Final Report
Contract No. NAS8-28071

ATOM BEAM SURFACE INTERACTION STUDIES:
EXPERIMENTAL SYSTEM DEVELOPMENT

by John C. Gregory

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**The University
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Submitted to:

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INTRODUCTION

It is clear from observations made during a variety of space flights that problems associated with outgassing and subsequent film condensation on sensitive surfaces will be present on the Skylabs and Space Stations of the foreseeable future. It does not appear likely that advances in materials development will occur which will enable contaminant sources of a hydrocarbon, silicone or siloxane nature such as potting compounds, sealants, adhesives, coatings and the like to be replaced soon.

Films of fresh contaminant deposited mainly during the early part of the orbital life of a spacecraft would generally be desorbed again from the surface as the partial pressure of adsorbable contaminant decreased were it not for the effect of solar radiation, both electromagnetic and particulate. Photons in the ultraviolet region and solar protons and electrons possess sufficient energy to cause fission of chemical bonds (commonly requiring about 5 e V of energy). The resulting free radicals may react in a wide variety of ways resulting in polymerization and cross-linking of a very complex nature and ultimately in the formation of a hard carbonaceous glaze of indeterminate stoichiometry and a thickness of perhaps some tens or hundreds of nanometers. Such films may significantly interfere with the primary objective of an experimental surface, and cleaning devices are under consideration to deal with this problem.

A phenomenon which will affect the amount and chemical condition of such a film at any time and which has received only cursory attention in this connection is the continuous bombardment of surfaces at Skylab altitudes by oxygen atoms. At altitudes in excess of 70 km, dissociation of the atmospheric gases occurs because of solar radiation. Above 120 km, atomic oxygen is a major constituent of the atmosphere, and in the exosphere and in interplanetary space the atmosphere is largely atomic hydrogen. The drag on satellites and other objects in the upper atmosphere is necessarily more complicated than in the lower atmosphere, which is composed of chemically stable systems, for in addition to thermal accommodation and the angular distribution of particles reflected by vehicle skins, it is necessary to consider (1) the reassociation of atoms into molecules at the surface, (2) the manner in which energy of reassociation is divided between kinetic energy of the newly formed molecules and surface heating and (3) the chemical reactions between the atomic atmosphere and the surface material of any vehicle. Under very-high-altitude flight conditions, the pressure is sufficiently low that the free molecular flow regime is realized, and the speed of the gas relative to the vehicle is of the order of 10^6 cm $\sec^{-1}$.

The natural oxygen atom concentration around 300 kilometers altitude varies widely with season, latitude, time of day, orbital phase, and sun activity, but a reasonable mean value is 1×10^9 oxygen atoms per cubic centimeter. Allowing for a gas temperature of 1000 to 1200°K at this altitude, the collision frequency of oxygen atoms with a surface is calculated from kinetic theory to be

$$z = \frac{P}{(2\pi m k T)^{1/2}}$$

$$= 5 \times 10^{13} \sec^{-1} \text{cm}^{-2}$$

This means that, on the average, every surface atom is struck by an oxygen atom every 20 seconds under conditions where the surface is moving slowly compared with the average gas species. When the surface is moving much faster than the gas species, the kinetic velocities of the molecules become unimportant. At orbital velocities (10^6 cm. sec.^{-1}) the impingement rate on the front surface of the spacecraft approaches 1×10^{15} oxygen atoms cm^{-2}. sec.^{-1}. Moreover, the kinetic energy of the O atoms is increased to 5.3 eV. Whereas the physical chemistry of ion-sputtering is fairly well understood, at least from the empirical standpoint, this is not true for the effect of active atom beams.

Both oxygen and nitrogen atoms have been shown to be chemically extremely reactive, and both have been demonstrated to cause macroscopic etching of graphite and polymer surfaces.[1,2] This writer [3] has shown that chemisorbed oxide layers, stable at 1000° C on a nickel crystal surface, were removed by three-second bombardment of nitrogen atoms (which are quite similar to oxygen atoms in their chemical behavior).

The mechanism of oxidation of organic materials by oxygen atoms is believed to be quite different from that by thermal oxidation in the presence of oxygen molecules. Initiation of simple thermal oxidation requires the slow formation of hydrocarbon radicals by thermal dissociation as shown in Equation 1:

$$RH \xrightarrow{\text{slow}} R^{\cdot} + H^{\cdot}$$

or (1)

$$RH \rightarrow R'^{\cdot} + R''^{\cdot} \quad .$$

These radicals then rapidly react with oxygen molecules:

$$R^{\cdot} + O_2 \xrightarrow{\text{rapid}} ROO^{\cdot} \ . \tag{2}$$

Further reactions are as follows:

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \tag{3}$$

$$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH \quad . \tag{4}$$

Oxidation by oxygen atoms proceeds by a rapid attack requiring only a small activation energy, or none at all, as shown in Equation 5:

$$RH + O^{\cdot} \xrightarrow{\text{rapid}} R^{\cdot} + {}^{\cdot}OH$$

or $\qquad$ (5)

$$RH + O^{\cdot} \rightarrow R'^{\cdot} + R''O^{\cdot} \quad .$$

Accessible alkyl (or other) radicals then probably react rapidly with other O atoms:

$$R^{\cdot} + O^{\cdot} \xrightarrow{\text{rapid}} RO^{\cdot}$$

$$R'^{\cdot} + O^{\cdot} \rightarrow R'O^{\cdot} \quad .$$

Oxidation by oxygen atoms proceeds rapidly at the surface without heating, with loss of material to the gas phase as volatiles of low molecular weight $\left(CO,\ CO_2,\ H_2O,\ HCHO,\ HCOOH,\ etc. \right)$.

Hydrogen molecules are readily thermally dissociated into atoms. H atoms formed by thermal dissociation of H_2 on hot (1500° C approx.) tungsten ionization gauge filaments have been recognized to cause contamination problems by surface chemists working with hydrogen. The H atoms react with hitherto inert organic residues bound to the walls and form volatile products (Hickmott, 1960)$^{(4)}$.

TECHNICAL APPROACH

For investigations of atom-surface interactions under these conditions, the use of beams of hydrogen and oxygen atoms is particularly appealing. However, a basic difficulty resides in tracing an atomic beam of number density of the order of 10^8 atoms, cm^{-3} through the residual gas of similar or higher number density. (10^8 atoms cm^{-3} corresponds to approximately 2.5×10^{-9} torr). This difficulty is overcome by modulating the atomic beam, usually by mechanically interrupting it at a frequency of the order of 10^2 Hz. Under these conditions, any effect arising from the beam may be identified by its occurring at the modulation frequency and in a specified phase. Using this modulation technique, it becomes possible to use mass-spectrometric detection of the beam, since the electron-impact ionization cross-sections for hydrogen, oxygen, and nitrogen atoms are known.

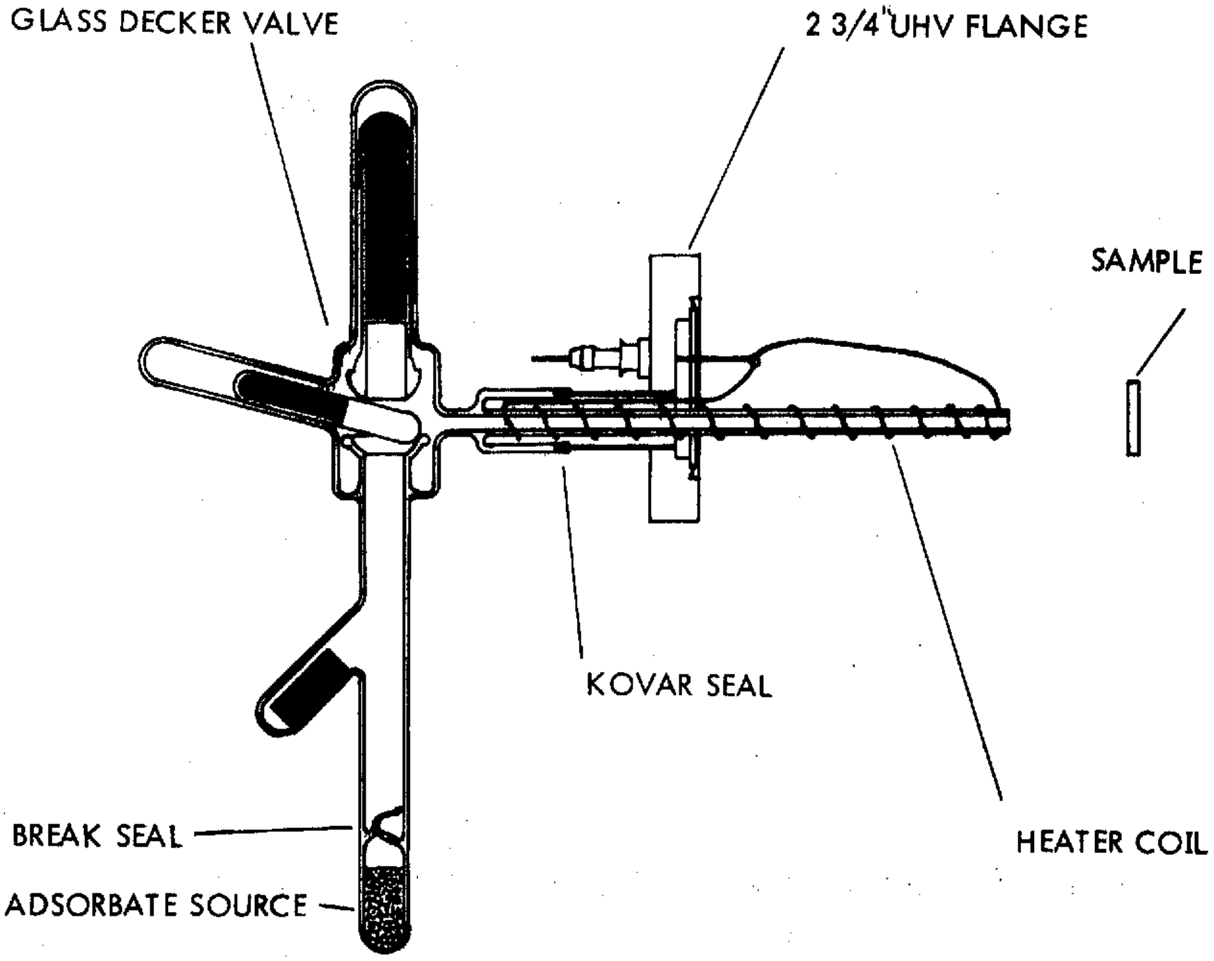
The experimental program now commencing in the Surface Physics Laboratory at MSFC Space Sciences Laboratory will involve quantitative deposition by standard techniques of adsorbates containing C and Si onto selected substrates and studying the kinetics of interaction of a beam of oxygen, nitrogen, or hydrogen atoms of known flux by means of Auger electron spectroscopy and LEED. Desorbed molecules will be analyzed by mass-spectroscopy using modulated beam techniques. Experimental conditions permitting, the two sets of measurements will be correlated.

ADSORBATE DOSING SYSTEMS

An ideal system for dosing gas onto a substrate mounted within a UHV Auger spectrometer chamber would provide a beam of known uniform flux of adsorbate confined to the substrate surface to prevent contamination of the walls of the chamber. Such beams are provided by molecular beam apparatus and may be chopped or varied in temperature and intensity. The problem is great elaborateness and cost of engineering physics design and fabrication of such systems, and such sophistication is only justified if the adsorption process itself is of prime interest. A cheaper and more manageable molecular beam dosing system can be made of pyrex glass if the services of a skilled glassblower are available. This system is described later in this report.

Simple Dosing System

A very simple dosing system which can handle troublesome organic or silicone liquids and solids is shown in figure 1. The adsorbate phase is contained within the breakseal portion into which it was distilled from an ancillary vacuum system. The temperature of the adsorbate may be below or above room temperature depending on its vapor pressure and the dose required. If the source is heated above room temperature the glass tube conduit into the Auger chamber may be heated by the resistance wire shown to prevent condensation in the tube. The flux may be momentarily cut off by the Decker valve, or by immersing the source in a cold bath. Complete cut-off is achieved by pulling off the glass tube between the Decker valve and the break-seal. Several tubes may be joined in this region providing a variety of adsorbates without shutdown of the system.



SIMPLE DIRECTIONAL DOSING SYSTEM

FIGURE 1.

Molecular Beam Dosing System

Pyrex molecular beam systems are relatively easy to construct, and are being used by several groups of surface chemists to measure sticking coefficients, adsorption kinetics and surface processes. The apparatuses of Hayward and Chappel (1969)[5) and King and Wells (1972)[6) were examined in detail and discussed with their designers and users. It would seem very feasible to build a modification of these apparatuses which would be useable as demountable facility on the Auger spectrometer chamber. This is shown in figure 2.

This beam system is constructed of pyrex glass, bakeable to 400°C, with background pressures of ~ 1×10^{-10} Torr achieved using mercury diffusion pumps. It might well be convenient to replace these with a modern turbopump. There are six chambers in series, chamber 1 containing the source of gas (at 10 - 100 Torr), chamber 6 being the Auger bell-jar, and the four chambers in between acting, with their orifices, to collimate the beam to the desired diameter, (a few mm). Chambers 4 and 5 are also titanium getter pumped.

The nozzle-skimmer system is all glass, the nozzle being made of a syringe with a 1 cm long, 0.01 cm dia capillary attached. The skimmer is a cone with a 0.05 cm dia orifice. Nozzle-skimmer separation can be varied (but remains fixed during an experiment). Magnetically operated beam-stoppers are shown as B4 and B5. These are used to cut off gas supply abruptly in the beam. The whole assembly of orifices may be aligned perfectly with a small laser. King and Wells report useful beam fluxes of nitrogen of 10^{12} to 10^{13} molecules cm^{-2} sec^{-1} over a target area of ~ 4×10^{-2} cm^2 with negligible out of beam leakage into the interaction chamber 6.

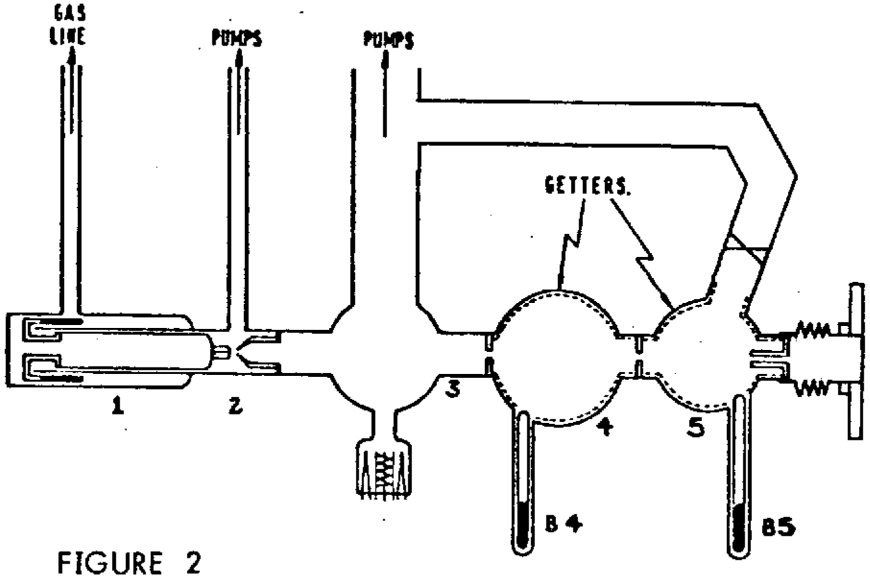


FIGURE 2

PYREX MOLECULAR BEAM DOSING SYSTEM

Alignment, testing and calibrations would all be done prior to mounting the assembly onto the Auger spectrometer. Chambers 1 through 5 are mounted on a rigid frame together with pumps and gas supply. Interface with the Auger spectrometer is through a glass to Kovar seal (after the exit capillary), a stainless steel bellows, a 2 3/4 inch and an 8 inch Varian flange. After joining of the beam with the Auger system fine adjustment of the beam onto the sample is made with the laser beam by moving the entire beam frame.

It is expected that this beam system could be used without chopping and phase-sensitive mass-spectrometer detection.

EVALUATION AND DESIGN OF SOURCES OF OXYGEN, NITROGEN AND HYDROGEN ATOMS.

Thermal dissociation and electron-impact dissociation by direct current, radio frequency or microwave discharge have all been used to produce atoms from molecular H_2, O_2, and N_2. Hydrogen is relatively easily dissociated at reasonably accessible temperatures ($< 3000^{\circ}K$) and tungsten sources of H atoms have been described.[7,8] Brennan and Fletcher[9] studied the experimental dissociation kinetics of H_2 on W. They give the absolute reaction velocity, v_a (atoms cm^{-2} sec^{-1}) as

$$v_a = 18 \times 10^{24} (P)^{1/2} \exp\left(- \frac{52,600}{RT}\right)$$

where P is the hydrogen pressure in torr, T is the absolute temperature and R is 2 cals $mole^{-1}$ deg^{-1}.

Nitrogen is only dissociated less than 1% at $3000^{\circ}K$, however, and oxygen lies between hydrogen and nitrogen in its ease of dissociation. No thermal sources of O atoms have been noted in the literature but it seems that an iridium oven at $2400^{\circ}C$ would provide a useable source of O atoms.

The disadvantage of the classical oven sources is that their energies do not normally exceed 0.5eV, which is much lower than the orbital impact energy. However, much useful and original information can be gained from experiments using these convenient sources.

The neutralised ion beam system, is the only method capable of providing a beam of oxygen or nitrogen atoms of energy 5-15eV under conditions suitable for surface invesigations. The system is conveniently divided into three parts; ion source, beam transport system, and target. The target is of course the substrate surface mounted in the Auger spectrometer chamber.

The ion source may be one of several types but must, as with all components, be compatible with UHV requirements. At present the most suitable appears to be the r.f. source. This is shown schematically in figure 3 and the actual hardware in figure 4 . This is an evolution of the ORTEC tube and was redesigned and built to conform with our requirements. It may be used directly without a beam transport system for rough studies of surface cleaning.

The beam transport section requires by far the most effort in design and construction. If it desired to proceed with this it is recommended that a laboratory design and development procedure be followed. The section includes ion lenses and accelerator, magnetic analyser for mass or energy selection, decelerator, ion neutraliser and deflection plates. A schematic is shown in figure 5 .

An example of such a system is described by Boring and Humphris.10) The beam species is first produced, ionized, and accelerated to the desired energy and neutralized by charge transfer in a gas. The difficulty with the method lies in the low intensity available particularly at low energies caused by space-charge spreading of the ion beam prior to neutralization. Boring and Humphris report reduction in space-charge spreading when free electrons are injected into the ion beam from a tungsten filament just prior to the deceleration stage.

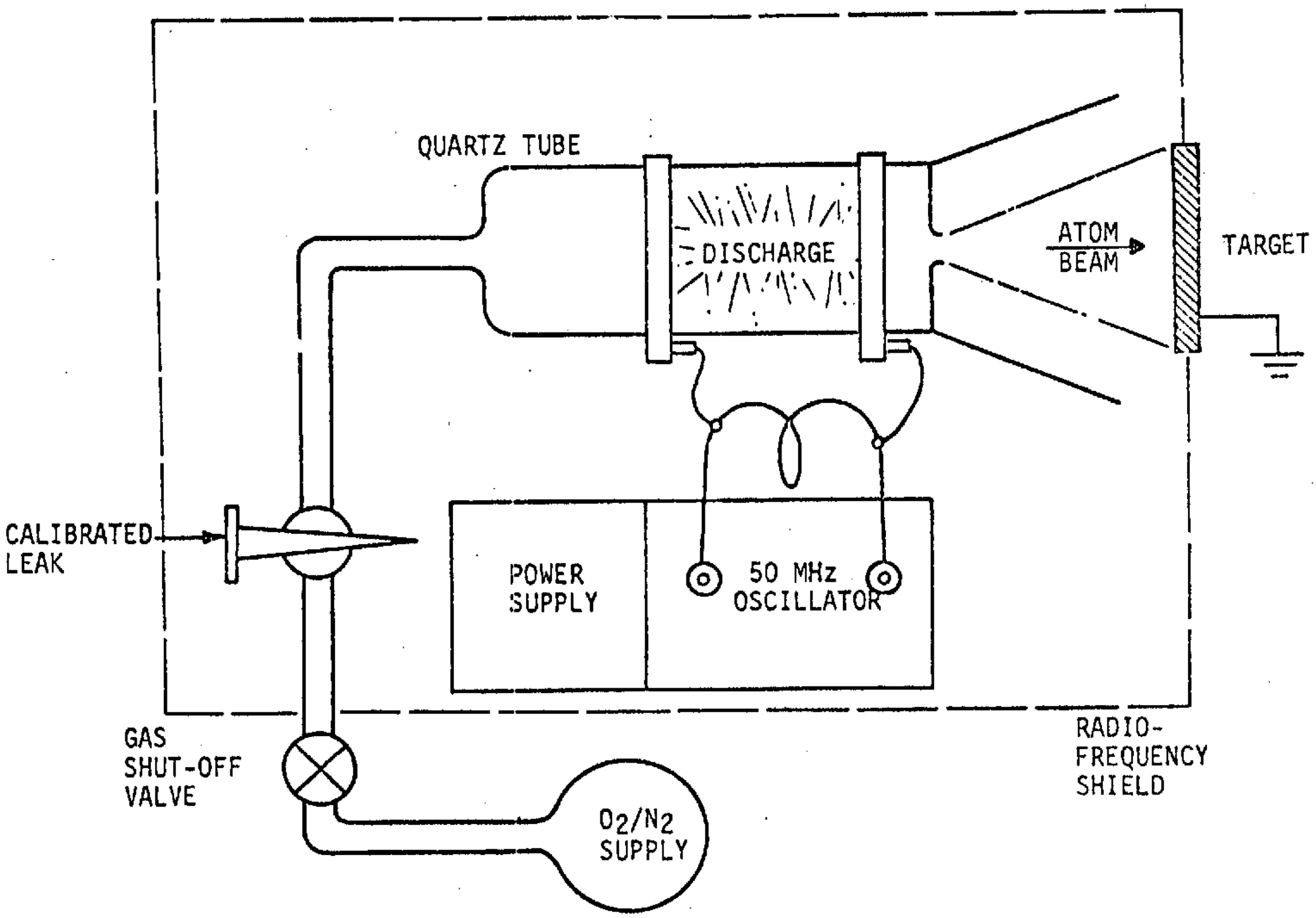


FIGURE 3 OXYGEN OR NITROGEN ATOM BEAM SOURCE

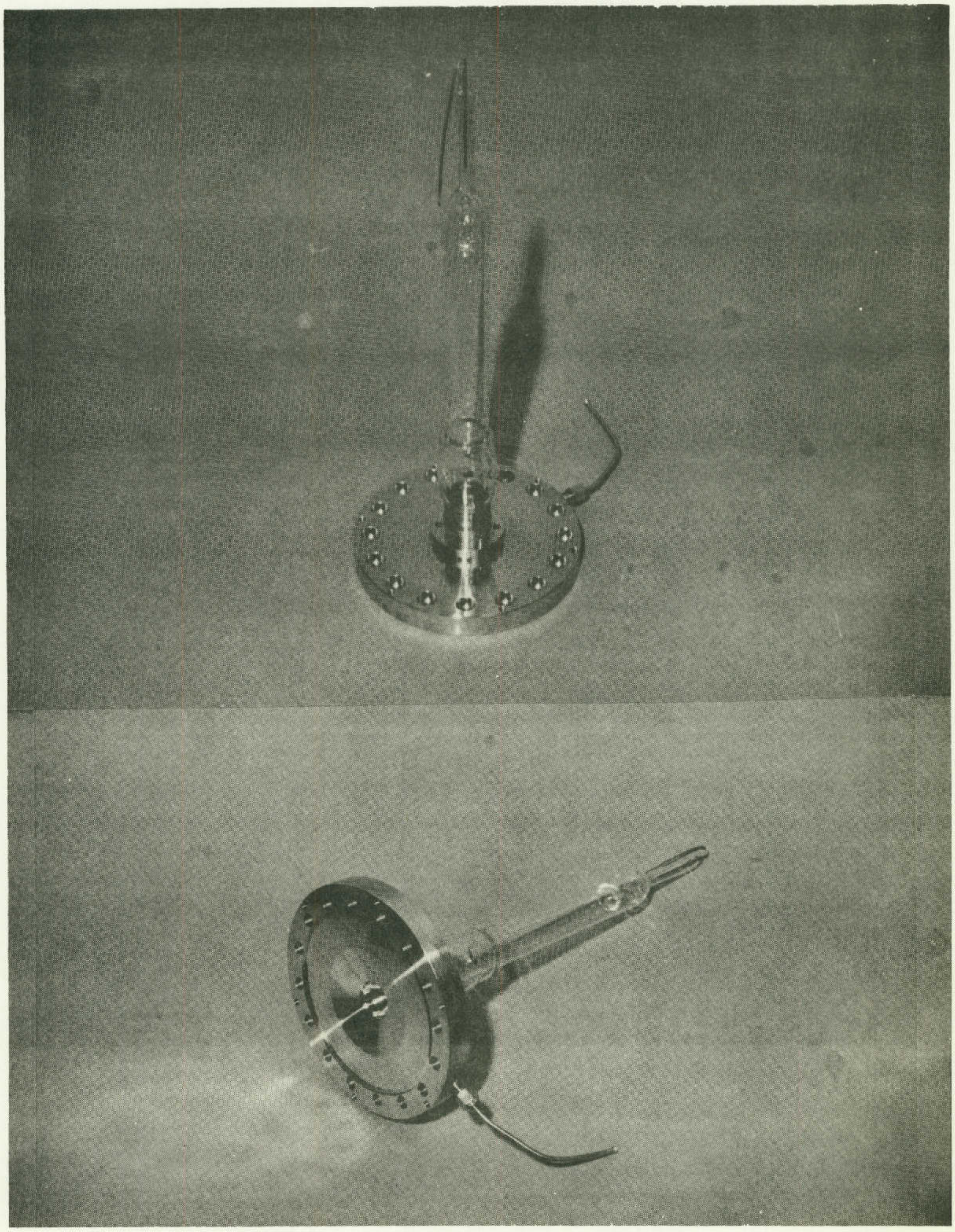


FIGURE 4: PYREX- STAINLESS STEEL UHV RF ION SOURCE

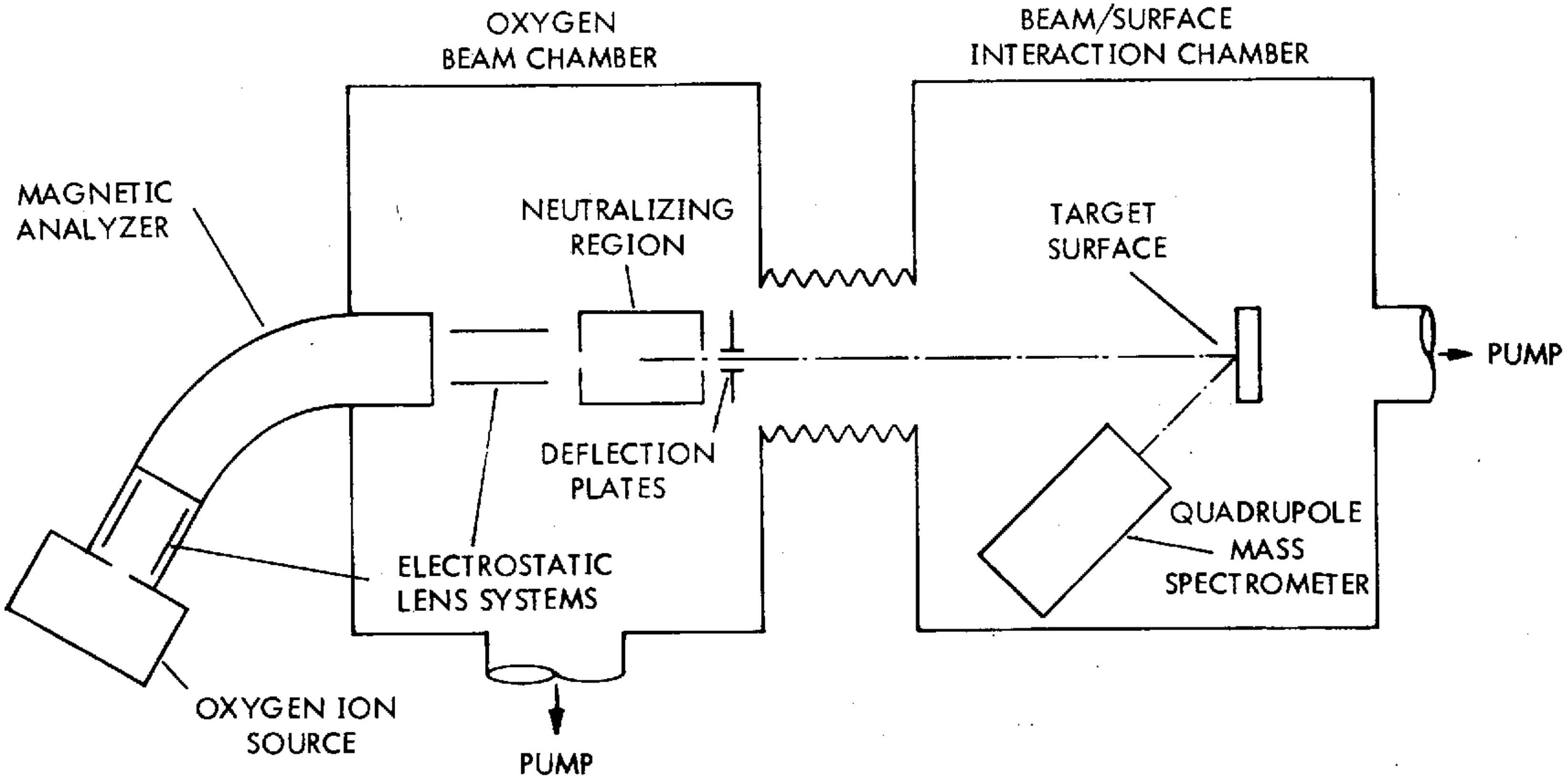


FIGURE 5. NEUTRALIZED ION OXYGEN ATOM SOURCE

Production of O atoms for the ion neutralization source may be by the oven source previously described, by a radio-frequency source similar to that shown in figure 4, or by microwave discharge cavity.

A review of the latest literature on ion beam techniques and technology is given by a recent book Ion Beams by Wilson and Brewer.$^{11)}$ Valuable technological detail is given for the construction of ion sources, ion optics and other components of the beam transport system.

REFLECTED ATOM BEAM DETECTION SYSTEM

The detector system using an Extranuclear quadrupole mass filter has been designed, built, and installed in a UHV chamber for testing. It is shown in figures 6 and 7 . The incident atom beam is not shown, but would be entrant at a port at 45 degrees to the large ports shown in figure 6 . For an atom beam normally incident upon the substrate surface, the detector may view the reflected beam from 25 degrees from the normal to parallel with the substrate surface.

Direct viewing of the beam (without a surface interaction) will allow accurate calibration of the various beam systems, both molecular and atomic, described in this report. Since cross-sections for the electron impact ionization of most simple molecular gases are known, and those for atomic hydrogen and oxygen have been recently determined, 12) the mass-spectroscopy technique provides quantitative measurements of processes under study. These processes may be:

- angular distribution of reflected particles
- thermal accommodation coefficient
- reassociation probability at the surface
- reaction cross-sections, activation energies for surface reactions
- energy distribution in reaction products

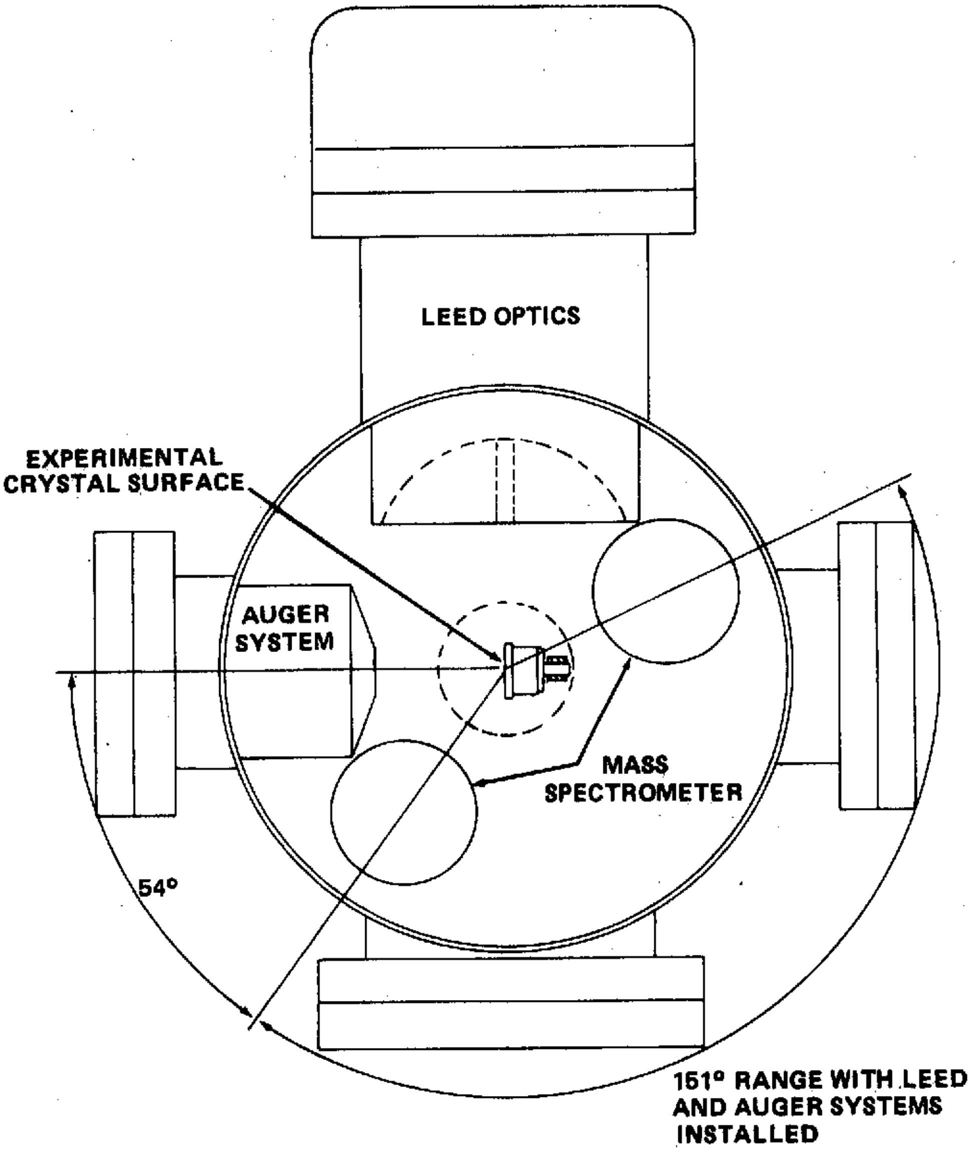


FIGURE 6.

PLAN OF ATOMIC BEAM SCATTERING SYSTEM

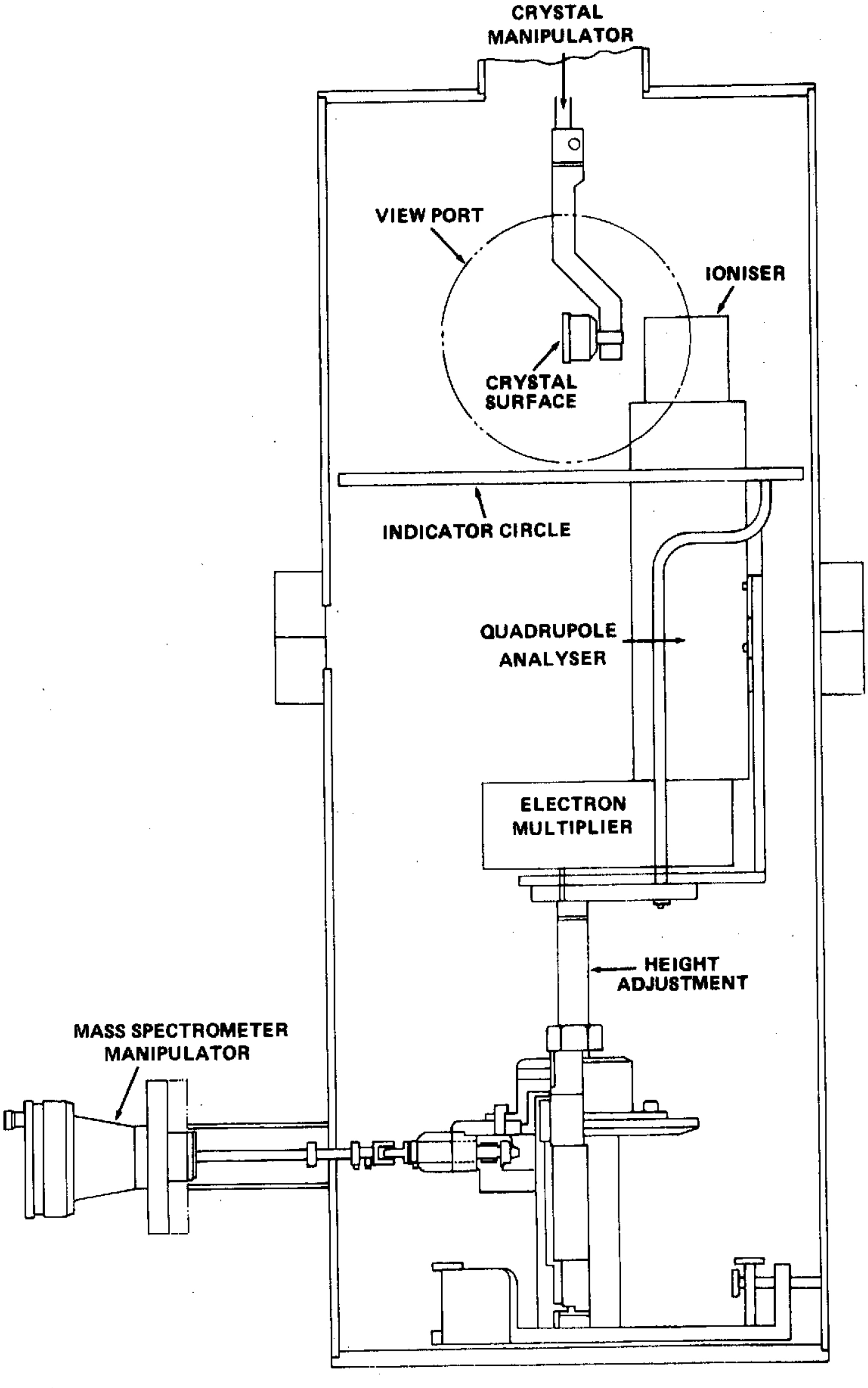


FIGURE 7. **ATOMIC BEAM SCATTERING DETECTOR SYSTEM**

ULTRAVIOLET REFLECTANCE AND AUGER ELECTRON SPECTROSCOPY OF CONTAMINATED SURFACES.

Ultraviolet experiments and techniques for deployment in earth-orbit on Skylab or Shuttle vehicles are very sensitive to contaminant deposition on optical elements. Little experimental research has been done using new powerful surface techniques such as Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) together with ultraviolet spectroscopy techniques principally because of the incompatibility of the vacuum hardware commercially available for these two disciplines. Since these problems of contamination remain unresolved and largely unquantified, and since this represents a relatively uncharted region of UV spectroscopy of intrinsic interest, it was decided to proceed to design special hardware to facilitate experiments in this area. A system has been designed which will allow:

- dosing of a substrate with an adsorbate without contaminating the Auger-LEED chamber
- UV irradiation and reflection spectroscopy of adsorbates on a substrate without allowing the surface to come into contact with the atmosphere and without contaminating the Auger-LEED chamber.
- periodic Auger analysis of the substrate surface under study
- ion bombardment cleaning of the substrate surface.

The insertion tube assembly, (Drawing No. UAH 5002), and the accompanying housing weldment, (Drawing No. UAH 5000), are combined to make a multipurpose instrument to be attached through a 6 inch gate valve to an existing 12 inch LEED-Auger chamber. Only the main assemblies are shown in this report. Copies of these and the part and sub-assembly drawings (total 19) have been delivered to the Government.

The insertion tube housing (figures 8 and 9) contains ports for ion bombardment, UV source, monochromator, electron multiplier, pumps and insertion tube assembly, and a mechanical feedthrough for manipulation of the insertion tube.

The insertion tube assembly, figure 10, will hold the crystal sample for cleaning and analysis in the auxillary chamber formed within the housing assembly. This chamber may be differentially pumped by closing the gate valve. When the sample is prepared for insertion into the LEED-Auger chamber for further analysis, the gate valve is opened and the sample extended by rotation of the mechanical feedthrough. The insertion tube assembly allows 15.1 inches of linear travel of the sample substrate (but no rotation). The sample may be transferred from the insertion tube to a sample manipulator in the LEED chamber. The insertion tube is then withdrawn and the gate valve closed. Upon completion of studies in the LEED-Auger chamber, the sequence may be reversed and the sample removed from the system.

PREPARATION OF SUBSTRATE SAMPLES FOR SKYLAB

Several nickel single crystals were oriented, cut and polished at Space Sciences Laboratory. These were to be mounted on the T-027 sample array and would be returned to SSL for surface contamination analysis by Auger electron spectroscopy.

Argon ion bombardment and crystal heating regimes were established for control samples.

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