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BROAD-BEAM MASS SPECTROMETER HAVING PARTICLE
ENERGY SELECTION MEANS
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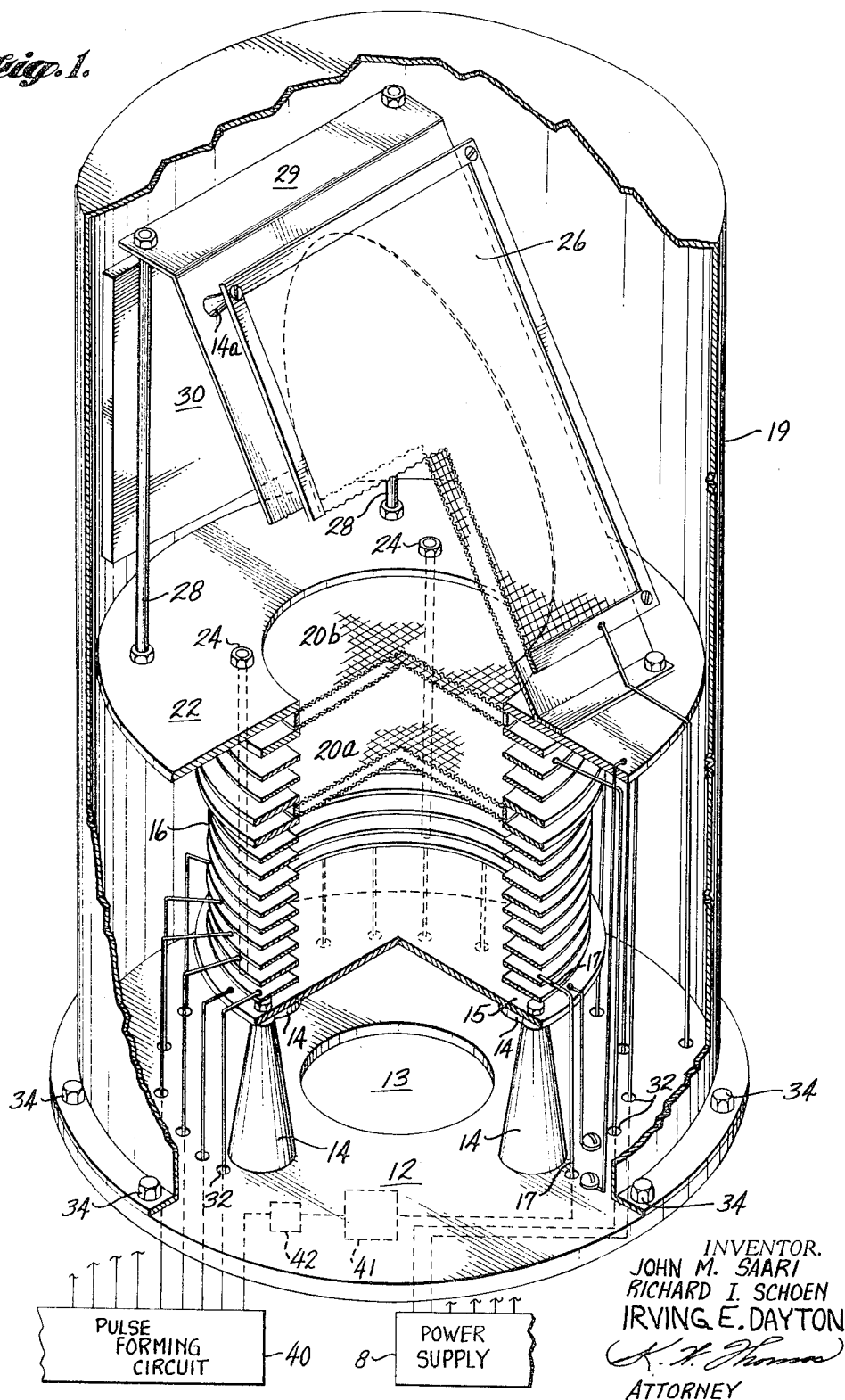
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Fig. 1.



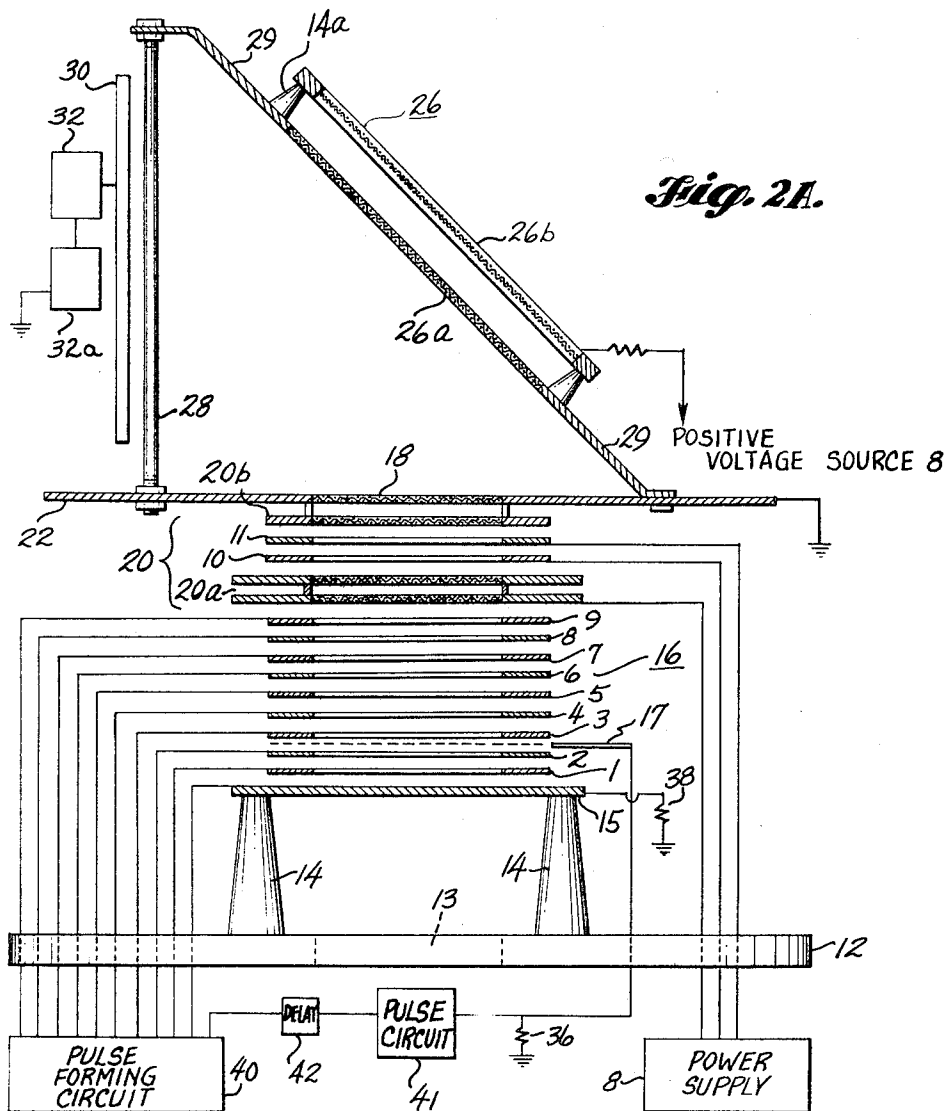
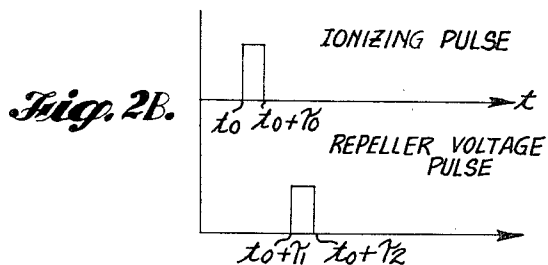
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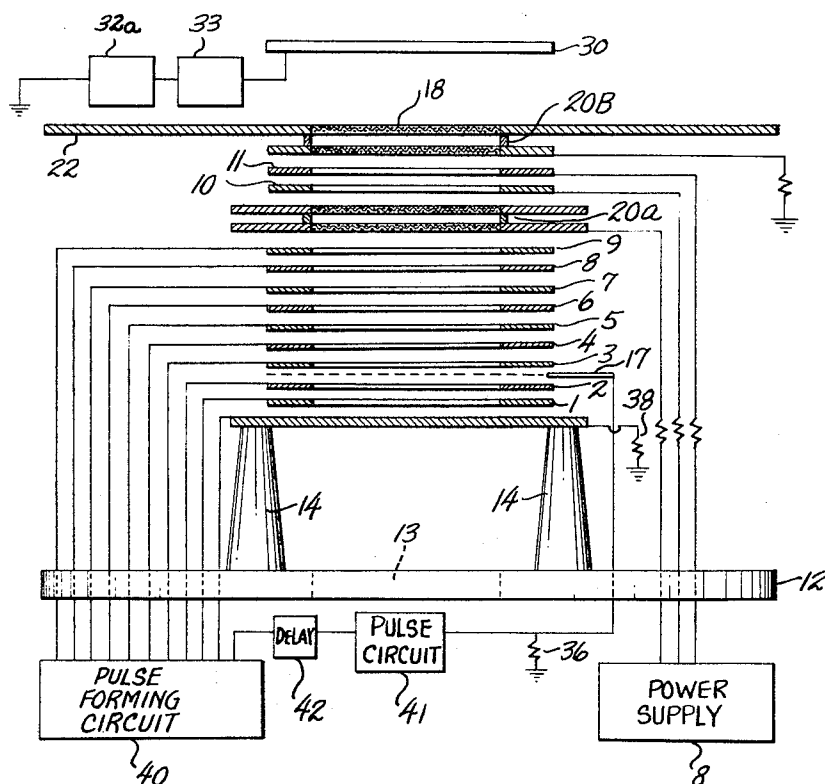
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Fig. 3.



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BROAD-BEAM MASS SPECTROMETER HAVING PARTICLE ENERGY SELECTION MEANS

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ABSTRACT OF THE DISCLOSURE

An apparatus for selecting ions of predetermined masses having an ion source producing pulses of ions. Electrodes defining the ion source are energized to impart substantially constant momentum to the ions in a first direction. A transparent intercepting grid imposes a force on the ions in a second direction parallel but opposite to the first direction so that only those ions exceeding a predetermined energy level pass through the intercepting grid. Of these ions, those below a predetermined energy level are reflected by a second intercepting grid to a collector electrode to be measured.

This invention relates to apparatus for the analysis of molecules present in an unknown mixture. More particularly, the instant invention relates to apparatus for separating ions having differing masses by the use of electrostatic techniques so as to provide a determination of the masses of the different ions and to thereby identify the different ions.

It is well known in the mass spectrometer art to analyze an unknown mixture of molecules by imparting velocity to ions of the differing molecules and subjecting the ions to a magnetic field which causes the ions to deviate from a linear path. The amount of deviation each ion experiences as a result of the applied force field is directly dependent upon the mass of the individual ion; the ions of different mass become separated as they travel through a relatively great distance. By collecting the ions and measuring the amount of deviation of each group of unknown ions, from the direction of initial velocity, the mass of the ions in the unknown group can be determined.

An example of the mass spectrometer art is presented in United States Patent No. 2,774,882 by William H. Wells, assignor to Bendix Aviation Corporation. As taught in the Wells patent, mass spectrometers which employ a magnet to produce deviation of moving ions are not entirely desirable for several reasons. For example, relatively large magnets must be used, necessitating apparatus which is fairly heavy, bulky and relatively expensive. Furthermore, as taught in the Wells patent, spatial dispersion of ions due to a magnetic force field does not have a linear relationship with respect to the mass of the ions, so that special circuits or additional computations are required to determine the ions of different mass in an unknown mixture. In the prior art, use of D.C. amplifiers to amplify the output signals caused by ion impingement upon collector plates is not desirable since such amplifiers cannot provide the sensitive response which is characteristic of A.C. amplifiers.

As taught in the Wells patent, it is desirable to construct mass spectrometer apparatus having means for applying a force on a pulse of ions for a predetermined period of time in a first direction so as to impose a constant momentum to the ions. Such a mass spectrometer preferably includes apparatus for imposing an electrostatic field on the pulse of ions in a second direction; as taught in the Wells patent and in the general mass spectrometer art, this second direction is substantially perpendicular

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to the first direction so as to produce a linear separation of the ions in the second direction on the basis of their mass. As will be taught below, the instant invention provides an improvement over the Wells patent and other mass spectrometer patents by imposing at least one electrostatic field on the pulse of ions in a second direction parallel and opposite to the first direction. In mass spectrometer art, as exemplified by the Wells patent, ions are detected by their displacement in a second direction, i.e., transverse to a first direction, after they have traveled a relatively great distance in the first direction. Since the spatial dispersion of the ions in the second direction is linearly related to the masses of the different ions, a simple determination of ion masses can be made by comparing the spatial dispersion acquired with the unknown ions with the tabulated and recorded dispersion of known ions. As taught in the Wells patent, this determination is enhanced by the use of A.C. amplifiers which are employed and are resonant at the repetition rate for producing the ion pulses.

The instant invention proposes apparatus for the determination and discrimination of the masses of an unknown ionized mixture of molecules which is not limited to a narrow beam of ions, moving in a first direction, as the Wells patent is limited. By comparing the method of selecting ion masses according to the teachings of the instant invention, which depends upon energy of ions all having constant momentum, with the aforementioned Wells method, we note in particular that the instant invention is not limited by slits in portions of the apparatus which restrict ion beam width. Therefore, in the instant invention, the ionized beam may be wide initially or may be fairly narrow initially and may be allowed to expand in width in practice of the method according to the instant invention. Furthermore, the resolution of the instant apparatus does not depend upon the width of the ion beam. In prior art spectrometers the ion beam cannot be allowed to expand because of loss of resolution caused by the finite width of the beam compared to the width of the opening through which the ion beam is discharged toward a collector plate. This limitation does not apply to the instant invention.

There is a second feature which distinguishes the instant invention over the prior art, and, in particular, the patent to Wells, in addition to the feature noted above, i.e., the capability of the instant invention to handle an ion beam with minimum dimensional restriction. In particular, the second feature of the instant invention provides for mass separation of ions in a second direction on a nonlinear basis, rather than a linear separation of ions in a second direction with respect to the first direction given to the ions at the time velocity is imparted to them. Thus, the instant invention can be used to advantage in certain situations in which the prior art cannot be used to such advantage. For example, it may be desirable during ion separation and differentiation to allow ion molecule reactions to take place. In such a situation according to the teachings of the instant invention, there will be a controlled variable pause between the end of the ionizing pulse and the initiation of the velocity imparting repeller voltage pulse. During this pause, ion molecule reactions will be allowed to take place and the beam will expand; that is, ions will move around, and the ion beam will increase in width. Another example involves a situation of monomolecular decomposition in which situation, as in the above noted example of ion molecule reactions, the ions would be caused to lie or to be situated within a chamber where ionization is caused between a repeller plate which imparts velocity to the ions in a first direction and a first grid or force field parallel to and opposite to the ion beam moving in a first direction for a period of time which

would be varied according to conditions under the particular experiment.

An object of this invention is to provide apparatus for determining the masses of ions in an unknown mixture including means for imposing substantially the same momentum on all of the ions and means for selecting those ions whose energies lie within a narrow predetermined range.

A second object of the instant invention is to incorporate relatively inexpensive and compact features into a mass spectrometer through the use of an electrostatic field to produce a separation of ions on the basis of mass.

A third object of the instant invention is to utilize A.C. or D.C. amplifiers in mass spectrometer apparatus in order to obtain a determination of the masses of the different ions in an unknown mixture and to provide a sensitive and reliable indication of the said ion masses.

A still further object of the instant invention is to provide a mass spectrometer capable of separating ions in a beam of greater size than heretofore possible with known apparatus.

Still another object of the instant invention is to provide apparatus for a mass spectrometer wherein analysis of pulsed ions can be made while allowing ion molecule reactions to take place.

A still further object of the instant invention is to provide ion mass analysis using mass spectrometer apparatus wherein ions are analyzed while allowing for monomolecular decomposition to occur.

Briefly, the instant invention comprises means for providing pulses of ions, means for imposing a force on the ions in a first direction for a predetermined period of time, means for imposing a force on the ions in a direction substantially parallel and opposite to the first direction to provide a selection of the ions on the basis of their energy. The selection of the ions on the basis of energy can be related to the mass of the ions in the following manner: the well known equation for kinetic energy may be written in terms of momentum as:

$$\frac{1}{2}Mv^2 = \frac{P^2}{2M} = E \quad (1)$$

in which M is the mass of each individual ion, v the velocity of each individual ion, and P the momentum of each individual ion. Since by the teachings of this invention each individual ion is given substantially the same momentum as every other ion, it is readily seen from Equation 1 that selection of the ions on the basis of energy produces mass selection.

Other objects and advantages will be apparent from the detailed description of the invention which follows and from the appended drawings and claims.

In the drawings:

FIGURE 1 is an isometric perspective illustrating an embodiment of the instant invention;

FIGURE 2A is a cross-sectional view through the mid-plane of the embodiment of FIGURE 1;

FIGURE 2B is a diagram illustrating time versus intensity of ionizing beam and repeller voltage pulses; and

FIGURE 3 is a view in cross-section showing a modification of the apparatus shown in FIGURE 1 and FIGURE 2A.

Referring to FIGURE 1, a mass spectrometer according to the teachings of this invention is shown. A partial vacuum bell-jar 19 (not shown in FIGURE 2A and FIGURE 3) is provided having bolt fastening means 34 for a removable cover plate 12; the cover plate 12 including means defining a sealable opening 13 to permit passage of gas molecules into bell-jar 19 from an exterior container (not shown). The bell-jar 19 shown in FIGURE 1 encloses: means for providing pulses of ions within the bell-jar 19 including an electron gun 17 disposed to be connected through a sealed opening 32 in plate 12 to a first pulse forming circuit 41; means for imposing

a force on the ions in a first direction for a predetermined period of time including a voltage repeller plate 15 supported on plate 12 by insulating members 14, and connected by a lead through a hole 32 in plate 12 to a second pulse forming circuit 40, which in turn is connected by delay circuit means 42 with the first pulse forming circuit 41; and means to provide a selection of the ions on the basis of their energy including means for imposing a force on the ions in a direction substantially parallel and opposite to the first direction, at least one means for reflecting ions having energies within a narrow predetermined range, means for collecting the ions and indicator means for indicating the current imposed by the ion impingement upon said means for collecting the ions.

As seen in FIGURE 1 and FIGURE 2A, the means imposing a force on the ions in a direction substantially parallel and opposite to the first direction includes a grid system 20 having a first grid 20a acquiring a potential from a power source 8 and a second grid 20b which is grounded; the means for reflecting ions includes a grid system 26 having a first grid 26a which is grounded and insulated by supports 14a from a second grid 26b which is given a predetermined potential from a power source (not shown); the means for collecting the ions includes an ion collector plate 30 (having support members not shown). The indicator means includes an electrometer 32a for indicating the current by ion impingement on plate 30, and in the embodiment of FIGURE 1 and FIGURE 2A a D.C. or an A.C. amplifier 32, to amplify the current at plate 30 due to ion impingement.

In combination with the means described above and similarly enclosed within bell-jar 19 are: the plurality of insulating members 14 disposed for attachment to plate 12 and supporting in conjunction with supporting bolts 24 a system of uniform plates or discs 16. The discs 16 are numbered 1 through 11, disposed substantially parallel to one another, and the distances separating discs 1 through 9 and discs 10 and 11 are uniform. The discs 16 are connected through a number of resistance leads to the second pulse circuit 40 in such a way as to maintain a uniform voltage gradient, between any two of the plates 16, at a time coinciding with the voltage on plate 15. In their central portion the discs 16 collectively include means defining a chamber 18 within bell-jar 19 within which the gas coming through opening 13 is ionized and accelerated by plate 15. The grid system 20 is disposed in combination with the discs 16, substantially parallel thereto. A structural member 22 is disposed substantially parallel to the plates 16 and is secured therein by the bolts 24. As seen in FIGURES 1 and 2A, a second grid system 26 is supported upon member 22 by members 28 and 29. The system 26 is disposed transverse to the plane of the member 22 and includes the parallel grids 26a and 26b separated by the insulators 14a. In FIGURE 2A the ion collection plate 30 is disposed substantially perpendicular to the plane of the member 22 by support means (not shown). It is to be understood, however, that collection plate 30 is not restricted to its position relative member 22 as shown in FIGURES 1 and 2A but may be disposed at any angle to the plane of member 22. The cover plate 12 includes means defining a plurality of sealable openings 32 through which resistance leads are passed for interconnecting the plates 16 with the second pulse circuit 40, and the grid 20a of FIGURE 3 and grids 20a and 26b of FIGURE 2A with the power source 8.

Referring to the embodiment shown in FIGURE 3, it is readily seen that the means for reflecting ions having energies within a narrow predetermined range and the accompanying supporting structure thereto, as described above in the description of the embodiment of FIGURE 1 and FIGURE 2A, are not included in the embodiment of FIGURE 3.

As seen in FIGURES 1, 2A and 3, ion-producing elec-

tron gun 17 is disposed between the second and third discs of discs 16. The grid 20a, is disposed between and substantially parallel to discs 9 and 10. Disposed above disc 11 and substantially parallel thereto is grid 20b.

As seen in FIGURE 2A, the gun 17 and the repeller plate 15 are connected to ground through resistors 36 and 38, respectively, so as to be substantially at ground potential in the steady state operation. In the steady state operation ionization is created by the ionizing beam from electron gun 17 represented by a dotted line between discs or plates 2 and 3. This ionizing beam from electron gun 17 may be a beam of electrons; or the means of ionization may include instead of gun 17 other charged particles, high speed uncharged particles, or a beam of photons. According to the instant embodiment the beam emitted from electron gun 17 is a pulsed beam derived through pulses of voltage of substantially equal magnitude applied from a pulse-forming circuit 41. The delay circuit 42 provides means for varying the time between the production of ions by gun 17 and the imposition of the accelerating force to the ions, by the potential pulsed to repeller plate 15. This variable pause controlled by circuit 42 allows time for ion molecule reactions to take place resulting in ion beam expansion. In the diagram of FIGURE 2B there is illustrated the ionizing sequence of the instant invention with a time versus intensity diagram. First, the ionizing pulse from electron gun 17 is initiated at a time t_0 , and it is turned off at a short time later at $t_0 + \tau_0$. During their travel through the space or region occupying chamber 18, the electrons from electron gun 17 impinge upon molecules of gas and vapor introduced into chamber 18 from a container (not shown) exterior to bell-jar 19 and entering chamber 18 through opening 13 in the bell-jar cover plate 12. This causes the molecules in chamber 18 to be ionized into electrons and positive ions, most of which have a unitary charge.

By interrupting the electron stream coming from electron gun 17, the ions are made available for easy impartation of velocity thereto upon the imposition of a positive voltage pulse on the repeller plate 15. This voltage pulse is applied to plate 15 from the second pulse-forming circuit 40. As seen in the diagram of FIGURE 2B, this pulse is applied at the time $t_0 + \tau_1$. This pulse, as noted above, causes the ions to be driven through chamber 18 by the repeller plate 15 toward the grid systems 20 and 26 of FIGURE 1 and FIGURE 2A and toward the grid system 20 of FIGURE 3. The pulse is applied to the plate 15 for a relatively short time, such as one or two microseconds, and is cut off. While the ionizing beam from electron gun 17 is pulsed on and at all other times except when the repeller voltage is on plate 15, the repeller plate 15 voltage is the same as the voltage applied to the first grid 20a of grid system 20. The voltage on grid 20a, when dealing with positive ions, is at some negative value $-V$. The voltage on grid 20b of grid system 20 at this time is zero, grid 20b being grounded; the voltage on grid 26a of system 26 is zero, grid 26a being grounded; and the voltage on grid 26b of grid system 26 is at some value $+\Delta V$, a small value. These grid system voltages are produced through resistors to the power supply 8 as indicated above. At this time, ion collection plate 30 is grounded through an electrometer 32a. The repeller voltage on plate 15 is pulsed on after the ionizing pulse on filament 17 is turned off. That is, the repeller plate 15 voltage from the second pulse circuit 40 is turned on for a time which is short ($\tau_2 - \tau_1$) compared with the transit time of the ions to grid 20a. This repeller voltage pulse is indicated in the diagram of FIGURE 2B. Because the voltage on grid 20a is maintained at a potential $-V$, there is an electric field generated between the repeller plate 15 and grid 20a. This field is made more uniform by the existence of plates or discs 1 through 9, connected through resistors to the second pulse circuit 40. The discs 1 through 9 have a uniformly decreasing potential on each disc, i.e., disc 1 is at a higher potential

than disc 2, etc. Thus a uniform electric field gradient is maintained between repeller plate 15 and grid 20a of FIGURES 1, 2A and 3. The electric field, uniform along the path the ions move in the first direction, effects the same force on each ion thus giving each ion the same momentum. When the repeller plate 15 and discs 1 through 9 are pulsed to a positive voltage by circuit 40 driving positive ions toward grid 20a, constant momentum is acquired by all ions in chamber 18 having the same charge and provided only that the time during which the pulse from circuit 40 is turned on is short compared to the transit time of the ions. As seen in the diagram of FIGURE 2B, this time is $(\tau_2 - \tau_1)$. Thus, all ions reach grid 20a with substantially the same momentum. At this time there is a voltage difference between grid 20a and 20b, since 20b is grounded and grid 20a has a potential $-V$. The plates 10 and 11, which as noted above in part form the plate system 16 are used to maintain this potential gradient uniform. Thus as the ions enter the region between grid 20a and 20b there is a force caused by the uniform electric field due to grid system 20 and plates 10 and 11 which retards the ions. This force is in the direction opposite to the direction in which the ions are moving. If the ions have an energy which is sufficient to overcome the potential difference V between grids 20a and 20b, then they pass into the equipotential regions between grid 20b and grid 26a. If these ions do not have such energy then they are reflected back into the chamber 18 by the force due to potential difference V . Ions which have the necessary energy or more, that is, an energy equal to the charge of the electron times the potential V or more, will pass through grid 20b (a highly transparent grid, as is grid 20a) and approach grid 26a. If these ions have enough additional energy, they surmount the potential barrier between grids 26a and 26b which amounts to ΔV , a small amount (a few volts) as compared with several hundred volts, perhaps, between grids 20b and 20a. If these ions have the additional energy to surmount the potential difference between grids 26a and 26b they will pass therethrough. If they have less energy than is necessary to traverse the region between grids 26a and 26b, they will be reflected as light waves against a mirror from this region toward the collection plate 30 and will be collected there. The current developing at collector plate 30 from ion impingement is measured with an electrometer 32a. In the steady-state operation which has been described, the measured current at the collecting plate 30 is a pulsed current which may be measured by D.C. or A.C. methods.

By altering the instant apparatus, as seen in FIGURE 3, it is feasible and often desirable to apply to grid 20a a negative voltage $-V$ plus a voltage $V_0 \sin \omega t$ which is a small A.C. voltage derived from power source 8. Grid 20b is maintained at zero potential as in FIGURE 2A. This applied modulated voltage will cause the ions to produce an alternating current voltage on the collection plate 30 of frequency $\omega/2\pi$. The measurements will be made with an alternating current apparatus amplifier 33 and an electrometer 32a as seen in FIGURE 3 instead of the direct current amplifier. One can compare the embodiment of FIGURES 1 and 2A and the embodiment of FIGURE 3. In the embodiment shown in FIGURE 1 and FIGURE 2A, one collects all ions which have been given an energy (by the voltage pulse from circuit 40 applied to repeller plate 15 and discs 1 through 9) between the energies of V and $V + \Delta V$ times the charge on the electron in each case. In the embodiment shown in FIGURE 3, the instant invention collects all the ions which have been given an energy greater than $V + V_0 \sin \omega t$. Since the value of $\sin \omega t$ varies with time, the minimum energy of the ions reaching the collector 30 in FIGURE 3 varies with time and the output signal will have an alternating current component caused by ions with energies in the range from $V - V_0$ to $V + V_0$. The frequency $\omega/2\pi$ of the voltage applied to grid 20a of FIGURE 3, must be small

compared to the pulsing frequency of the voltage applied to the repeller plate 15. In both embodiments in order to vary the mass collected, one varies the voltage on grid 20a, that is, V. One does this by varying the voltage continuously and slowly as one pulses the ionizer many times per second. As mentioned earlier, if the momentum given to each ion is represented by P, M as the mass of an ion, and q as the charge of an electron, which is considered to be substantially the amount of charge on each ion, then we have in the embodiment of FIGURES 1 and 2A, using the approximation that ΔV is small compared with V, the statement that the ions will be collected if they have an energy qV which is equal to $P^2/2M$. Similarly, in the embodiment shown in FIGURE 3 we will get an alternating current signal on the collection plate 30 for those ions for which the same equation applies, provided only that V_0 is small compared with V. Thus, as one scans the voltage with increasing V, one goes to smaller and smaller values of M, that is, the mass collected is inversely proportional to the voltage applied at grid 20a.

Since numerous changes may be made in the above apparatus and different embodiments may be made without departing from the spirit thereof, it is intended that all matter contained in the foregoing description referring to apparatus or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. In a mass spectrometer, the combination comprising:
 - (a) means for providing pulses of ions;
 - (b) means for imposing a substantially constant momentum on the ions in a first direction, including a plurality of discs disposed substantially parallel to one another, said plurality of discs being connected by circuit means to a source of potential, said plu-

rality of discs including means defining a chamber through which the ions pass in a first direction and said plurality of discs providing a uniform electric field giving the ions constant momentum;

- (c) first grid means for imposing a force on the ions in a direction substantially parallel and opposite to the first direction including a direct current voltage source; and
 - (d) second grid means for reflecting ions having energies within a narrow predetermined range and moving in the first direction, including a direct current voltage source, said second grid means being so disposed as to reflect only ions having energies within a narrow predetermined range of those ions having sufficient energy to pass through said first grid means to provide a selection of ions on the basis of their energy.
2. The mass spectrometer of claim 1 wherein said first grid means and said second grid means each includes a pair of grids positioned substantially parallel to one another and having means for imposing a voltage difference across said pair of grids.
 3. The mass spectrometer of claim 2 including means for collecting the ions and indicator means for indicating the current imposed by the ion impingement upon said means for collecting the ions.

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