

FOREWORD

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This report summarizes work done under this contract and covers the period from 1 July 1958 to 31 August 1960.

Laboratories for Applied Sciences personnel who participated in the work covered by this report include: L. DeVaux, R. Gabriel, R. Harada, W. Harvey, J. Kristoff, M. Mapp, M. Remdt, F. Rieke, J. Tribby, M. Weber, and D. Williams. Professor M. Inghram of the Department of Physics, The University of Chicago, has acted as consultant.

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ABSTRACT

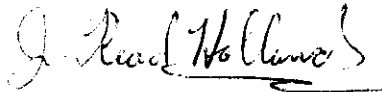
Experiments are being undertaken to study the reactions that occur when free radicals, atoms, or ions impinge upon various types of surface. A molecular beam containing free radicals, etc., is to impinge upon a prepared surface and the reaction products that are reflected or evaporated from the test surface are to be analyzed by means of an analytical mass spectrometer. Conditions will be such that the analysis is uncomplicated by reactions in the gas phase or at walls of the apparatus.

This report describes the instrumentation that has been designed and constructed for the experiments described above.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



J. READ HOLLAND, Actg. Chief,
Advanced Metallurgical Studies Branch
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Contract
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1. INTRODUCTION

1.1 PROBLEM

The aim of this research is the experimental investigation of the phenomena that occur when molecular fragments--ions, free atoms, and free radicals-- impinge upon solid surfaces. As an example of the sort of problem we should like to investigate, we consider oxygen atoms impinging upon a face of a single crystal of graphite. It is conceivable that an atom may (a) be reflected, (b) be adsorbed, (c) combine with a carbon atom and immediately evaporate as a CO molecule, or (d) strike an O atom previously adsorbed on the surface and immediately evaporate as a CO or CO₂ molecule. In case (b), the O atom may (1) diffuse into the crystal or (2) diffuse along the surface of the crystal until it reacts with a C atom of the crystal or with an O atom, or other molecule such as CO, adsorbed on the crystal face, and then evaporate as CO, O₂, or CO₂.

We contemplate observing in as direct a manner as possible which of the above processes occur, and how the probabilities of the various processes depend upon initial conditions such as momentum of the incident O atom, crystallographic plane of the graphite, angle of incidence, temperature of the graphite, roughness of the surface, and degree of surface coverage by adsorbed atoms or molecules.

1.2 METHOD AND APPARATUS

The apparatus and methods we propose to use do afford the possibility of investigating the above questions in what is, so far as we can see, the greatest detail practicable. The type of experiment planned is illustrated schematically in Figure 1.

The reacting species are introduced in the form of a molecular beam that will, in general, contain free radicals and undissociated molecules in a known ratio. The means by which the composition of the beam is determined is not indicated in Figure 1, but will be discussed later. The molecular beam impinges upon a target surface that is to be studied. At the surface, the respective species contained in the beam may undergo various processes; however, in any event they will either stick to the target or will reissue from it in changed or unchanged form. The aim of the experiment is to measure the composition of the beam from the target; by comparing it with that of the incident beam one can deduce the nature of the reactions that occur at

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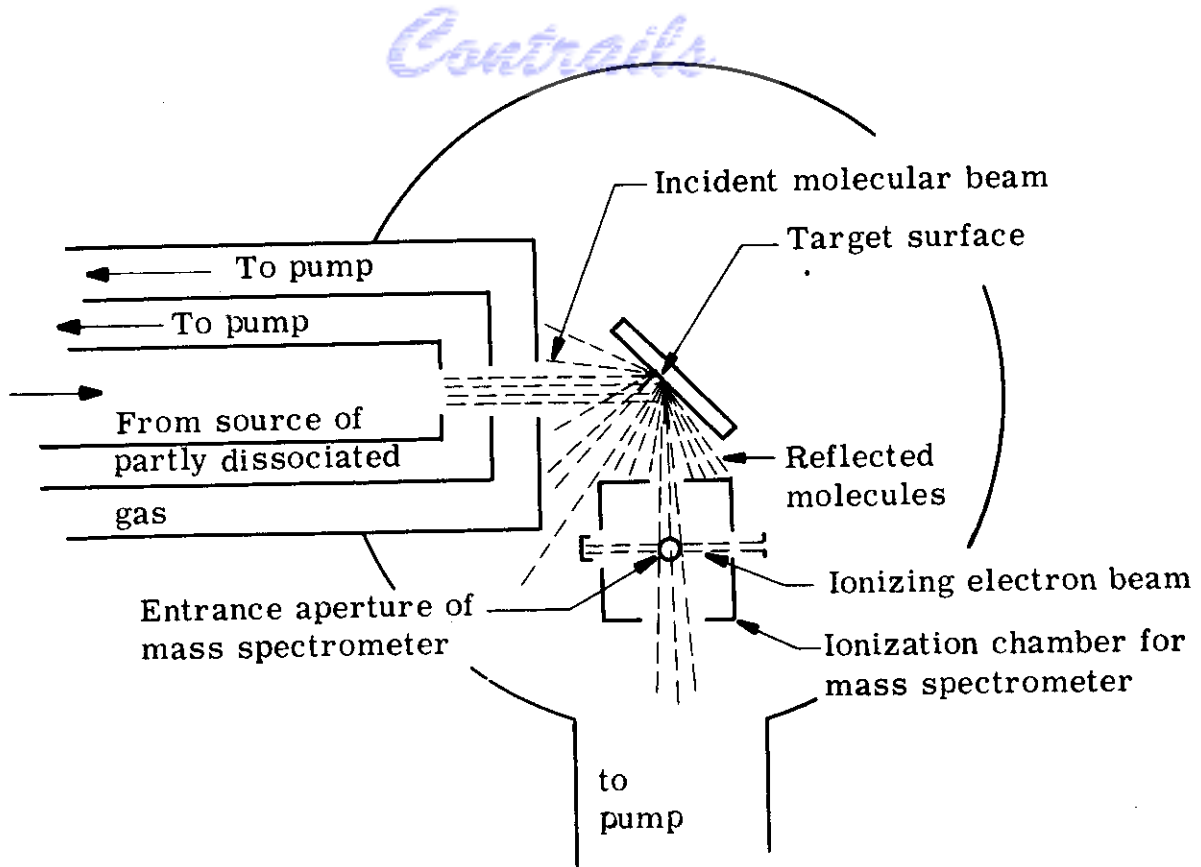


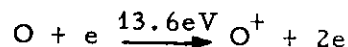
Figure 1. Apparatus for Investigation of the Recombination of Free Atoms on Surfaces (schematic)

the surface. The composition of the beam from the target is to be measured with a mass spectrometer.

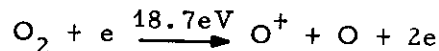
The outstanding feature of the experiment as outlined above is that the reaction at the target surface can be isolated from all other reactions, either at walls or in the gas phase. This isolation can be accomplished because, thanks to the very great sensitivity of the mass spectrometer, the experiment can be carried out with collimated beams of molecules and with exceedingly small ambient pressure in the target chamber. To complete the description of the experiment, three basic requirements are discussed.

1. Provision must be made for measuring the composition of the incident beam. This is accomplished, as shown in Figure 13, by providing a direct path from the molecular-beam source to the ionization source of the mass spectrometer. By means of a shutter, the molecular beam may be directed in turn directly to the ionization source or to the target.

2. Provision must be made for positive identification of chemical species in addition to the determination of mass/charge ratio as measured by the mass spectrometer. This identification is accomplished by the method of controlled electron impact. In this method, the ion current at a particular mass number is observed as a function of the energy of the electrons used for producing ionization. Thus, for example, if one observes ions of a mass-ratio corresponding to singly-charged oxygen atomic ions, such ions may be the consequence of either of the processes



or



provided the incident electrons have sufficient energy. The first of the processes requires the smaller energy; by observing how the ion current depends upon incident energy, we can distinguish the first reaction from the second and thus determine the proportions of atomic oxygen and molecular oxygen in the beam entering the ionization source.

3. It is necessary to distinguish the beam molecules passing through the ion source as against the random background molecules due to ambient gas pressure in the ion source. Since the beam will itself, after striking walls, contribute to the ambient pressure in the source, it is not possible to observe a true background current by merely shutting off the beam. Rather, we must observe the current for the molecular beam passing through the ionizing electron beam (beam plus background) and compare it with the current for the beam passing into the ion source but not through the ionizing electron beam (background only). The provision for such a sequence of measurements will be discussed in Section 3.1, Item c.

1.3 PROGRAM

The number of specific chemical systems that eventually warrant investigation by the methods outlined above is very large. We have decided that reactions of hydrogen atoms on a variety of typical materials such as tungsten, graphite, quartz, etc., will be studied first. Before experiments can be started, however, the instrumentation must be provided; this in itself is a large enterprise and will be the exclusive subject of the remainder of this report.

Actual research will be conducted and reported under contract AF 33(616)-7106.

2.1 GENERAL DESCRIPTION

The analytical mass spectrometer built for this research is a magnetic deflection, 60-degree sector instrument with a 12-inch deflection radius. It is of a design developed by Professor M. Inghram over several years at the Argonne National Laboratory and in the Physics Department at The University of Chicago. Many such instruments have been built and are in operation at the above laboratories and elsewhere, and they have been applied successfully in a variety of chemical problems. Professor Inghram provided us with a complete set of detailed drawings and has consulted with us frequently during construction. The instrument has been built in our own shop. The electronic units associated with it have also been built principally by LAS personnel. Inasmuch as the development of this instrument has not been a part of this project, we shall not undertake to include working drawings in this report. Rather, we shall aim at describing the physical design and function of the instrument.

The gross features of the mass spectrometer tube are indicated in Figure 2. Photographs of the instrument and the control console, taken during tests, are shown in Figures 5 and 6. Practically all metal parts are of Inconel metal, joined by inert-gas welding. Demountable joints employ gold wire gaskets. Inconel was chosen because it is a clean vacuum metal and maintains its shape and dimensions well during temperature cycling; it is practicable to out-gas the entire tube by baking at 400° C.

The mass spectrometer functions in the following way: Molecules enter the ion source, where they are bombarded with electrons and converted to ions. The ions are accelerated and focused at the entrance slit of the analyzer. Within the analyzer the electric potential is constant and the ions move with constant kinetic energy qV where q is the charge on the ion and V the acceleration potential. The ions enter the magnetic field of strength H where they move along circular paths of radius R given by the expression:

$$R = \frac{1}{H} \sqrt{2V m/q} \quad (1)$$

where m is the mass of the ion. When the ions leave the magnetic field, they again travel in linear paths, but in directions that are different for each value of m/q . Those particular ions that have followed paths of 12-inch radius are deflected through 60 degrees and pass through the exit slit to the detector; all others are rejected at the exit slit. To perform an analysis, the magnetic field is varied slowly; as it passes through a valve that permits ions of a particular species to pass the exit slit, the detector current rises to a peak; the area under the peak is a measure of the concentration of a particular species of ion in the beam leaving the entrance slit.

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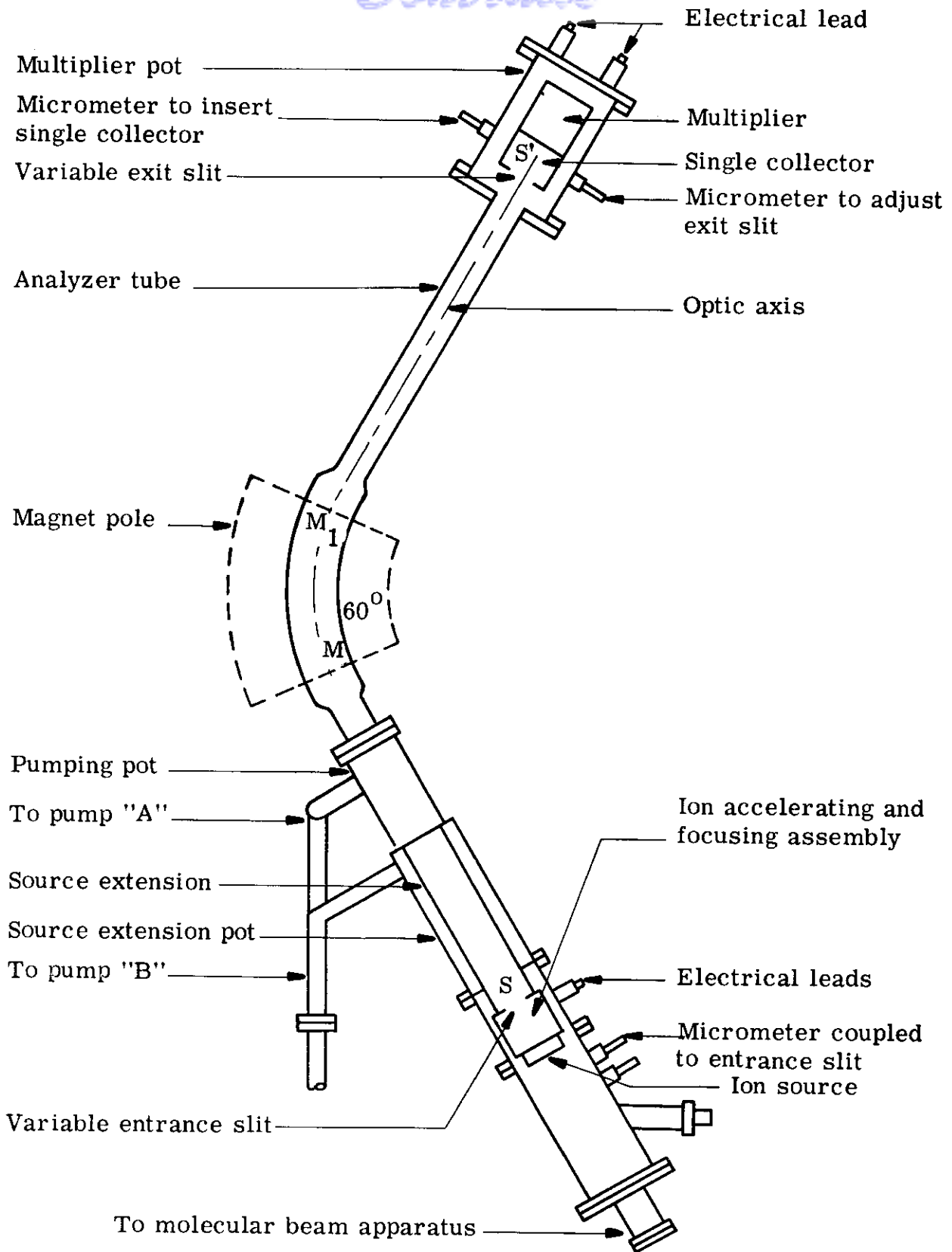


Figure 2. Mass Spectrometer (schematic)

The above is, of course, an abbreviated description. To perform the functions of ionizing, focusing, deflecting, etc., in a reliable, precise, and efficient manner requires elaborately designed apparatus. The mass spectrometer shown in Figures 2 and 5 contains 55 electrodes that must be operated at precisely controlled, generally different, potentials; there are 51 insulated electrical leads through the vacuum envelope. The electronic control system directly connected to this unit (see Figure 6) contains 232 vacuum tubes and a number of silicon diodes. The remainder of this section will indicate the functions of the various parts of the spectrometer, and of the units of the control console.

Reviews of the theory of the mass spectrometer may be found in the following articles.

Inghram, M., "Modern Mass Spectroscopy," Adv. in Electronics, Vol. 1, Academic Press, New York (1948), p. 219.

Inghram, M., and Hayden, J., Mass Spectroscopy, Publication 311 of the NAS and NRC, Washington, D. C. (1954).

Kerwin, L., "Mass Spectroscopy," Adv. in Electronics, Vol. 8 (1956), p. 187.

2.2 ION SOURCE

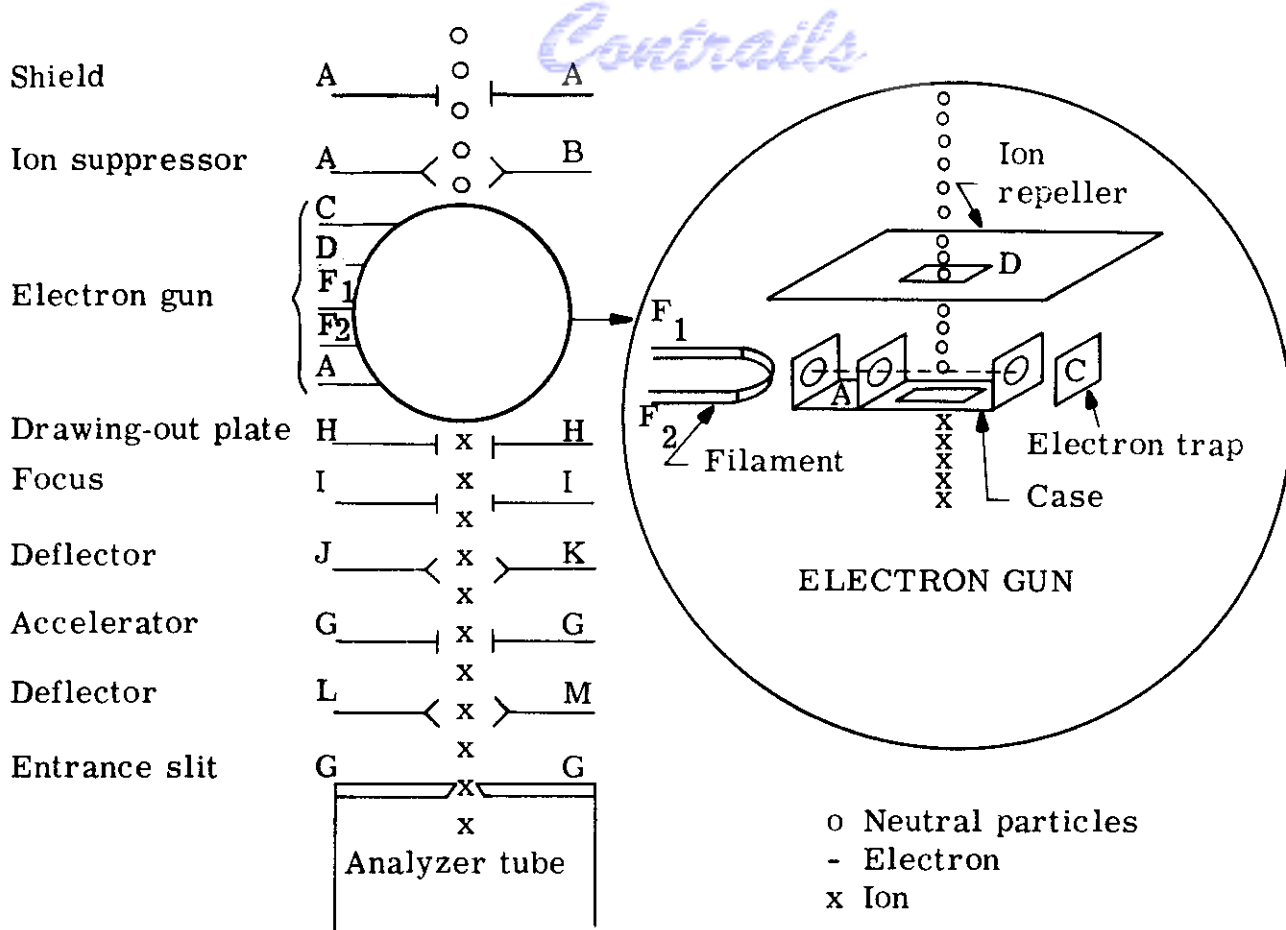
The ion source has the functions of bombarding molecules with electrons of well defined energy to form ions, of collecting and accelerating the ions so formed to a kinetic energy of about 10^4 ev, of focusing them onto the entrance slit, and directing them accurately down the axis of the analyzer tube. The arrangement of electrodes and potentials is illustrated schematically in Figure 3; the actual construction is illustrated by the photograph in Figure 7. Typical values and ranges of the potential for the ion source electrodes shown in Figure 3 are given in Table 1.

The metal vacuum envelope of the spectrometer is at ground potential, so the ions must be formed in a region maintained at the accelerating potential; normally about 10 kv, positive for positive ions. Thus the entire source above the accelerator electrode is at high potential with respect to ground and must be insulated accordingly. The various electrodes function as indicated below.

The shield has more a mechanical than electrical purpose; it serves as a pressure plate to hold the rest of the assembly together.

The ion suppressor provides a lateral electric field to remove ions from entering the molecular beam.

The case of the electron gun assembly is designed to provide a nearly field-free region where ions are formed by electron impact.



Typical values of these potentials for positive ions are listed in Table 1.

Figure 3. Controlled Electron Impact Ion Beam Source (schematic)

The repeller provides a small electric field that tends to move the ions toward the exit slit at the bottom of the case.

The filament supplies electrons; the electron energy is determined by the potential difference between the case and the center of the filament. The total emission current is monitored and maintained constant by a servo-circuit; therefore, the filament must be well insulated from the case. Only a fraction of the total emission passes through the beam-defining apertures to form the electron beam; the beam current is collected by the electron trap and conducted to a meter.

The drawing-out electrode provides an electric field that penetrates into the case through the exit slit and tends to draw ions out.

Continued

Table 1. Typical Values and Ranges of the Potentials
for the Ion Source Electrodes (see Figure 3)

Electrode	Typ. Values (Volts)	Range (Volts) (for positive ions)
A	+10,000	0 - 10,000
B - A	+300	0 - 300
$C - (F_1 + F_2)/2$	+150	0 to +225
D - A	+5	0 to +30
$F_1 - F_2$	5v, RMS, 3KC A.C.	3 - 5v RMS
$[(F_1 + F_2)/2] - A$	-75	0 to -150
H - A	-50	0 to -300
I - A	-450	0 to -750
J - A	-2500	-300 to -4000
K - A	-2500	-300 to -4000
J - K	0	-250 to +250
G - ground	0 (Ground)	
L - ground	0	-250 to +250
M - ground	0	-250 to +250

The drawing-out, focusing, and accelerator electrodes together form an electrostatic lens system that accelerates the ions and also focuses them sharply on the entrance slit of the spectrometer.

The two pairs of deflector electrodes provide transverse electric fields so that the ion beam can be bent in two places along its length. By having two bends, it is possible both to center the beam on the entrance slit and to control the direction in which it passes through the slit.

The entrance slit is one of the defining slits of the analyzer; its width is adjustable through a micrometer sealed by a slyphon bellows.

2.3 ANALYZER

2.3.1 Tube

The analyzer tube is illustrated in Figures 2 and 5. The main section of the tube, which passes between the magnet poles, was formed from a length of 2-inch outside diameter, 3/32-inch wall Inconel tubing, using bending and pressing dies borrowed from The University of Chicago Central Shop.

2.3.2 Magnet

The shape of the pole face is indicated in Figure 2; the general construction in Figure 5. The magnetic circuit is of Armco iron. The gap is 2.18 cm. The coils each have about 30,000 turns of #22 wire on a 9-inch core; total coil resistance is 3000 ohms. The field in the gap is about 35 oersteds per ma for a magnet current up to 6,000 oersteds. Saturation field is 8100 oersteds at 320 ma.

2.4 ION DETECTOR

Two arrangements are available for measuring the analyzed ion current.

1. The ions may be collected (single collector) and measured as current by a vibrating-reed electrometer
2. The ions may impinge upon a dynode and generate secondary electrons; the secondaries are amplified by an electron multiplier the output of which may be read as pulses by means of a linear amplifier and scaler or as integrated current by means of the electrometer

The detector assembly is illustrated schematically in Figure 4. Table 2 indicates the function and potentials of the various electrodes. Photographs of the single collector and photomultiplier assemblies are shown in Figure 8.

The single collector consists of a defining slit S', a secondary electron suppressor, and a collector plate plus guard ring assembly. The width of the exit or defining slit S' is adjustable by a micrometer and bellows connection from outside the vacuum system. The single collector plate can be moved in or out of the incident ion beam path by means of another micrometer and bellows connection. With the single collector plate open the ion beam is allowed to pass through the deflector plate and guard ring assembly (2) to the first (or conversion) dynode of the 16-stage electron multiplier detector. The repeller and shield produce an electric field that forces secondary electrons liberated from the conversion dynode to travel to the second dynode rather than to other, more positive, surfaces in the neighborhood. The final collector may be connected to a pulse amplifier and scaler, or to an electrometer that measures

Controls

Table 2. Typical Values and Ranges of the Potentials
for the Ion Detectors (see Figure 4)

Electrode	Typ. Values (Volts)	Range (Volts)
Sup-ground	-300	-300
GR1-ground	0	0 - ±45
GR2-ground	0	0 - ±45
DP1-ground	0	±250
DP2-ground	0	±250
DP1-DP2	0	-500 to +500
SHD-ground	-4500	-4500
Rep-ground	-4500	-4000 to -4500
Conversion dynode-ground	-4000	-4000
Dynode 2-Dynode 3	-300	-270 to -350
Dynode 16	-45	0 to -45
Collectors	0	0

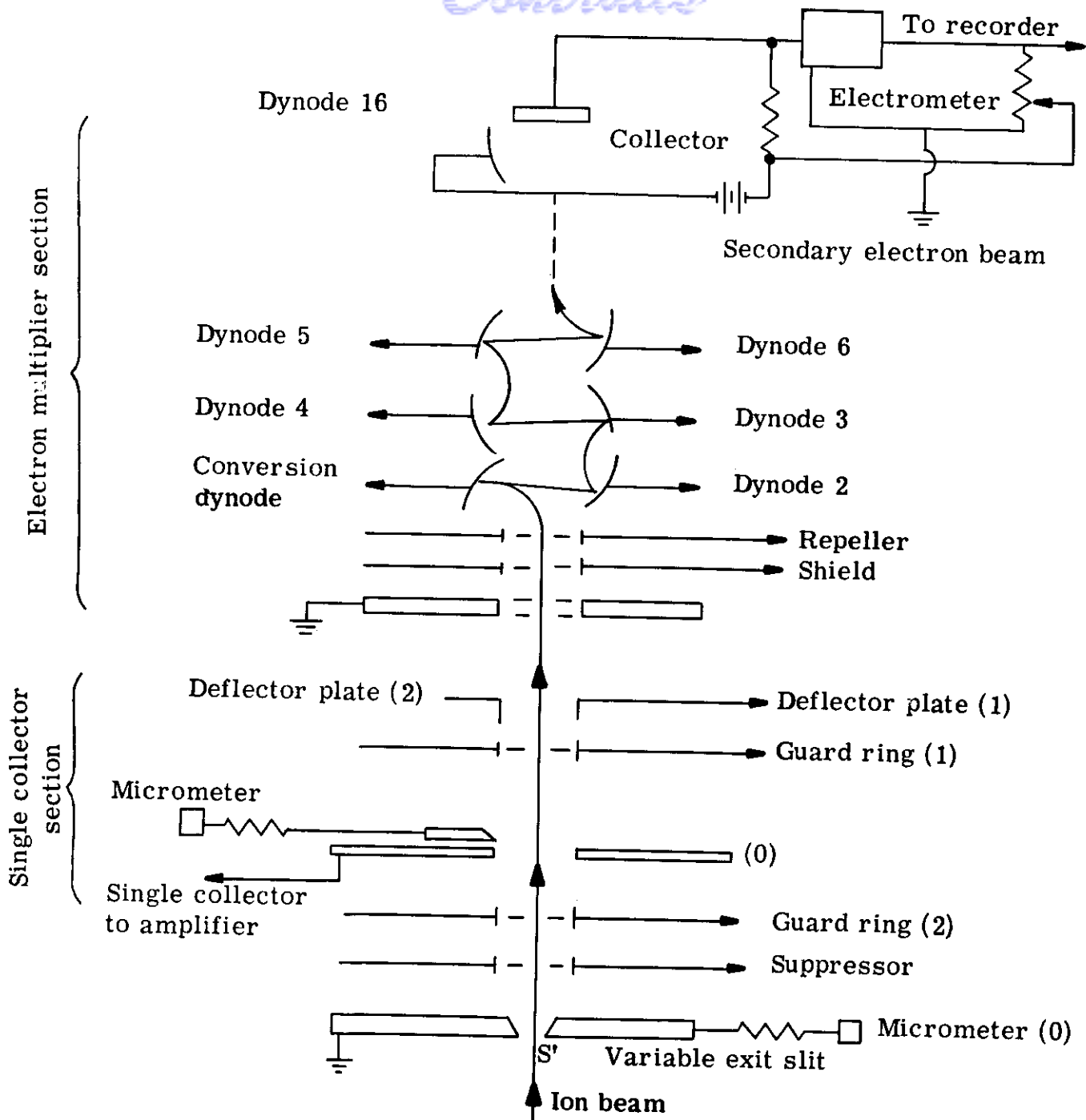
integrated output current. In this instrument the gain of the multiplier is $(2.6)^{16}$ or about 2.5×10^6

The electron multiplier has the advantage of extreme sensitivity and rapid response. However, it responds differently to ions of different types, and so must be calibrated when actual ion currents are to be compared. The single collector provides the means for such calibrations.

2.5 ELECTRONIC CONTROL SYSTEM

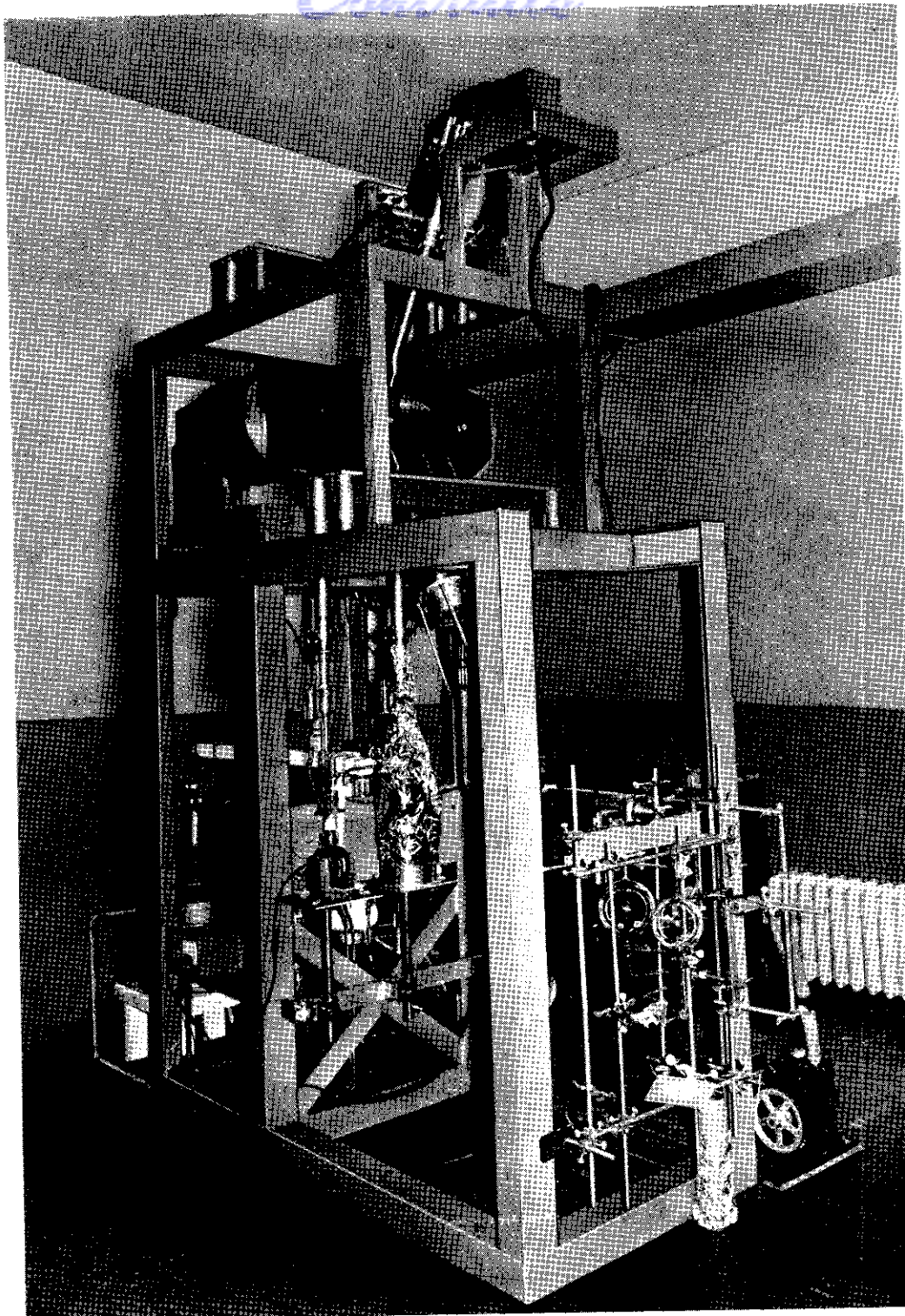
The electronic control system, contained principally in the console, fulfills the following functions:

1. To supply current to the magnet and provide for its precise adjustment and variation.
2. To supply potentials to the mass spectrometer, as indicated in Figures 3 and 4.



Typical values of the potentials of these electrodes are listed in Table 2.

Figure 4. Single Collector and 16-Stage Electron Multiplier Ion Detectors (schematic)



A temporary ion-source cover has been installed for testing and adjusting the mass spectrometer. The temporary gas leak and supply system are also shown. The ion-source cover will eventually be replaced by the molecular-beam apparatus shown in Figure 14.

Figure 5. Mass Spectrometer

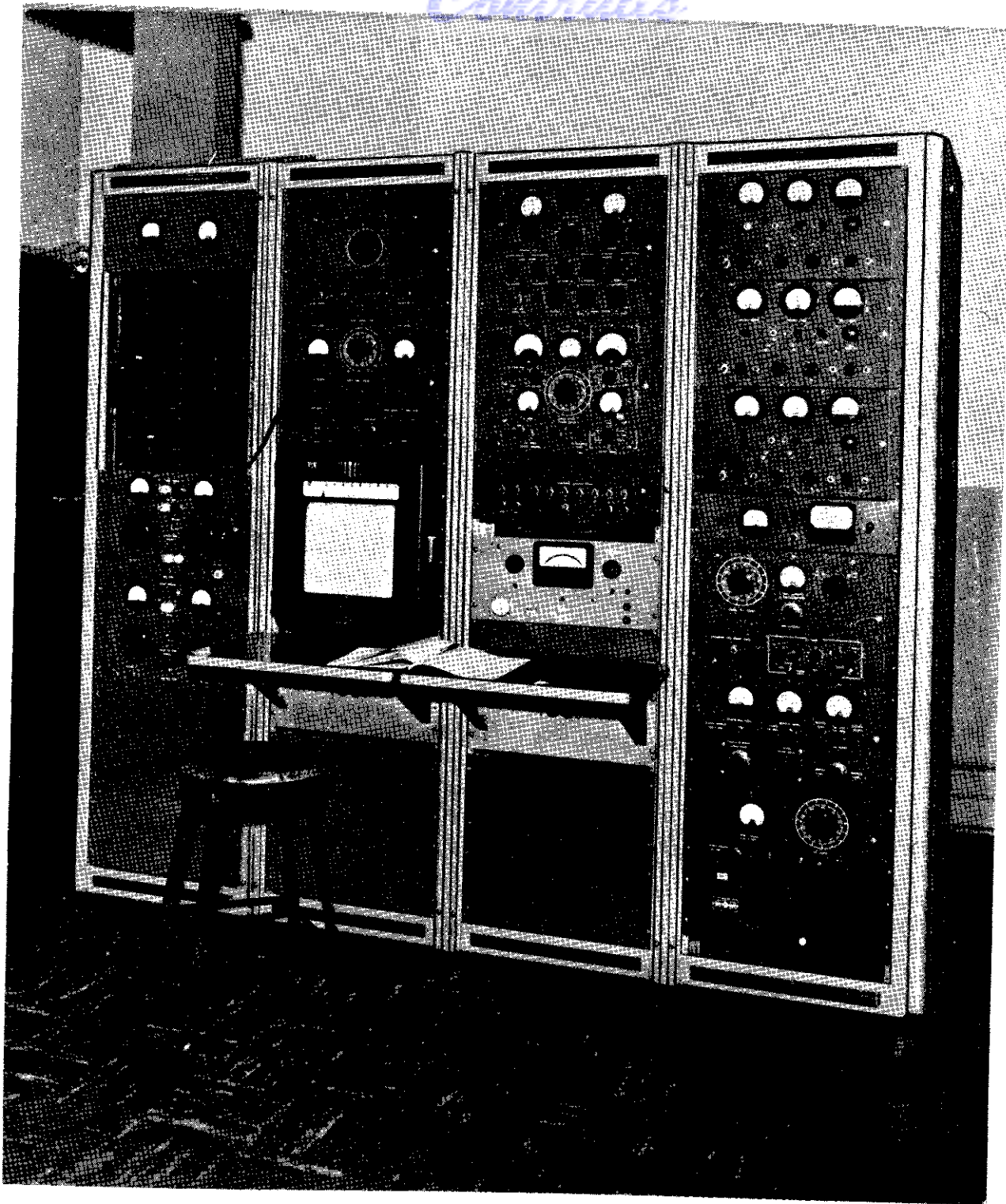


Figure 6. Electronic Control Console

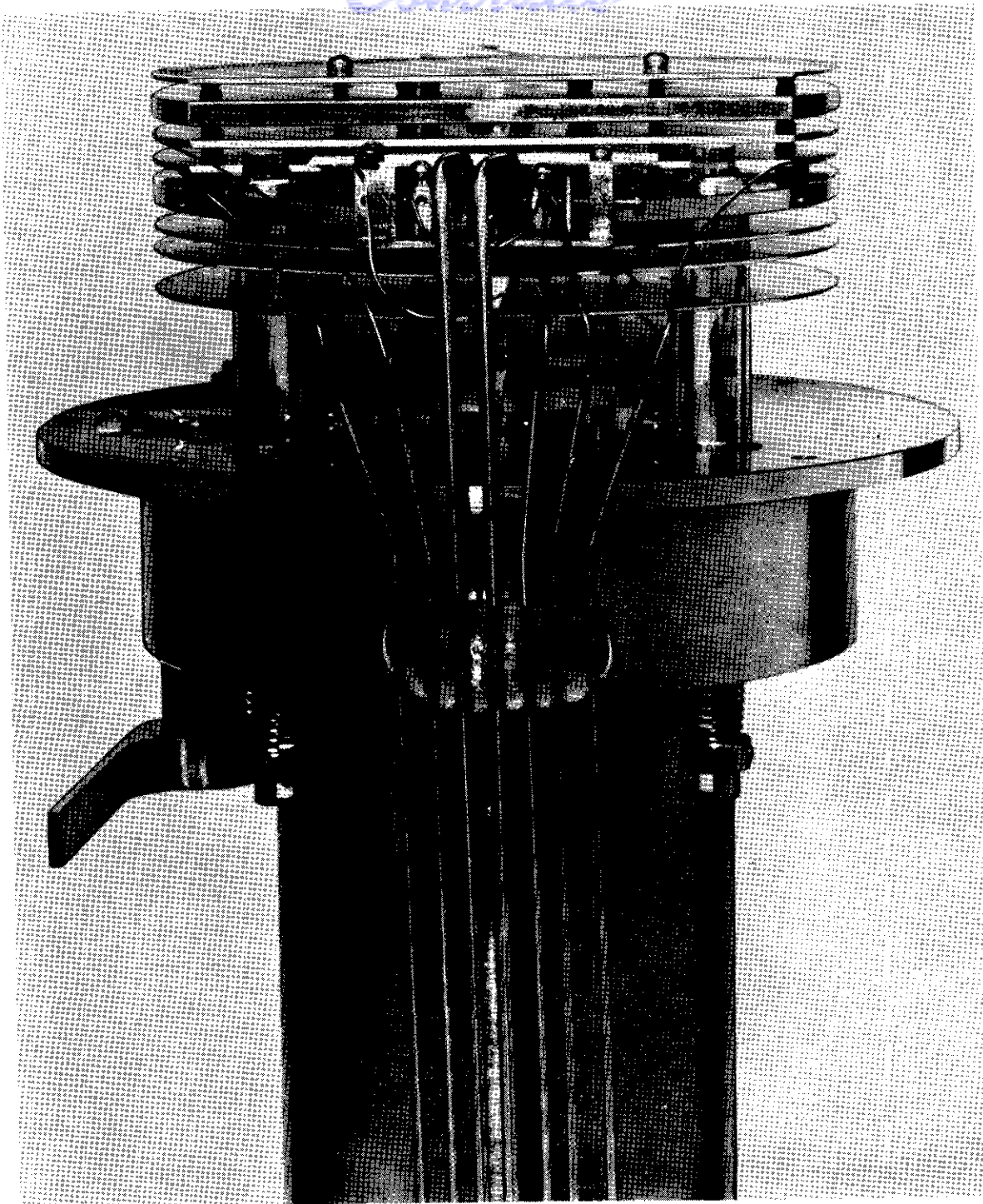
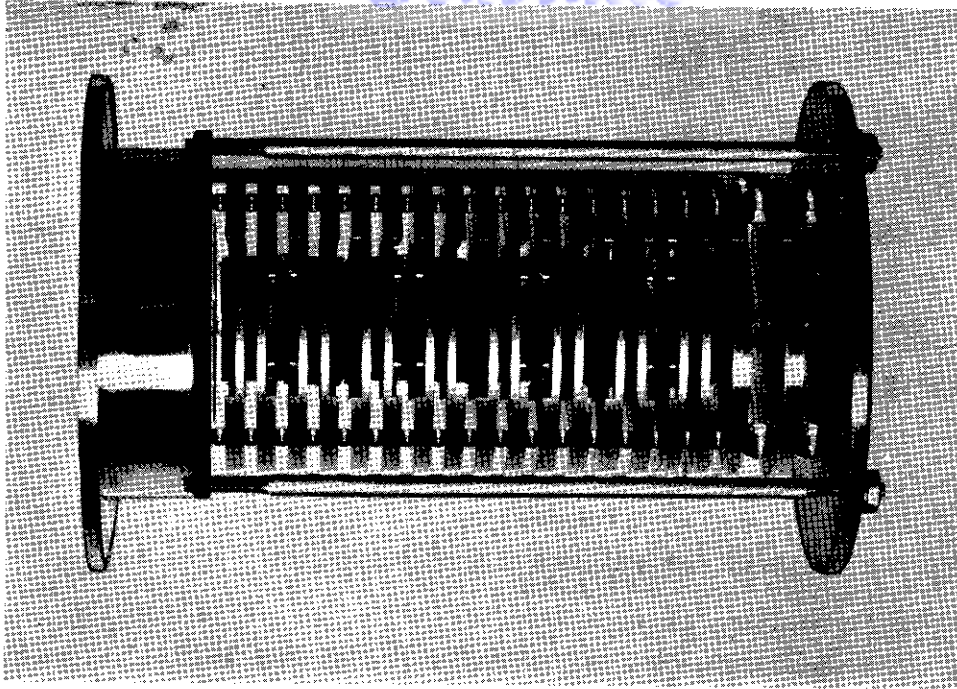
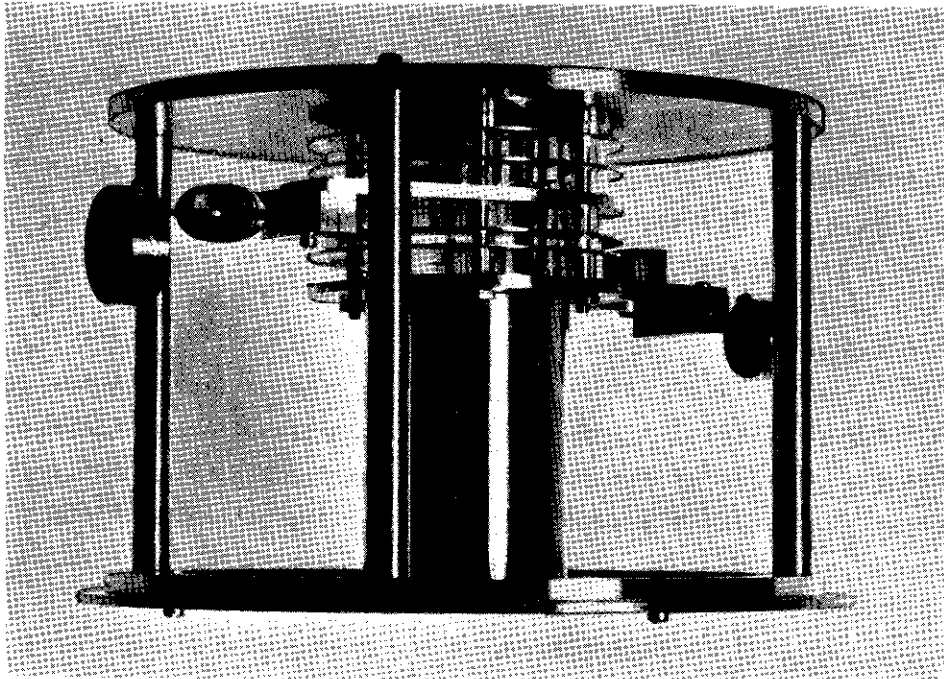


Figure 7. Electron-Impact Ion Source



(a)



(b)

Figure 8. Ion Detectors (a) Single Collector (b) Electron Multiplier

3. To provide an electron-current regulator for the filament of the ion source.
4. To display or record data, principally the magnet current and the detector output.
5. To control ion gauges attached to various vacuum compartments.
6. To control pumps.
7. To provide safety interlocks and shut-offs to protect the apparatus from incorrect procedures and from failure of electrical and mechanical components and of electric and water supplies.

The following units have been purchased:

General Radio 5 kva line-voltage regulator
Baird-Atomic linear amplifier and scaler
Carey vibrating-reed electrometer
Leeds and Northrup two-channel recorder.

The remaining units have been constructed in the laboratory; the operating principles of the more important ones are reviewed in following sections. We shall not, however, describe in detail the electronic circuitry, which is conventional.

2.5.1 Magnet-Current Supply

If the theoretical resolving power of the spectrometer is to be realized, the magnet current must be stable and free of ripple within a few hundredths of a percent. For recording, it should be possible to make the current vary with time smoothly and at a chosen rate, either upward or downward. The regulating circuit that serves the purpose is shown schematically in Figure 9.

The magnet current i_m flowing through the current measuring resistor R_1 produces a potential $i_m R_1$ at a. The difference amplifier compares $i_m R_1$ with the potential at b that exists because of charge on the low-leakage capacitor C. If V_a is not equal to V_b , an error signal is generated and fed through the d. c. amplifier to the grid of the series regulator, which adjusts i_m so that $V_a = V_b$.

The circuit so far discussed servo-regulates the magnet current to whatever value corresponds to the reference potential V_b , and by virtue of high gain around the servo-loop, renders the magnet current constant in spite of ripple and power-line variations in the 1800 v supply. All adjustments of magnet current are effected by varying the reference potential V_b .

The circuitry to the right of C is the sweep circuit; by means of it the potential across C, and thus the magnet current, can be made to vary linearly with time or to remain stationary. The differential amplifier and follower circuits have very high input resistances, so that the potential across C changes only by the flow of current through the resistor R_2 ; that is to say

$$\frac{dV_b}{dt} = \frac{1}{R_2 C} (V_e - V_b)$$

The follower circuit is a unity gain amplifier; it has a high input resistance and low output resistance; its function is to make the potential at d follow accurately that at b. If the switch S is in the uppermost position, the capacitor C must charge at a constant rate; in the lower position, discharge; and in the middle position, remain fixed. By varying the magnitude of R_2 , the rate of change can be regulated. In case one wishes the magnet current to remain very accurately at a fixed value for extended periods, a reference voltage derived from a cascade of voltage regulator tubes may be applied at b. By these means, adequate control of the magnet current is achieved.

Although voltage sources are indicated as batteries in Figure 9, the actual circuits are all battery-free, with V-R tubes as constant-voltage sources.

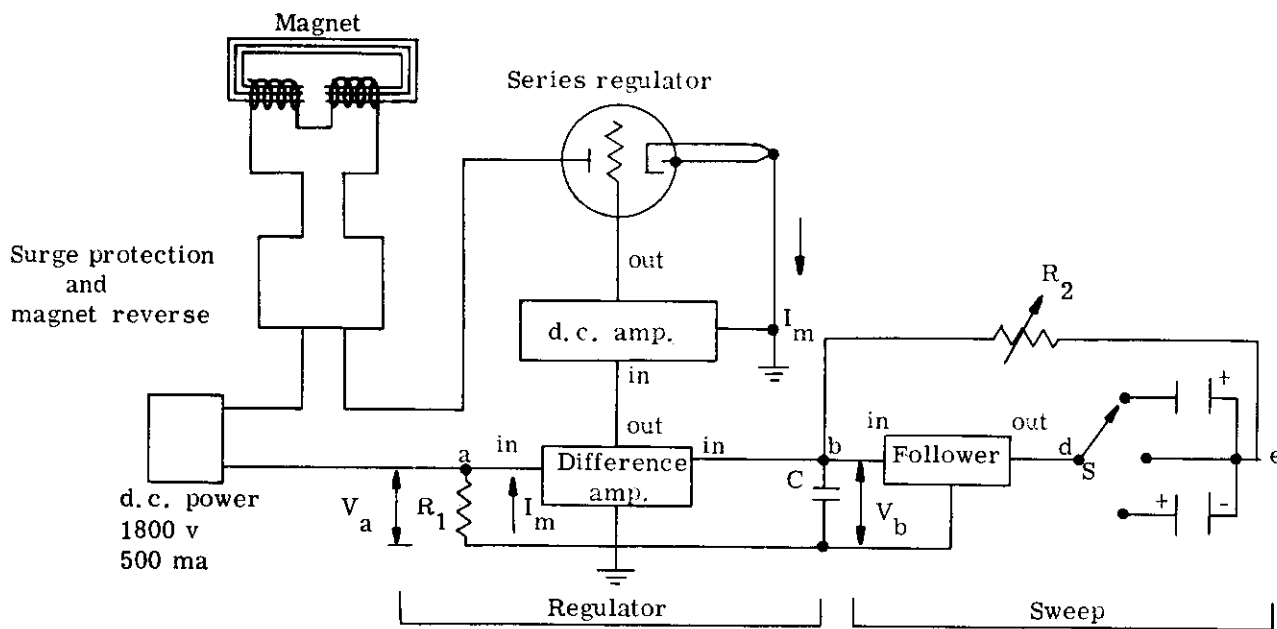


Figure 9. Schematic Block Diagram of Magnet-Current Regulator and Sweep Circuit

2.5.2 Accelerating-Voltage Supply

The accelerating voltage, just as the magnet current, must have short-term constancy within a few hundredths of a percent if maximum resolution of the mass analyzer is to be realized. The regulating circuit is shown schematically in Figure 10. The essential feature of this circuit is a radio frequency high-voltage supply in which control is effected through the voltage applied to the screen-grids of the 450 k. c. oscillator tubes. The output voltage V_o is servo-regulated to bring the voltage $V_1 = [R_1 / (R_1 + R_2)] V_o$ to equality with a reference voltage V_R . Control of the output voltage is effected by adjustment of the reference voltage, which may be derived either from V-R tubes and voltage-dividers or from a linear-sweep circuit similar to that in the magnet supply.

The entire supply is built on a well-insulated chassis and is powered through an isolation transformer, so that either terminal may be grounded, according to whether positive or negative ions are to be analyzed.

2.5.3 Ion-Source Current and Voltage Regulator

For many applications the electron beam current must be maintained constant over a wide range of accelerating potentials (i.e., filament-to-case potential difference), or reciprocally, the electron energy may be required to remain constant while the beam current is varied over a wide range. In the present apparatus, it is actually the total

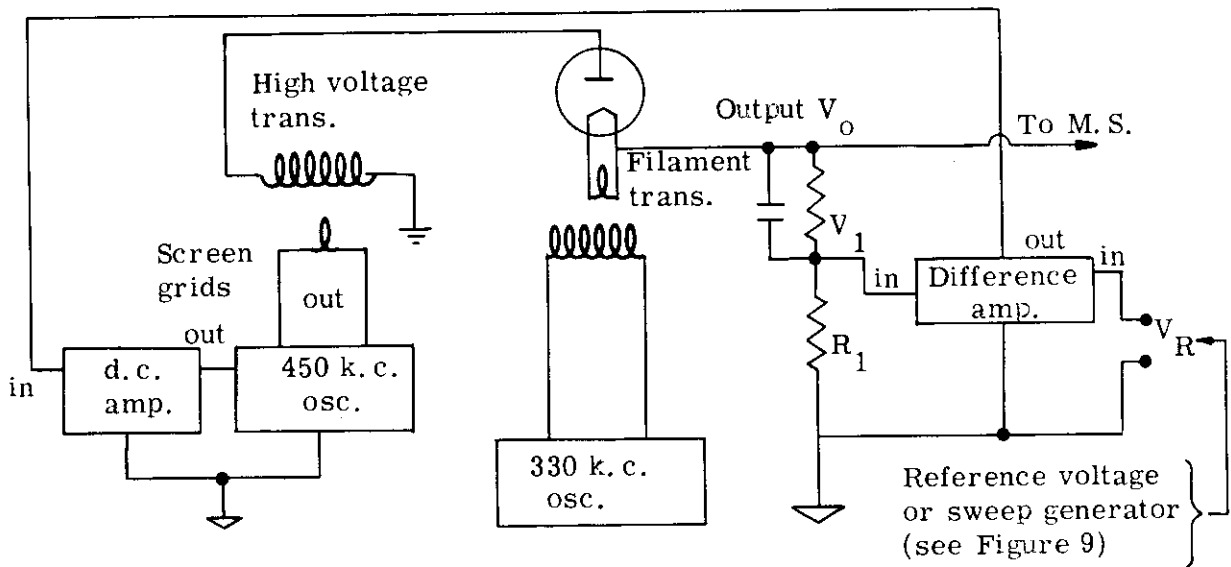


Figure 10. Accelerating Voltage Supply (0-10 k. v.)

emission current rather than the beam current that is controlled; the beam current is very nearly proportional to emission current and can be measured by means of the meter connected to the trap. In this apparatus, the total emission current can be varied from 0.05 to 25 ma and maintained constant to within 0.1% for a 25% change in line voltage. The maximum ripple in the emission current is less than 1% and the average long-term drift is less than 0.01% per hour. The electron energy is governed by the filament-to-case potential difference, which is continuously variable from 150 volts downward. At very low voltages, however, the emission current is limited by space charge and can be regulated only below the space charge limited value.

The above results are accomplished by means of the circuits represented schematically in Figure 11. The left half of the diagram relates to control of emission current. The electron current emitted by the filament flows to the case and repeller and

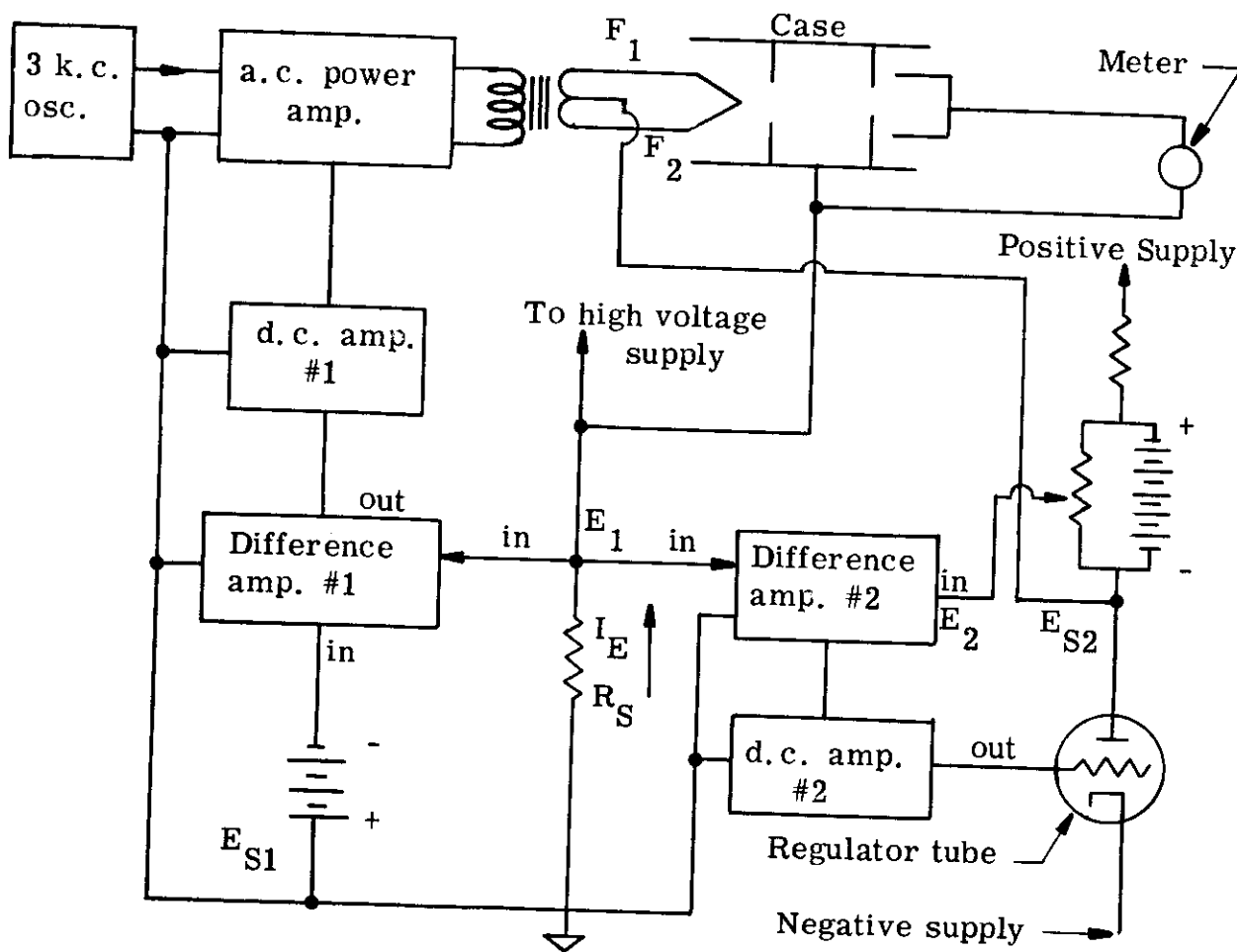


Figure 11. Block Diagram of Emission-Current and Electron-Energy Regulator

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then through the current-measuring resistor R_S to the chassis. The differential amplifiers connected to R_S have extremely high input resistances and draw negligible currents. The potential E_1 developed across R_S is applied to one input of difference-amplifier #1; the reference potential E_{S1} is applied to the other input. The amplified difference between these two potentials is applied to the filament power-amplifier in such a way as to control the power delivered to the filament. With increasing power, the temperature of the filament rises and consequently its electron emission (unless the emission is already limited by space charge, in which case the control fails), which in turn influences E_1 in such a way as to bring it nearer to equality with E_{S1} .

A feature not indicated in Figure 11 is a clamping circuit that prevents the control circuit from pushing the filament current beyond a safe limit when emission is inhibited by space charge or surface poisoning. The reason for using a. c. power for heating the filament is convenience in electronically controlling a low-voltage, high current circuit. The use of 3 k. c. current eliminates temperature ripple.

The circuit in the right-hand half of Figure 11 is designed to maintain a constant difference between the potential E_1 of the case and the potential E_{S2} of the midpoint of the filament. As a servo-mechanism, it controls the current through the regulator tube so as to maintain equality between the input voltages E_1 and E_2 of the difference amplifier #2, and thus to maintain the filament at potential $E_{S2} - E_2$, relative to the case. Because the voltage-gain around the servo-loop is very large, the potential difference $E_{S2} - E_1$ is practically unaffected by variations in emission current or fluctuations in the supply voltages.

2.5.4 Miscellaneous Supplies and Controls

Potentials A--B, H, I, J of Figure 3 and Table 1 are derived from a conventional electronically-stabilized RF voltage supply and voltage dividers. Potentials G--L, M of Figure 3 and Table 1 are derived from a voltage divider across a bank of V-R tubes fed from a simple d. c. supply.

The electron multiplier is powered by an RF voltage supply, similar to that for the accelerating voltage except that maximum output is 5 kv, plus voltage dividers. Potentials for the deflector plates and suppressor (Figure 4 and Table 2) are derived from a voltage divider across a bank of V-R tubes fed from an electronically stabilized voltage supply.

Three control units and electrometers for 5 vacuum ion-gauges and 3 thermocouple gauges are included in the console. These units are designed according to more exacting standards than are any units available commercially, but are otherwise conventional.

All of the units mentioned in Sections 2.5.1 through 2.5.4 draw 60-cycle, 115-volt power through a 5 kva General Radio Variac voltage regulator.

2.5.5 Safety Controls

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Automatic safety controls of several sorts are necessary to prevent damage to the apparatus in case of (a) improper operating procedures, (b) unforeseen failure of the water coolant supply to diffusion pump, (c) interruption of line power, (d) vacuum leaks resulting in a rise of pressure to a level higher than the minimum required for safe operation of the system. The importance of the safety controls is evident not only because they are automatic and fast and eliminate the human error factor and the slow response of the operator but because some of the equipment, e. g., vacuum pumps, will run continuously for long periods of time and therefore much of the time without attendance.

Table 3 lists the types of failures that are foreseen and the preventive or corrective action that is taken automatically.

Table 3. Types of Failures and Preventive or Corrective Measures for Mass Spectrometer Apparatus

Type of Failure	Preventive or Corrective Measure
1. Improper procedures on part of the operator.	Power inputs to all high voltage and filament power supplies are connected through a relay in the ion gauge vacuum indicator circuit. If vacuum is not below a certain preset level these units can not be turned on.
2. Insufficient flow of water through a diffusion pump.	Power to boiler of pump shut off until restored manually.
3. Vacuum falls below preset level.	Power to high voltage and filament supplies shut off until vacuum level is restored to preset value.
4. Line power is interrupted.	Entire system is shut down. Must be restored manually.

3. MOLECULAR-BEAM APPARATUS

The molecular-beam apparatus that has evolved from the basic idea indicated in Figure 1 is illustrated in Figure 12. The configuration of the molecular beams is drawn to scale in Figure 13. It is to be noted that this design permits a direct comparison to be made between the composition of the beam issuing from the source and the composition of the beam reflected from the target; no intermediate calibrations are necessary. This feature, which was developed at Professor Inghram's suggestion, will both simplify experiments and make them more accurate.

The requirements that had to be met are reviewed in Section 3.1. The theoretical calculations used as a guide for the design are given in Section 3.2. The final drawings are the result of a series of drafting-board experiments, each successive one representing improvements in mechanical features and calculated performance.

The actual apparatus, nearly completed, is shown disassembled in Figure 14. Details, mode of construction, and material resemble closely those of the mass spectrometer.

3.1 REQUIREMENTS

Intensity. It is necessary that the species to be detected arrive in the ionization region of the mass spectrometer at a rate high enough to be counted with a reasonably small statistical error. To secure high intensity the distance from the source slit S to the target T (see Figure 13) and the distance from the target to the ionization region R have to be small, and the limiting slits should have large areas.

Ambient Pressure In the Space Between S and D (See Figure 13). The pressure must be low enough so that the molecular beam is not scattered by gas collisions. This condition is favored by a small area for S and by high pumping speed for the region A to S.

Ambient Pressure In the Target Chamber. The ambient pressure should be low enough so that the random flux of molecules to the target surface is small compared to the flux of the incident beam. This condition is favored by a low pressure in the space A to D and large pumping speed for the target chamber.

Ambient Pressure In the Ion-Source Region. The pressure should be extremely small, to minimize the background of ions formed from the ambient gas. This condition necessitates that the target and the ion source be placed in separately pumped vacuum chambers connected only by the small apertures G and F.

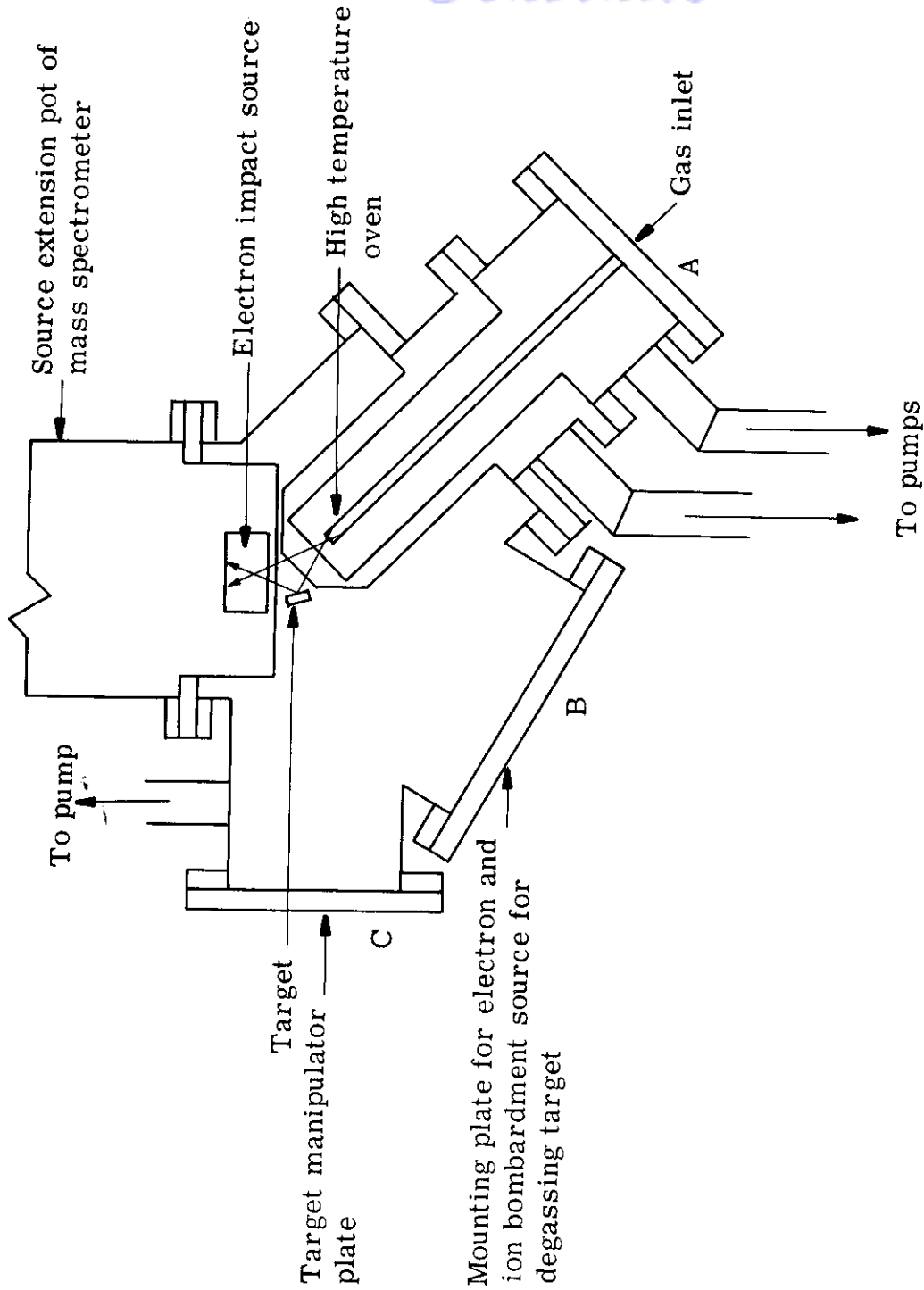


Figure 12. Molecular-Beam Apparatus (schematic)

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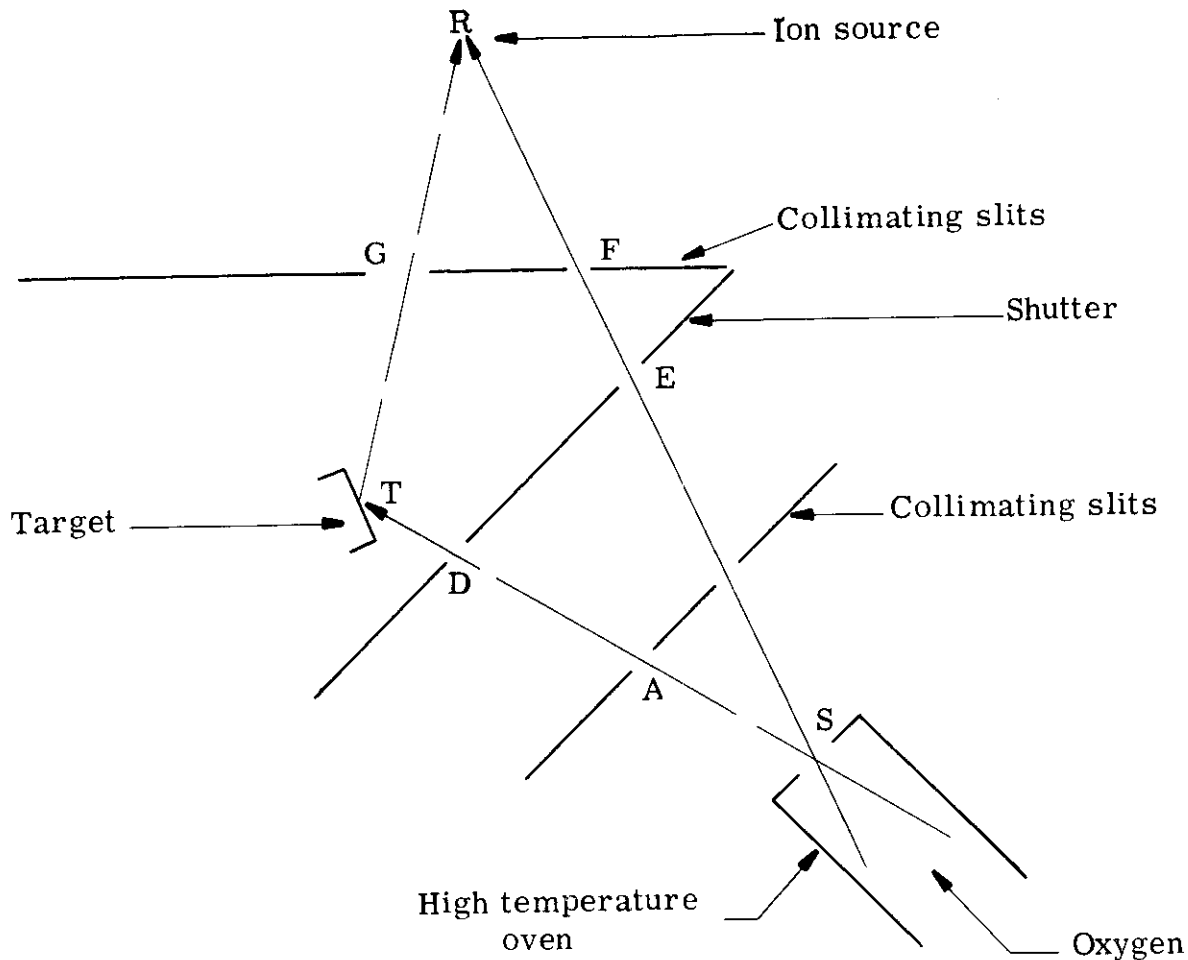


Figure 13. Configuration of Molecular Beam (schematic)

Background Ion Current. For stable molecules, the response of the mass spectrometer will usually be partly to ambient pressure and partly to beam molecules, in spite of precautions taken to reduce ambient pressure in the ion-source chamber to a minimum. Thus, provision must be made for independent readings of background and background-plus-beam. Because the ambient pressure is caused in part by the beam itself, it will not do to simply turn off the beam; instead the beam should be swept across the sensitive region without other alteration. This operation has been provided for by making the shutter D and the collimating slit G movable in a direction perpendicular to the plane of Figure 13 (similarly with F, for the direct beam).

Flexibility. Because construction of this type of apparatus is expensive and time-consuming, it should be so designed that it can be adapted, without major reconstruction, to experiments on many different materials under a wide range of conditions.

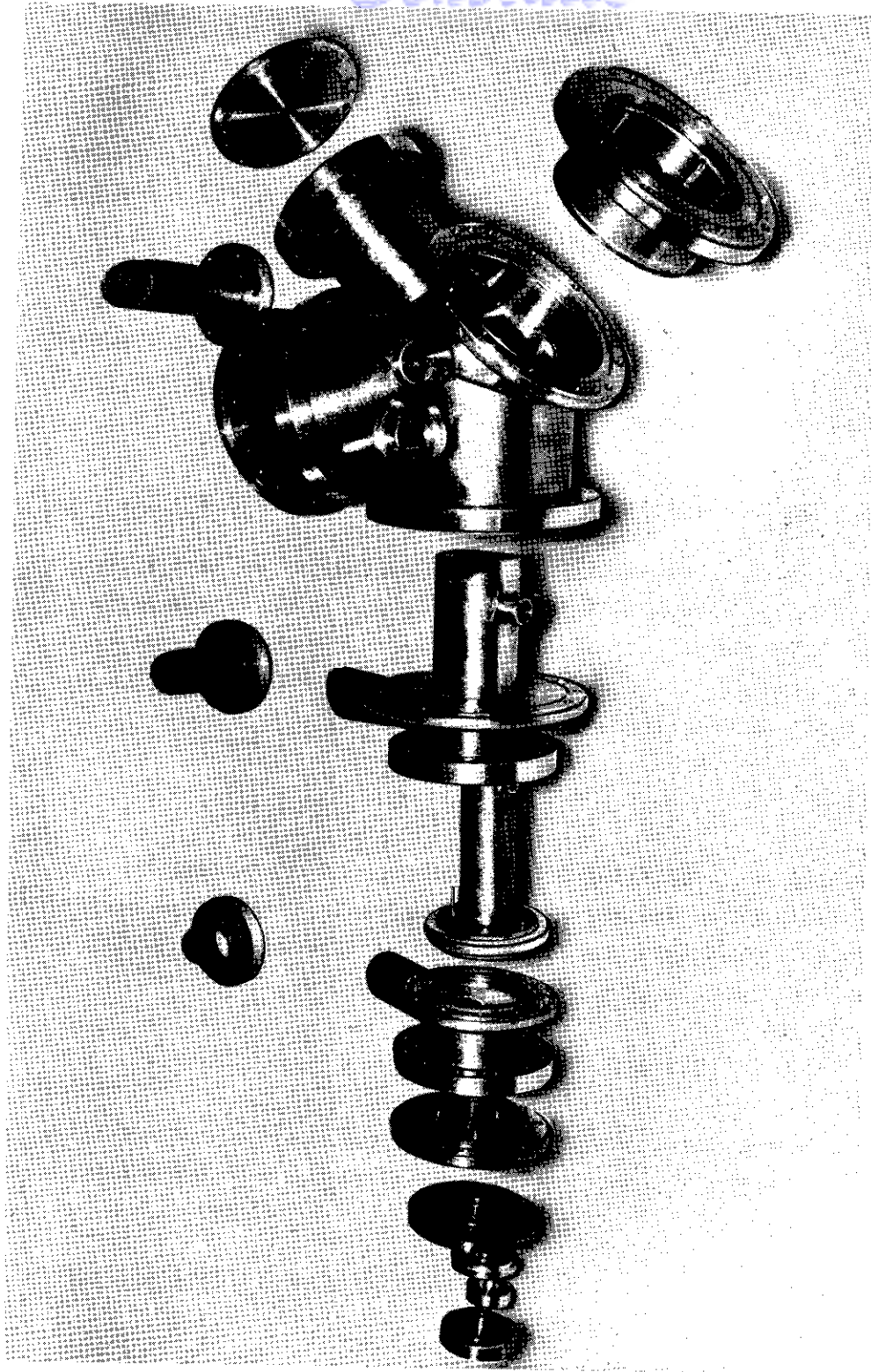


Figure 14. Unassembled Molecular-Beam Apparatus

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This requirement has been met by providing three large, gasketed cover plates A, B, and C of Figure 12, as carriers of observation ports, source ovens, and target manipulators.

Mechanical Features. The apparatus had to be designed so that the parts could be machined and could be joined by inert-gas welding. Moreover, it had to be strong enough to be self-supporting with pumps attached, so as to avoid thermal stresses during bakeout.

To some extent the requirements conflict with one another, so compromises had to be worked out carefully. We believe that, in an extended program of experiments, the effort expended upon the design of the apparatus will be fully justified.

3.2 GAS FLOW-THEORY AND CALCULATIONS

In the molecular beam apparatus the pressure will be low enough so that the flow of gas is governed by the laws of molecular flow rather than hydrodynamics. The necessary condition is that the mean free path λ be large compared with the pertinent dimensions of the apparatus. The mean free path is an inexactly defined quantity; for air, (N_2 , O_2 , and A) at $500^\circ K$ it is given approximately by

$$\lambda = 5 \times 10^{-3} \text{ cm/p} \quad (2)$$

where p is expressed in mm Hg. For H_2 , λ is twice as large as for air; for He, three times. The number of molecules per second dQ that will pass through an aperture of area A_s traveling within a solid angle dW centered about a direction making an angle θ , with normal to the aperture, is given by

$$dQ = \frac{dW}{4\pi} \quad nv \cos \theta \quad A_s \quad (3)$$

where n is the number of molecules per unit volume and v the average molecular speed. The number Q per second that pass through in one direction is found by integrating Eq. (2) over a hemisphere; i. e.,

$$Q = \frac{1}{4} \quad nv \quad A_s \quad (4)$$

Equation (4) has to be modified if the sides of the aperture are thick. (The modification is appreciable only where tunnel-like passages are concerned and are not important in the cases with which we shall deal.)

The mean speed is given by

$$v = 1.46 \times 10^4 \sqrt{\frac{T}{m}} \frac{\text{cm}}{\text{sec}} \quad (5)$$

where T is the absolute temperature and M the molecular weight. Equation (4) can be used to compute pumping speeds $\frac{Q}{\lambda}$ of apertures by inserting the proper value of v. It will be more convenient, however, to make calculations in terms of effective pumping apertures A. For air at 300°K, Eq. (4) predicts a pumping speed of 12l/sec per cm² of aperture.

The spatial distribution of beam intensity that results when two rectangular apertures are used to define a pencil-beam can be calculated from Figure 15.

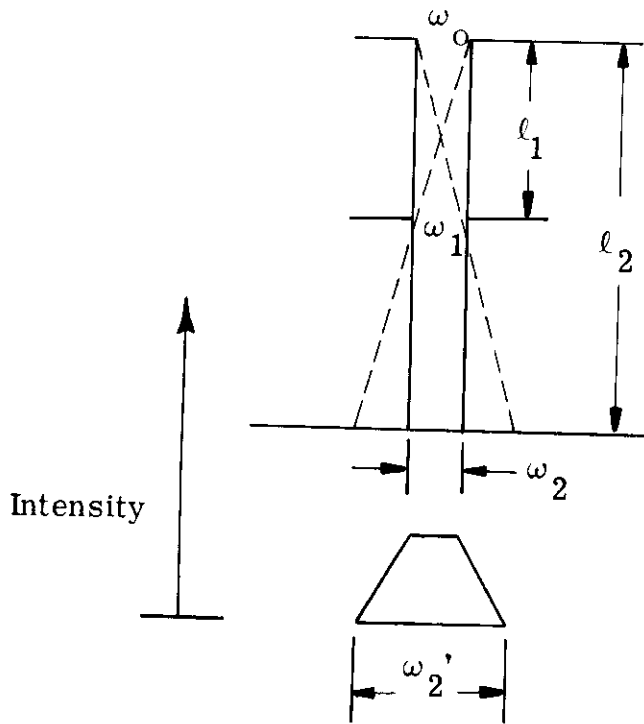


Figure 15. Intensity Distribution in a Molecular-Beam Limited by Two Apertures

The source aperture has a width w_0 ; the defining aperture has a width w_1 and is at a distance l_1 from the source. At a distance l_2 from the source, the beam has a core in which the intensity is a maximum and is uniform. The width of the core is given by

$$w_2 = \frac{l_2}{l_1} (w_1 - w_0) + w_0 \quad (6)$$

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Outside the core, the intensity falls off linearly, the total width of the beam w'_2 is given by

$$w'_2 = \frac{\ell_2}{\ell_1} (w_1 + w_0) - w_0 \quad (7)$$

Similar relations will hold for the second dimension h of the apertures and beam.

The particle-flux Q_0 of molecules through the source aperture, using small-angle approximations, is given by

$$Q_0 = \frac{1}{4} w_0 h_0 n_0 v_0 = \frac{1}{4} A_0 n_0 v_0 \quad (8)$$

That through the beam restricting aperture Q_1 is given by

$$Q_1 = Q_0 \frac{w_1 h_1}{\ell_1^2} = \frac{n_0 v_0}{4\pi} \frac{A_0 A_1}{\ell_1^2} \quad (9)$$

The flux density I_2 in the core of the beam at ℓ_2 is given by

$$I_2 = Q_0 \frac{1}{\pi \ell_2^2} \quad (10)$$

The particle density n_2 in the core of the beam at ℓ_2 is given by

$$n_2 = \frac{I_2}{1.18 v_0} \quad (11)$$

The factor 1.18 enters because the average molecular speeds are different for source and beam. Concentration $n(\text{cm}^{-3})$ is related to p (in mm Hg) and $T(^{\circ}\text{K})$ according to

$$n = 9.65 \times 10^{18} p/T \quad (12)$$

The relations given above will now be used to estimate pressures and beam fluxes in the apparatus illustrated in Figure 12. For convenience, the apparatus is shown schematically in Figure 16, where the various vacuum compartments are indicated. Areas of beam-limiting apertures are represented by a's; of effective pump apertures, by A's. The aim of the calculation is to estimate backgrounds and beam strengths accurate within a factor of 2. To avoid unnecessary complication, insignificant terms will be dropped without comment. Although the source will in general contain a mixture of molecular species, it is necessary to calculate for one component only, since each

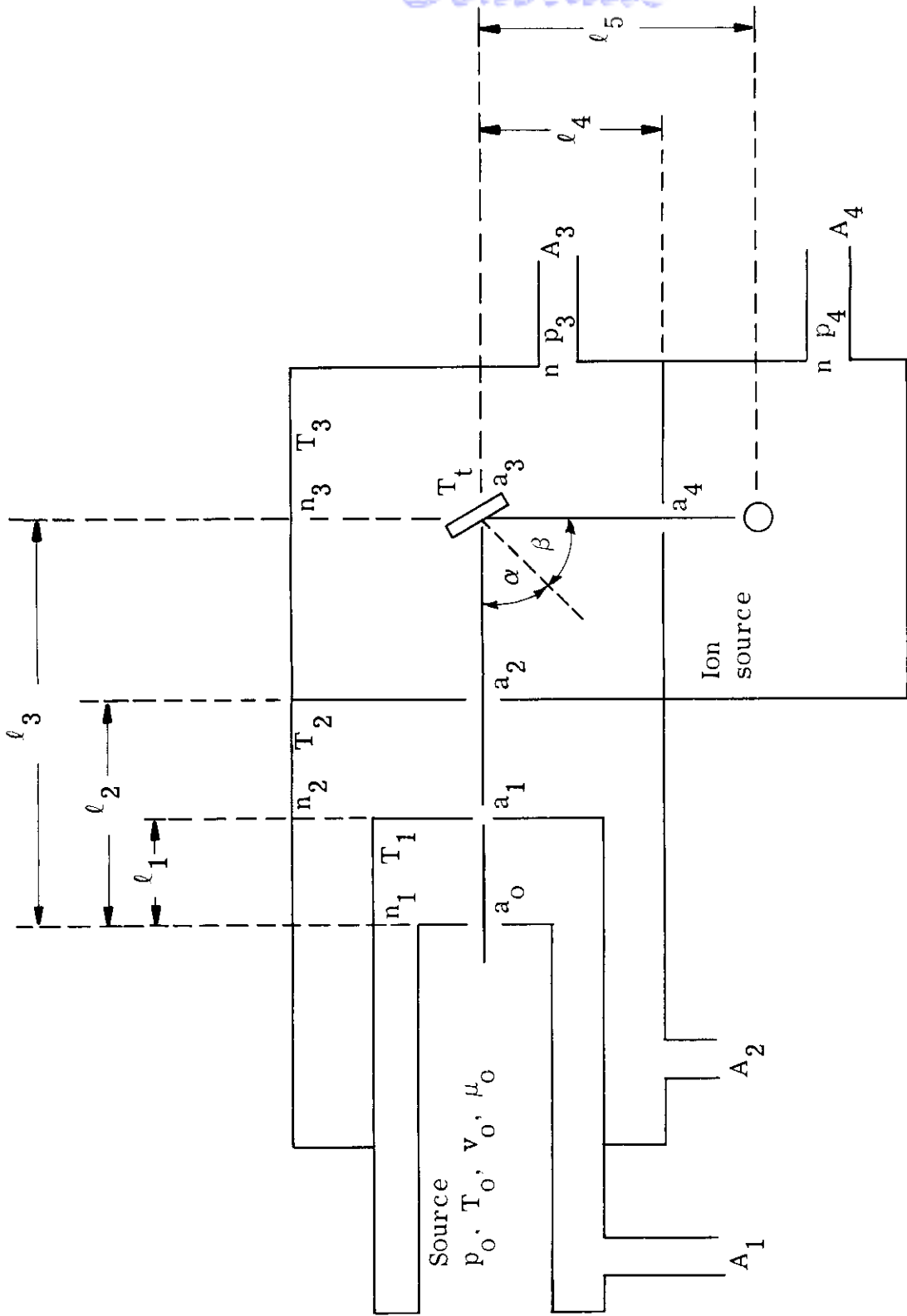


Figure 16. Molecular-Beam Flux Pattern (schematic)

species will effuse independently. If large temperature differences exist within the apparatus--as when high temperature is used to produce dissociation in the source--the molecular speeds will vary from place to place in the apparatus according to the temperature of adjacent walls. We will assume nv , or $n\sqrt{T}$ to be constant throughout each vacuum compartment, since collisions of molecules are primarily with walls rather than with other molecules.

Along with development of formulas, computed numerical values will be indicated for various terms. These computations are based on the actual dimensions of the apparatus, as given in Table 4. All pumping apertures are somewhat arbitrarily taken as 1 cm^2 . In addition, the following values are used

$$\begin{aligned}
 p_0 &= 1 \text{ mm Hg} \\
 T_0, \dots, T_5 &= T_t = 300^\circ\text{K} \\
 M &= 1 \text{ (atomic hydrogen)} \\
 n_0 &= 3.2 \times 10^{16} \text{ cm}^{-3}
 \end{aligned}$$

Values pertaining to other conditions can be readily found from those given by inspection of the formulas.

Table 4. Dimensions of Molecular Beam Apparatus

$a_0 = 10^{-2} \text{ cm}^2$	
$a_1 = 3.9 \times 10^{-2} \text{ cm}^2$	$l_1 = 1.35 \text{ cm}$
$a_2 = 3.2 \times 10^{-2} \text{ cm}^2$	$l_2 = 2.69 \text{ cm}$
$a_3 = 7.7 \times 10^{-2} \text{ cm}^2$	$l_3 = 3.55 \text{ cm}$
$\cos \alpha = \cos \beta = 0.59$	
$a_4 = 10.3 \times 10^{-2} \text{ cm}^2$	$l_4 = 1.55 \text{ cm}$
	$l_5 = 3.55 \text{ cm}$
	$l_e = 1.2 \text{ cm}$

The beam fluxes through apertures a_0 , a_1 and a_2 are given by

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$$Q_o = \frac{1}{4} n_o v_o a_o \quad (13)$$

$$Q_1 = Q_o \frac{a_1}{\pi \ell_1^2} = \frac{n_o v_o}{4\pi} \frac{a_o a_1}{\ell_1^2} \quad (14)$$

$$Q_2 = Q_o \frac{a_2}{\pi \ell_2^2} = \frac{n_o v_o}{4\pi} \frac{a_o a_2}{\ell_2^2} \quad (15)$$

(a_2 will always be within the core of the beam formed by a_o and a_1).

The ambient pressure in space 1 can be found by equating Q_o to the pump flux through A_1 ; i. e.,

$$\frac{1}{4} n_o v_o a_o = \frac{1}{4} n_1 v_1 A_1 \quad (16)$$

from which

$$\frac{n_1}{n_o} = \frac{n_o v_o}{v_1} \frac{a_o}{A_1} = \sqrt{\frac{T_o}{T_1}} \frac{a_1}{A_1} \quad (17)$$

The total flux through a_1 into space 2 is Q_1 plus that caused by effusion of the ambient gas from space 1. When this is equated to the pump flux through A_2 one obtains

$$\begin{aligned} \frac{n_2}{n_o} &= \sqrt{\frac{T_o}{T_1}} \frac{a_o a_1}{\pi \ell_1^2 A_2} \left(1 + \frac{\pi \ell_1^2}{A_1} \right) \\ &= 6.8 \times 10^{-5} \times (1 + 5.7) = 4.5 \times 10^{-4} \end{aligned} \quad (18)$$

Making a similar calculation for space 3 one obtains

$$\frac{n_3}{n_o} = \left(\sqrt{\frac{T_o}{T_3}} \frac{a_o a_2}{\pi \ell_2^2 A_3} \right) [18] \quad (19)$$

where

$$[18] = 1 + \frac{a_1}{A_2} \frac{\ell_2^2}{\ell_1^2} + \frac{a_1 \pi \ell_2^2}{A_1 A_2}$$

then

$$\frac{n_3}{n_o} = (1.42 \times 10^{-5}) [1 + 0.15 + 0.88] = 2.9 \times 10^{-5}$$

The term in the parentheses is the particle density that would exist in space 3 if Q_2 were the only entering flux. The excess of the square bracket [18] over unity indicates the relative contribution of stray molecules that occur because of the finite speed of the pumps attached to spaces 1 and 2. One goal of the design is to make this excess small.

At the surface of the target the normal component of the flux of particles carried by the beam is given by

$$I_t = \frac{n_o v_o a_o \cos \alpha}{4\pi l_3^2 3.0 \times 10^{-17}} \tag{20}$$

That caused by ambient pressure in the target chamber is given by

$$I'_t = \frac{n_3 v_3}{4} \tag{21}$$

The ratio I'_t/I_t can be expressed

$$\begin{aligned} \frac{I'_t}{I_t} &= \frac{a_2 l_3^2 [18]}{A_3 l_2^2 \cos \alpha} \\ &= 0.19 \end{aligned} \tag{22}$$

In order to calculate the response of the mass spectrometer to the beam reflected from the target, it will be necessary to first calculate the density of molecules in the ion source at l_5 . We assume that the beam molecules incident on the target are totally reflected with a cosine distribution and that they travel with a speed that corresponds to a temperature T_t . The density n_{t5} of reflected molecules traveling in a beam within the ion source is given by

$$\begin{aligned} \frac{n_{t5}}{n_o} &= \sqrt{\frac{T_o}{T_t}} \frac{a_o a_3 \cos \alpha \cos \beta}{4\pi^2 l_3^2 l_5^2} \\ &= 4.3 \times 10^{-8} \end{aligned} \tag{23}$$

There will also exist in the ion source a background concentration n_4 because of both the beam and the ambient pressure in compartment 4. The ratio of this concentration to that in the beam is given by

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$$\frac{n_4}{n_{5t}} = 4 \sqrt{\frac{T_t}{T_4}} \frac{a_4}{A_4} \frac{\ell_5^2}{\ell_4^2} \left(1 + \frac{\pi \ell_3^2 \ell_4^2 a_2}{\ell_2^2 A_3 a_3 \cos \alpha \cos \beta} [18] \right)$$

$$= 2.16 \times (1 + 32) = 71 \quad . \quad (24)$$

The value 71 for the background-to-signal ratio is on its face alarming, but for a number of reasons does not represent the value to be expected. This ratio can be lowered, however, by increasing the effective pumping apertures A_3 and A_4 above the assumed values of 1 cm^2 , which corresponds to a pumping speed of 12 l/sec. for air. A_3 , connected with the source-pot of the mass spectrometer, will be limited by the pump lead, which is a length of $1-7/8''$ (4.75 cm) tubing. For a circular cylinder of diameter D and length L the effective pumping aperture is given approximately by

$$A = \frac{\pi}{4} D^2 / (1 + \frac{4}{3} L/D) \quad .$$

By using an ion or getter pump and avoiding cold traps it will be easy to make A_1 as large as 2 or 3 cm^2 . Similar considerations hold for A_4 , except that it can be increased to 3 cm^2 easily. Moreover, by adapting the flanged access ports, which are three inches and six inches in diameter, as pump leads, effective areas up to 100 cm^2 can be arranged with only moderate inconvenience. Thus, if necessary, the background/signal ratio as computed from Eq. (24) can be reduced to about unity. Above all, it should be kept in mind that the above numbers apply strictly only to stable species; for unstable species, the metal walls of the apparatus will tend to catalyze recombination, and thus act as pumping apertures, so that background/signal ratios will be much smaller than those indicated above.

The background will present less of a problem than may appear from the discussion above, inasmuch as it will be very much smaller than that calculated when one is dealing with free atoms or radicals, which will combine on walls of the apparatus and thus have very great effective pumping apertures.

Estimates have been made also for the direct beam shown in Figure 13. With other conditions equal, the signal will be about a hundred times greater than for the reflected molecules, and the background will be smaller than the signal.

From the molecules carried through the ion source, an ion current i_I is produced

$$i_I = i_e \ell_e n_{5t} \sigma \quad (25)$$

where i_e is the electron current that intersects the molecular beam, ℓ_e is the length of its

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path through the beam, and σ is the ionization cross section. It is estimated that about 2% of the ion current formed is collected and registered at the detector of the mass spectrometer.

A conservative value for i_e is 2×10^{-5} amperes. Ionization cross sections for simple ionization usually have maximum values of about 10^{-16} cm^2 at electron energies several times the ionization energy. When the appearance potential method is used, the cross sections will be much smaller; it seems conservative to take 10^{-18} cm^2 in our calculations. Assuming $\sigma = 10^{-18}$ cm^2 and a collection efficiency of 2%, we derive from Eq. 25 that

$$i_i \text{ (collected)} = 5 \times 10^{-25} n_{5t} \text{ amp cm}^2$$

and for the number of ions collected per sec,

$$\frac{i_{IC}}{e} = 3 \times 10^{-6} n_{5t} \text{ cm}^2 .$$

From our standard assumed conditions and Eq. 23, one obtains

$$\begin{aligned} \frac{i_{IC}}{e} &= 4.1 \times 10^3 \text{ ions/sec collected, for } a_2 p_0 \\ &= 10^{-2} \text{ cm}^2 \text{ mm/Hg at } 300^\circ\text{K} . \end{aligned}$$

We now examine what conditions in the molecular beam source are practicable. The width w_0 of the source slit should not be greater than the mean free path of the gas molecules within the source. From the relations

$$w_0 = \lambda_0 = \frac{5 \times 10^{-3}}{p_0} \text{ cm/mm Hg}$$

one obtains $w_0 p_0 = 5 \times 10^{-3}$ cm/mm Hg. The maximum height of the slit that can be accommodated is about 2.5×10^{-1} cm, so the maximum area a_0 compatible with the condition on λ_0 is $a_0 p_0 = w_0 h_0 p_0 = 1.2 \times 10^{-3}$ $\text{cm}^2/\text{mm Hg}$, which is about 1/8 of that under our standard conditions. Because the molecular species one is interested in may make up only a fraction, say 1/3 of the total pressure in the source, one should assume a value of $a_0 p_0$ perhaps 1/25 of the standard condition. Then one obtains, finally

$$\frac{i_{IC}}{e} = 160 \text{ ions collected/sec}$$

With the multiplier-detector it will be possible to count individual ions, so the accuracy of the results will involve counting-statistics. The counting rates are large enough, however, so that it will be possible to secure accurate data with observation periods of

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a few minutes. Thus long-term stability sources will not be crucial.

The above calculations are conservative and give every reason to anticipate that the apparatus will be fully adequate for the experiments contemplated.

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