion of the detector through the atmosphere would greatly exceed the number produced by local photoionization of NO. Most of the ions could be removed before they enter the photoionization region by auxiliary electrodes. (The current to these sweeping electrodes would be informative in itself.) However, the reactive species of the upper atmosphere may react either with themselves or with the electrode surfaces to produce ionization. To discriminate against such ionization (which would not be larger than that produced by local photoionization of NO) the ionizing light source should be modulated (chopped) and only the modulated component of the ion current amplified and detected. Care must be taken to prevent photo-ejection of electrons from the electrode surfaces by stray or scattered radiation. Simple constructions can prevent photo-ejection by solar radiation without materially affecting the free sampling of the atmosphere by the detector. The effects of the electrode surfaces on the equilibrium concentrations of NO in a system of O, N, N₂, and O₂ must be evaluated.

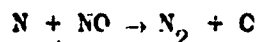
It is quite difficult to obtain extremely strong sources of Lyman- α radiation needed for this experiment. A more suitable source is the krypton resonance line at 1236 A. Absorption of this ionizing radiation by molecular oxygen will not be serious. At 1236 A the absorption cross section of molecular oxygen is $5 \times 10^{-19} \text{ cm}^2$; consequently, $10[\text{O}_2] \times (5 \times 10^{-19}) \times 100\%$ of the radiation will be absorbed in passing through the electrode system. At 60 km $[\text{O}_2] \approx 10^{14}/\text{cc}$ and $\approx 0.05\%$ absorption occurs, which is inconsequential and becomes of even less consequence at higher altitudes. Since the sensitivity of the detector is proportional to the ionizing light flux, a simple nitric oxide (Chubb and Friedman, 1959) or iodine (Brackman, Fite, and Hagan, 1958) photoionization chamber should monitor it. Large variations in the output of the light source are not expected over the relatively short measuring time offered by rocket probes.

PROGRESS

A. D-Region Simulator

The D-region simulator is a device capable of creating, in varying degrees, all the phenomena which the measuring device might encounter during its passage through the D-region except those relating to high speed motion in the upper atmosphere, and direct solar illumination of the device. The effects of solar radiation on the D-region itself are duplicated.

To simulate the D-region a low pressure environment composed of atomic oxygen, nitrogen, excited molecular nitrogen and oxygen, and the chemical products resulting from the interaction of these species is required. This is accomplished by passing highly purified nitrogen through a powerful microwave discharge in a low pressure, fast flow system. The partially dissociated nitrogen is then reacted with a stream of nitric oxide.



which generates atomic oxygen from atomic nitrogen. By varying the original atom density (i.e., by adjusting the pressure, flow rate, and microwave power), and the amount of NO added, the total atom content and the ratio of $[O]/[N]$ can be set. Molecular oxygen can then be added to whatever concentration is desired. By discharging the oxygen as it passes through an auxiliary inlet coated with HgO, varying amounts of excited O_2 (with no associated oxygen atoms) can also be added. This mixture reacts to establish a steady state nitric oxide concentration in exactly the same way that occurs in the D-region. Furthermore, chemionization processes generate NO^+ , the predominant positive ion in the D-region.

The D-region, despite the simplicity of chemical elements present, is a very complex medium when the energy states of its constituents and the ionic species present are taken into account. Hence it is not surprising that a complicated series of preparations are necessary to duplicate its essential features. Because of this complexity, relatively

elaborate measurements must be made and considerable preliminary investigation is necessary to characterize the resulting medium in which the NO measuring device is to be tested. The simulator in operation is shown in Figs. 3, 4, 5, and 6.

The major analytical tools used in the present simulator are optical radiation detectors which monitor the excited molecular and atomic states directly and the ground state reactants indirectly through previously studied chemiluminescent reactions. Although not now in use, absorption measurements and a quadrupole mass spectrometer will soon be applied to further define the test media.

Figure 7 shows schematically the essentials of the simulator. Six filtered photomultipliers (Fig. 8) which detect emission from $N_2(B^2\Pi)$, $NO(^2\Pi)$, $O_2(a'^1\Delta_{v=0})$, $O_2(b'^1\Sigma_{v=0})$, $O_2(b'^1\Sigma_{v=1})$, $O_2(^3\Sigma)$, O_4^* , and NO_2^* can be seen pointing into the observation bulb. Typical variations of these bands with $[O]$, $[N]$, $[N_2]$, $[O_2]$, and the interdependencies of some of the emission resulting from reactions among excited species are shown in Figs. 9, 10, and 11.

Titration inlets where NO (which measures $[N]$ or $[O]$ through the reaction $N + NO \rightarrow N_2 + O$) and NO_2 (which measures O by $NO_2 + O \rightarrow NO + O_2$) can be seen in each segment of 4-inch-diameter pyrex tubing which transports the gas from the 1 kw microwave generator (Fig. 12) to the 72-liter bulb. Calibrated reservoirs (Fig. 13) equipped with calibrated diaphragm transducers are used to derive titrant flow rates from the rate of pressure change in the reservoirs.

Other inlets (Figs. 12 and 14) can be seen for the addition of other gases to selectively quench (i.e., deactivate) excited molecules. The slanted wooden table (between the reservoirs in Fig. 15) will hold a movable photomultiplier to observe the transition from a steady state of the gas above a circular inlet (to promote mixing) to a new steady state which is caused by the gas addition. Below the two parallel pipes can be seen the second discharge system (Fig. 14) for adding excited O_2 separately.

The 6-inch metal piping leads through the wall and connects to a high capacity Roots pump and large oil pump. These pumps will empty a 220-cubic-foot cylinder of gas in 150 minutes at a system pressure of 10.0 mm Hg. The pumps operate efficiently to 10^{-3} mm Hg and measurements have been made at 10^{-2} mm Hg. Two high pressure gas storage manifolds are located outside the building on a porch, each drawing gas from four large cylinders.

The large wooden box (Fig. 16) contains a PbS infrared detector, filters, light chopper, and amplifier. All the other amplifiers, balance and time constant circuits, and recorders are centrally located on a table near strategic gas valves (Fig. 17). The photomultiplier high voltage supplies are above the 72-liter bulb (Fig. 19).

Several optical spectrographs are available for use, only one of which is shown in operation (Fig. 16). The large bulb has several entrance ports through which the test device (shown in Fig. 2) enters the test environment.

B. The NO Measuring Device

Figure 2 shows the current device under test. The outer electrode structure completely surrounds the central signal electrode which measures the ionization produced by the Kr resonance radiation excited in the high intensity lamps. To date this design has proved adequate.

C. High Intensity Vacuum Ultraviolet Lamps

These lamps required considerable development. LiF is cleaved by the device in Fig. 19 to $\approx$ 1-mm-thick windows and sealed to the lamp body by various techniques (AgCl on Pt and various epoxy resin cements). A quartz wool plug is then inserted from the other end followed by uranium filings and the complete assembly is attached to the high vacuum filling system shown in Fig. 20. After a preliminary pump-down and flaming, hydrogen is admitted and the uranium reacted by slow and careful heating of the filings. Furnaces are then raised about the lamps, the system opened to the pumps, and the uranium hydride (formed when the uranium reacted with H_2) is slowly decomposed, yielding an activated uranium

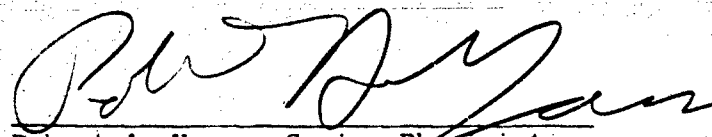
getter. Krypton is now admitted to the proper pressure and the tube sealed off. The lamps are then tested for total emission intensity using a nitric oxide ion chamber shown in Fig. 21, and their spectral characteristics determined on the spectrometer shown in Fig. 22.

The present lamps produce $\approx 10^{15}$ photons/sec but this flux decays rapidly with time, as Fig. 23 indicates. Although lamps have been operated for ≈ 10 hours, their real usefulness is limited to ≈ 1 hour or less. It is believed that the rapid decay of lamp intensity is due to radiation damage of the LiF window. Investigation is continuing to verify this.

Usually the lamps are excited by a microwave cavity and generator, but excitation at lower frequency (Fig. 21) is of comparable efficiency. Low power, low frequency (≈ 100 mc) light-weight excitation oscillators are under development, and efforts are continuing to improve lamp intensity.

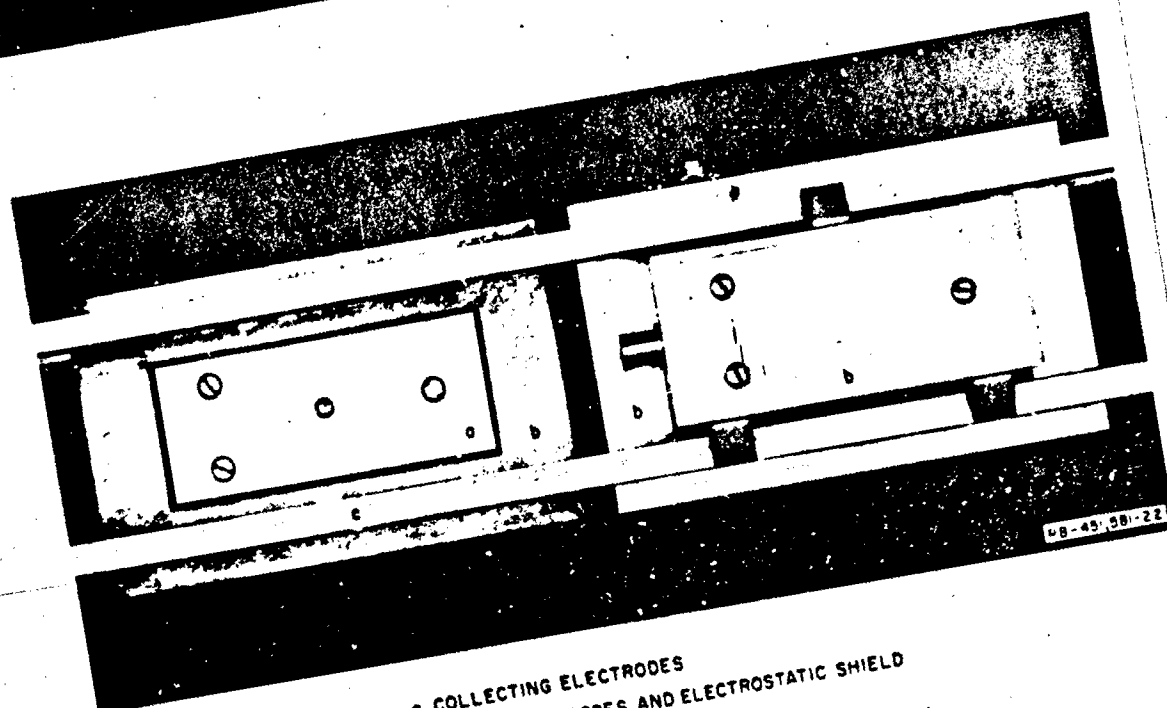
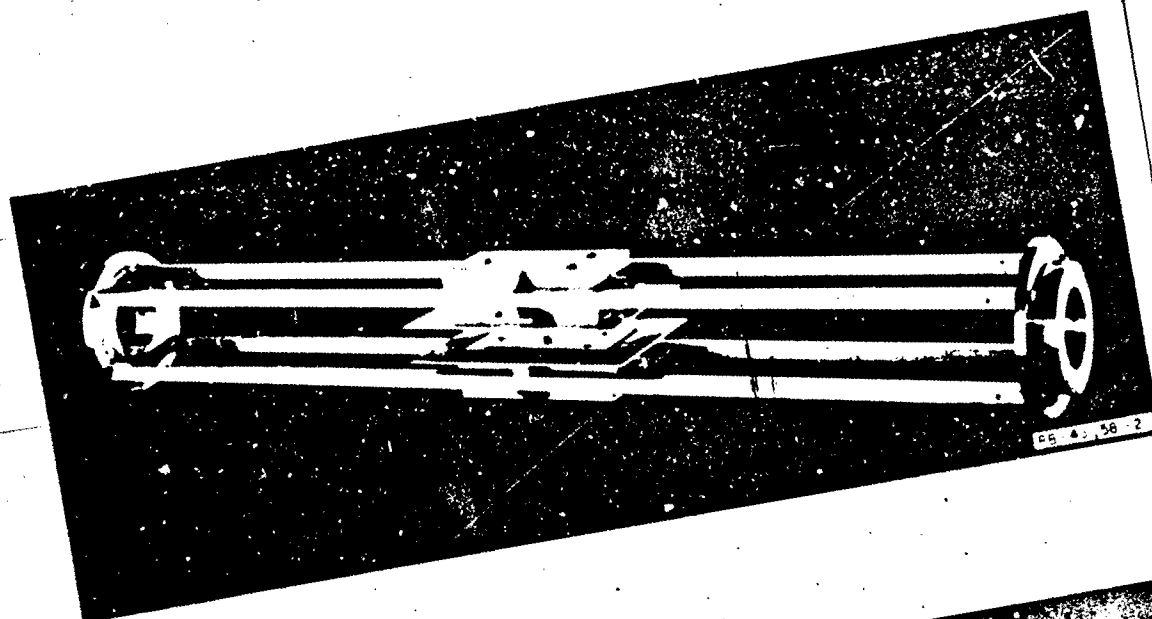
D. Current Status

Only very preliminary tests of the prototype NO measuring device have been completed because of the long construction period required for the D-region simulator and the extensive lamp development program. However, no serious difficulties have yet been experienced in using the prototype device. It is anticipated that ≈ 4 months will be required to verify the original estimates of its sensitivity and specificity for detecting NO. A parallel engineering development of a flight certifiable instrument is planned.


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Department of Atmospheric Sciences

Approved:


Charles J. Cook, Executive Director
Chemical, Theoretical, and Applied Physics



- a COLLECTING ELECTRODES
- b GUARD ELECTRODES AND ELECTROSTATIC SHIELD
- c ELECTRODE SUPPORTS

FIG. 1 PROTOTYPE ELECTRODE ASSEMBLY

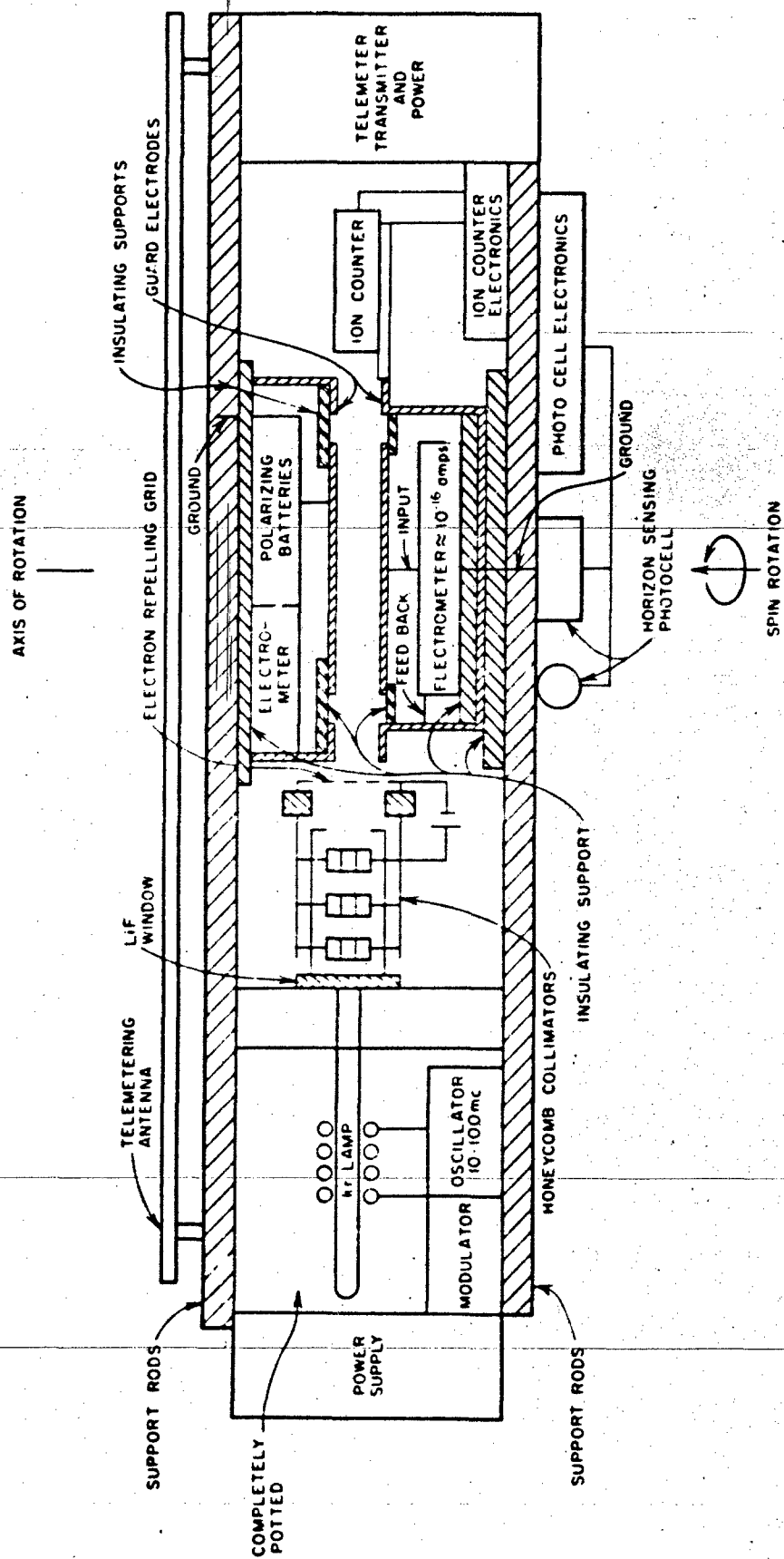


FIG. 2 PRELIMINARY SKETCH OF THE ROCKET-BORNE NO MEASURING DEVICE

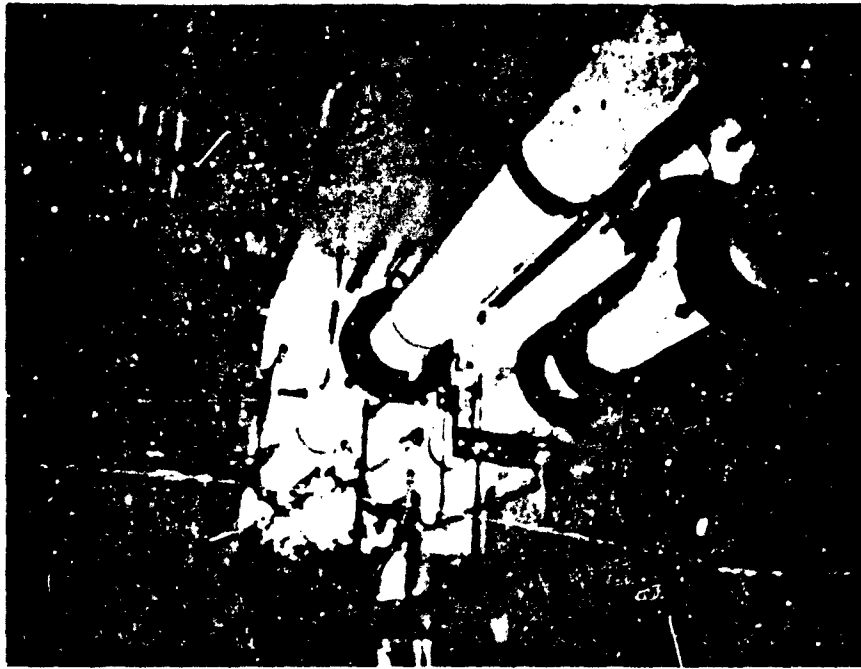


FIG. 3 THE SIMULATOR IN OPERATION LOOKING TOWARD
THE DISCHARGE

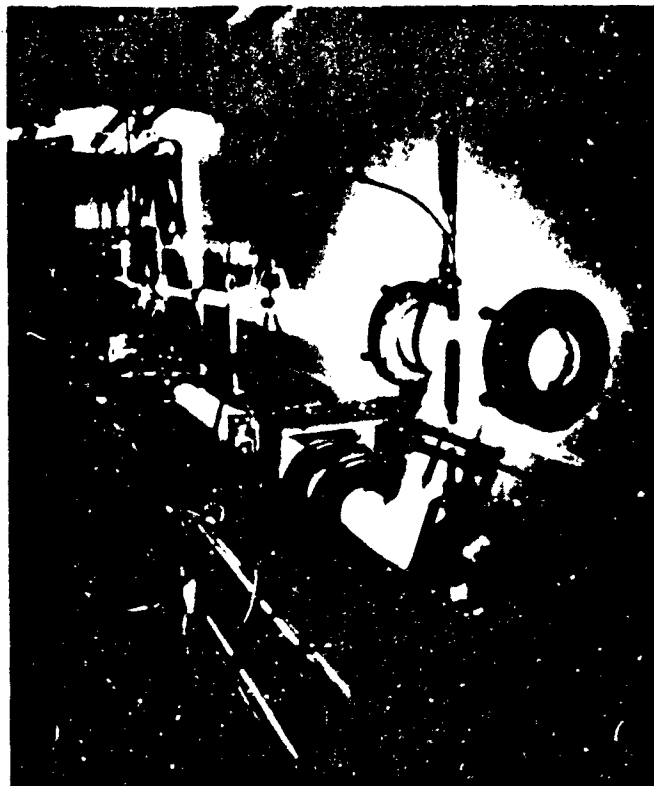


FIG. 4 THE SIMULATOR IN OPERATION LOOKING TOWARD
THE DISCHARGE



FIG. 5 THE SIMULATOR IN OPERATION LOOKING
TOWARD THE OBSERVATION BULB

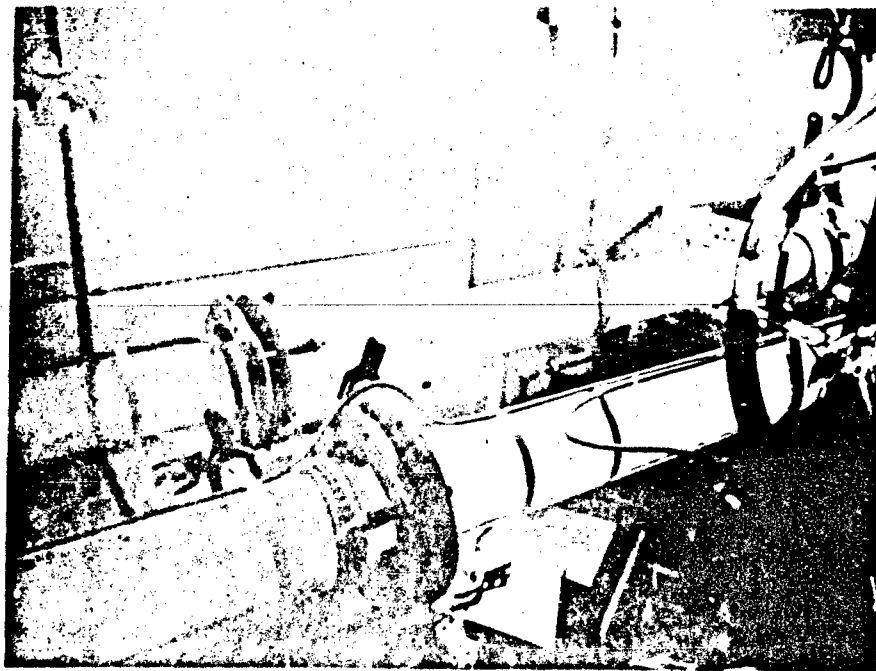
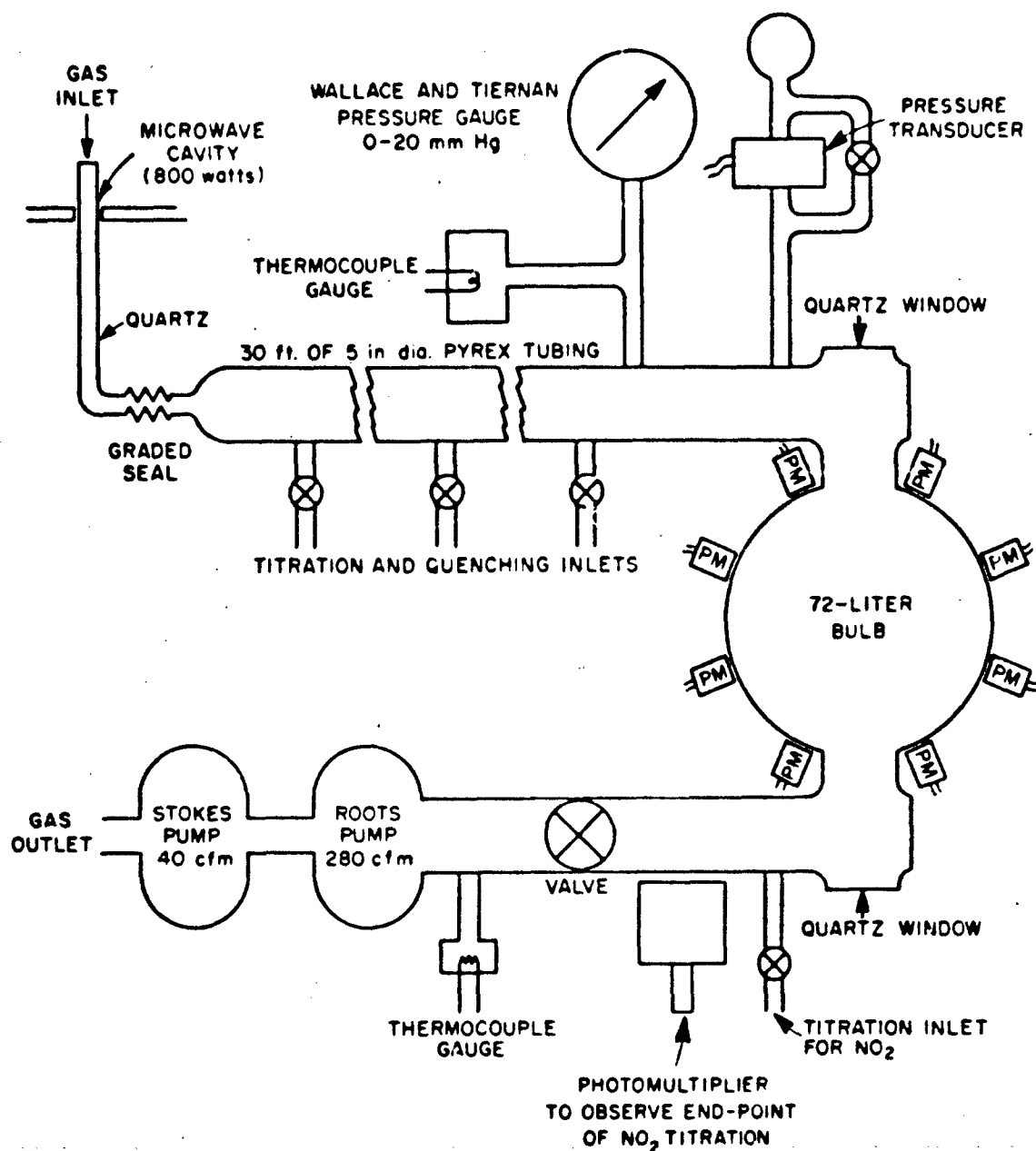


FIG. 6 THE CENTRAL TITRATION REGION



P.M. = PHOTOMULTIPLIERS TO OBSERVE AT FOLLOWING WAVELENGTHS

- | | |
|----------------|-----------|
| 1. 3200-3900 Å | 5. 6340 Å |
| 2. 4000-4500 Å | 6. 7618 Å |
| 3. 5300-5700 Å | 7. 7708 Å |
| 4. 5577 Å | 8. 1.27 μ |

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FIG. 7 SCHEMATIC DIAGRAM OF D-REGION SIMULATOR



FIG. 8 THE OBSERVATION BULB WITH PHOTOMULTIPLIERS

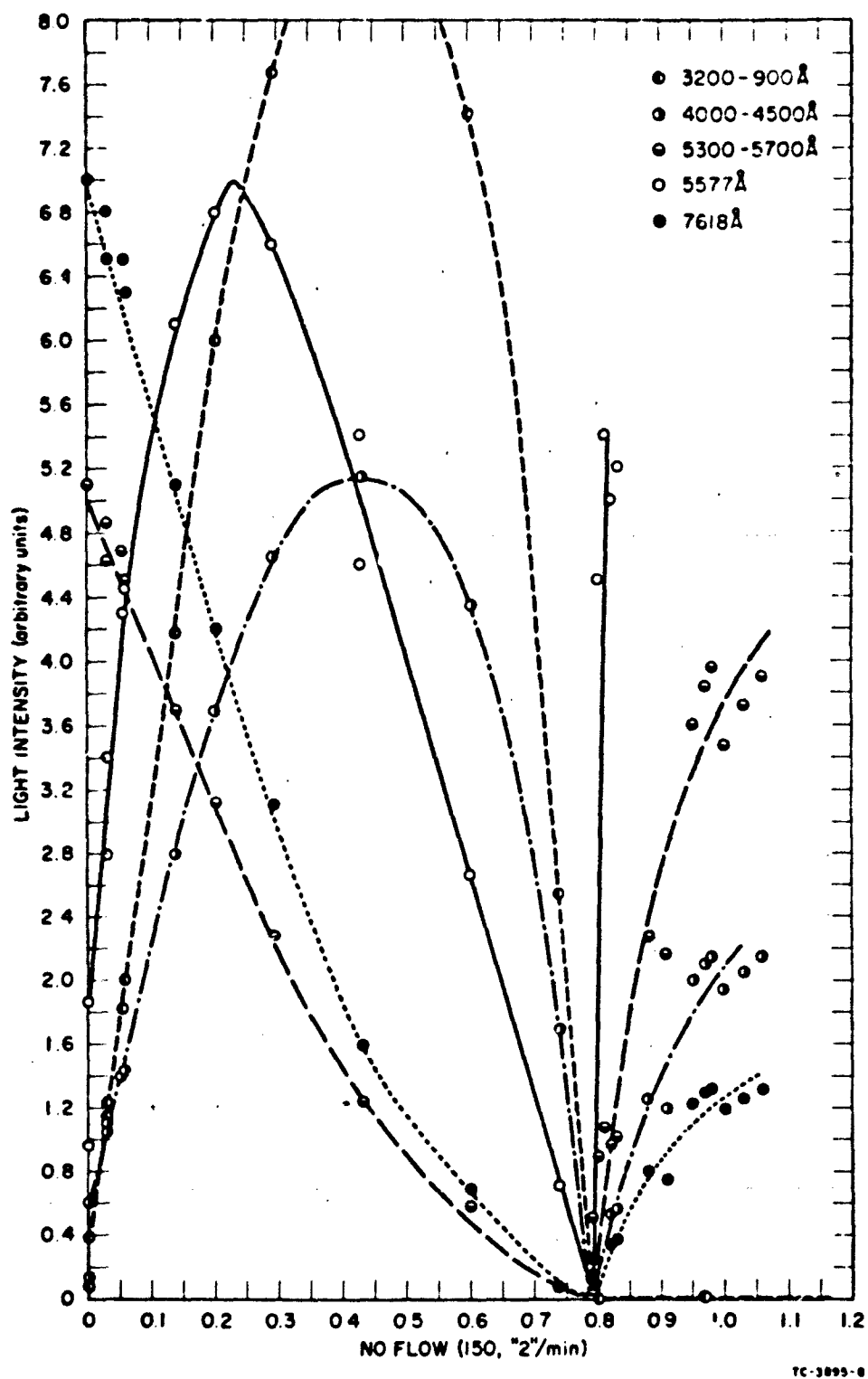
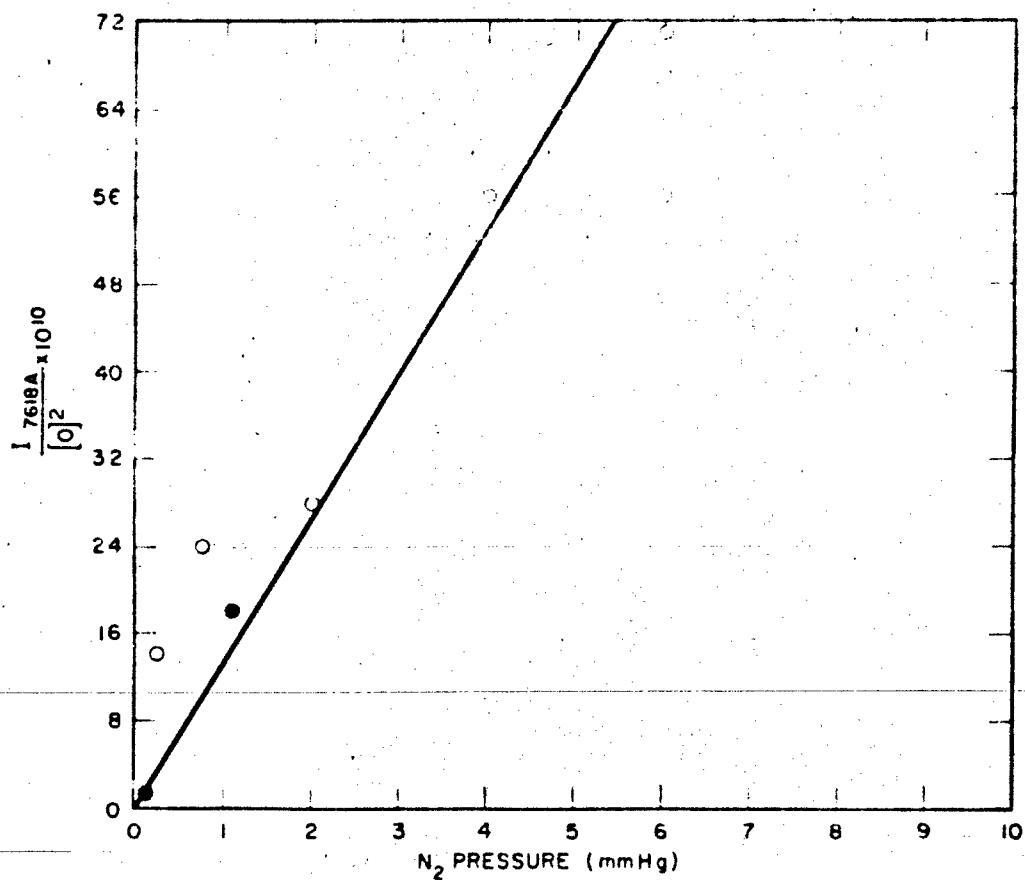
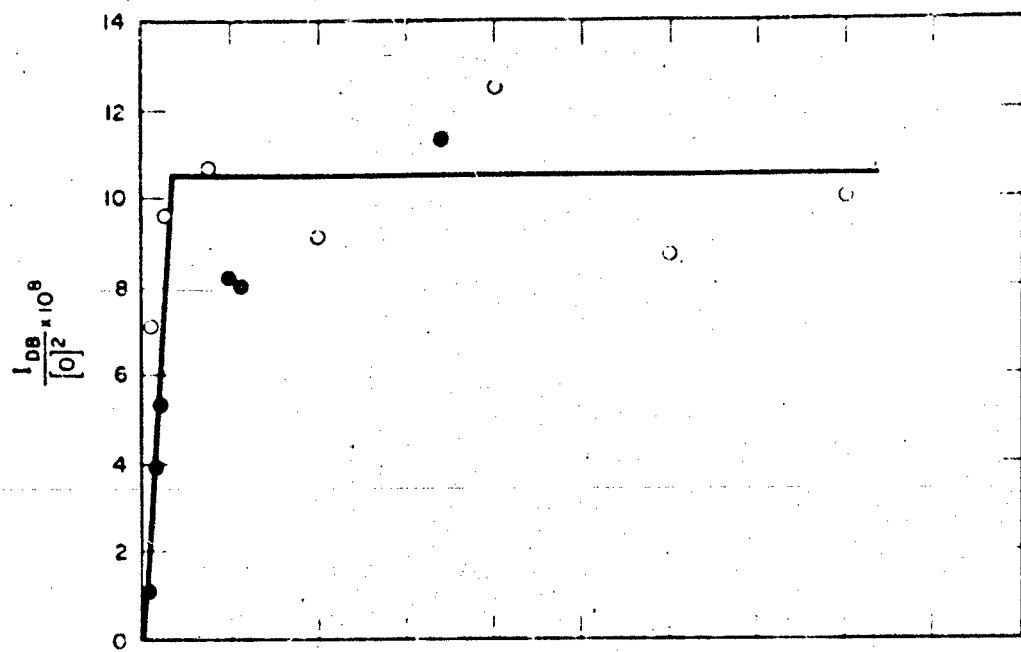
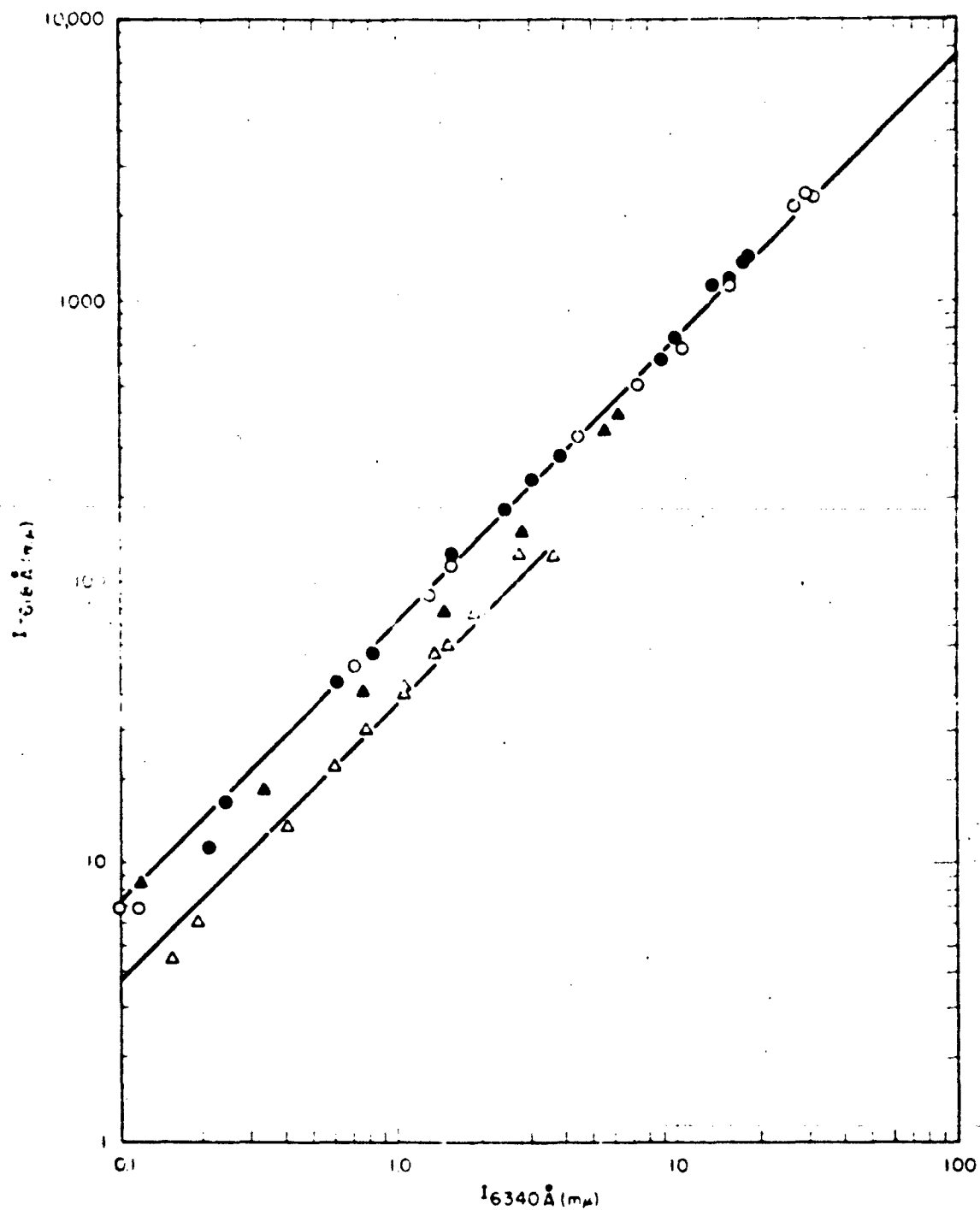


FIG. 9 LIGHT INTENSITY vs. ATOMS IN DISCHARGED N₂



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FIG. 10 LIGHT INTENSITY vs. PRESSURE IN DISCHARGED N_2 TITRATED WITH NO



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FIG. 11 LIGHT INTENSITY AT 7618 vs. LIGHT INTENSITY AT 6340 IN DISCHARGED O₂ WITH O REMOVED

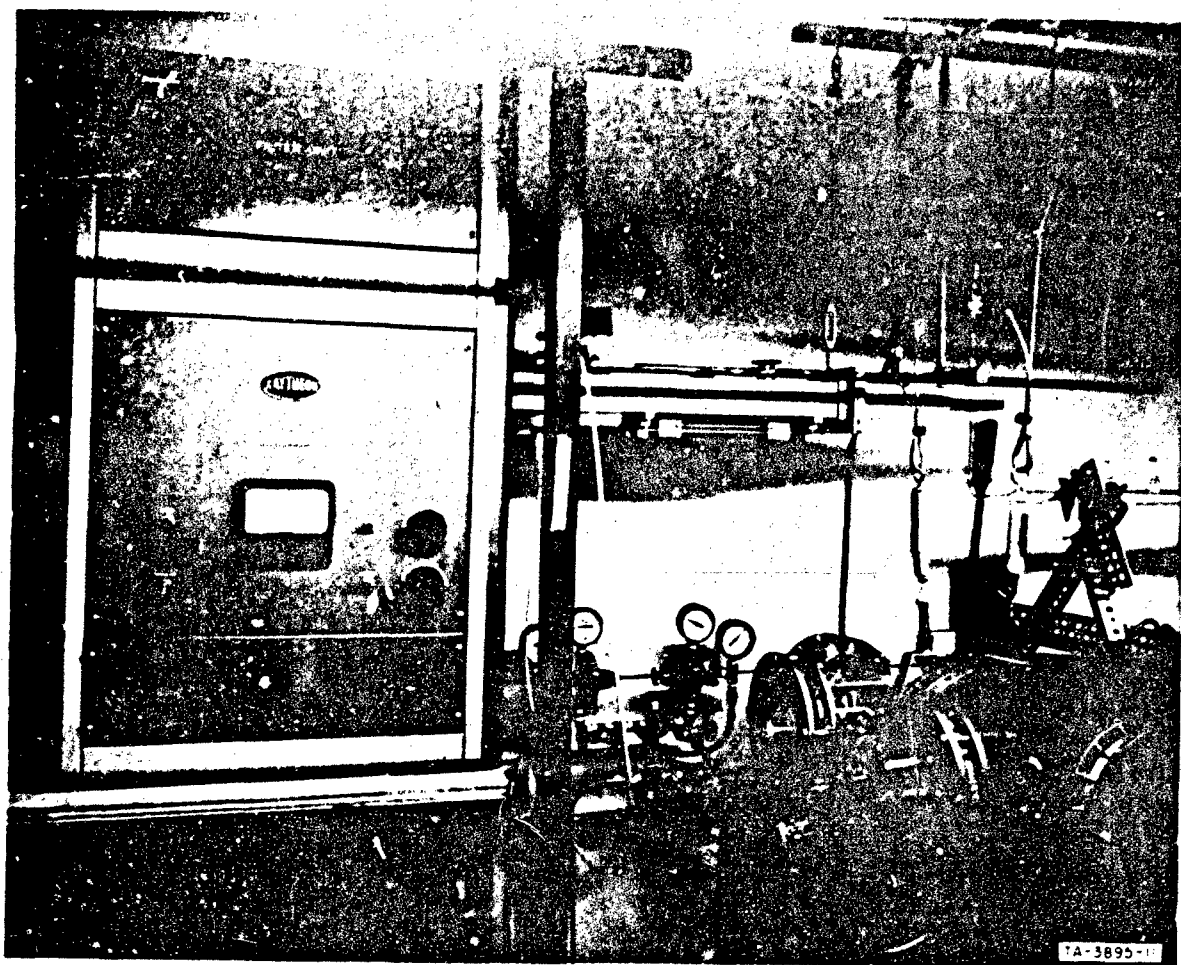


FIG. 12 THE 1-km MICROWAVE DISCHARGE SOURCE AND INPUT FLOW MANIFOLD

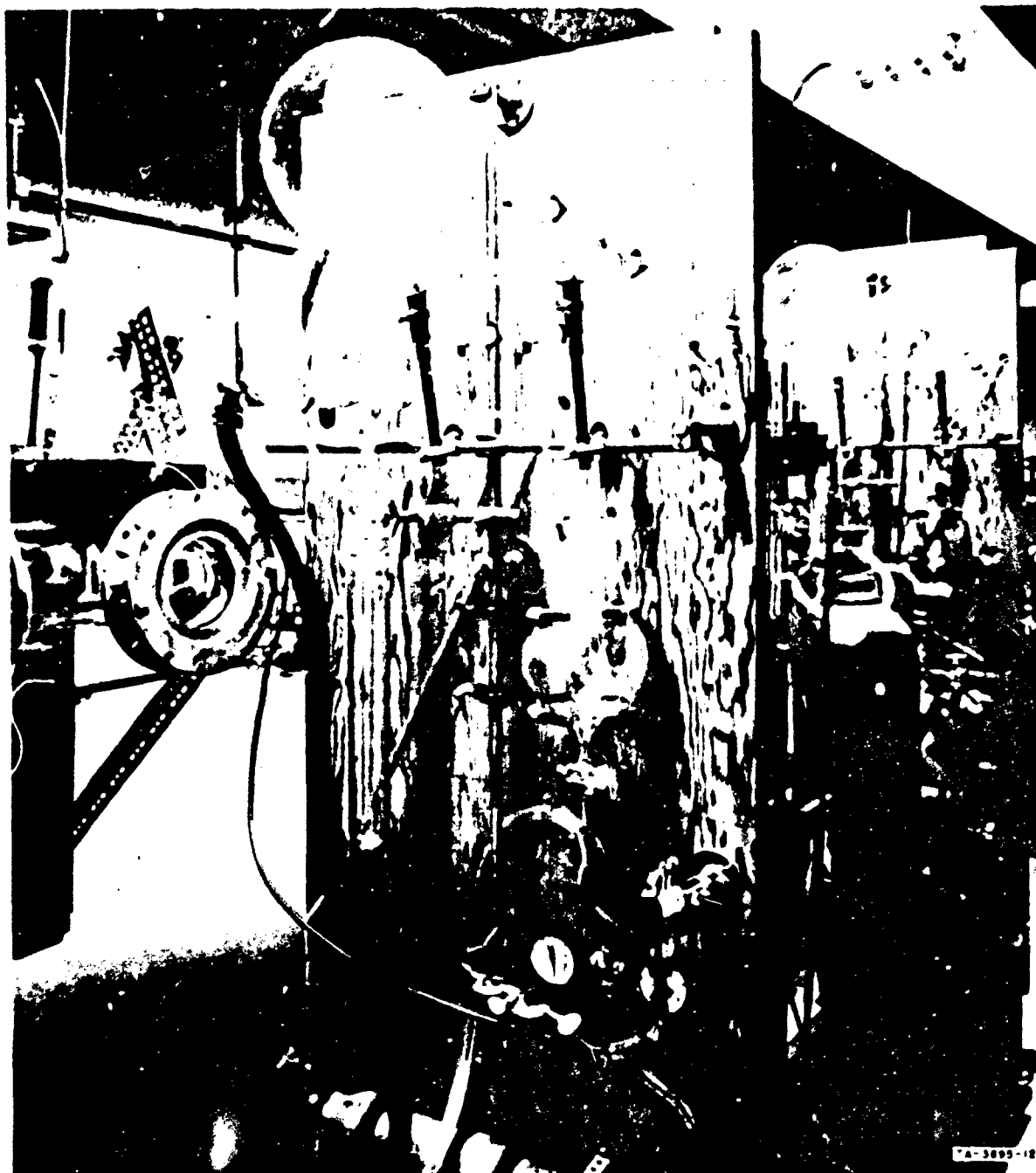


FIG. 13 THE CALIBRATED RESERVOIRS FOR NO AND NO₂ ADDITION

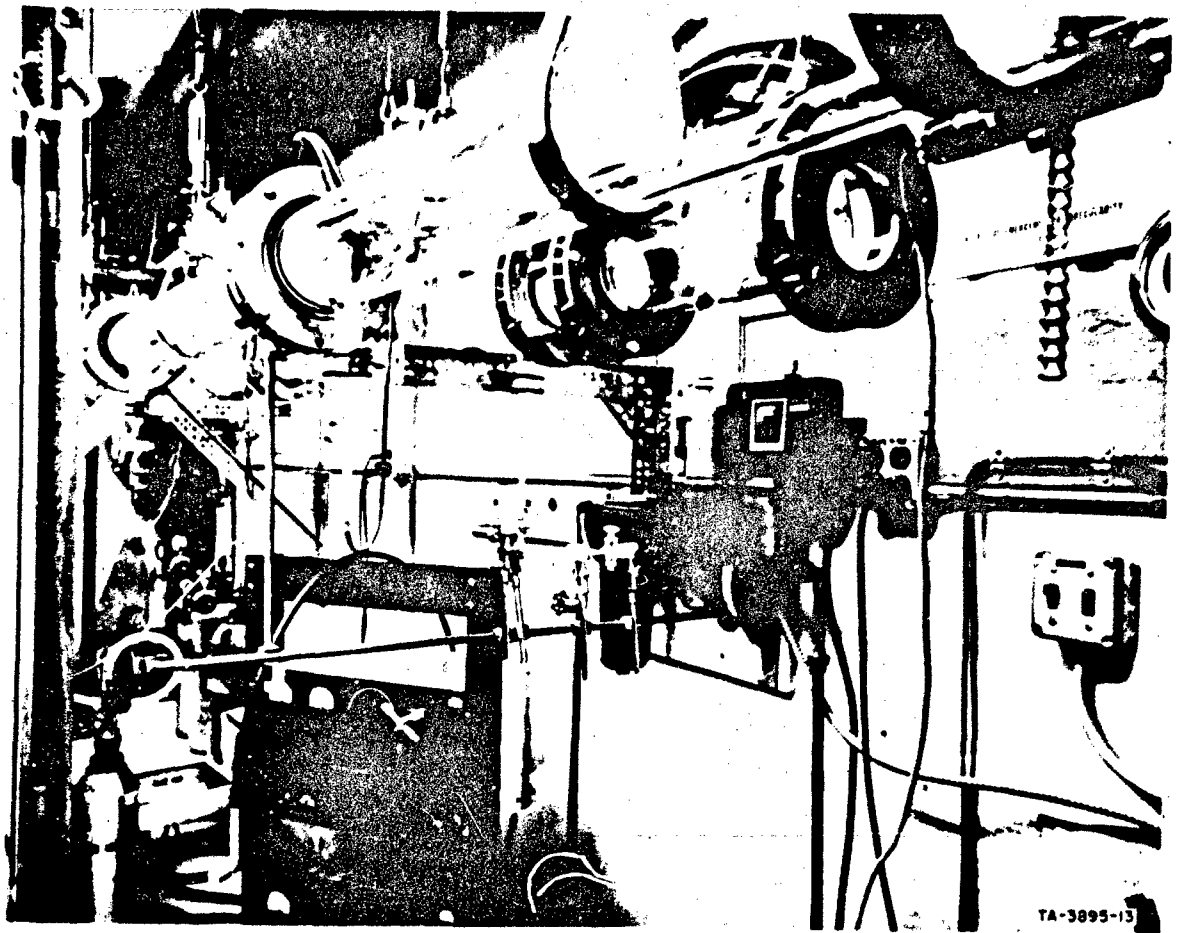


FIG. 14 OVER-ALL VIEW OF THE FLOW SYSTEM
LEADING TO THE OBSERVATION BULB

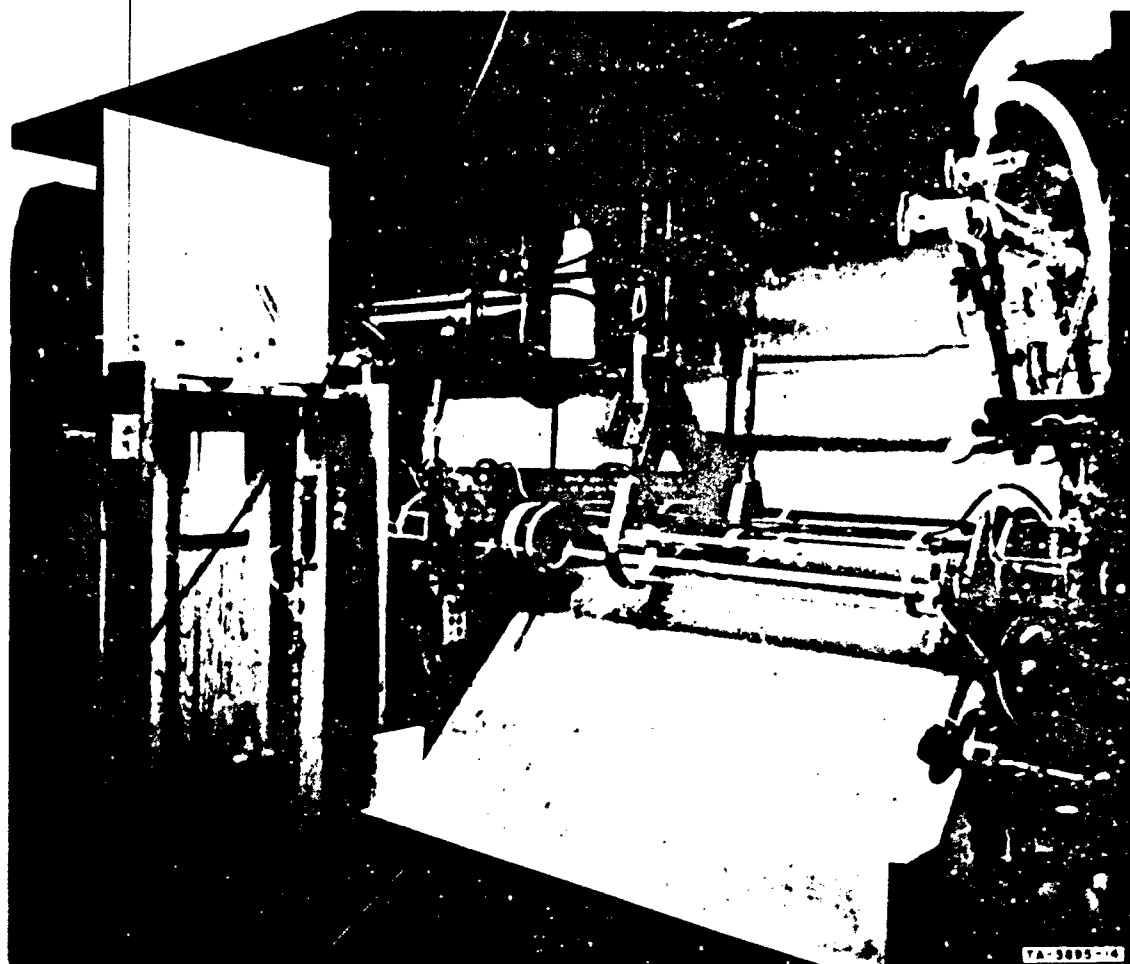


FIG. 15 TRANSIENT STUDY REGION OF THE FLOW SYSTEM

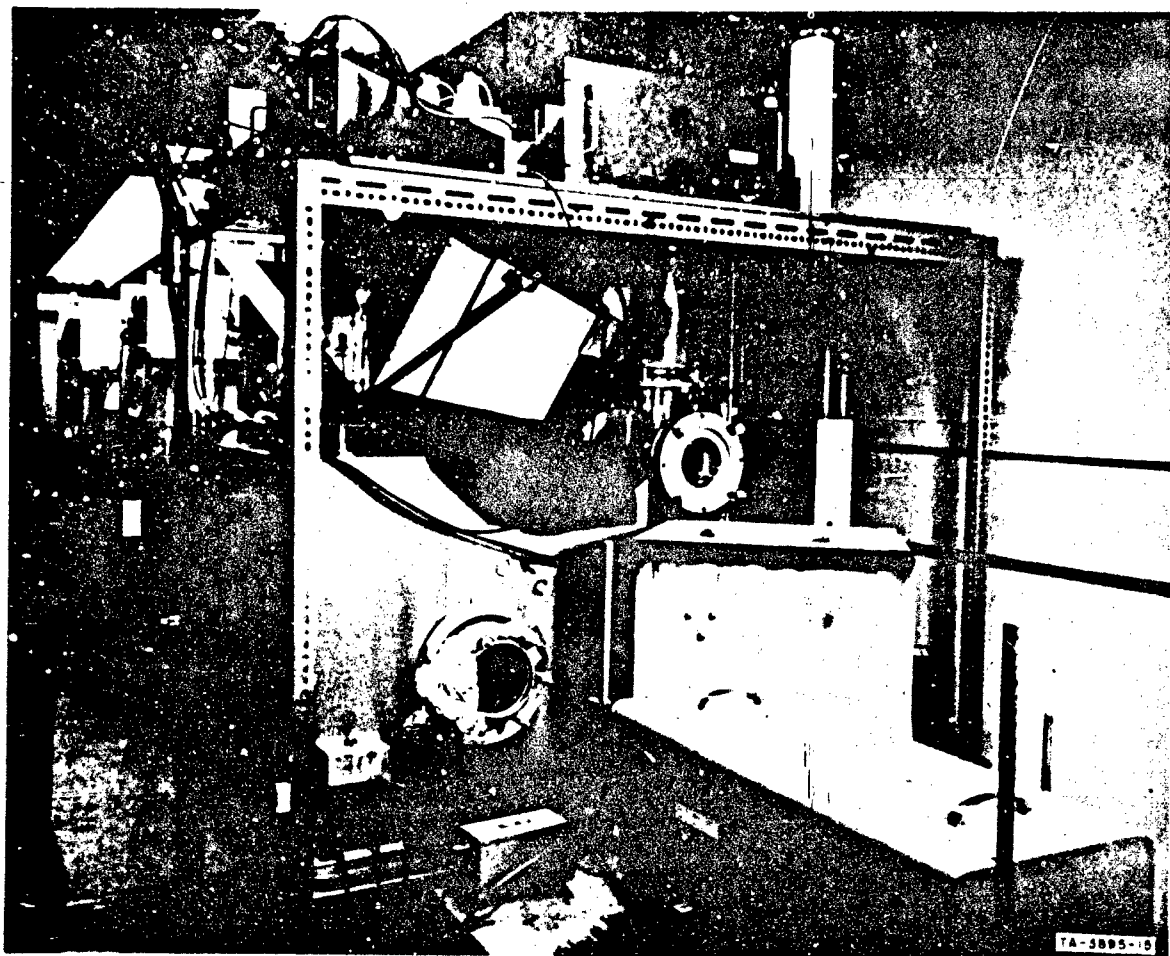


FIG. 16 THE OBSERVATION BULB WITH INFRARED DETECTORS
AND SPECTROMETERS

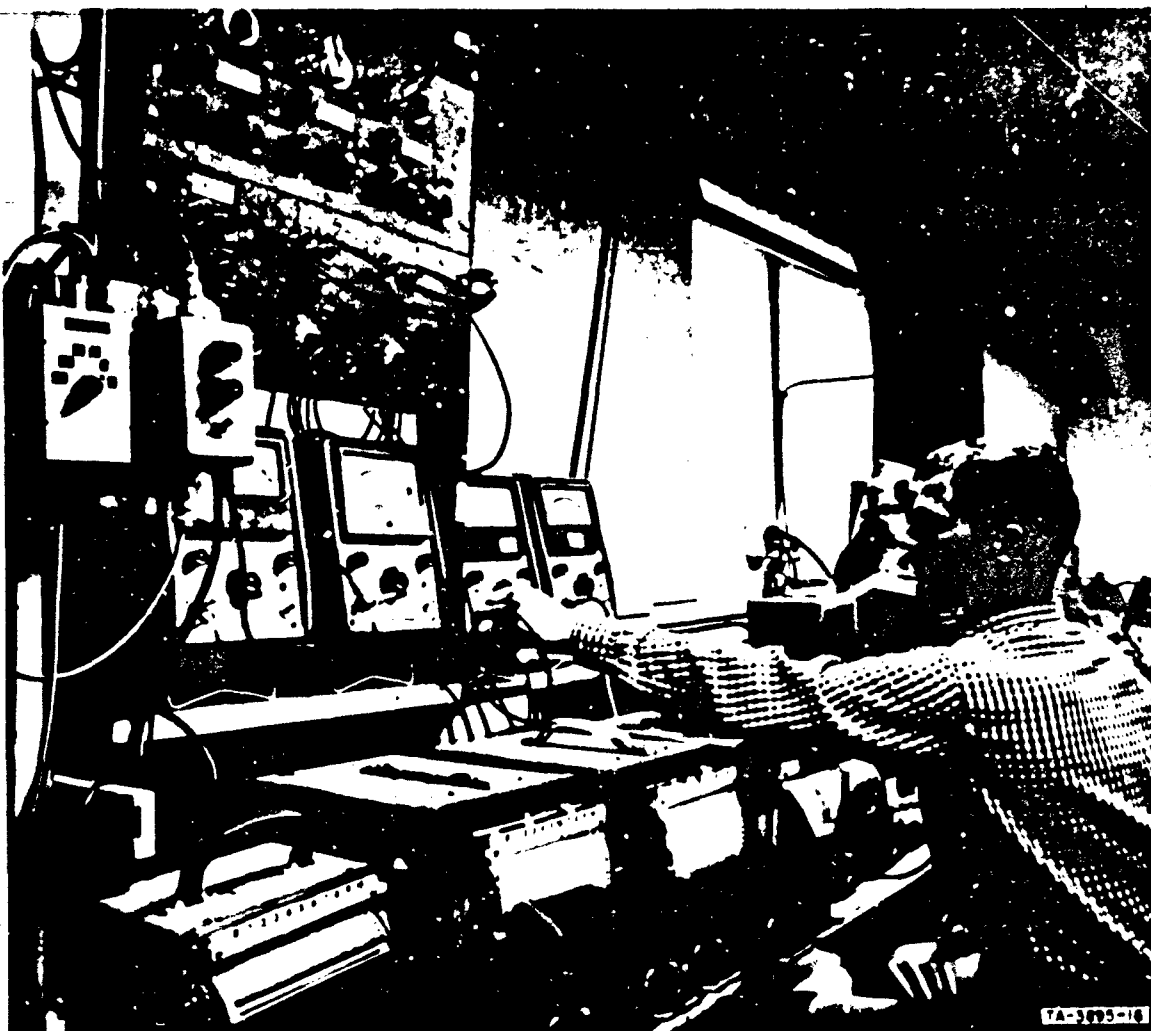


FIG. 17 OPERATOR AT INSTRUMENT CONSOLE

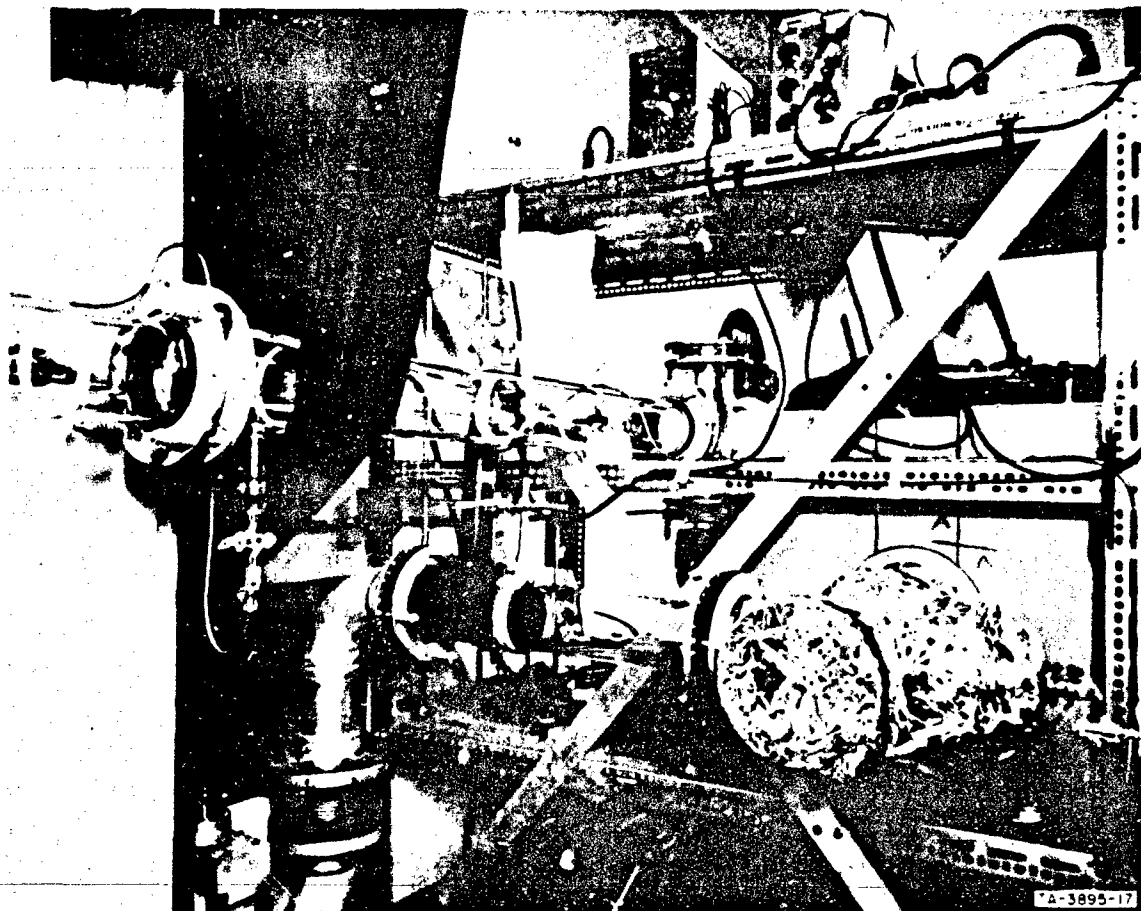


FIG. 18 THE 72-LITER OBSERVATION BULB AND CONNECTIONS

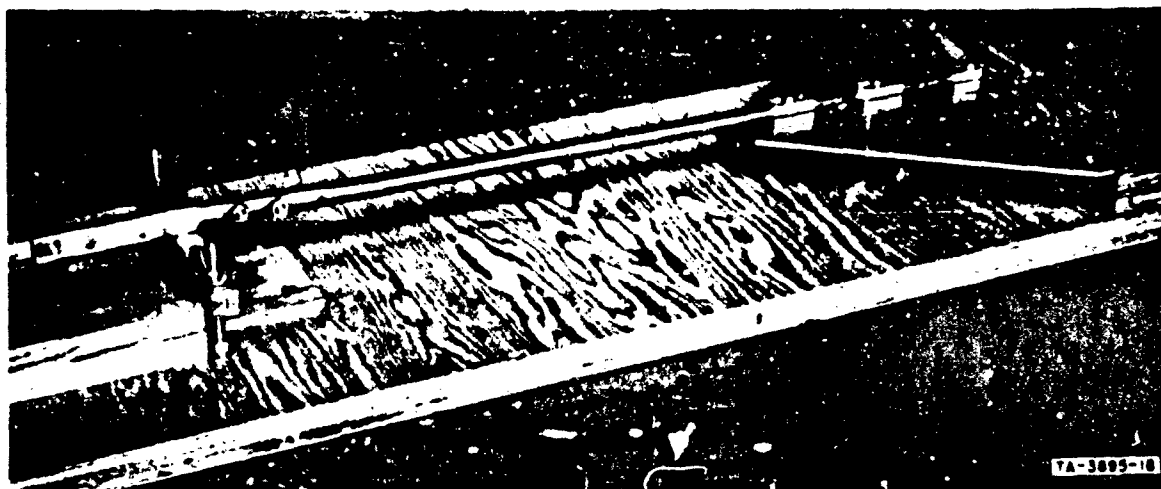


FIG. 19 THE LIF CLEAVER

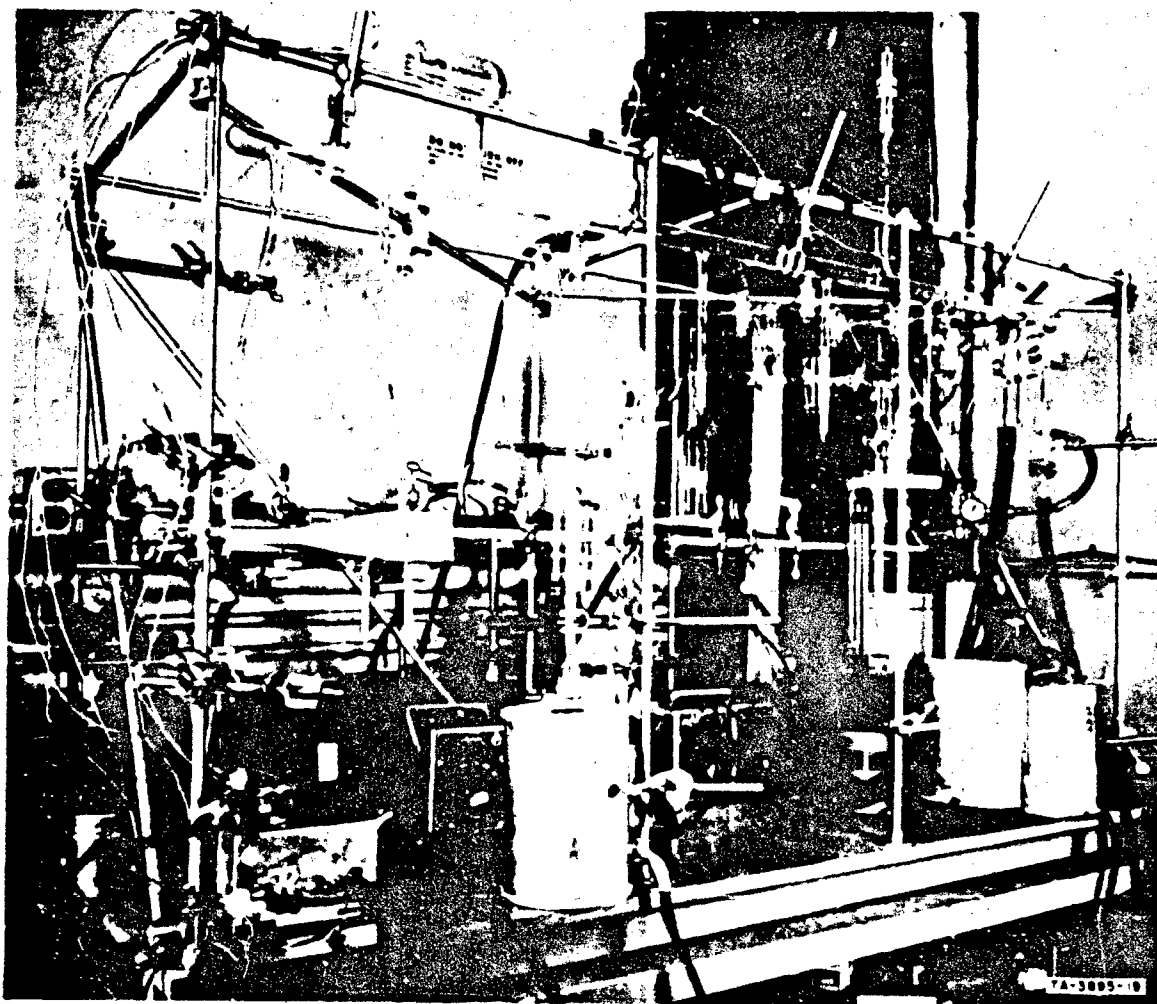


FIG -20 THE LAMP FILLING SYSTEM

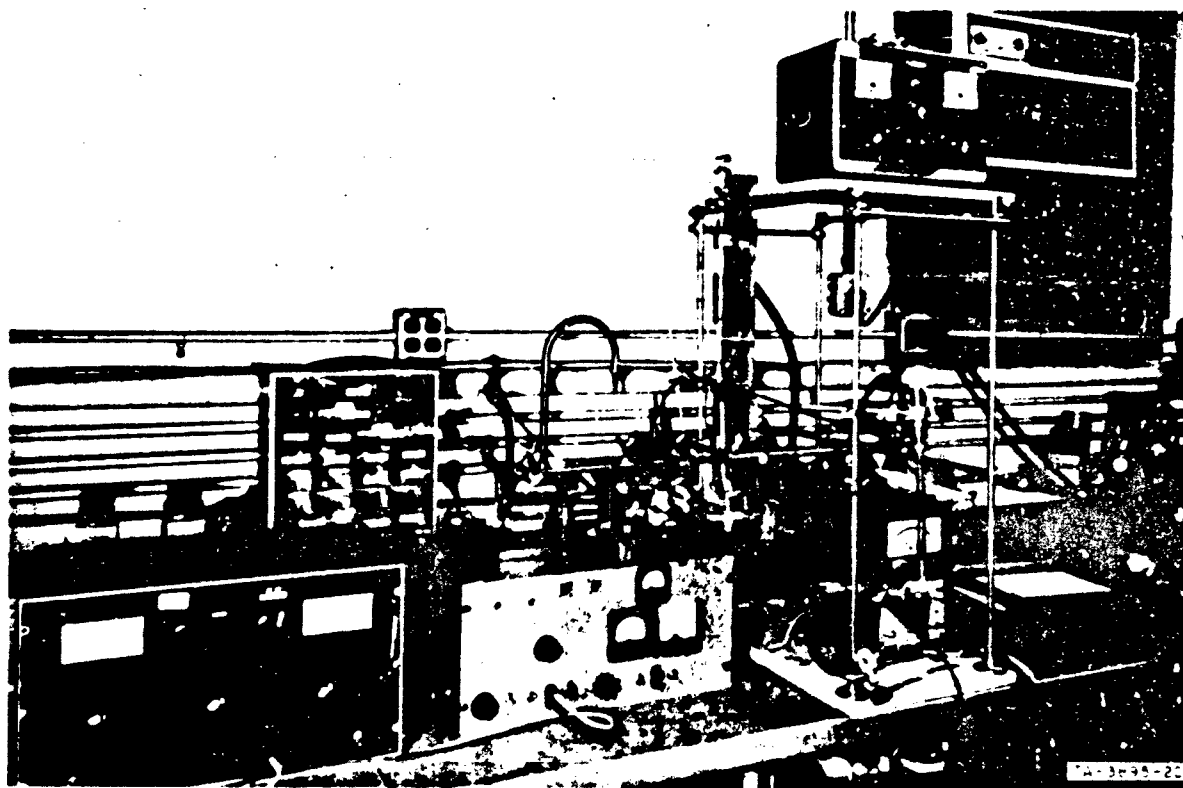


FIG. 21 THE LAMP INTENSITY MEASURING APPARATUS

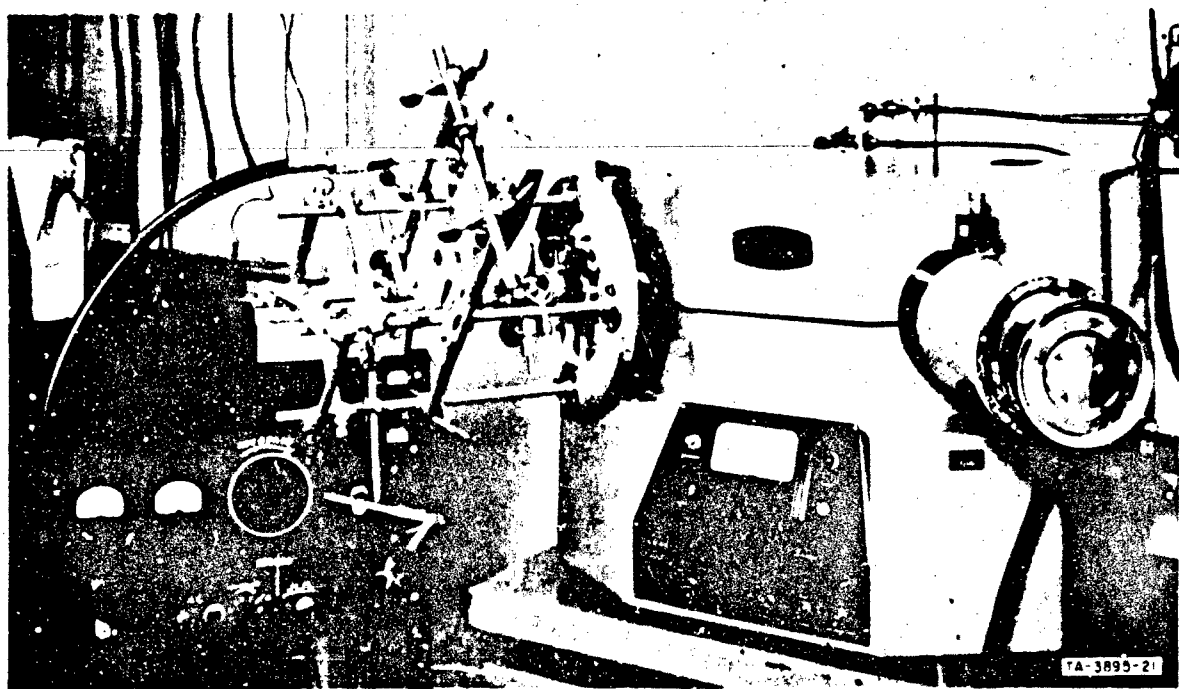
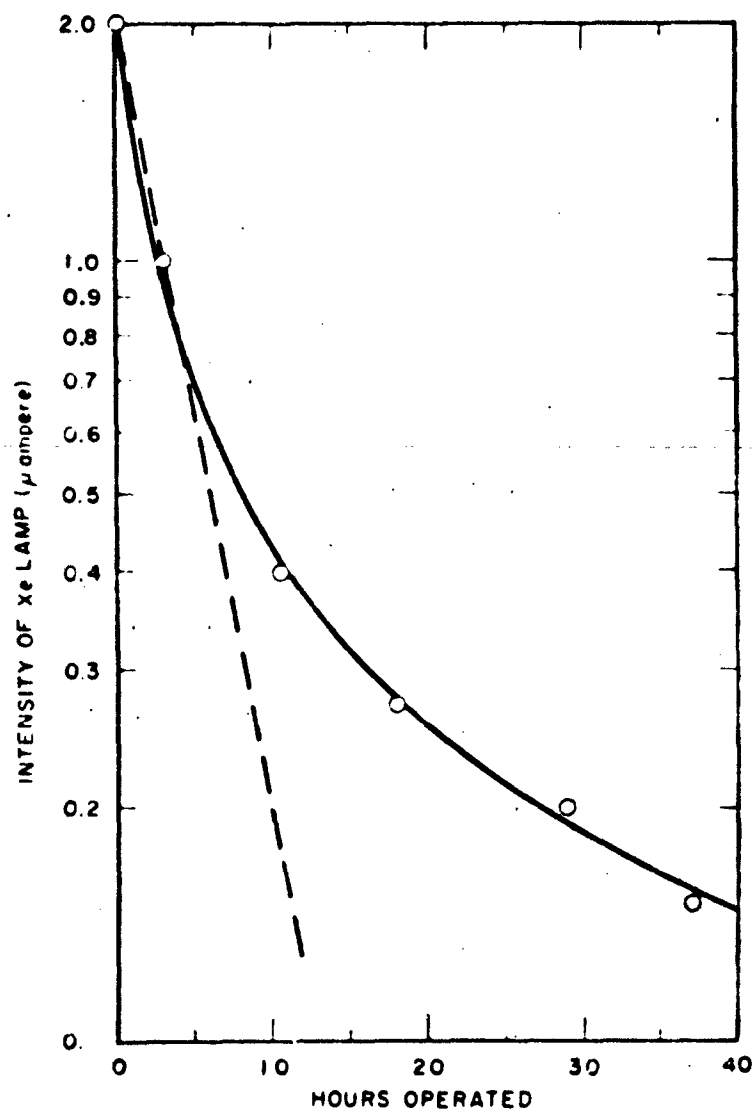


FIG. 22 MEASURING THE SPECTRAL DISTRIBUTION OF THE PHOTOIONIZING LAMPS



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FIG. 23 LAMP INTENSITY vs. TIME

Unclassified

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