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- [73] Assignee **the United States of America as represented by the Secretary of the Air Force**

[56]

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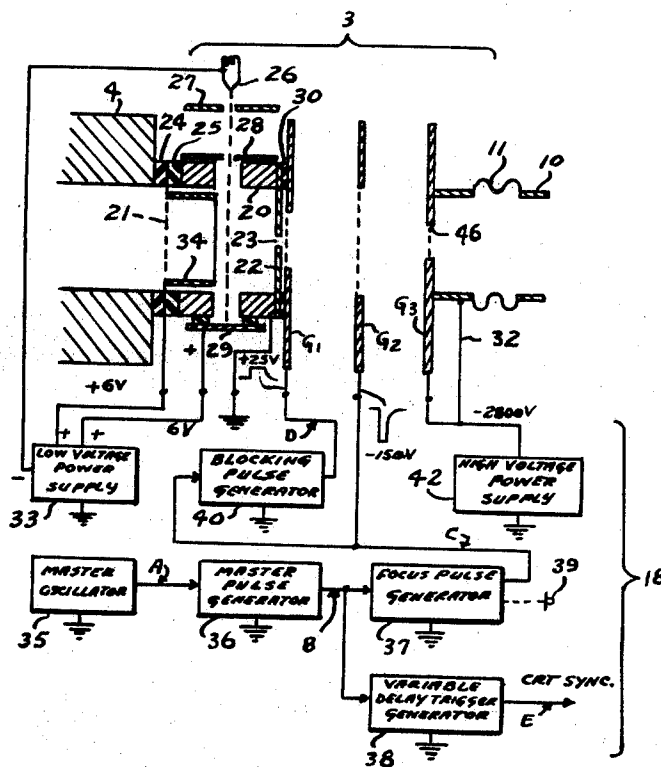
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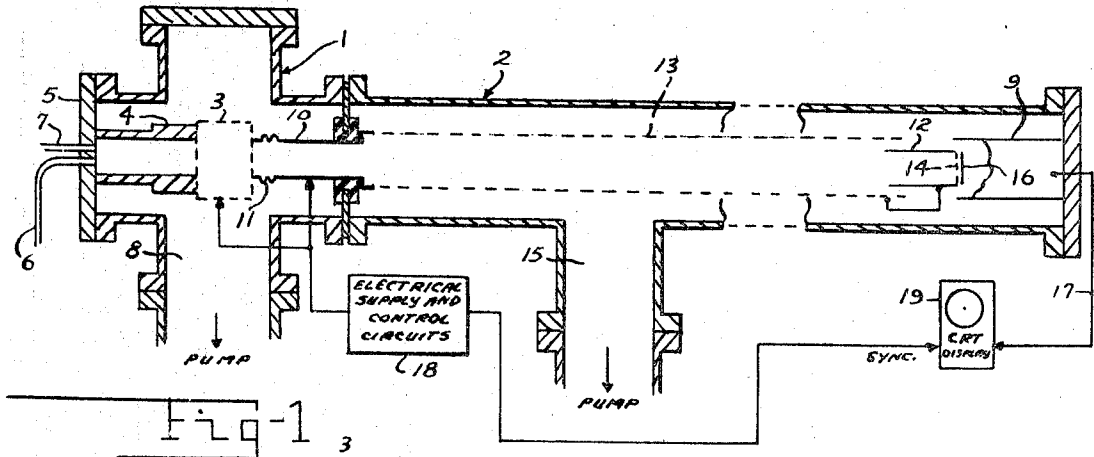
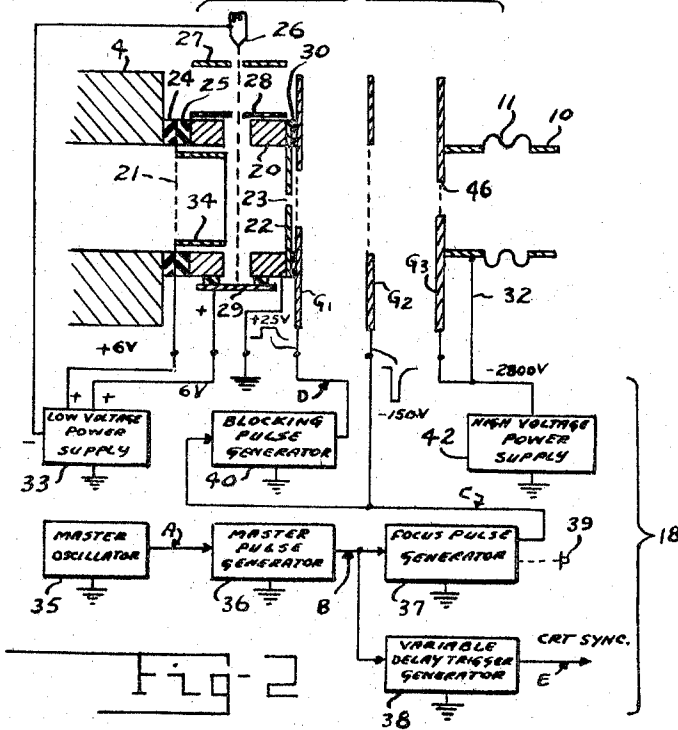
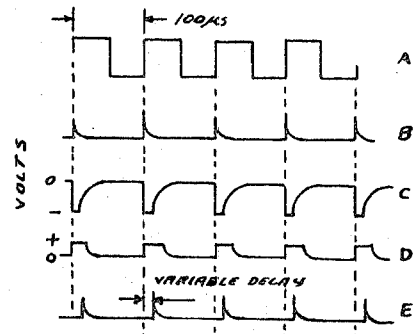
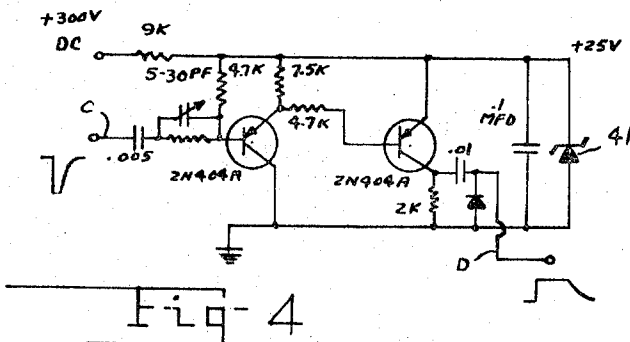
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[54] **TIME-OF-FLIGHT MASS SPECTROMETER OPERATIVE AT ELEVATED ION SOURCE PRESSURES**
5 Claims, 7 Drawing Figs.

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- [51] Int. Cl. H01J 39/34
- [50] Field of Search 250/41.9(G),
41.9(ISB), 41.9(1)

ABSTRACT: A time-of-flight mass spectrometer for the investigation of ion-molecule reactions at ion source pressures up to about 1 Torr. The ion source is operated with a continuous electron beam and a constant repeller voltage of the minimum value necessary to extract ions from the source. A shaped repeller and low electron trap potential are used to provide a uniform field in the source, resulting in a minimum kinetic energy range for the extracted ions. Focusing takes place in the low-pressure region outside the source bounded by the first and second grids between which the focusing pulse is applied. A concurrent blocking pulse is applied to the first grid to prevent ions entering the focusing region during the focusing operation.





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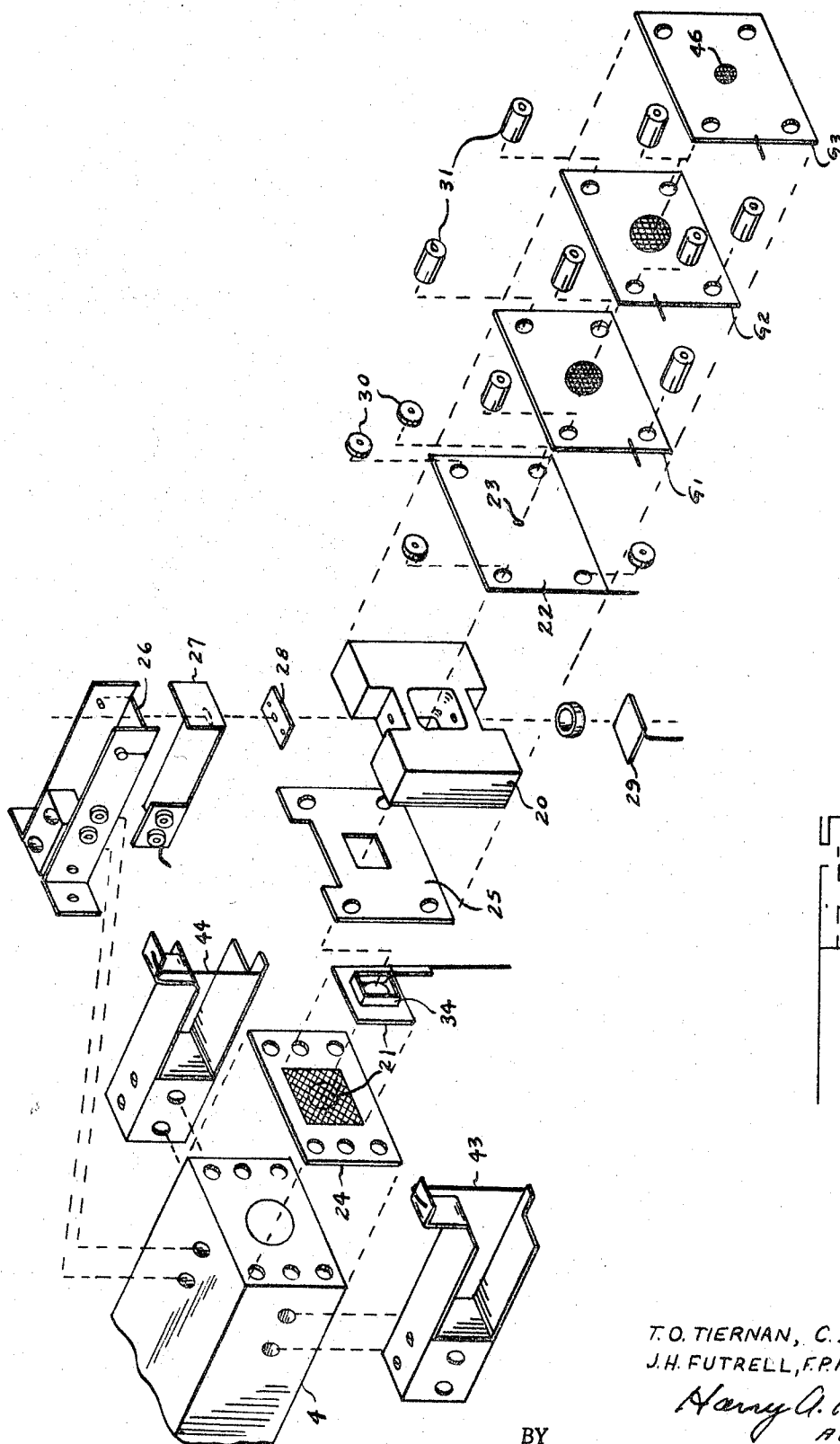


FIG. 5

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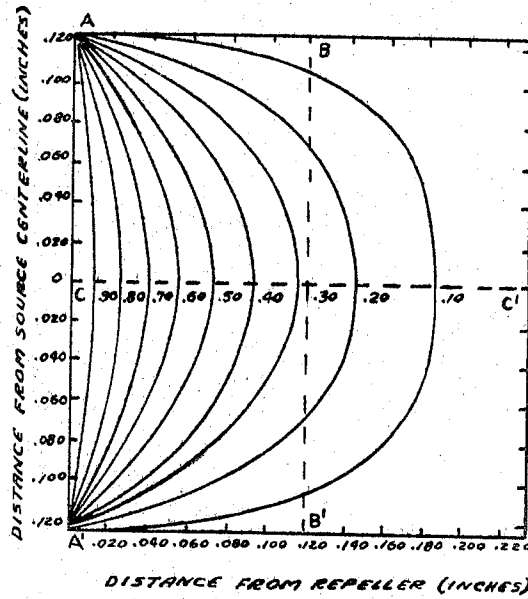


Fig-6

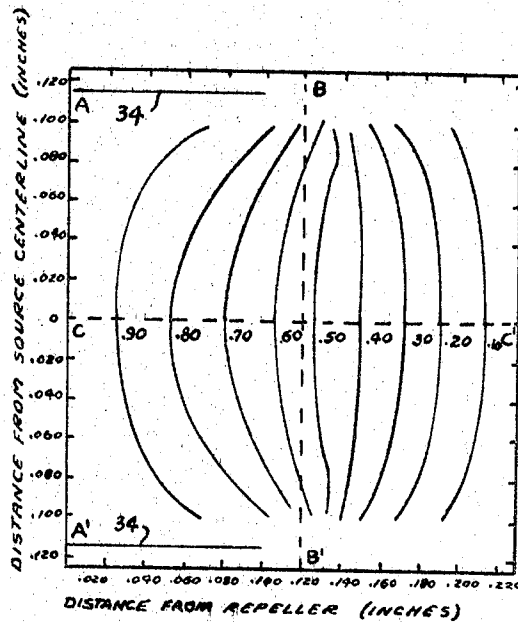


Fig-7

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TIME-OF-FLIGHT MASS SPECTROMETER OPERATIVE AT ELEVATED ION SOURCE PRESSURES

BACKGROUND OF THE INVENTION

The invention relates to time-of-flight mass spectrometer and particularly to relatively high-pressure ion sources for such spectrometers.

For the study of ion-molecule reactions, time-of-flight mass spectrometers have been devised in which the ion source is enclosed to permit a considerably higher pressure in the ionization region than in the ion source housing and drift tube. Descriptions of such an instrument may be found in an article by D.C. Damoth in *Advances in Analytical Chemistry and Instrumentation*, C.N. Reilly, Editor, Vol. 4, pages 371—407, John Wiley and Sons, 1965, and an article by Futrell et al. applicants, in *The Review of Scientific Instruments*, Vol. 39, No. 3, pages 340—345, Mar. 1968.

Present "high" pressure time-of-flight mass spectrometers, however, suffer a serious loss of spectral quality and mass resolution at source pressures higher than the relatively modest values of 0.03—0.05 Torr. Investigation has shown this to be due largely to the strong electric field within the ion source that results from the application of the relatively high voltage ion focus pulse between the backing plate of the ion source and the first grid, i.e., the grid adjacent to the ion exit aperture of the source. This pulse actually has two purposes: one, to draw ions out of the ion source into the ion acceleration region of the apparatus; the other, to achieve space focus of the ions at the target electrode of the ion detector located at the end of the drift or flight tube of the instrument, or, more specifically, to cause all ions which have the same mass-to-charge ratio, but which may start from points in the source at different distances from the exit aperture, to reach the target electrode at the same time. The magnitude of the pulse required to achieve this space focus depends upon the parameters of the particular instrument, a typical value being -175v. The magnitude is manually adjustable and is normally set to the value giving the best overall focus.

The above focus conditions will be achieved only if the spread in kinetic energies of the ions of the same mass-to-charge ratio leaving the source is essentially that due to the focus pulse. Any other factors in the source tending to modify the kinetic energies of the ions will reduce the sharpness of focus and degrade the mass resolution of the spectrometer. The principal factor producing undesirable changes in ion kinetic energy is the occurrence of collisions between particles in the source. At low source pressures the probability of collision is slight and the loss of resolution from this cause is insignificant. However, at even moderate pressures, enough collisions occur to spread the energy range from a very low value for an ion that has undergone a maximum energy absorbing collision to a kinetic energy equal approximately to the average value for ions that escaped collision, or about 87 ev. for a focusing pulse of -175v. An energy dispersion this great seriously degrades the resolution of the spectrometer, and the problem becomes more severe as the pressure is elevated and the probability of collisions increases. Moreover, at an ion kinetic energy of 87, ev., endothermic charge transfer reactions are possible and the ions thus formed also will not have the proper energy to be focused in a discrete mass spectrum. The field strength within the source is thus an important contributing factor to the energy defocusing problem. Further, the problem of high field strength can not be solved by reducing the magnitude of the focus pulse since its value, as already stated, is dictated by the parameters of the instrument.

Another factor that adversely affects the focus and therefore the mass resolution is a nonuniform electric field in the ion source. Factors contributing to this are the ionization chamber structure and a high electron trap voltage. In the latter case, with high trap or anode potentials, primary ions formed in the trap region are accelerated transversely to the path of ion extraction and may undergo dissociative charge exchange reactions in the source chamber.

SUMMARY OF THE INVENTION

The purpose of the invention is to provide an ion source construction and mode of operation that provides good spectral quality and mass resolution in a time-of-flight mass spectrometer at source pressures as high as 1 Torr.

In accordance with the invention a high electric field strength in the ion source is avoided by removing the ion focus region from the source chamber to the low-pressure region outside the chamber. The ion source is operated with a continuous electron beam and a continuous backing plate or repeller potential which is made only high enough to extract ions from the source. This reduces the maximum kinetic energy of the extracted ions from the high value that results when focusing is accomplished in the source, for example 87ev. as given above, to a much lower value, for example 3ev. for a repeller potential of 6v. The maximum kinetic energy range of ions leaving the source is therefore considerably less than 3ev. which greatly reduces the focus problem.

The ions leaving the source pass through the first grid into the region between the first and second grids where focusing is accomplished by application of the focus pulse between these two grids. The sample of ions focused is that existing between the two grids when the focus pulse is applied. A blocking pulse concurrent with the focus pulse is applied to the first grid to prevent the passage of ions from the source into the focusing region during the focusing operation. Since the pressure in the focusing region is low, the probability of collision is low and the effect of this factor on the quality of focus is negligible. The usual final acceleration of the focused ions occurs in the acceleration field established between the second and third grids in conventional manner.

In addition, the range of kinetic energies of the ions derived from the source is further reduced and the mass resolution correspondingly improved by the use of a shaped repeller electrode and a reduced electron trap voltage to provide a more uniform electric field in the ion source chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the general arrangement of the principal elements of a time-of-flight mass spectrometer to which the invention applies;

FIG. 2 illustrates schematically an ion source together with the ion focusing and accelerating apparatus constructed in accordance with the invention;

FIG. 3 shows waveforms occurring in FIG. 2;

FIG. 4 is a schematic diagram of a suitable blocking pulse generator for use in FIG. 2;

FIG. 5 is an exploded view of a physical embodiment of the apparatus shown schematically in FIG. 2; and

FIGS. 6 and 7 illustrate the improvement in ion source field uniformity brought about by the shaped repeller electrode.

DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 shows the general arrangement of a typical time-of-flight mass spectrometer for use at elevated source pressures. The instrument is contained in gastight housing having two principal sections designated 1 and 2. Section 1 contains, in the location defined by block 3, the ion source, the ion focusing apparatus and the ion acceleration apparatus, which are the parts of the spectrometer to which the invention pertains. The apparatus in block 3 is supported by a hollow standoff 4 attached to cover plate 5. The sample to be analyzed, in gaseous form, is introduced into the interior of support 4 through sample input tube 6. Tube 7 also communicates with the interior of support 4 and may be used to monitor the gas pressure in the interior or, in automatic pressure control systems, to provide an input pressure to automatic pressure control apparatus (not shown) which automatically regulates the sample input flow through tube 6 in such manner as to hold the pressure inside support 4 at a constant preset value. The sample gas in support 4 can flow freely into the ion source in block 3 through its porous backing plate as we will be seen later. The

ion source chamber, as will also be seen later, communicates with the interior of housing section 1 only through two small openings which are no larger than required for entry of the ionizing electron beam through one and the exit through the other of ions formed in the chamber by collisions between electrons and the sample particles. These restrictive openings permit the interior of section 1, which is connected to a fast acting evacuating pump through port 8, to be maintained at a pressure much lower than that in the ion source chamber, for example, 10^{-4} Torr.

The ions generated, focused, and accelerated in the apparatus represented by block 3 enter the field-free drift tube of the spectrometer which terminates in the ion detector 9. The drift tube, except for its extension 10 at the input end, and the ion detector 9 are located in section 2 of the housing. Extension 10 has a spring bellows section 11 which forces the input end of the drift tube into physical contact with the last electrode of the apparatus represented by block 3, as we will be seen later. The ion detector 9 has a stack portion 12 which in effect is an output extension of the drift tube. The drift tube therefore consists of extension 10, main portion 13, and stack 12, and terminates at grid 14 at the end of stack 12. The entire drift tube is maintained at the same electrical potential, which is that of the last electrode in block 3. The main portion 13 of the drift tube is porous, for example, a metal mesh, so that the pressure within the tube is the same as that in section 2 of the housing which is connected through port 15 to a second evacuating pump. As will be apparent later, the only communication between section 2 of the housing and section 1 is through a restricting aperture in the last electrode of the apparatus in block 3 which permits section 2 to be maintained at a lower pressure than section 1, for example, 10^{-6} Torr. Ions passing through grid 14 strike the target electrode 16 of the ion detector. This electrode is an ion cathode which emits electrons in proportion to the number of ions striking it. These electrons are amplified in number by an electron multiplier forming part of the ion detector 9 which produces an output signal on line 17 proportional to the abundance of the ions striking target electrode 16.

Operating and control potentials are supplied to the spectrometer by suitable circuits represented by block 18. Periodically for example at a rate of 10kHz, a focus pulse is applied to block 3 causing a sample of focused and accelerated ions to enter the drift tube. Ideally, these ions all have the same kinetic energy, except for the energy differences produced by the focus pulse as required to achieve space focus of all ions of the same mass-to-charge ratio at target electrode 16. Since the ions move down the drift tube with velocities inversely proportional to the square roots of their mass-to-charge ratios, ions of the same mass-to-charge ratio tend to move down the tube in clusters of increasing separation due to the different velocities. Therefore, the ions of different mass-to-charge ratios arrive at the target electrode 16 of the ion detector at different times, those with the lowest ratio arriving first, so that mass-to-charge ratios are displayed along the horizontal or time axis of oscilloscope 19. The abundance of ions is displayed along the vertical axis by deflecting the beam vertically in accordance with the output of ion detector 9.

FIG. 2 shows schematically the construction of the apparatus of block 3, FIG. 1, in accordance with the invention. An actual physical embodiment is shown in FIG. 5. The ion source chamber is defined by the main body 20, the backing plate 21 which in this case is termed the repeller electrode, and metal plate 22 having an ion exit aperture 23. Repeller electrode 21 is insulated from support 4, body 20 and plate 22, all of which are at ground potential, by insulators 24 and 25. The repeller electrode is porous, for example, a metal mesh, to permit the gas sample to pass from the interior of support 4 into the ion source chamber and to maintain equal pressures in these two spaces. The ionizing electron beam is produced by cathode 26 and, after passing through control grid 27 and the aperture in electron entrance plate 28, passes centrally through the ion source chamber to a positive anode or elec-

tron trap electrode 29 which has an insulating seal to the ion source body 20.

Grids G_1 , G_2 and G_3 are situated outside the ion source in the interior space of housing section 1 and are electrically insulated from the source by insulating spacers such as 30 and from each other as by insulating spacers such as 31 (FIG. 5). The drift tube extension 10 is urged into physical and also electrical contact with G_3 by spring bellows 11. Equal potentials on the drift tube and G_3 may be insured by an electrical connection 32 if necessary.

The basic components of the various electrical circuits 18 in FIG. 1 are shown in block form in FIG. 2. Low voltage supply 33 supplies direct operating potentials to repeller electrode 21, the anode or electron trap 29, and cathode 26. The trap electrode is operated only about 6v. positive relative to the grounded body of the ion source in order to reduce to a negligible amount any transverse acceleration of ions due to its field. Cathode 26 may be operated negative relative to ground by a sufficient amount to produce the required operating potential between it and the trap electrode 29.

The repeller electrode 21 is operated at no higher positive potential than is required to expel ions through the ion source exit aperture 23. This potential may be about +6v. As stated earlier, the repeller electrode is shaped to produce a more uniform expelling field within the ion source chamber and to thereby narrow the kinetic energy spread of the ions exiting through aperture 23. This is accomplished by a conductive extension 34 of the repeller electrode into the ion source chamber. The extension is in the form of an open ended box as seen more clearly in FIG. 5. In the embodiment shown, the ion source chamber has a height and width of about .025 inch and a length along the axis of the instrument of about .022 inch. The projection extends to a point just short of the electron beam B-B' at the center of the space. FIGS. 6 and 7 show the equipotential lines at intervals of 0.10 the total voltage drop without and with the extension 34, respectively. It will be seen that in FIG. 7 the 0.50 line occurs more nearly at the center of the space and that from the center where the electron beam B-B' is located to point C' where the exit aperture 23 is located the field is very uniform.

The cyclic operation of the spectrometer is under the control of master oscillator 35 which produces a square wave having a period of 100 μ sec. (10kHz) as represented by waveform A of FIG. 3. This is converted by master pulse generator 36 to a series of sharp pulses at 100 μ sec. intervals as represented by waveform B. These pulses trigger focus pulse generator 37 to produce the focus pulses represented by waveform C and the variable delay trigger pulse generator 38 to produce the sweep trigger pulses for oscilloscope 19 represented by waveform E. The focus pulses, which may have a magnitude of about -150v. are applied to grid G_2 . Adjustment of the focus of the spectrometer is accomplished by varying the magnitude of the focus pulse as by manual control 39. Blocking pulse generator 40 converts the focus pulse produced by generator 37 to a positive pulse of constant magnitude and somewhat greater duration than the focus pulse. A suitable circuit for generating this pulse is shown in FIG. 4. The magnitude, for all values of the focus pulse, is +25v. as established by Zener diode 41. The blocking pulses are applied to grid G_1 .

Accelerating grid G_3 as well as the entire drift tube 10-13-12 are held at a suitable constant direct potential of, for example, -2,800 by high voltage source 42.

The ion source of FIG. 2 is operated with a continuous electron beam and constant repeller 21 voltage so that ions are continuously being generated in the source chamber. During the intervals between blocking pulses D, ions are expelled through aperture 23 by the electric field inside the source chamber and pass through G_1 into the space between G_1 and G_2 . Upon the simultaneous application of blocking and focus pulses to G_1 and G_2 , respectively, the entry of ions into the space between the two grids is blocked and the sample of ions in the space at that instant is subjected to the focus pulse. The field produced between G_2 and G_1 by the focus pulse ac-

celerates the ions toward G_2 through which they pass into the space between G_2 and G_3 . Since the length of time an ion is acted on by the focus pulse and therefore the increase in its velocity due to the focus pulse is directly related to its distance from G_2 , a proper selection of the focus pulse magnitude in relation to the other parameters of the spectrometer can cause ions of the same mass-to-charge ratio to arrive at target electrode 16 (FIG. 1) at substantially the source time although starting from different points in the focus region between G_1 and G_2 .

The space focused ions passing through G_2 are subjected to the constant accelerating field that exists between G_2 and G_3 due to the -2,800v. potential on G_3 . This field increases the kinetic energies of the ions equally and by a large amount relative to the kinetic energies received in the ion source and in the focus region between G_1 and G_2 . The accelerated ions pass through aperture 46 of G_3 into the drift tube. Except for the energy differences imparted to the ions by the focus pulse as described above, the ions enter the drift tube with substantially the same kinetic energies so that their velocities are proportional to the square roots of their mass-to-charge ratios, causing ions of different mass-to-charge ratios to arrive at the target electrode 16 (FIG. 1) at different times, as already mentioned.

When ion sources are operated at high pressures a severe loss of ion intensity can occur after a short period of operation due to a build up of surface charge in the source. This problem can be completely overcome by heating the ion source to a temperature of about 250° C. In the embodiment shown in FIG. 5, this heating is accomplished by electrically heated filaments 43 and 44, made of tantalum for example, supported adjacent to the sides of ion source body 20. Insulating materials used in the ion source must be able to withstand this temperature, mica being a suitable material.

It is desired to obtain a mass spectrum which is representative of the actual composition of the ions existing in the ion source. As already discussed, however, the mode of operation described here results in the focusing of only those ions which are in the space between grids G_1 and G_2 when the focus pulse is triggered. This concentration is a function not only of their original abundance in the source but also of their velocities which result form the expelling field in the source. Thus the observed data exhibit a velocity discrimination which is created by the method which is employed here to achieve space focusing. Assuming that all ions leaving the source have equal energies, then the velocity of a given ion is proportional to the inverse square root of its mass. This gives rise to a square root-of-mass dependence of the steady state concentration of ions in the sampling space between G_1 and G_2 . Therefore the observed spectra should be corrected by dividing each ion intensity by the square root of the ion mass.

We claim:

1. Apparatus situated in the evacuated housing of a time-of-flight mass spectrometer for generating, focusing and accelerating ions for introduction into the drift tube of said spectrometer, said apparatus comprising: an ion source structure providing an enclosed ionization chamber having an electrically insulated porous repeller plate and an exit plate containing a small exit aperture as parallel opposite walls, means providing a continuous electron beam passing centrally through said chamber, means for introducing a gas under relatively high pressure into said chamber through said repeller plate, and means for applying a constant small positive potential to said repeller plate for expelling ions through said exit

aperture; ion focusing means comprising two spaced grids located outside said source structure in the evacuated space of said spectrometer housing and situated parallel to said exit plate and opposite said exit aperture for receiving ions expelled through the aperture into the space between said grids, and means for periodically and concurrently applying a positive blocking pulse to the grid nearer the exit aperture and a larger negative focusing pulse to the other grid; and ion accelerating means comprising a third grid parallel to and spaced from the grid receiving said focusing pulse, and means for maintaining said third grid at a constant high negative potential.

2. Apparatus as claimed in claim 1 in which means are provided for heating said ion source structure to a temperature high enough to prevent the formation of a surface charge on the walls of said chamber.

3. A time-of-flight mass spectrometer having, in a gas tight housing under constant evacuation, a unipotential drift tube, an ion detector located at the exit end of the drift tube, and apparatus for generating, focusing, and accelerating ions for introduction into said drift tube, said apparatus comprising: an ion source structure situated opposite and spaced from the entrance to said drift tube and providing an enclosed ionization chamber centered on the extended axis of said drift tube and bounded on two opposite sides by an electrically insulated porous repeller plate and an exit plate both normal to said extended axis, a said exit plate being nearer the drift tube entrance than said repeller plate and having a small exit aperture concentric with said extended axis, means providing a continuous electron beam passing centrally through said chamber and normal to the extended axis of the drift tube, means for introducing a gas for analysis under relatively high pressure into said chamber through said porous repeller plate, and means for applying a small constant positive direct potential to said repeller plate for expelling ions from said chamber through said exit aperture; first, second, and third grids normal to the extended axis of the drift tube and situated between said exit plate and the entrance to said drift tube, said first grid being close to said exit aperture, said third grid being at the entrance to said drift tube, and said second grid being intermediate the first and third grids; means for periodically applying a negative focus pulse to said second grid; means synchronized with said focus pulse for applying concurrently therewith a positive pulse to said first grid for blocking the exit of ions from said chamber during said focus pulse; means for continuously maintaining said third grid at a high negative potential; and means for maintaining said drift tube at the potential of said third grid.

4. Apparatus as claimed in claim 3 in which said repeller plate is provided with an extension into said chamber, said extension being in the form of an open ended box only slightly smaller than said chamber and extending to a point near said electron beam for making the electric field in said chamber produced by the potential of said repeller plate more uniform particularly in the region between the beam and the exit aperture.

5. Apparatus as claimed in claim 4 in which said electron beam is established between a cathode and a plate acting as an electron trap both situated outside and on opposite sides of said chamber with said beam passing through apertures in opposite walls of said chamber, and in which said plate is maintained at a low positive potential relative to the walls of said chamber to reduce the field in said chamber due to said plate.