

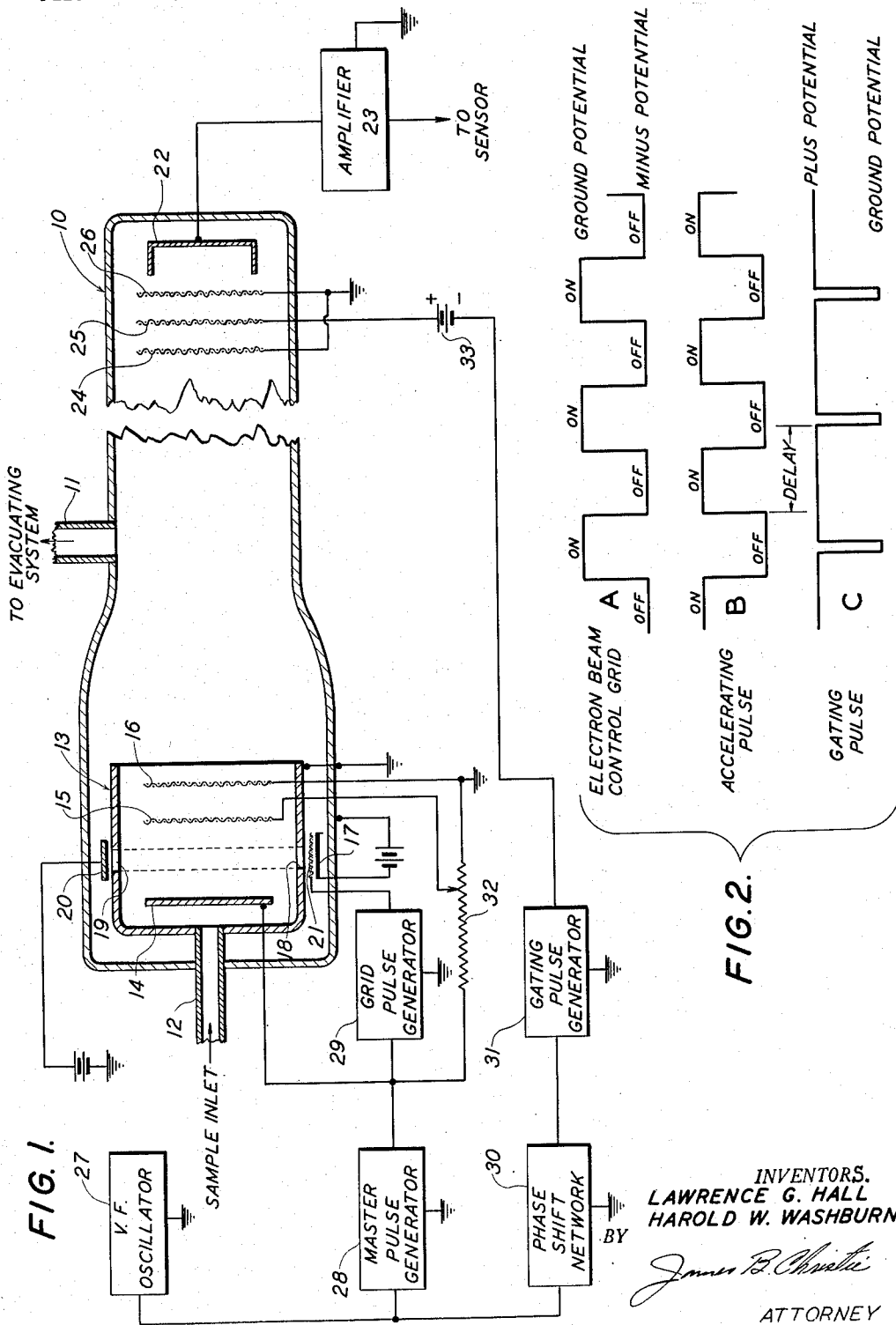
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L. G. HALL ET AL
MASS SPECTROMETRY

2,810,075

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2 Sheets-Sheet 1



INVENTORS.
LAWRENCE G. HALL
HAROLD W. WASHBURN
BY *James B. Christie*
ATTORNEY

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FIG. 3.

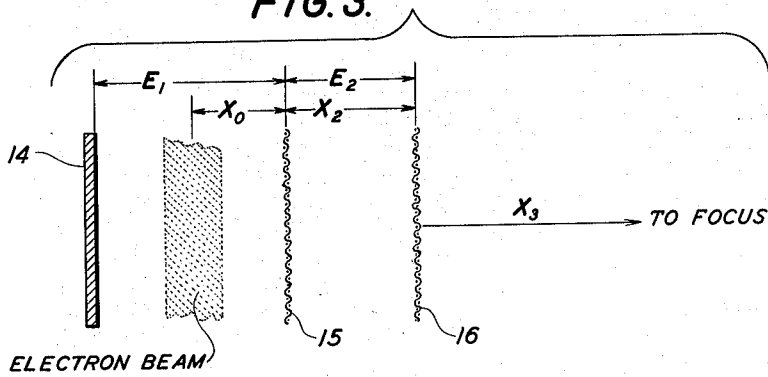
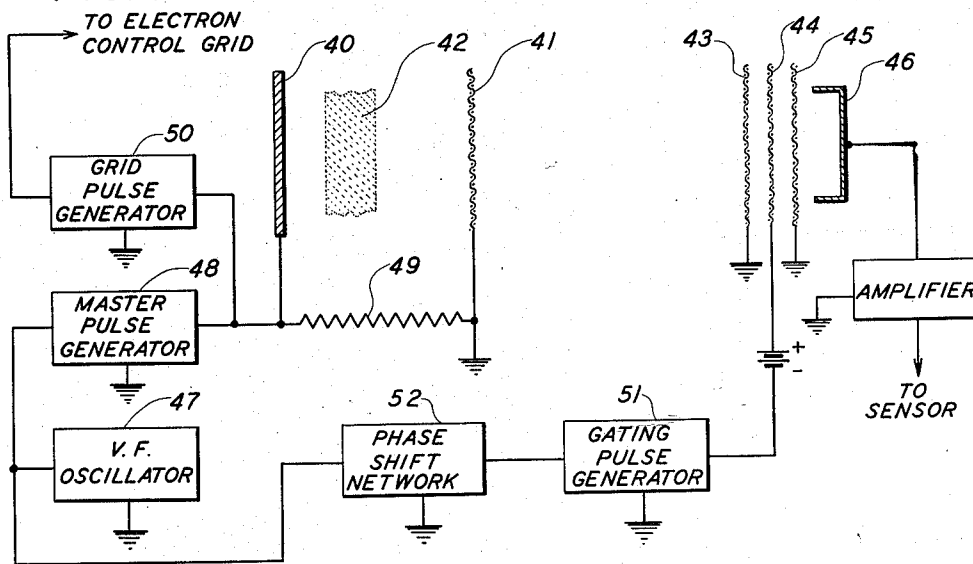


FIG. 4.



INVENTORS.
LAWRENCE G. HALL
HAROLD W. WASHBURN
BY

James B. Christie

ATTORNEY

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MASS SPECTROMETRY

Lawrence G. Hall, West Covina, and Harold W. Washburn, South Pasadena, Calif., assignors, by mesne assignments, to Consolidated Electrodynamics Corporation, Pasadena, Calif., a corporation of California

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2 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometry and more particularly to an improved instrument of the type which has become known as a "time of flight" mass spectrometer.

In mass spectrometry a sample of material to be analyzed is ionized by any one of several known means, and the ions thus formed are separated as a function of mass-to-charge ratios. Separation of the ions in accordance with mass-to-charge ratio is generally accomplished under the influence of electric or magnetic fields, or both, to effect spatial separation thereof. Ions of a given mass-to-charge ratio may then be directed upon an ion collector or target and discharged, whereby a measure of the resulting ion current may be obtained.

In a so-called time of flight mass spectrometer separation of ions is normally accomplished by taking advantage of the characteristic accelerations imposed on ions of differing mass-to-charge ratio by an accelerating electrical field. Generally the ions, after formation or upon formation, are subjected to the influence of a propelling electrical field and are allowed to travel along a so-called drift tube wherein the ion masses separate as a consequence of their characteristic and differing response to the imposed acceleration. In one instrument of this type a collector electrode is provided in the drift tube, and the sensing circuit associated with the collector electrode is periodically actuated so as to sense only those ions of a given mass which strike the collector electrode.

Such selective actuation of the sensing system represents one form of "gating," whereby resolution is obtained between the spatially separated ion bunches.

In time of flight mass spectrometers which employ a drift tube, as above described, and a gating system within the tube to resolve ions of differing mass, it is highly desirable that ions of any given mass be made to coincide in space and time at the gating system and differ in position from ions of any other mass. If the ion source has a potential gradient across the region in which ions are formed, those ions will differ in energy upon emission from the ion source into the drift tube and will, as a result, be difficult to form into an image in space and time at the gating system. For this reason, an extended region of ion formation is avoided in the presently conventional mass spectrometer of this type.

We have now found that it is unnecessary to avoid an extended region of ion formation and that in fact an ion energy spread as produced by a potential across the region of ionization is a form of ordered energy and can be made to form a fine image in space and time by proper adjustment, design and operation of the ion source.

The invention contemplates in a mass spectrometer the combination comprising an evacuable envelope, means for periodically forming ions in the envelope, ion collecting means disposed in the envelope remote from the region of ion formation, the intervening region com-

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prising a drift tube as above described, means for periodically propelling ions from the region of ion formation toward the collector electrode, and means for synchronizing the periods of ion formation and ion propulsion so that these periods are alternate and substantially mutually exclusive in time. Some form of gating is provided either within the drift tube or in association with the collector electrode circuit, in either case to limit the collector electrode to predetermined response periods.

These predetermined periods of collector electrode response are selected such that the collection system including the collector electrode is sensitive only to pulses of ions of a given mass-to-charge ratio. The sensitivity of the collection system may be determined by an actual gating grid system preceding the collector electrode in the spectrometer tube, so operated that only ion pulses of a given mass-to-charge ratio are passed through the gating system. Alternatively, the collection system to which the collector electrode is electrically connected may be actuated only in periods to be responsive to ion pulses of a given mass-to-charge ratio.

In a preferred embodiment of the invention a system is provided whereby the energy of the formed ions can be controllably ordered so as to produce a sharply focused image of ions of a given mass-to-charge ratio at a desired point in the drift tube. In a somewhat simpler embodiment of the invention means are provided which are operable to formation of an image at a fixed distance from the source of ions.

These embodiments of the invention will be clearly understood with reference to the following detailed description thereof as taken in conjunction with the accompanying drawing in which:

Fig. 1 is a schematic diagram in longitudinal section of a preferred form of mass spectrometer in accordance with the invention;

Fig. 2 is an illustration of the wave forms of certain energizing signals developed in the circuit of Fig. 1;

Fig. 3 is an exploded or enlarged schematic reproduction of the electrode array of the ion source of Fig. 1 identifying certain critical dimensions and values of an electric field determinative of the operation of the instrument; and

Fig. 4 is a schematic diagram of a simpler embodiment of the invention.

The mass spectrometer in Fig. 1 comprises an evacuable tube 10 provided with an outlet 11 for connection to an evacuating system (not shown) and an inlet 12 for introduction of a gaseous sample from a sample source (not shown).

An ion source 13 is disposed in one end of the tube 10 and is connected to the inlet 12 for introduction of the sample directly into the ion source. Electrodes 14, 15 and 16 are mounted in the source, the electrodes 15 and 16 being in the form of grids or perforate plates to permit passage of ions therethrough. A conventional electron gun 17, illustrated as an electron emitting filament, is mounted adjacent a wall of the source 13 and positioned to direct electrons through a first aperture 18 in the source wall to traverse the source and pass through a diametrically opposed aperture 19 in the source wall to strike and discharge at an electron target 20. An electron control grid 21 is disposed between the gun 17 and the aperture 18, the grid 21 being operable to control and determine the electron flow from the gun 17.

A collector electrode 22 is mounted at an end of tube 10 opposite the source 13 and is connected to a conventional amplifier 23 which, in turn, may be connected to a conventional sensing or recording system (not shown). A series of closely spaced electrodes 24, 25 and 26 are

arranged serially immediately ahead of the collector electrode 22, these electrodes functioning as a gate to determine ion access to the collector electrode 22.

The invention is not directed or limited to any particular form of gating system. The illustrated "gate" is intended only to represent one operable form. As pointed out above, effective gating may be accomplished in the output circuit of the collector electrode or in control of the sweep voltage in a display cathode ray tube. These are all presently known expedients and are compatible with the invention, controlled operation thereof being achieved in the illustrated manner. In fact, the invention is susceptible of use without any form of gating system, as for example where the entire spectrum is desired to be displayed on a cathode ray tube.

The operation of the tube is controlled by a circuit including a variable frequency oscillator 27, a master pulse generator 28, an electron grid pulse generator 29, a variable phase shift network 30, and a gating pulse generator 31. The variable frequency oscillator 27 feeds into the master pulse generator which generates a pulse of the type shown in curve B in Fig. 2. This pulse is applied directly to electrode 14 in the ion source and through a potentiometer 32 to electrode 15 of the source. As illustrated, the accelerating pulse is applied across the boundary electrodes of the source. Alternatively, the pulse may be applied across electrodes 14 and 15 with electrode 16 being held at a uniform negative potential with respect to electrode 15. The master or accelerating pulse is also fed to the electrode grid pulse generator 29 which develops a pulse as illustrated in curve A of Fig. 2 and feeds this pulse to the electron control grid 21.

A signal from the oscillator is also applied to the variable phase shift network 30, the output of which triggers the gating pulse generator 31. This develops a pulse as shown in curve C of Fig. 2 which is delayed with respect to the accelerating pulse as a function of the setting of the phase shift network. This gating pulse is impressed on electrode 25 of the ion gate. The delay in impressing the gating pulse on electrode 25 relative to the application of the accelerating pulse to electrodes 14 and 15 in the ion source is shown in Fig. 2 as relative to curves B and C thereof. Electrode 25 is biased positively by battery 33 so that positive ions are blocked except when the gating pulse is applied to drive the electrode negative with respect to its bias potential.

The operation of the instrument of Fig. 1 is as follows: Ions are formed by the electron beam between electrodes 14 and 15. Ion formation by means of an electron beam is quite common, although the instrument of the present invention is not limited to this manner of ion formation. For example, if it is desired to analyze a solid sample, the electron gun 17 may be replaced by an emitter of the sample whereby emitted ions will be directed under the influence of grid 21 into the region wherein ionization takes place in the illustrated instrument.

A voltage pulse derived from the master pulse generator 28 is applied to electrode 14 and in the proportion of the setting of potentiometer 32 to the grid 15 and with respect to the grid 16 and the drift tube. This pulse directs the ions into the drift tube and remains on until the heaviest mass ion in the system has cleared grid 16 and then remains off until the heaviest mass ion has been collected at the collector electrode or eliminated at the gating system. During the period of pulse application to the electrodes 14, 15, in which period ions are propelled from the ionizing region into the drift tube, the electron control grid 21 is pulsed to an off or blocking condition, whereby no electrons are admitted into the ion source. In other words, ions are not formed during the period of propulsion and conversely there is no propulsion field during at least the major portion of the period of ion formation.

Repetitive pulsing of the source in this manner causes the ions to leave the source in bunches which, at a given

time thereafter, will be separated in space as to mass-to-charge ratio. During the time the voltage pulse is off, ions of the following bunch are formed. The formed ions remain in the region of formation pending an accelerating pulse and under the influence of the negative space charge of the electron beam. During the time the accelerating voltage pulse is on, the means of formation of ions must be removed or turned off as described above in order that ions will not be formed which are unrelated to the aggregate subjected to the propulsive pulse.

Due to the presence of a source of ions of appreciable thickness as indicated by the width of the illustrated electron beam, the formed ions will have a considerable spread in voltage if the field between electrodes 14 and 15 is appreciable during the voltage pulse. Ions which originate within the boundaries of the electron beam most closely adjacent electrode 14 will fall through a greater voltage than ions originating adjacent the boundary of the electron beam most closely proximate to the grid 15, and as a consequence can be made to overcome, after a specified time of travel, this difference in point of origin. By this means a clear image of the ions of any given mass may be formed at some point in the drift tube at a given time, the point being a function of the magnitude of the field existing between electrodes 14 and 15 of the source.

The ions thus formed into spatially separated clearly defined bunches may be discriminated by providing suitable gating at or adjacent the collector electrode. In the illustrated embodiment the gating is accomplished by electrodes 24, 25 and 26, a pulse being applied to electrode 25 as indicated in curve C of Fig. 2 so synchronized with the pulsation of the source as to pass only ions of a given mass-to-charge ratio from each burst of ions issuing from the ion source. The timing of the gating function is accomplished in the phase shift network 30 and may be selected in relation to the potentials applied to the ion source and the periodicity thereof to select the desired ion mass to be passed to the collector electrode.

Fig. 3 shows an exploded view of the electrode array of the ion source of Fig. 1 enlarged to permit application of indicia of dimension thereon. From this figure the following discussion is developed.

It can be shown that the approximate equation relating the dimension and fields of the ion source with the distance in the drift tube required for focusing, is as follows:

$$X_3 = 2 \left(X_0 + \frac{X_2}{a} \right) \left((1-a) \sqrt{1 + \frac{X_2}{ax_0}} + a \right) \quad (1)$$

where:

X_3 = distance from grid 16 to point of focus (cm.),

X_0 = distance from grid 15 to central region of ion formation (cm.),

X_2 = spacing grid 15 to grid 16 (cm.),

$$a = \frac{E_1}{E_2}$$

E_1 = field existing between electrode 14 and grid 15 (volts/cm.),

E_2 = field existing between grid 15 and grid 16 (volts/cm.).

Fields are in such a direction as to propel ions into the drift tube and are assumed constant during the application of the voltage pulse. This assumption is made to facilitate mathematical explanation. However, in practice, it may be desirable to vary the configuration of the accelerating pulse to meet particular requirements.

It can also be shown that under a given set of imposed conditions, the time (t) in seconds required for an ion to reach the gate is proportional to the one-half power of the mass-to-charge ratio:

$$t = K \sqrt{(m/q)} \text{ sec.} \quad (2)$$

K is dependent upon the geometry and field strengths involved and need not be a fixed quantity for successful operation of the instrument.

Thus, if the measuring device is made sensitive for a short period at a time:

$$ta = K\sqrt{(m/q)a} \quad (3)$$

After application of the voltage pulse the ion of desired mass-to-charge ratio $(m/q)a$ will be measured, and undesired mass-to-charge ratios having been rejected by or not yet approached the gate will not be measured.

In order to avoid harmonics, the period τ between voltage pulses should be sufficiently long that the heaviest ion of appreciable abundance has been or is about to be collected. The frequency of operation may be greater than $1/\tau$ with the attendant possibility of measuring ions of undesired mass-to-charge ratio.

Fig. 4 shows in diagrammatic form an alternative electrode array and circuit arrangement wherein common elements of the apparatus, such as the evacuable tube and the like, have been omitted from the drawing. The instrument of Fig. 4 comprises electrodes 40 and 41 defining the boundaries of an ion source wherein ionization may be accomplished by an electron beam outlined in section at 42. The electron beam may be formed by a gun, controlled by a control grid and trapped by an electron target, all in the manner as shown in detail in Fig. 1. A series of electrodes 43, 44, 45 are positioned ahead of a collector electrode 46, the space between the electrodes 41 and 43 defining a drift space. Electrode 46 is connected to an amplification and sensing system in a conventional manner.

As in the embodiment of Fig. 1 the circuit of Fig. 4 includes a variable frequency oscillator 47, a master pulse generator 48 which is connected to electrode 40 and through a suitable resistor 49 to electrode 41. An electron grid pulse generator 50 is connected to the master pulse generator and feeds a controlling pulse to the electron control grid (not shown) which functions in the manner of the grid 21 of Fig. 1. A gating pulse generator 51 is connected to the oscillator through a variable phase shift network 52, the output of the gating pulse generator being impressed on the gating electrode 44.

The apparatus of Fig. 4 differs from that of Fig. 1 in the elimination of one of the field-forming electrodes in the Fig. 1 apparatus. The result of this lesser number of electrodes is that the instrument of Fig. 4 is in essence what may be considered a fixed focus instrument; that is, the point of formation of the crystallized image of the several ion masses is fixed in space with respect to electrode 41 so that the geometry of the system must be carefully controlled to place the gating network at such fixed distance from the electrode 41. In contrast, the instrument of Fig. 1 is controllable to the extent that the point of desired image formation with respect to spatial departure from the ion source may be selected by suitable control of the various operating parameters as demonstrated by the foregoing mathematical formulae.

The circuit elements associated with the illustrated spectrometer tubes are all conventional in themselves and, apart from their combination in the illustrated manner to function as described, do not represent a part of this invention. Therefore, any detailed illustration or description of the various elements such as the pulse generators, oscillators, phase shift network and the like is not required for an understanding of the invention.

The invention has been described with relation to two specifically illustrated embodiments wherein it has been necessary to show determinative potential relationships between the various portions thereof. However, it should be mentioned that reference potential need not be ground as illustrated specifically in Fig. 1, and if it becomes desirable to otherwise fix the potential of the drift tube or

other elements of the device, which are illustrated as being at a fixed potential, such can be done without departing from the scope of the invention. These elements that are illustrated at ground potential in the drawing are so illustrated merely to indicate that they are at a fixed potential differing in the relation described from the potentials of the other portions of the apparatus.

Also, as described and illustrated, a constant field is placed across the ion source in pulses, this illustrating one acceptable and convenient mode of operation. However, to increase the duty cycle of the device, and this is particularly true with respect to the simplified embodiment of Fig. 4, it may be desirable to vary the propulsion field during each pulse from one value at the beginning of the pulse to a higher value at the end of the pulse. Such variation has the effect of accelerating the delineation of the ion masses whereby the time interval between propulsion and collection may be reduced and the repetition rate of ion formation and ion propulsion may be increased. Such variation in the propulsion field may be accomplished without alteration of the apparatus as illustrated by simple and obvious selection of the character of the pulse generating means.

We claim:

1. In a mass spectrometer the combination comprising an evacuable envelope, means for periodically developing ions within a restricted region of the envelope, a plurality of electrodes disposed adjacent the restricted region of the envelope and arranged on opposite sides of such region, means for applying a potential pulse to the electrodes on opposite sides of the region of ionization for periodically propelling ions from said region, means for causing such pulse to increase in magnitude between the initiation and extinguishment of the pulse, means controlling the application of said propelling pulse so that periods of ion formation and ion propulsion are alternate and substantially mutually exclusive in time, an ion collector electrode disposed in the envelope remote from the region of ion formation and oriented along the line of ion propulsion from the region of formation, means connected to the collector electrode for sensing ion discharge thereon, and means for limiting to a predetermined ion mass the sensibility of the sensing means.
2. In a mass spectrometer the combination comprising an evacuable envelope, means for periodically developing ions within a restricted region of the envelope, a plurality of electrodes disposed adjacent the restricted region of the envelope and arranged on opposite sides of such region, means for applying a potential pulse to the electrodes on opposite sides of the region of ionization for periodically propelling ions from said region, means for causing such pulse to increase in magnitude between the initiation and extinguishment of the pulse, means controlling the application of said propelling pulse so that periods of ion formation and ion propulsion are alternate and substantially mutually exclusive in time, an ion collector disposed in the envelope remote from the region of ion formation and oriented along the line of ion propulsion from the region of formation, means connected to the collector electrode for sensing ion discharge thereon, at least one electrode grid disposed adjacent the collecting face of the collector electrode, and means for applying a pulsed potential to the electrode grid in matched periods with relation to the periods of ion propulsion to pass to the collector electrode only ions of a given mass-to-charge ratio.

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