FINAL REPORT

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A MULTIPOINT FIELD IONIZATION SOURCE

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From

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ABSTRACT

An investigation has been made of the use of field ionization and field emitted electrons as ion sources for use with a quadrupole mass spectrometer.

It has been possible to replace the normal filament type electron source with a field emission electron source in the form of a 100-point comb. Results with this source have been very satisfactory. The electrons generate a normal bombardment ion spectrum.

Operation of this comb as a direct field ion source has not been too successful. It appears that a field ion source cannot be used for direct injection into a quadrupole type mass spectrometer. The requirements for low energy ions and a straight-through geometry are too severe.

In the next three months we hope to install an energy analyzer to swing the ion beam about 100°. This will give us better control and focusing of the ions as they enter the spectrometer and should aid in removal of the high energy electrons and neutrals which introduce high noise levels.

I. INTRODUCTION

Investigation of the atmosphere of the planets is an important mission of the National Aeronautics and Space Administration in the coming decade. The primary instrument for this type of research is the mass spectrometer. Devices of this type have been studied and used for many years, and some flight programs have been successful, but the ion source for the mass spectrometer remains a major problem in every experiment.

The commonly used ion source is of the electron bombardment type where the source of electrons is a relatively fragile filament. The heating current needed for this filament imposes a heavy burden on system power supplies.

Alternatives to the hot-filament electron bombardment ion source include the well-known spark source of Dempster, the gas-discharge tube used by Aston and in the Mattauch-Herzog mass spectrograph, and the inverted magnetron of Herzog and Poschrieder. However, all these approaches involve compromises in performance or added complexity. Recently Muller (1) and others (2, 3, 4) have reported on the use of field ionization sources for mass spectrometry. These devices have proved to be most useful for this purpose and are potentially equal or superior to hot-filament electron bombardment sources in both simplicity and performance. These sources require only very low currents and they are orders of magnitude more resistant to impact and vibration than conventional hot-filament sources.

This report summarizes work done at the University of Arizona Field Emission and Space Systems Laboratory on developing field-ionization sources for mass spectrometry. The work accomplished may be divided into two categories: (a) that concerned with the production of ions through direct molecule-electric field interaction and (b) that involving ion production by molecule bombardment with field emitted electrons.

Both approaches are applicable to systems requiring ruggedness, simplicity, and low power comsumption, and a change from one type of operation to the other requires only a change in voltages--no change in structure or physical arrangement is involved.

II. THEORY OF FIELD PHENOMINA IN THE VICINITY OF METAL SURFACES

Field Ion Emission

If a free atom is considered as a potential trough in which the valence electron is at a ground state V_I, then the potential walls can be altered by the application of an external electrical potential U (Fig. 1). Quantum mechanics predicts a probability of ionization by the tunneling of a valence electron into the metal through the potential barrier distorted by the external field.

In circumstances where the external field is produced by a metal tip of small radius acting as an anode, there are further interactions (Fig. 2) (4). Several image potentials are produced (the most important of which is that of the valence electron) which considerably increase the penetration probability (5). The Fermi level in the metal must be considered in the experiment (shaded area in Fig. 2), because tunneling can occur only if the ground state of the valence electron is raised, by the external field, to at least the Fermi-level (μ) of the metal. This implies a certain minimum distance of several Å between the atom and the metal surface approximated by:

$$d_{min} \simeq \frac{V_I - \phi}{F}$$

where V_I = ionization potential
ϕ = work function
F = external field strength

The emitted ion current is the product of the penetration probability and the supply function. The penetration probability is a function of the applied electric field, the molecule involved and its distance from the metal. Ultimately a zone-of-ionization is defined as the volume in which the ionization probability is 100%. The supply function is then the rate of atom or molecules entering the zone of ionization. The expressions for current derived from these considerations are complex (especially for molecules) and not completely verified (6). However, the range of current has been calculated and experimentally shown to be on the order of 10^{-5} amp/torr (2).

The energy distribution of field emitted ions has been shown to be quite narrow (see Fig. 3) (7). Thus a field-ion source may approach more closely, than a conventional bombardment source, the ideal of a mono-energic ion supply for mass spectrometry.

In considering the application of field ionization to mass spectrometry, the emission angle is an important factor. In a single tip source, the total ion current is realized over a solid angle of approximately 120°; the aperture angle of an ion beam entering a mass spectrometer should be on the order of 1°. Work done on focusing ions emitted from a single tip into a mass spectrometer has yielded transmissions on the order of 1/200 (2). Thus the effective ion current supplied by a single point source is about $5 \cdot 10^{-8}$ amp/torr. This provided the motivation for investigating multi-point field-ion sources to achieve greater effective currents for mass spectrometry work.

Field Electron Emission

If the vacuum space immediately adjacent to a metal surface is subjected to a field on the order of 0.3 to 0.6 V/Å, interaction with the metal barrier potential yields a resultant composite potential of the form shown in Fig. 4. Electrons in the conduction band with energies near the Fermi level can quantum mechanically tunnel through this deformed barrier and thus escape from the metal. This may be contrasted with thermionic or photoemission where electrons must be excited to energies above 2 ev in order to surmount the metal barrier potential.

The magnitude of the field-emitted electron current is predicted by the Fowler-Nordheim equation (6),

$$I = (6.2)\ 10^{6}\ [(\mu/\phi)^{1/2}/\mu + \phi]\ F^{2}\ \exp\ [-6.8 \cdot 10^{7}\ \phi^{3/2}/F]$$

Here F is the field strength in V/cm, μ= Fermi level, and φ = work function. The temperature dependence is small at normal temperatures $I_{300^{\circ}K} = 1.03 I_{0^{\circ}K}$ and can be neglected in first-order calculations.

Typical current values are 10^2 to 10^4 amp/cm^2, and net currents are generally in the fractional microamp range, though long-term currents as high as 1 ma from a single tungsten tip have been reported (8).

Thus it appears possible to use field emitted electrons (preferably from an array of tips for higher currents) as a substitute for thermionic generators in a bombardment-type ion source.

III. EXPERIMENTAL WORK DONE ON A DIRECT FIELD ION SOURCE

As the first field ion source, a 50-tip array ("brush") was formed from .010" diameter tungsten wire sharpened by electrolytic etching in KNO_3 solution. This brush was mounted in the configuration shown in Fig. 5. The screen in Fig. 5 was a stainless steel mesh of .025 inch diameter wires spaced at .125 inch intervals.

Initial testing in air at a pressure of $8 \cdot 10^{-4}$ torr with the brush at +16 kv and the screen grounded through a nanoammeter yielded a screen current of 10^{-9} amps and a maximum collector current of $6 \cdot 10^{-10}$ amps. The latter current that passed the screen and migrated down the drift tube was of interest, since that is the current available for focusing into a mass spectrometer.

Continued operation showed a slow decay of current with time which indicated possible this effect, a 50-tip platinum brush was fabricated. This new brush was quite stable and yielded a maximum collector current of $3 \cdot 10^{-10}$ amps at $8 \cdot 10^{-4}$ torr with 16 kv biasing.

Along with the new brush, the layout of Fig. 5 was modified in anticipation of use directly with a mass spectrometer (Fig. 6). As seen in Fig. 6 a number of focusing rings were provided along the drift tube. Since the mass spectrometer entrance is at ground potential, the ion energy on entering is determined explicitly by the potential of the emitting tips. Thus the brush must be held at a relatively low potential (<100 v) and the ionizing field must be provided by the screen. The new configuration provided insulation for screen biasing up to 25 kv.

Using -25 kv on the screen, ion currents of 1×10^{-9} amps at 8×10^{-4} torr were measured. Ion energy investigations took into account the peculiarities of our particular mass spectrometer, an Ultek quadrupole unit. The maximum allowable ion energy is 30 ev and care must be taken to avoid secondary electrons and high energy neutrals because of the quadrupole's line-of-sight construction and use of a multiplier as a detector.

Figure 7 shows the results of an ion energy and secondary electron investigation with the brush held at +30 volts and the collector voltage cycled ±150 volts. The data of Fig. 7 was subjected to the following interpretation. The field emitted ions were at a maximum energy at the screen (25 kev). At this energy, any collision with the screen material will produce multiple secondary electrons. Since the screen is a potential hill with respect to electrons, any secondary electrons on the collector side of the screen will fall toward the collector through a net potential of 25 kv. Thus an essentially constant electron current can be expected at the collector over the relatively small variations of the collector voltage (±150 volts). This means that the true ion current is the sum of the positive current and the electron current ($\cong 5 \times 10^{-9}$ amp at $V_{collector} \overline{<} 0$).

The fact of the ion current dropping to zero at $V_g = +50$ v indicates that most of the ions were in the proper energy range (~ 30 ev).

The actual secondary electron production was estimated to be somewhat greater than the measured electron current due to some reflection from the collector plate with the high energy impact.

Another reason for considering secondary electrons was the possibility of producing ions by bombardment. If ions were produced by this secondary electron bombardment on the collector side of a small positive gradient generated by element 8, they would be detected; if produced anywhere else they would fall back to the negative screen. The gradient generated by element 8 was less than or equal to +50 volts. Thus any ions produced by bombardment would have energies $\leq$ 50 ev, which was exactly the range of energies detected.

To further investigate these complications the system was modified to direct ions into the Ultek mass spectrometer (see Fig. 8). The same geometry was used, but the focusing element array was changed and an aperture placed at the entrance into the M.S. The other major change was the installation of a 2500-tip tungsten brush (from the Field Emission Corp., McMinnville, Oregon) for greater emission currents. This necessitated the use of dry gases for all operations in the field ion or field emission mode.

In the first tests, the configuration of Fig. 8 was capable of supplying ion current that the Ultek Quadrupole could differentiate into spectra. Spectrometer primary currents were 10^{-14} to 10^{-15} amps meaning that the transmission ratio was on the order of 10^{-4}. A typical spectrum (of N_2 and A introduced into the system) is shown in Fig. 9 with the corresponding focusing voltage indicated.

In all cases where spectra were obtained, element 4 was biased positive with respect to the brush. In this situation primary ions could not surmount the potential barrier of element 4 and it was finally concluded that the majority of the ions observed in the mass spectra were generated by secondary electron bombardment occurring between elements 4 and 6. That most of the observed ions were produced in this region was inferred by the absence of sufficient ion current for a spectra when $V_4 < V_6$; if element 4 were not positive in respect to element 6, then any secondary bombardment ions would fall back to the screen.

We are thus confronted with the following problem: If the emission field were produced by the brush being held at a high positive potential, then axial ion energies were much too great for the spectrometer; but if the screen were operated at a high negative potential, high energy secondary electrons were produced which created unwanted complications.

The first approach used to resolve this was to place the brush-screen axis at an angle of 90° to the mass spectrometer axis (Fig. 10). This was an attempt to "swing" the ion beam from the x-direction to the y-direction, the energy in the y-direction (along the axis of the spectrometer) being determined by the potential of element 3.

Operationally, spectra as in Fig. 11 were produced by the system. The maximum total ion primary current was approximately 10^{-15} amps, the same as in the previous system. However, the absence of any noise caused by secondary electrons entering the quadrupole resulted in much more sensitive and useful spectra than those obtained from the straight-line configuration.

Since element 4 was operated near ground (higher potentials upset the y-direction focusing), it was obvious that the primary x-direction ions were not being stopped and then re-accelerated along the y-direction. In fact, with element 4 removed from the system, essentially identical spectra (in shape and resolution) except smaller in absoluted magnitude by a factor of 10 were observed.

Two possible mechanisms for producing secondary ions, with negligible velocity in the x-direction, were considered. The first process was that of charge exchange. An ion moving in a partial vacuum has a finite probability of reacting at a distance (without the necessity of a collision) with the valence electrons of a neutral molecule. The ion becomes neutralized and the molecule is charged, but they both retain their original kinetic energies. The ratio between the current of charge exchange-produced ions and the primary ion current can be approximated by an equation given by J. B. Homer, et al (9):

$$\frac{I_s}{I_p} = FQ_RPd$$

where I_s = secondary ion current
I_p = primary ion current
F = constant
P = pressure
d = reaction path length
Q_R = reaction cross-section area

For the high velocity range of primary ions is our system, Q_R was an inverse function of ion velocity.

The second possible process was that of ion bombardment reactions. Even without element 4 in place, there were a number of metal surfaces subject to bombardment by 25 kev field ions (due to the ∿120° emission angle). Investigations by Fogel, et al (10), have determined the nature of surface emissions from metal subjected to bombardment by light ions with energies in the 20 kev range. They showed that both positive and negative ions were emitted, each with a current of several percent of the primary ion current, as well as a secondary electron current of several times the primary ion current. Further, the ions emitted were shown to be determined primarily by the gases adsorbed on the target metal surface. There was also a primary ion reflection of several percent, but in our situation this might be negligible due to a high degree of scattering.

Further investigation of the spectra obtained from the set-up of Fig. 10 indicated the latter mechanism as dominant: It was found that introducing gases into the system to high partial pressures (up to 10^{-5} torr) did not discernably affect the spectrum of Fig. 11. Since the spectra were not pressure independent the charge exchange process was discounted and it was assumed that detected ions were largely from the bombardment of the target metal (element 4) surface. The pressure independence to CO_2 and N_2 assumed these ions not to be the most active in exciting target emission during bombardment. This assumption is reasonable since Fogel, et al, found a definite variation of bombardment effects with different ion species used for bombardment.

Further evidence for the target bombardment mechanism was found by moderately baking the system (200^o C for 1.5 hours). This reduced the magnitude of the spectra by a factor of ∿50 while the primary brush current remained unchanged. Exposure to air at atmospheric pressure for one hour re-established the original spectra magnitude. This strongly indicated target surface-adsorbed gases as the source of the analyzed ion current.

This metal surface bombardment effect leads to the speculation on the possibility of exposing clean metal surfaces to an atmosphere of interest and subject them to analysis at a later time by high energy bombardment with direct field produced ions. The major problems in this would be differential adsorption (and desorption as ions) and ion dissociation (as indicated by the numerous fragment peaks in the spectrum of Fig. 11).

The difficulty in registering directly-produced field ions in the previous two systems prompted an attempt to build a modified straight-line type source to suppress secondary electron emission. Fig. 12 shows the aperture-focusing system that was built--there were no screens in the beam path to be sources of secondary electrons. The reduced brush structure had approximately ten active emitting tips.

In operation, the primary current supplied was on the order of 10^{-15} amps. Since this current was so small, the electron multiplier was required for detection and no direct current polarity measurements could be taken. However, operating the quadrupole filter gave an indirect indication; no spectrum was differentiated and the current profile vs. mass number was roughly decaying exponential. This pattern was characteristic of high energy electrons entering the quadrupole.

Thus secondary electrons were still being generated along the aperture fringes. From these results we tentatively concluded that a simple line-of-sight field ion source was not practical with a straight-through quadrupole mass spectrometer.

An energy filter or other device that would differentially alter ion and electron paths is considered to be the best approach to this problem. We hope to construct such a device during the summer of 1968. This filter will swing the beam through about a 100° angle. This will facilitate better focusing and rejection of high energy neutrals and electrons.

Experimental Work Done on Field Electron Bombardment Sources

The occurrence of ions from secondary electron bombardment during field ionization experiments provided motivation for developing a bombardment source using directly emitted electrons.

A preliminary experiment was run using the system of Fig. 10. The brush was set at -10kv, the screen at ground, and elements 3, 4, and 6 were adjusted to give the maximum ion current into the spectrometer. The total ion current was 5×10^{-14} amp at 8×10^{-7} torr. A typical spectrum of N_2, CO_2, and Ar is shown in Fig. 13. Fragmentation seen in Fig. 13 was expected because of the 10 kev electrons used in the bombardment. Nonetheless, this simple bombardment system demonstrated that field electron bombardment was possible and that further development might be fruitful.

Thus a more refined system was constructed. It incorporated much of the original Ultek ion source--the filament electron source being replaced with a field electron source but taking advantage of the existing bombardment geometry and ion optical arrangement. The field electron source was required to produce a ribbon-shaped electron beam in order to be compatible with the rest of the bombardment system. Thus a linear row of approximately 100 tungsten tips was used with slits cut in the draw-out field element and focusing elements (see Fig. 14).

Preliminary operation has been quite promising. Using field emitted electrons adjusted to an energy of 100 ev, very clear spectra were obtained with a maximum primary ion current on the order of 1×10^{-12} amp at 1×10^{-7} torr. A typical spectrum of air has been reproduced in Fig. 15.

Emitted electron currents ranged from .05 to .2 milliamps, with the higher values being in the range of currents used with the hot filament source. Since our ion currents were smaller than those of the conventional source by a factor of 10^2 to 10^3, there is consideraable room for increasing the electron current transmitted into the bombardment chamber by using shorter and more exact draw-out and focusing arrangements.

The primary problem in considering field emitted electrons is that of current stability. E. E. Martin, et al, outlined two mechanisms by which parameters of the Fowler-Nordheim equation are altered, thus altering the current to applied voltage ratio. First, electronegative gases can be adsorbed on the tip surfaces, changing the work function ϕ. This usually results in a reduction of current (to 10-20% of the initial value) in a relatively short period of time (on the order of one hour).

Secondly, there may be a change in geometry of the emitting tips with time due to ion bombardment. This is a longer term phenomenon than the former and is characteristically regenerative (i.e. sharp protrusions are caused by ion bombardment which increase the local field. This further increases electron current; more ions are produced by electron bombardment, and the tips become progressively more radically altered by the increased ion bombarding frequency). Electron current generally rises until a vacuum arc occurs either modifying or destroying the tip.

The period during which electron current remains relatively stable can vary from seconds to thousands of hours, depending on internal gas pressure and composition and the emitted current magnitude. A quantitative relationship has been found experimentally by Martin, et al:

$$\frac{1}{1}\frac{dI}{dt}\left(\frac{1}{\text{hours}}\right) = 10^{11}\, P(I)^{3/4}$$

where P = pressure in torr of helium
I = emitted current

We experienced both forms of current instability in our system. Initial electron current was several hundred micoramps with only 1.5 kv applied for field; within two hours of operation this dropped to less than 30 Ma and this required greater than 3 kv. From this point the second form of instability was observed. Current would periodically rise to 100 to 200 microamps and then fall abruptly to less than 10 microamps. This pattern of tip irregularities forming by ion bombardment and then deforming due to high current densities continued for two to three hours.

Measured pressure during these first hours of operation rose from a quiescent 5×10^{-8} torr to 2 to 3×10^{-7} torr. Since this was due to outgasing of metal surfaces subjected to electron bombardment, it was assumed that local pressure was even higher.

After four to five hours of operation (and 48 hours rest time) the pressure was down to 5×10^{-8} torr and we were able to get very stable electron currents. 50 micoramps ±2% was run for a period of five hours with no measurable increase in current. This performance was reproducable after a period of shut-down.

Thus it was concluded that stable electron currents could be obtained after two to three hours of "break-in" operation to stabilize the work function, eliminate local outgasing, and to provide for some "forming" of the tips.

There was evidence that emission along the row of tips was not homogeneous. It was found that two trials of the same electron current level would yield spectra of differing magnitude. Errors in the focusing geometry (i.e. fringing field effects at slit ends or the tip row not being accurately parallel to the slits) would account for differential transmission of emission along the row into the bombardment chamber.

Thus further work is indicated on focusing geometry to give a transmission into the bombardment chamber both more uniform and of a greater overall magnitude. Also, further investigations are indicated into emission homogeneity (since the more uniform the emission distribution along the tip row, the greater the total current and long term stability) and into very long term stability.

Conclusions

It was found that a field ion source cannot be simply incorporated along the axis of a line-of-sight quadrupole-type mass spectrometer. Because of the requirement for low energy ions, any configuration must unavoidably generate high energy secondary electrons which produce spurrious bombardment ions and/or upset mass spectrometer performance. In a curved path magnetic-type mass spectrometer or in systems requiring energy filtration this problem is reduced due to the alteration of the ion path and with such systems field ionization would appear more easily applicable.

In utilizing field-emitted electrons for producing ions by bombardment we have had very promising results. Clear spectra have been produced with half-height widths as small as 0.35 of a mass number. Using a multiple-tip electron source relatively stable currents of usable magnitudes have been achieved at pressures on the order of 5×10^{-8} torr. Required field voltages have ranged from 1 to 4 kv, small enough to be easily generated and controlled in an interplanetary package. Thus, with some further refinement, field emitted electron bombardment ion sources appear quite applicable for use in interplanetary spectrometry.

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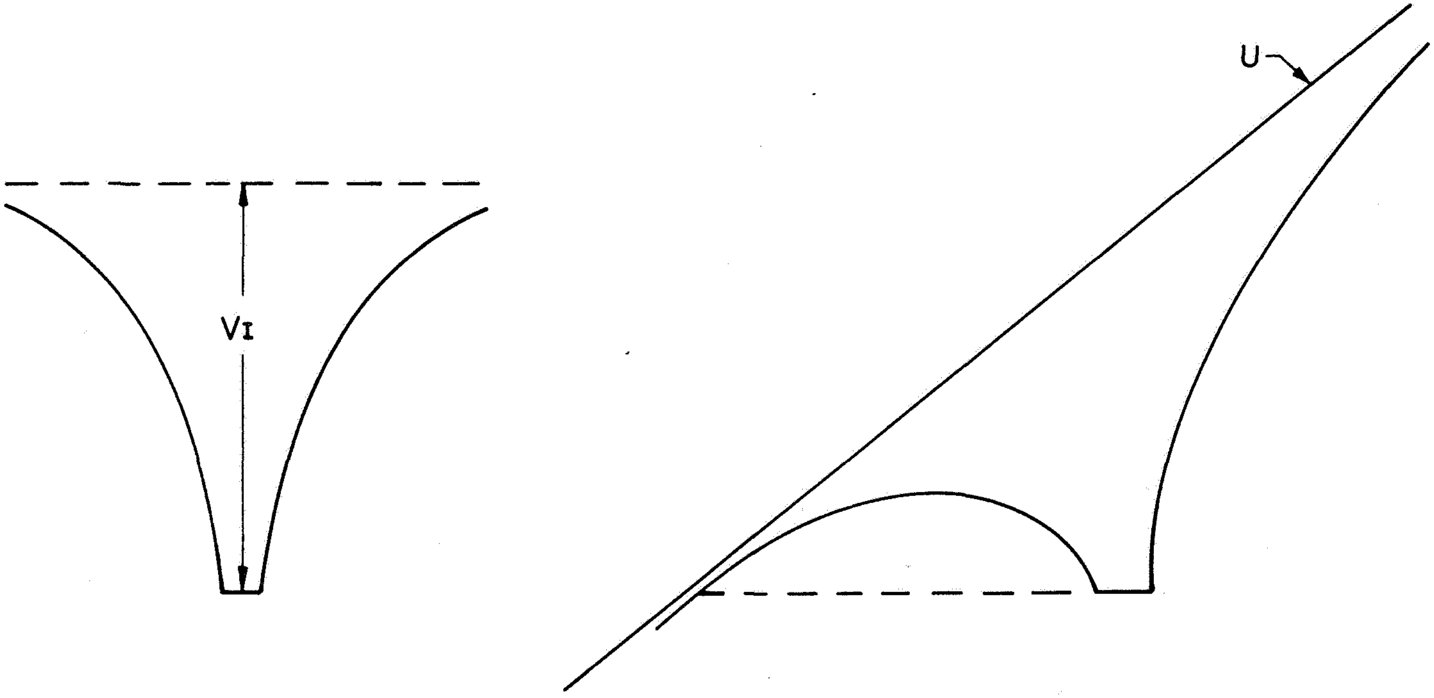
Figures



a.
Free Atom

b.
Atom Under Influence of High External Field

Figure 1. Potential Trough Representation of Atom

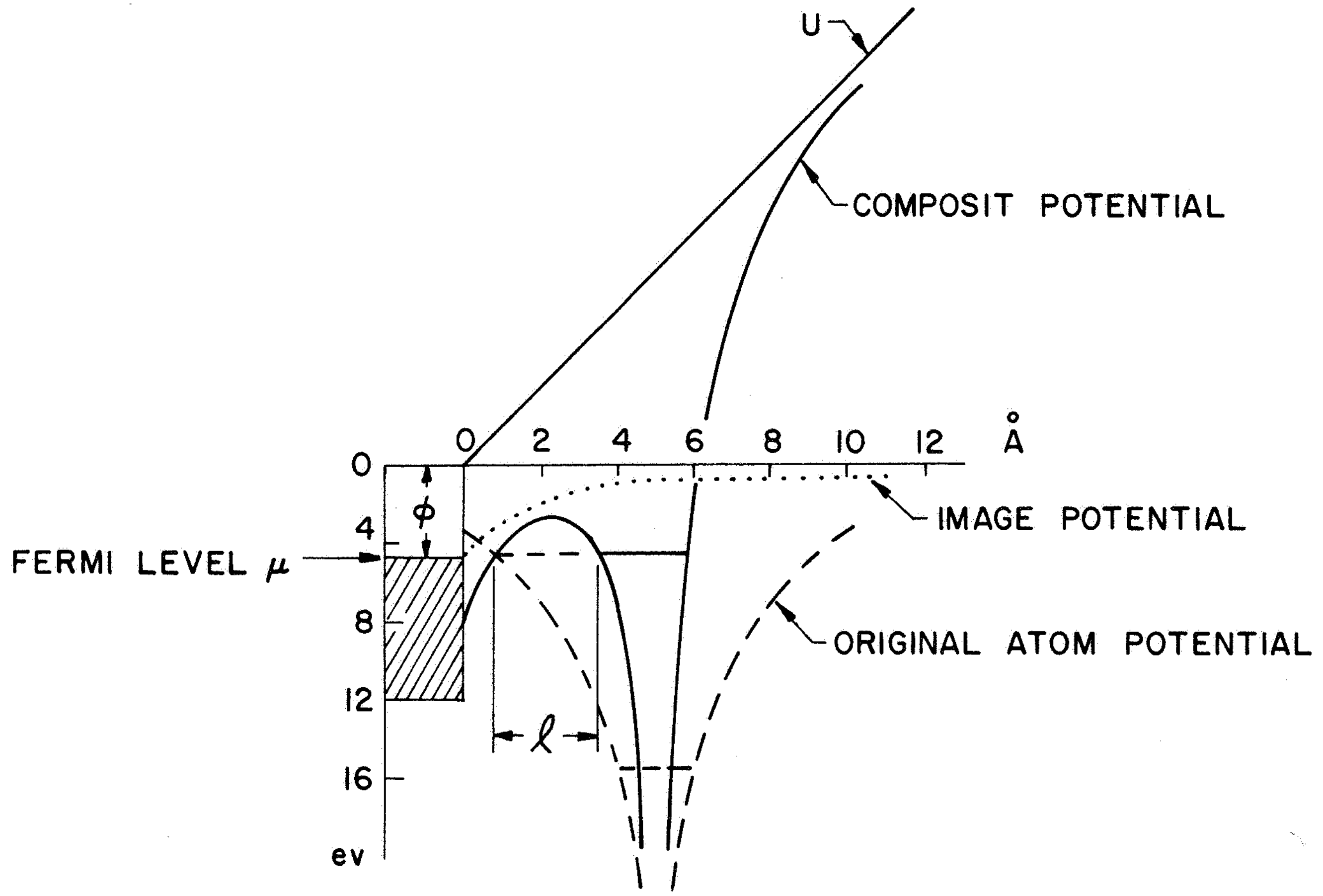


Figure 2. Potential Diagram of a Hydrogen Atom Near a Tungsten Surface

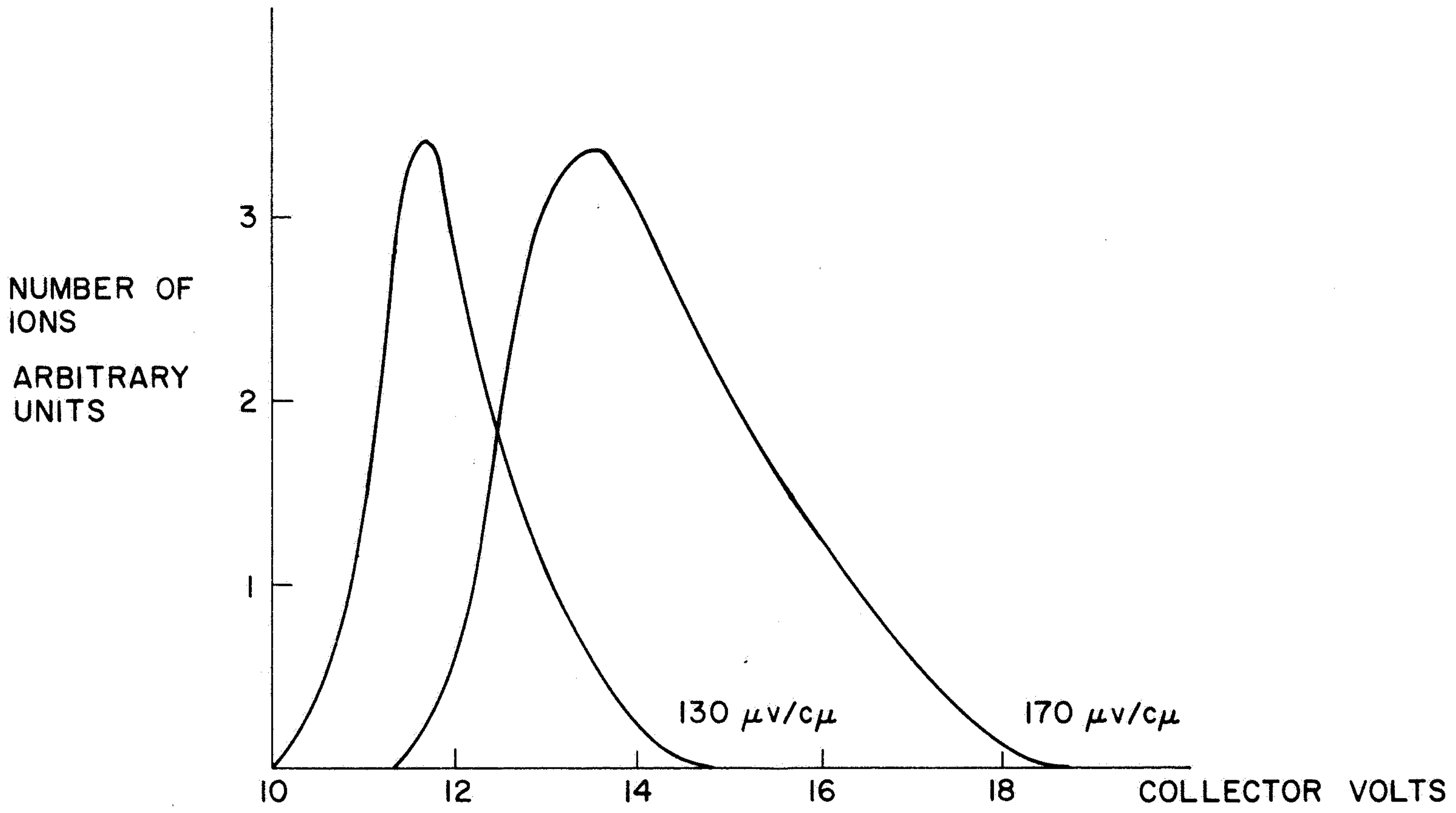


Figure 3. Typical Field Emitted Ion Energy Distribution

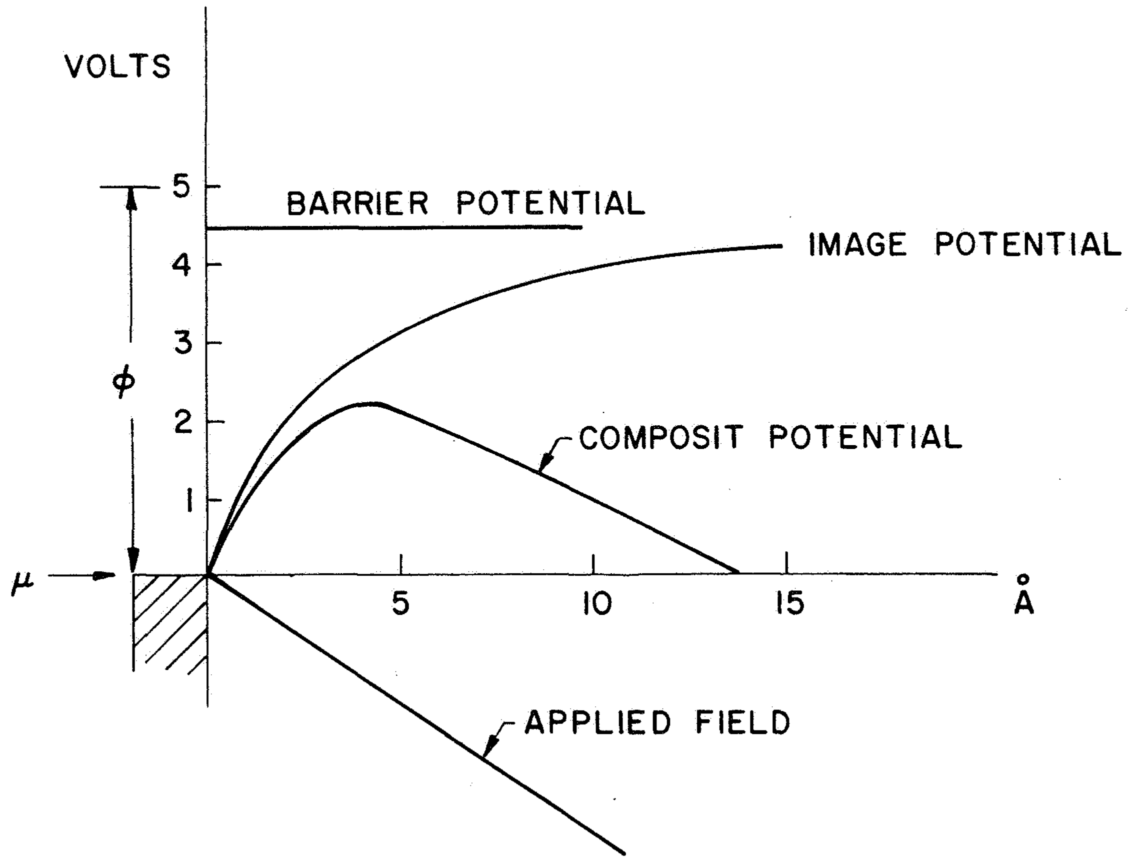


Figure 4. Potential Diagram for Electrons at a Metal Surface in the Presence of an Applied Field

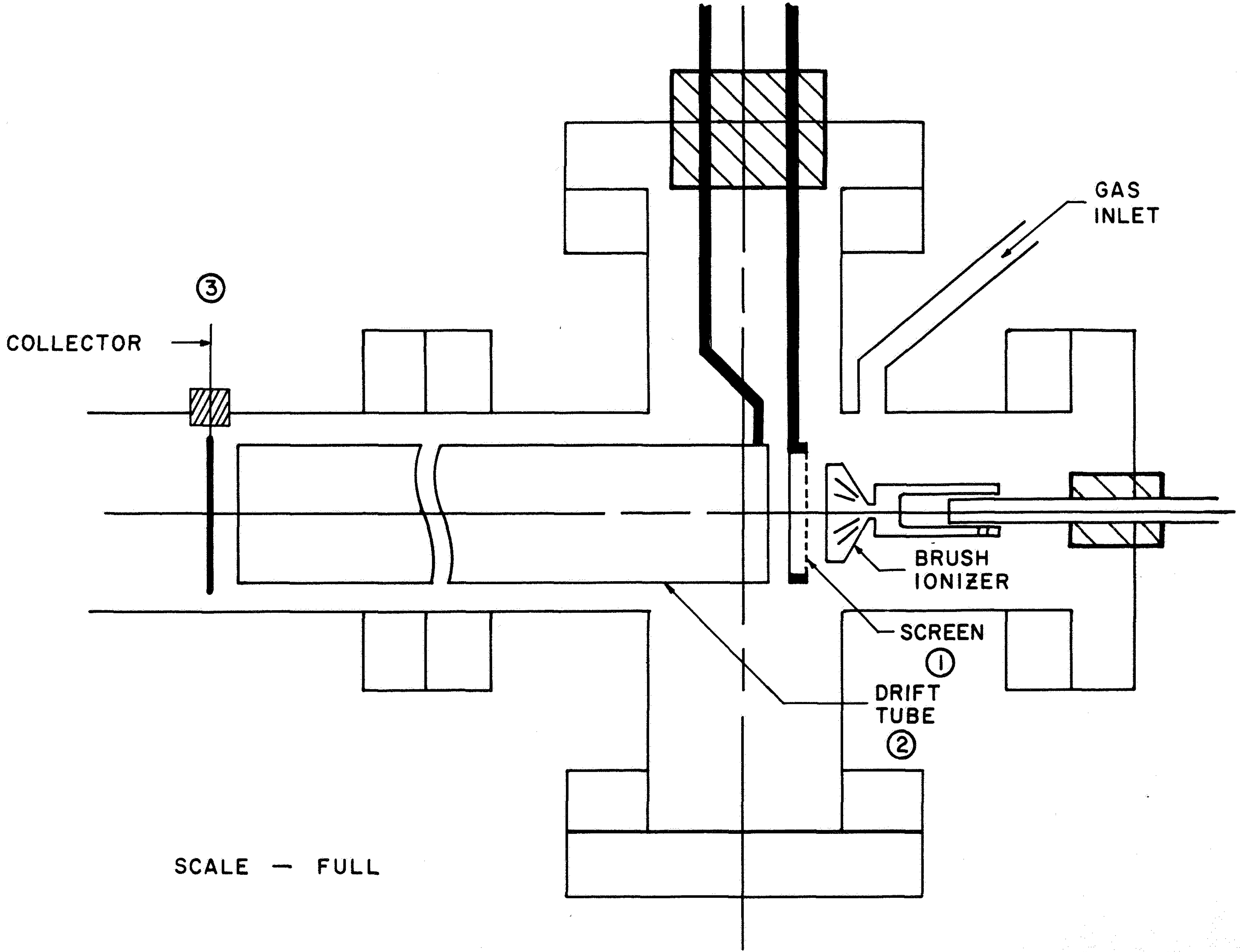
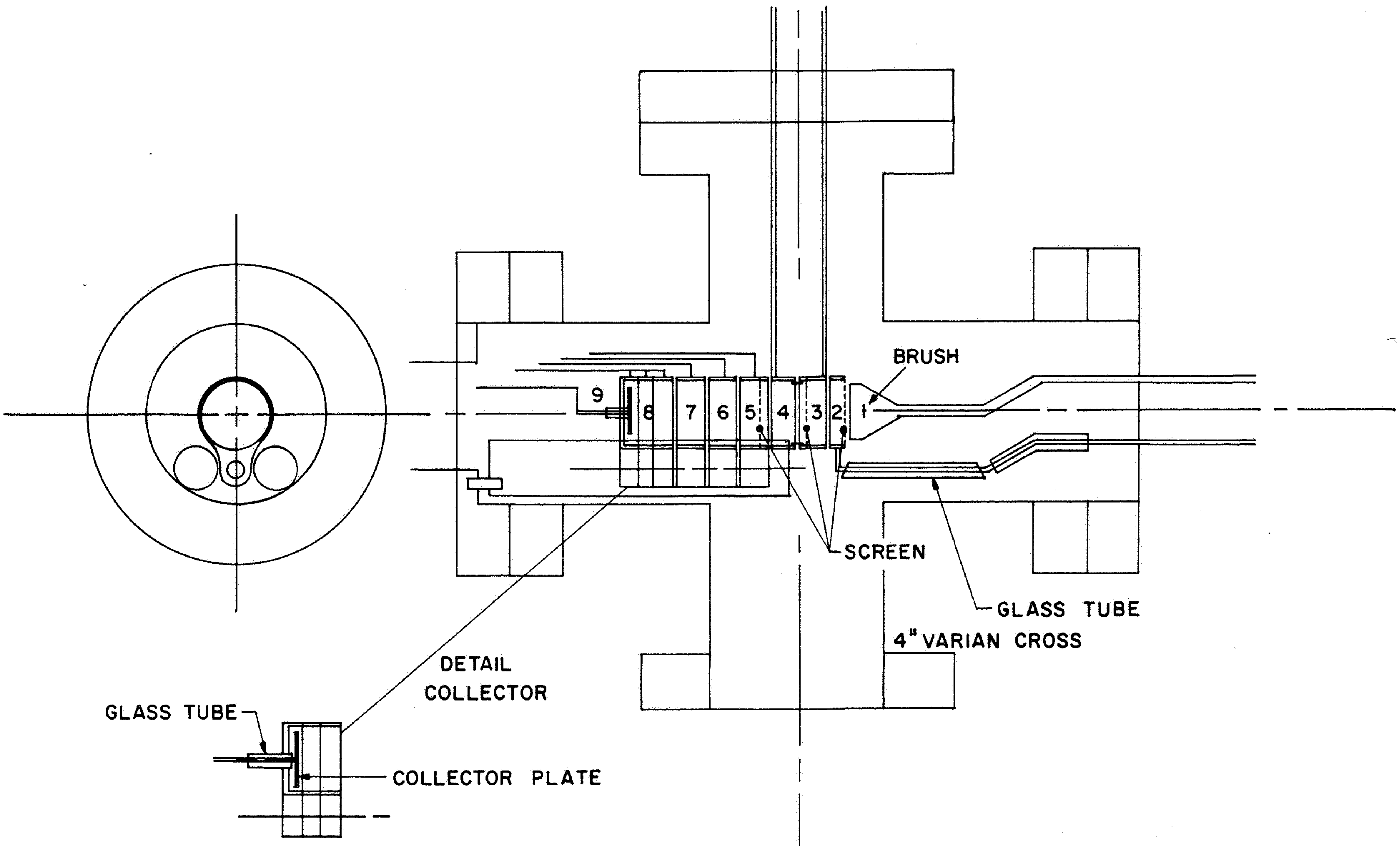


Figure 5. Initial Field Ionization Test System



APPROX. SCALE ONE-HALF

Figure 6. Refined Field Ionization Source

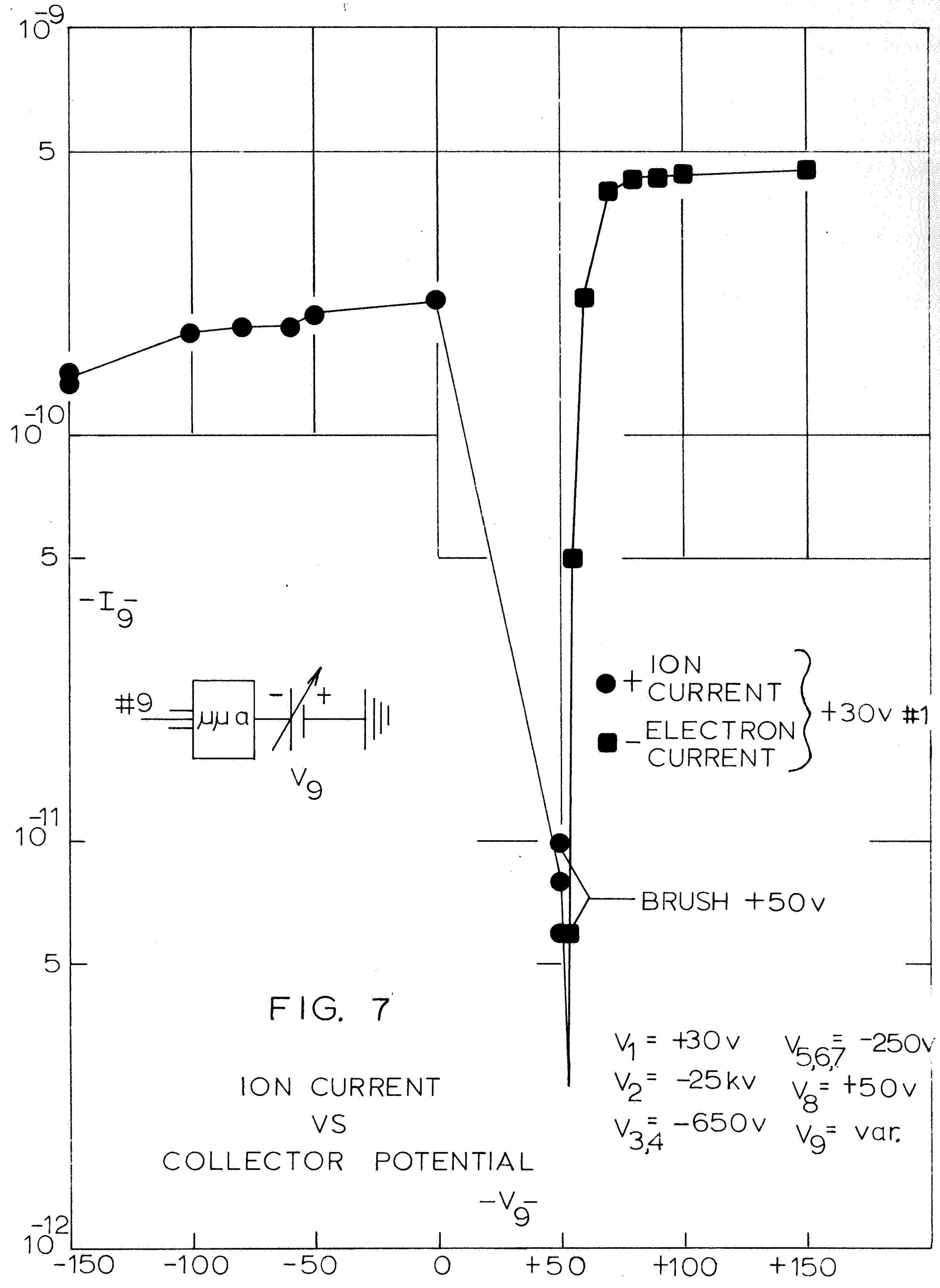


FIG. 7

ION CURRENT
VS
COLLECTOR POTENTIAL

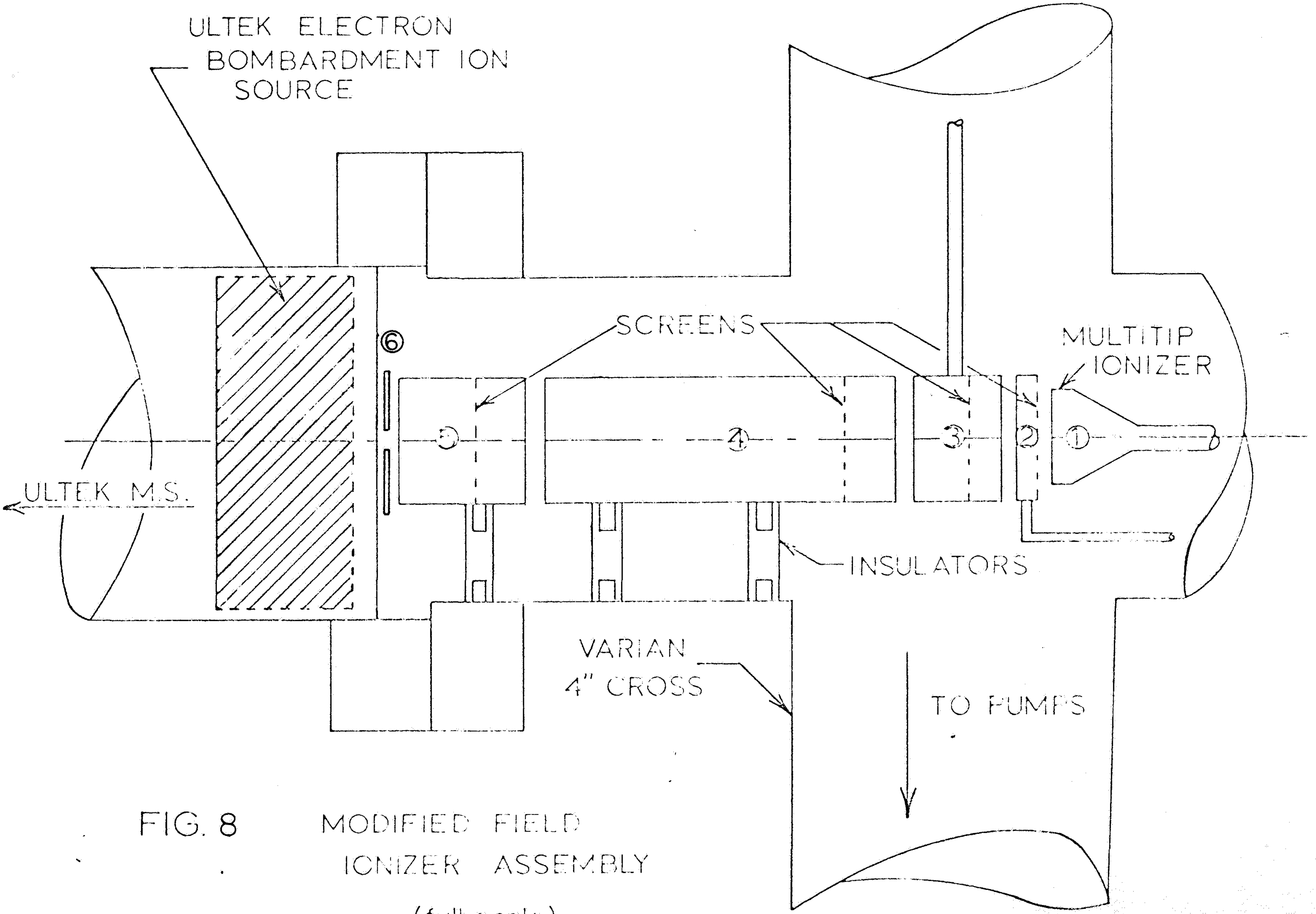


FIG. 8 MODIFIED FIELD IONIZER ASSEMBLY

(full scale)

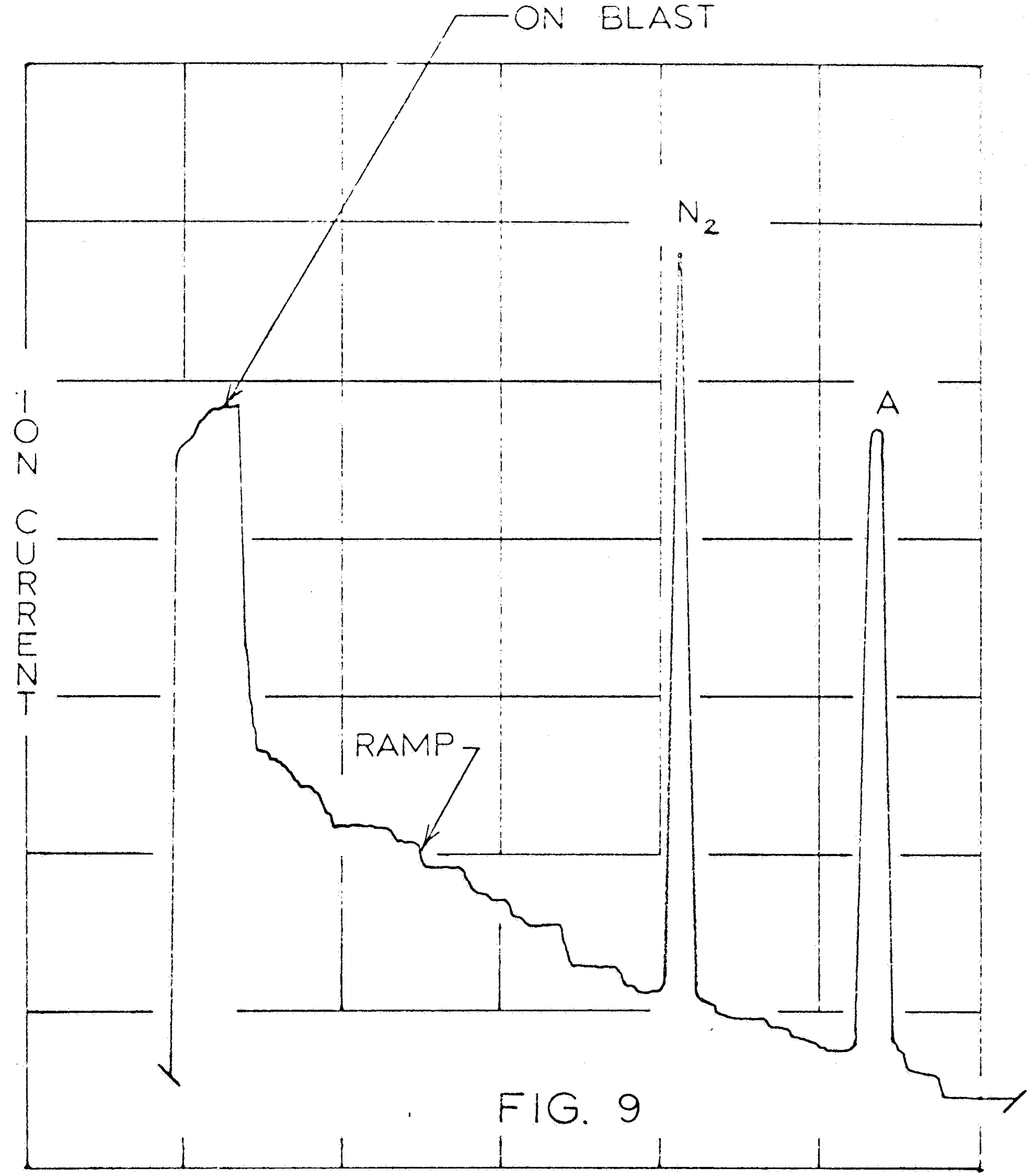


FIG. 9

FIELD ION SPECTRUM OF

N_2 + A

V_1 = +(30-50) V_4 = +(200-600)

V_2 = -25 kv V_5 = +(200-600)

V_3 = -3 kv V_6 = +100

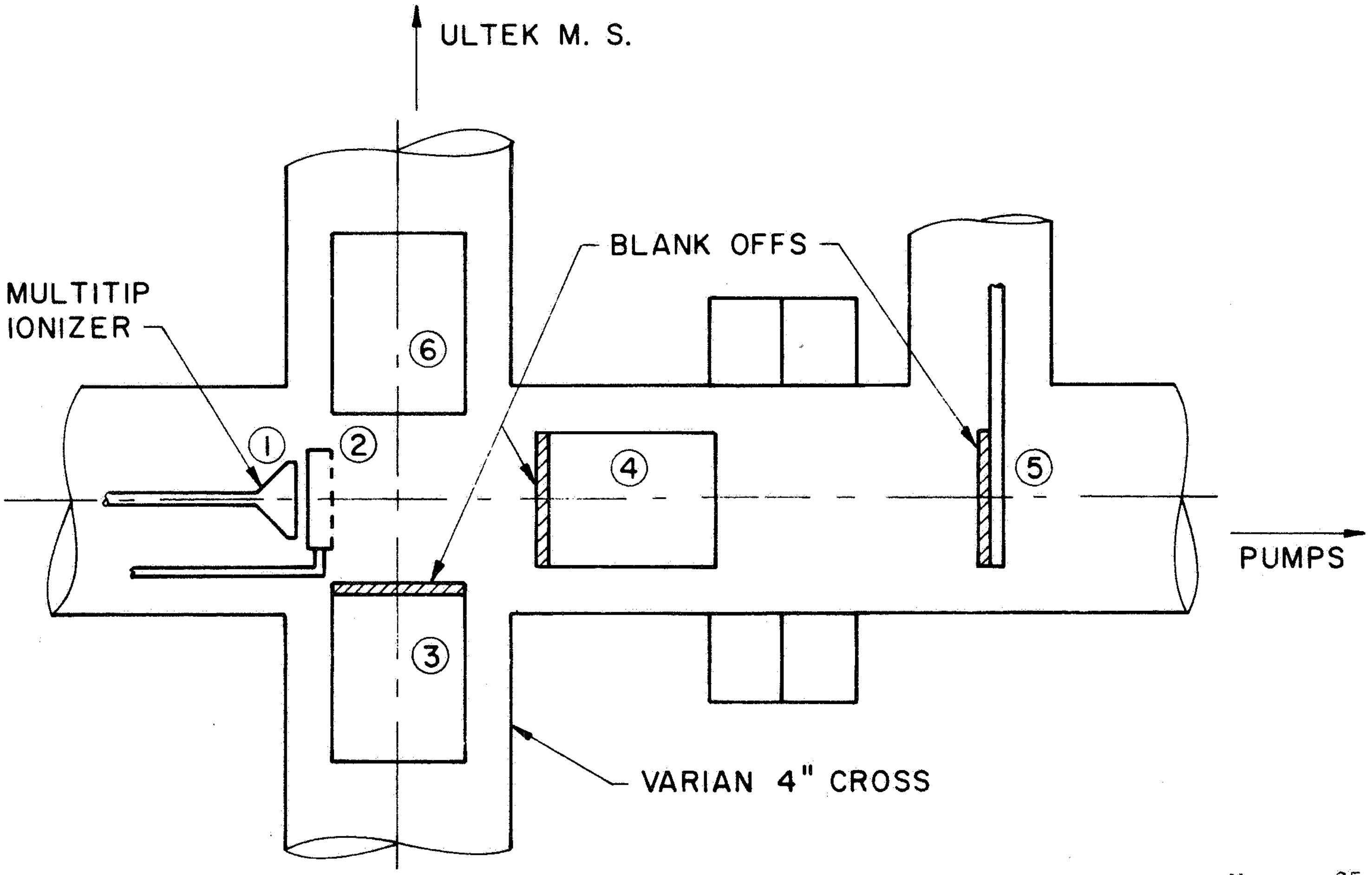


Figure 10. Rotation of MS Axis (Scale: 1/2)

V_1 = + 25 kv

V_2 = Ground

V_3 = +(0-300)v

V_4 = +(0-150)v

V_6 = +(100-200)v

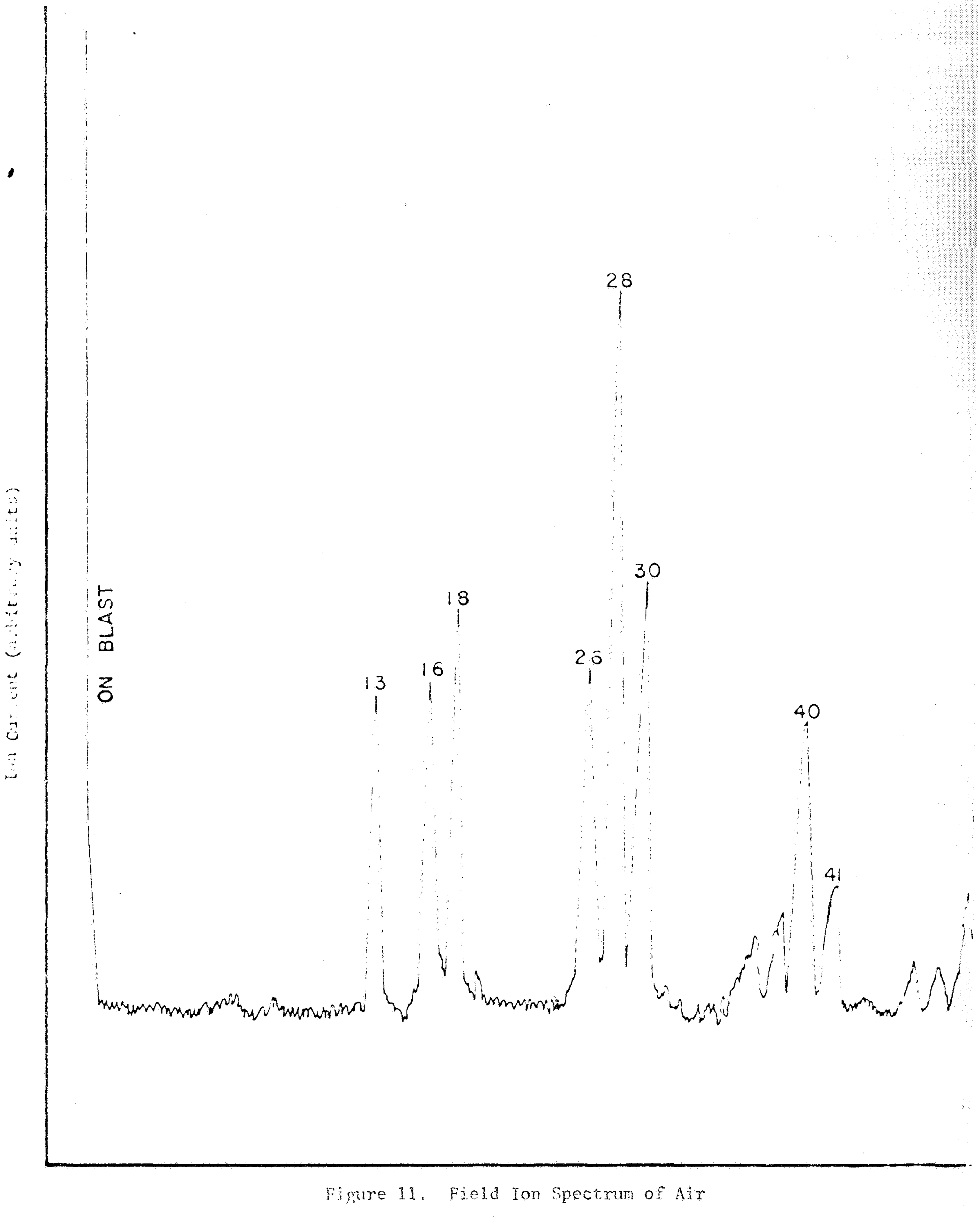
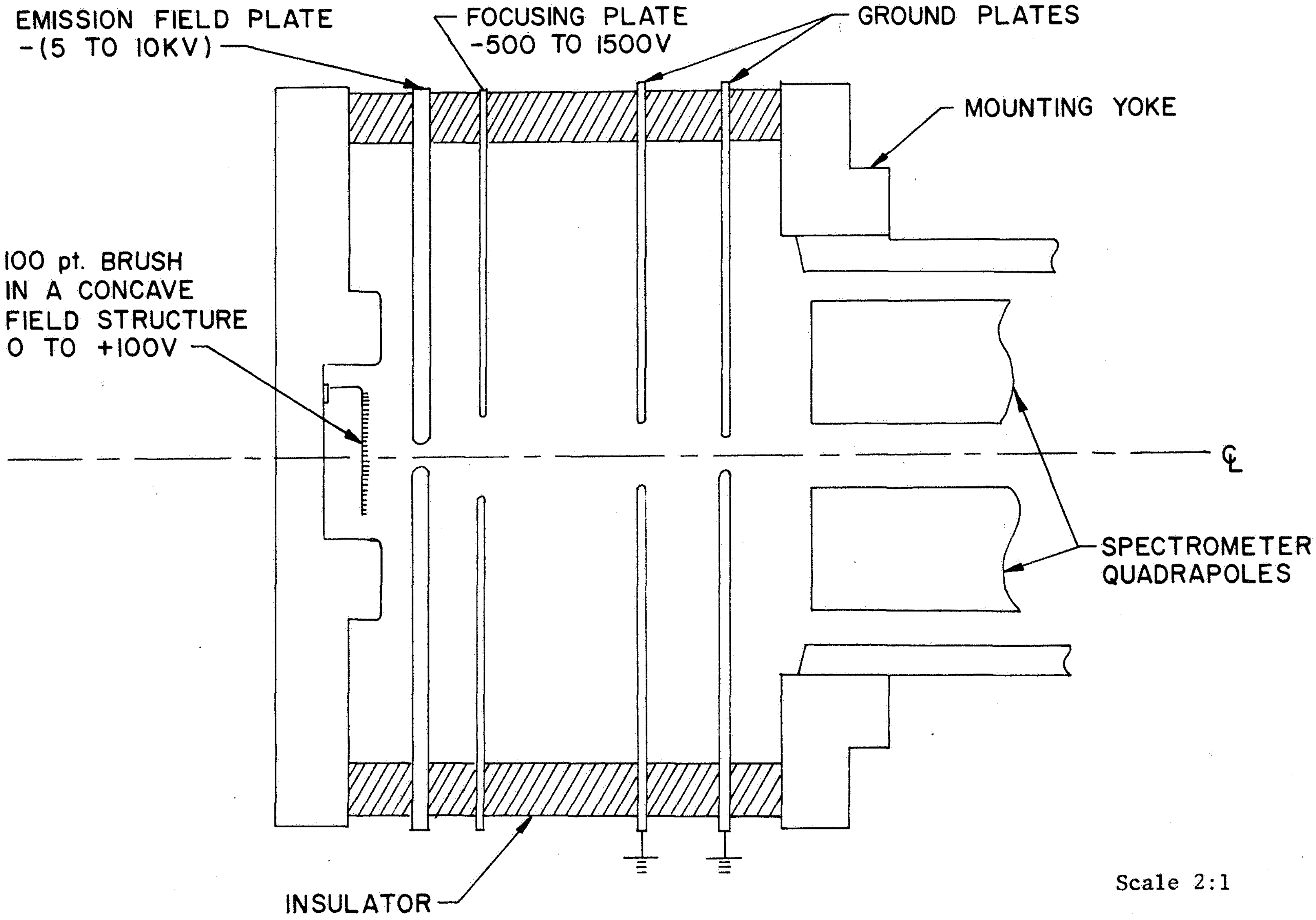


Figure 11. Field Ion Spectrum of Air



Scale 2:1

Figure 12. Aperture - Focusing Field Ion Source

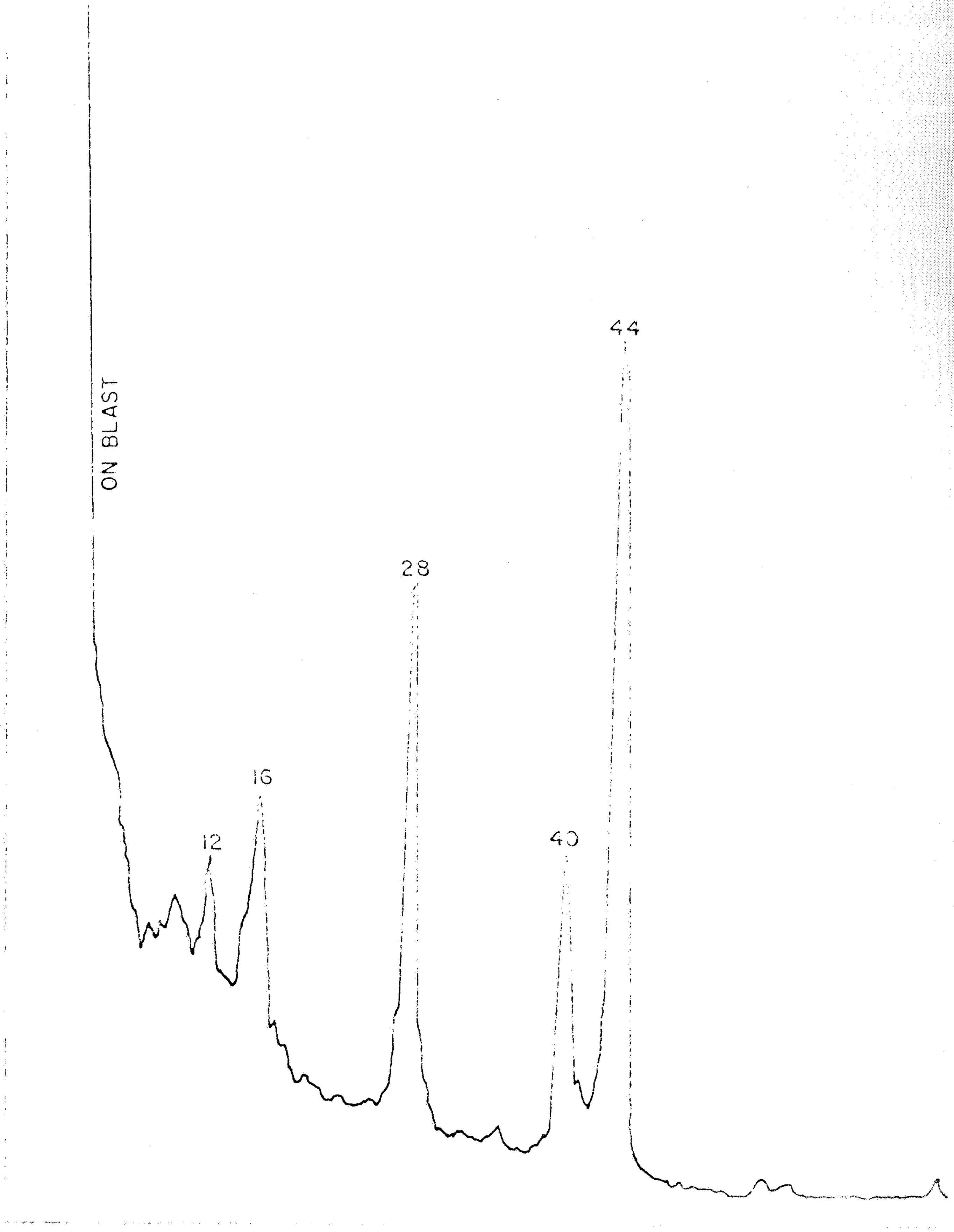


Figure 13. Field Electron Bombardment Spectrum of CO_2, A, and N_2

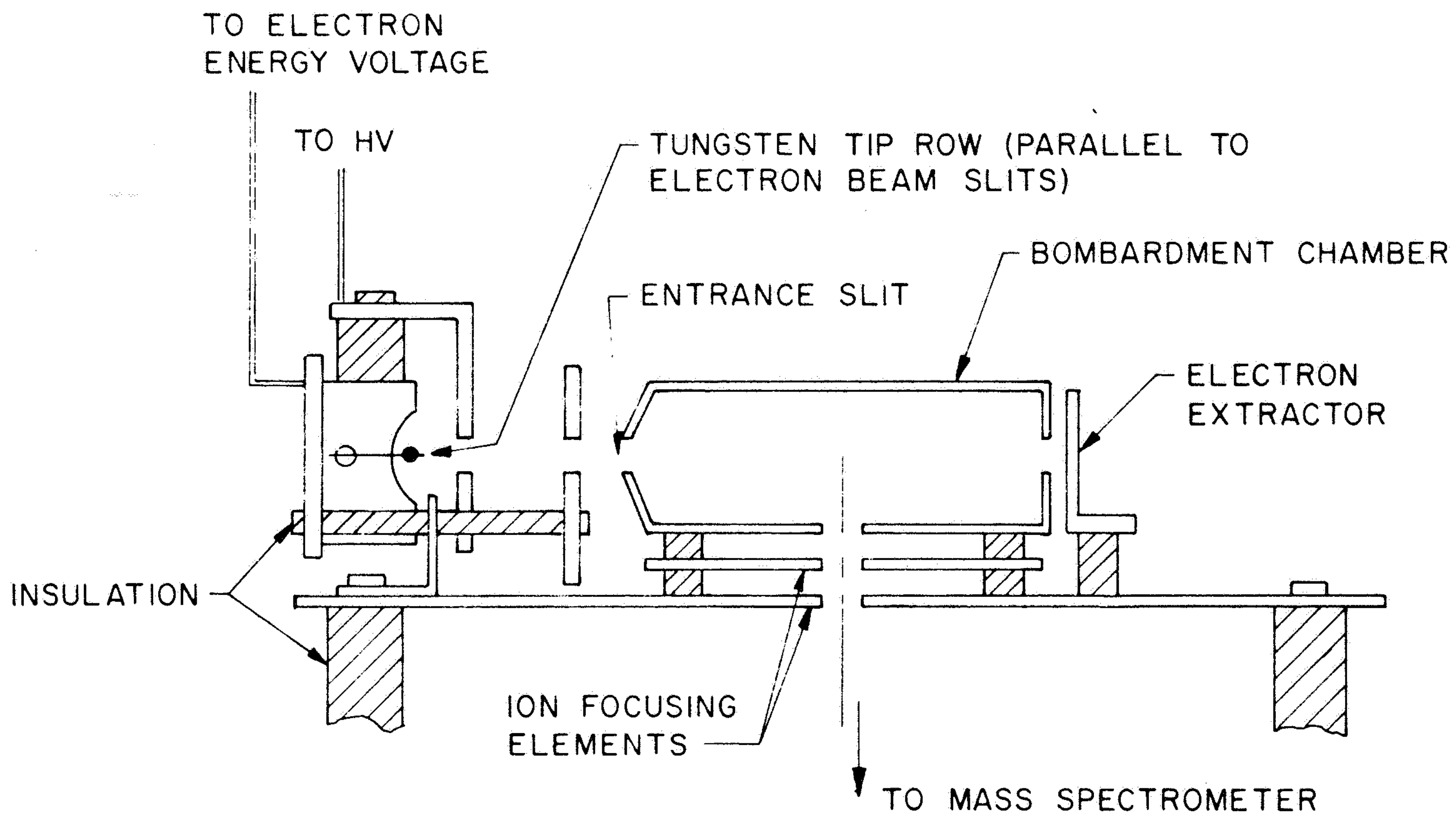
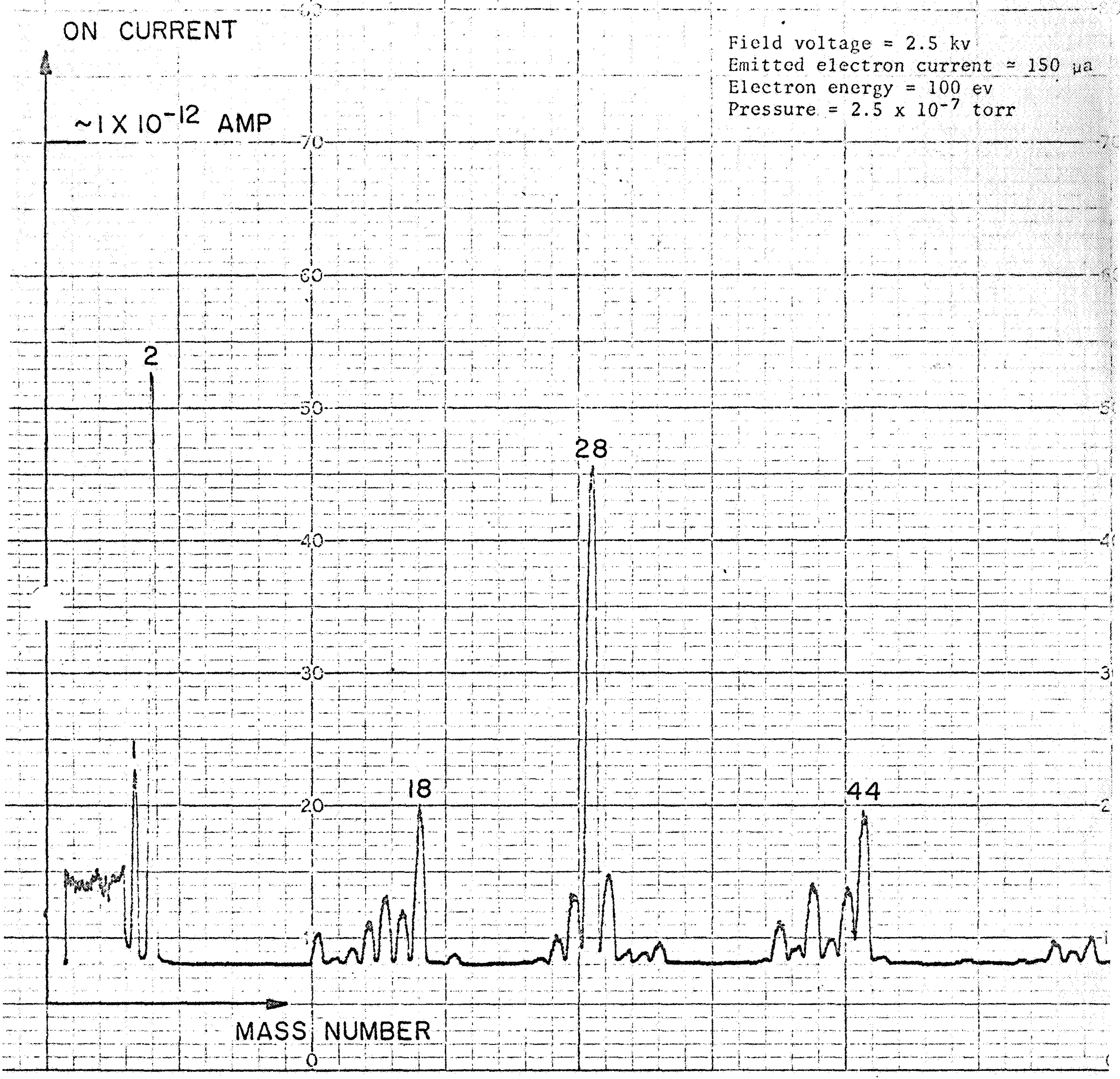


Figure 14. Cross Section of Refined Field Electron Bombardment Source (Scale 4:1)

Figure 15. Refined Field Electron Bombardment Spectrum



Field voltage = 2.5 kv
Emitted electron current ≈ 150 μa
Electron energy = 100 ev
Pressure = 2.5 x 10^{-7} torr