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DYNAMIC MASS SPECTROMETER WHEREIN IONS ARE PERIODICALLY OSCILLATED UNTIL SELECTIVELY ACCELERATED TO A DETECTOR

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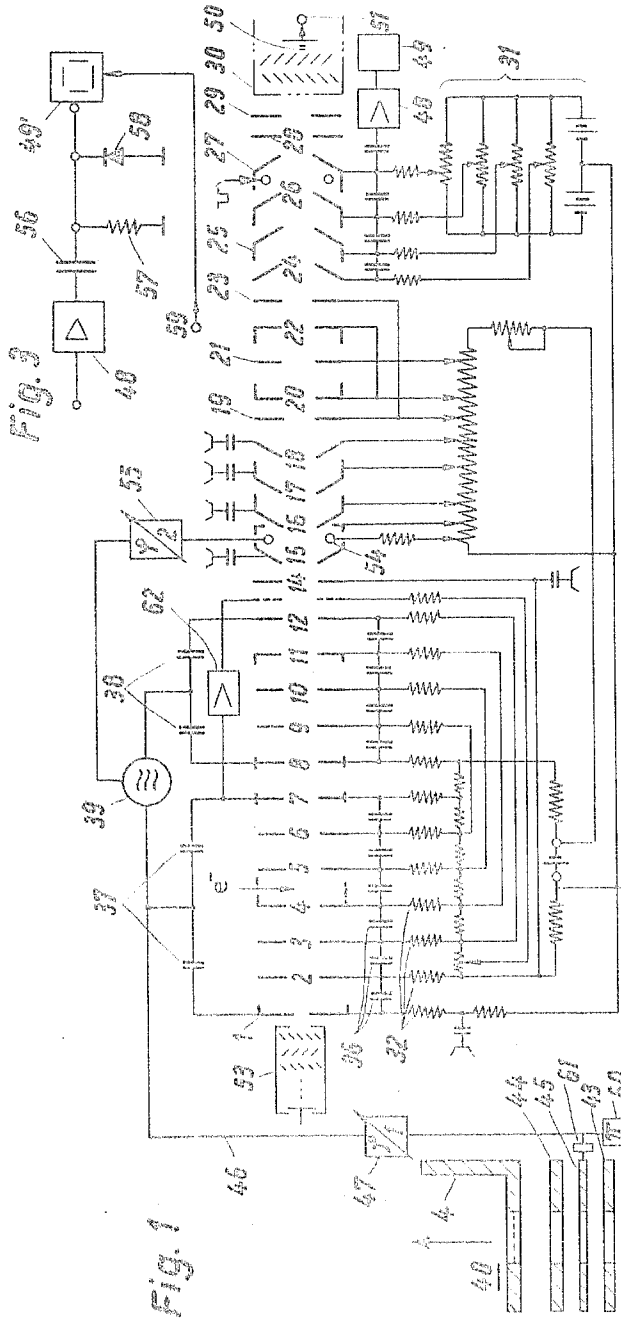


Fig. 1

Fig. 3

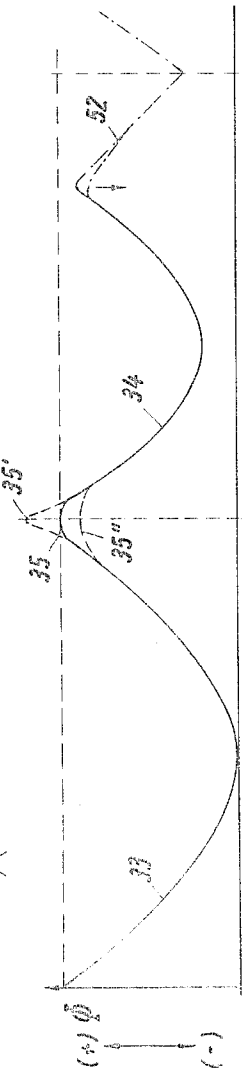


Fig. 2

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DYNAMIC MASS SPECTROMETER WHEREIN IONS ARE PERIODICALLY OSCILLATED UNTIL SELECTIVELY ACCELERATED TO A DETECTOR

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13 Claims. (Cl. 250—41.9)

The invention relates to a dynamic mass spectrometer, in which ions are selectively accelerated by high frequency voltage while executing approximately periodic oscillations in a potential trough.

In a known mass spectrometer of this type ions are produced approximately at minimum potential point of a parabolically shaped potential trough by means of an electron beam and then ions having a specific ratio of charge e to mass m are selectively accelerated by a high frequency voltage, when the frequency of oscillation of the ions in the parabolic potential coincides with the frequency of the applied high frequency voltage. The accelerated ions finally reach a collector. Indication results from measurement of the collector current (U.S. Patent 2,570,158) Journal of Applied Physics, 22, 680, 1951.

Another mass spectrometer has been proposed in which ions are periodically produced beyond the minimum of a parabolic potential trough. When the frequency at which the ions are produced coincides with the frequency of oscillation of a specific type of ion (specific e/m ratio) at the parabolic potential, in-phase accumulation of such ions results. The oscillating charge cloud thus produced can then be detected by means of a collector electrode or secondary electron multiplier (Zeitschrift f. angew. Physik, 11, 395, 1959).

In the following description ions of a specific e/m ratio which are selectively accelerated or accumulated will be referred to as "resonant ions" for the sake of brevity.

However, it has been discovered that the resolving power of the mass spectrometers described above is reduced because the A.C. fields employed for acceleration or accumulation, not only affect the resonant ions but also the homogeneous background of asynchronously oscillating ions of different sort. The ion background is thus modulated so that in the detection device, for instance an electrostatic collector electrode or a secondary electron multiplier, in addition to the signal produced by the resonant ions, a signal is produced which results from the modulation of the inherently continuous background or ion space charge. The amplitude of the background signal can quite easily attain the same order of magnitude as the signal emanating from the resonant ions and in extreme cases can even exceed this.

With known arrangements of this sort, a further adverse effect is exerted upon the resolving power thanks to the fact that the resonant ions must continuously oscillate within the space charge cloud forming the background and comprised of asynchronously oscillating ions of different sort. It is not difficult to visualize that the interaction between the different sorts of ions on the one hand

introduce scatter in the accumulated resonant ions and on the other brings about a certain degree of phase-focusing of other ions not in resonance although the object is to achieve the highest possible degree of phase separation.

Therefore, it is an object of the invention to reduce the above mentioned disturbing effects, i.e., the adverse influence of the space charge formed by the ions which are not in resonance, the spurious signals originating from a modulation of the continuous ion background, the scattering of the accumulated resonant ions, and the undesired phase-focusing of ions of different e/m ratios.

A further object of the invention is to provide an improved mass spectrometer which employs exclusively electric fields and which is physically small, compact and inexpensive.

Still a further object of the invention is to provide an improved mass spectrometer which is especially suitable for leak detection.

A mass spectrometer according to the present invention comprises a vacuum-tight elongated envelope; means for introducing a gas or vapor to be analyzed into said envelope; an ion source, an output electrode and a number of spaced electrodes having coaxial apertures in said envelope; means for applying inidividual potentials to each of said electrodes for producing during operation along an axis of said apertures a potential distribution which exhibits along said axis in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential, and a third point of relatively positive potential, said potentials being adjusted in such a manner that ions of a given e/m ratio exhibiting like oscillation frequencies when oscillating between the first and second points of relatively positive potential and between the second and third points of relatively positive potential. The ion source is provided between said first and second points of relatively positive potential and said output electrode, which is part of a ion detection arrangement, e.g., an electron multiplier, is arranged along said axis beyond said second point of relatively positive potential if seen from said ion source. The potential distribution thus comprises two adjacent potential sinks and preferably has at least approximately the form of two adjacent parabolas. The mass spectrometer further comprises means for periodically transferring ions of a specific e/m ratio which are generated by the ions source in the first potential sink simultaneously with ions of other e/m ratios over said second point of relatively positive potential into said second potential sink where they are exclusively accumulated and detected.

In a specific embodiment of this invention ions are produced at a point in the first potential sink, which latter is preferably of parabolic form, which is at a lower potential than the maximum potential between the two sinks. Ions of a specific e/m ratio are then continuously supplied with energy from a high frequency field and ultimately pass via the intervening maximum at the second point of positive potential to the second potential sink, in a manner which will be described later. This second potential sink, in which no A.C. field exists is likewise preferably shaped parabolically with the exception solely of a small region adjoining the intervening maximum. The sink is so dimensioned that the ions oscillate in it with the same frequency as in the first sink

which selection takes place. The ions periodically transferred to the second potential sink accumulate in known fashion but this is not, however, accompanied by the production of ions of different sort (which would be oscillating asynchronously in the same potential sink) in the manner described above for the second type of known mass spectrometer. The accumulated ions of one single sort can then be detected in known fashion, e.g., by means of a electrostatic collector or a secondary electron multiplier.

The invention will now be explained in more detail making reference to a non-limitative exemplary embodiment in conjunction with the drawing.

FIGURE 1 shows a schematic representation of a mass spectrometer tube and some associated circuitry, in accordance with the invention;

FIGURE 2 shows a diagram of the potential distribution along the axis of the spectrometer tube illustrated in FIGURE 1, on the same scale as FIGURE 1;

FIGURE 3 shows a preferred circuit arrangement for processing the output signal from the mass spectrometer tube illustrated in FIGURE 1.

The arrangement illustrated in FIGURE 1 comprises a number of coaxially situated spaced electrodes **1** to **30**, usually of disk or cup-like form, these being contained in a vacuum vessel (not shown for reasons of clarity) connected to a suitable vacuum system. For some part, the electrodes perform several functions.

The electrodes **1** to **30** have suitable connections passing from them outside the vacuum vessel and there connected to a voltage divider and potential supply arrangement, this in its entirety carrying the reference **31**. Some of the electrodes are connected to this voltage divider arrangement via isolating resistance **32**. Details will be evident from the drawing and from the explanation of FIGURE 2.

The electrodes **1** to **15** inclusive serve to produce a first potential sink **33** (FIGURE 2) along the axis of said electrodes, this sink preferably having a parabolic form. As will be well known to those skilled in the art, the frequency of oscillation of oscillating charge carriers is independent of amplitude where a parabolic potential exists. The electrodes **15** to **27** inclusive serve to produce a second potential sink which preferably substantially has the form of a parabola. More or less at the position of the electrode **15**, the potential distribution along the axis of the tube access has an intervening positive going maximum **35**.

The electrodes **1** to **7** inclusive and the electrodes **8** to **12** inclusive are connected together in A.C. fashion, to form two groups, by means of capacitors **36**. Each group is connected via capacitors **37** or **38** to the corresponding output terminals of an oscillator **39** which supplies antiphase high frequency voltages to the two electrode groups.

In the region of the part of the potential sink **33** facing away from the potential sink **34**, there is situated an arrangement for the production of ions which is indicated near the electrode **4** in purely schematic fashion by an arrow e^-. Preferably the device for the production of ions is constituted by an electron gun **40**, shown enlarged in FIGURE 1 and rotated through 180°, which produces an electron beam running perpendicularly to the tube access. The electron gun is constructed in the usual manner and contains a filament cathode **41**, a Wehnelt electrode **42**, a first accelerating electrode **43**, and a second accelerating electrode **44** which is followed by the electrode **4**. Between the first and second accelerating electrodes **43** and **44**, in accordance with the invention a further compensating electrode **45** is placed and this will be described later.

The control electrode **42** has applied to it during operation, an A.C. voltage of the same frequency as the accelerating voltage, e.g., by a line **46**. The voltage applied to the control electrode **42** preferably takes the form of a series of very sharp positive pulses and is so adjusted by means of a phase-shifting circuit **47** that the beam is injected when the resonant ions oscillate through the field of influence of the beam in the direction towards the potential minimum along the tube axis.

At the end of the potential sink **34** facing away from the intervening maximum **35**, there is situated an arrangement for the detection of ions oscillating in said second potential sink **34**. To this end the electrodes **24** to **27** for example can form an electrostatic collector arrangement and be interconnected by means of capacitors and further connected to a detection arrangement. The detection arrangement can contain an amplifier **48** and a display device **49**; the preferred embodiment will be discussed later in conjunction with FIGURE 3.

On the other hand, detection can be done by means of a secondary electron multiplier arranged after the last electrode **27** of the electrodes used for establishing the above described potential distribution along the axis of the electrode system. The ions oscillating beyond the electrode **27** are preferably accelerated by the application of increasingly more negative voltages to the electrodes **28**, **29**, **30**. The electrode **30** at the same time constitutes the input electrode of a multiplier arrangement **50** shown in schematic fashion only, at whose anode **51** the output signal can be picked up. The potential beyond the electrode **27** follows approximately the course indicated in FIGURE 2 by the chain dotted line **52**.

The arrangement thus far described works in the following manner:

In the first potential sink **33**, the ion source **40** preferably, but not essentially, produces ions in phase with the high frequency at a location at which a more negative potential obtains than at the location of the intervening maximum **35**. The ions of different charge/mass ratios then oscillate in the potential sink **33** with frequencies which are dependent upon this ratio. Ions whose frequency of oscillation coincides with the frequency of the voltage applied between the two electrode groups **1** to **7** and **8** to **12**, continuously accumulate energy on oscillations through the acceleration slot formed by the electrodes **7**, **8** and therefore oscillate with increasing amplitude while ions of other sorts on average extract but negligible energy from the high frequency field. Preferably, the voltage used for acceleration is not a sinusoidal one but rather a voltage having a pulse form with a relatively low mark-space ratio in order further to improve selection. The ions are preferably likewise produced in phase with the high frequency, in short-period fashion (e.g., during an interval of 0.1 microsecond), during the oscillation of the group of resonant ions through the intersection point between electron beam direction and tube axis in the direction towards the minimum point of the potential sink **33**.

In accordance with the invention, the resonant ions are separated from the other ions forming the space charge background, by selective transfer of the resonant ions to the second potential sink **34**. To do this, they must surmount the intervening maximum **35**.

In order for ions to be able to pass from the first potential sink **33** to the second potential sink **34**, the potential at the intervening maximum **35** must at least temporarily be made equal to or less than the potential at the lectrode **1**.

If the potential at the maximum **35** is equivalent to the potential at the electrode **1**, half the resonant ions pass over the intervening maximum **35** into the second potential sink **34** after appropriate acceleration, while the other half are either absorbed by the electrode **1**, where this is of imperforate construction, or, where the electrode **1** is of the apertured type, passed into a supplementary multiplier **53** which may be optionally arranged behind it and there detected.

The other possibility consists in the intervening maximum generally having a value 35' as illustrated by the dashed line and only temporarily being reduced, preferably synchronously with the accelerating voltage, to a value equivalent to the potential at the electrode 1 or preferably less than this as indicated by the dashed curve 35''. The reduction of the potential of the intervening maximum can be brought about by a ring electrode 54 situated inside the electrode 15 which produces the maximum and which is by-passed for A.C. voltages by a condensor, which ring electrode 54 is fed with a suitably phased voltage synchronised with the voltage of the high frequency generator 39. The phase shift can be brought about by means of a phase-shift circuit 55 and amounts to about 90° with respect to the accelerating voltage applied to the two electrode groups. It is not necessary to reduce the potential of the intervening maximum 35 for each cycle of the high frequency voltage, instead this being done at some submultiple of the accelerating frequency.

In order to prevent the separated ions oscillating in the potential sink 34 from returning to the first potential sink 33, such an amount of energy is extracted from the resonant ions on transfer into the second potential sink 34 that they are no longer able to oscillate quite up to the potential value which they have just exceeded. This braking action on the resonant ions is produced in the following manner:

The potential maximum 35 has at the instant of ion transfer a flat peak of finite width. This form results from interaction between the D.C. and A.C. potentials at the ring electrode 54 and the D.C. potential at the apertured electrode 15 to the left thereof. The ions pass with low velocity only from the potential sink 33 over the flat intervening maximum 35 into the second sink 34. The width of the intervening maximum over which the ions slowly pass is largely dependent upon the A.C. voltage at the electrode 54. If the A.C. voltage falls while the ions are passing across the flat intervening maximum into the sink 34, they lose energy and as a consequence can no longer exceed the intervening maximum in the return part of the oscillation. They remain in the right hand potential sink and are continuously decelerated by the non-parabolic potential region adjoining the maximum until they have finally left the field of influence of the ring 54. This takes place at a specific amplitude of oscillation and at this amplitude, the resonant ions are accumulated in the right hand potential sink. Alternatively, the potential distribution at the point of relatively positive maximum between the sink 34 and the accelerating shape 52 may have such a form (i.e., sub-linear potential) that ions entering said region are decelerated by amounts which are substantially proportional to the amplitude of oscillation.

The staggered electrostatic collector electrodes 24 to 27 must naturally be so arranged and biased that they can fully receive the signal produced by the oscillating ions. The same applies to the multiplier arrangement. In this latter, the potential threshold between the trough 34 and the input electrode of the multiplier can either be maintained at a potential which the accumulated ions can still exceed of preferably the height of the potential threshold is periodically reduced, after a specific accumulation time, so that the accumulated ions can "run out" into the multiplier. This can be done by means of the electrode 27' which is comparable in circuitry and function with the electrode 54.

To plot a mass spectrogram, the frequency of the oscillator 39 is made to pass through the desired range. In this way, the resonant ions are caused to collect in the second potential trough 34 and can be detected by the detection arrangement. The amplitude of the signal appearing at the inductive collector or at the anode of the multiplier (which is normally about on ground potential), corresponds to the proportion of the type of ion whose frequency of oscillation is in resonance with the instantaneous output frequency of the oscillator 39.

As FIGURE 3 shows, the output signal, possibly after amplification in amplifier 48, is differentiated by a differentiating network comprising a capacitor 56 and a resistance 57, and rectified by a rectifier 58 before being displayed on the screen of an oscilloscope 49'. The time-base of the oscilloscope is synchronised with the frequency of the oscillator 39 via a line 59.

Further improvements in the resolving power can be obtained by the following additional means:

It has been found that the A.C. voltages fed to the beam-producing system 40, and in particular to its control electrode 42, create electric fields in the region of the tube axis, these bringing about defocusing of the cloud of resonant ions by imparting undesirable and unpredictable momentums to the individual ions. This can be avoided by the insertion between the modulating electrode 42 and the region around the tube axis in which the resonant ions are situated at the instant of beam injection, of an additional electrode 45 to which a voltage of such phase is applied that the field produced by this electrode cancels out the disturbing field in the range concerned to the maximum possible extent. The electrodes 42, 45 can be fed with voltages from the same source although between the two electrodes a phase shift element 60 is inserted which is preferably adjustable and which produces a phase shift of approximately 180°. In the line to the compensating electrode 45 an attenuator 61, preferably variable, is also inserted. The acceleration electrodes 43, 44 are preferably bypassed to ground by capacitors.

Similar conditions obtain in the region of the potential maximum 35. Here, disturbances can be introduced as a result of the high frequency accelerating voltage applied to the electrodes 8 to 12. In order to compensate for the influence of this voltage, to the electrode 13 following the last electrode 12 supplied with a R.F. potential a voltage which is at least approximately 180° out of phase with the voltage at the electrode 12 is applied. This can be simply achieved by the insertion between the electrode 13 and the output of the high frequency generator feeding the other electrode group 1 to 7, of a preferably adjustable attenuator 62.

If the highest possible resolving power is required, the accelerating voltage is conveniently chosen small so that the energy increment per accelerating cycle is small. For other applications, for instance that of leak detector, a somewhat higher accelerating voltage is expedient since here in general a low resolving power is acceptable and a high response rate desired. For application as a leak detector and a constant test gas, e.g., helium, a fixed frequency oscillator can be employed.

The line sharpness can also be improved by using D.C. heating for the cathode 41.

The above described embodiments may be varied by those skilled in the art in various respect without departing from the invention. The potential distribution may be produced by a conductive coating applied to an inner surface of an elongated tube-like envelope. Instead of the single source 39 of A.C. energy several individual R.F. or pulse sources may be employed for supplying the respective electrodes, those sources being synchronized. Other kinds of ion sources may be used, e.g., plasma sources or nuclear radiation.

We claim:

1. A mass spectrometer comprising a vacuum-tight envelope; means for introducing a gas or vapor to be analyzed into said envelope; means for producing along an axis in said envelope a substantially uniform D.C. potential distribution having in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential and in the vicinity of which there is only a D.C. potential, and a third point of relatively positive poten-

tial; an ion source for ionizing said gas or vapor in a region between said first and second points of relatively positive potential at a point of said axis on which a potential prevails which is less positive than the potential of said second point of relatively positive potential; means for periodically transferring ions of a specific ratio of charge to mass over said second point of relatively positive potential into a region on said axis between said second and third points of relatively positive potential; means for retarding the transferred ions; and means for detecting the transferred ions.

2. A mass spectrometer comprising a vacuum-tight envelope; means for introducing a gas or vapor to be analyzed into said envelope; a number of spaced electrodes having coaxial apertures in said envelope; a D.C. potential source arrangement for biasing said electrodes to produce along an axis of said apertures a potential distribution having in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential and in the vicinity of which there is only a D.C. potential, and a third point of relatively positive potential; an ion source for ionizing said gas or vapor in a region between said first and second points of relatively positive potential at a point of said axis on which a potential prevails which is less positive than the potential of said second point of relatively positive potential; means for periodically transferring ions of a specific ratio of charge to mass over said second point of relatively positive potential into a region on said axis between said second and third points of relatively positive potential; means for retarding the transferred ions; and means for detecting the transferred ions.

3. A mass spectrometer comprising a vacuum-tight envelope; means for introducing a gas or vapor to be analyzed into said envelope; a number of spaced electrodes having coaxial apertures in said envelope; a D.C. potential source arrangement for biasing said electrodes to produce along an axis of said apertures a potential distribution having in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential and in the vicinity of which there is only a D.C. potential, and a third point of relatively positive potential; an electron gun for producing an electron beam crossing said axis at a point between said first and second points of relatively positive potential, where a potential prevails which is less positive that the potential of said second point of relatively positive potential; means for periodically transferring ions of a specific ratio of charge to mass over said second point of relatively positive potential into a region on said axis between said second and third points of relatively positive potential; and means for detecting the transferred ions.

4. A mass spectrometer comprising a vacuum-tight envelope; means for introducing a gas or vapor to be analyzed into said envelope; a number of spaced electrodes having coaxial apertures in said envelope; a D.C. potential source arrangement for biasing said electrodes to produce along an axis of said apertures a potential distribution having in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential and in the vicinity of which there is only a D.C. potential and a third point of relatively positive potential; an electron gun for producing an electron beam crossing said axis at a point between said first and second points of relatively positive potential, where a potential prevails which is less positive than the potential of said second point of relatively positive potential; a source of high frequency voltage; means for applying said high frequency voltage to at least one electrode but only between said first and second points of relatively positive potential; means for retarding ions transferred from between the first and second to between the second and third points of relatively positive potential; and means for detecting ions which have been accelerated by said high frequency voltage and transferred into the region of said axis between said second and third points of relatively positive potential.

5. A mass spectrometer comprising a vacuum-tight envelope; means for introducing a gas or vapor to be analyzed into said envelope; a number of spaced electrodes having coaxial apertures in said envelope; a D.C. potential source arrangement for biasing said electrodes to produce along an axis of said apertures a potential distribution having in the order named a first point of relatively positive potential, a first point of relatively negative potential, a second point of relatively positive potential, a second point of relatively negative potential and in the vicinity of which there is only a D.C. potential, and a third point of relatively positive potential; an electron gun for producing an electron beam crossing said axis at a point between said first and second points of relatively positive potential, where a potential prevails which is less positive than the potential of said second point of relatively positive potential; a source of high frequency voltage; means for applying said high frequency voltage to at least one electrode and only between said first and second points of relatively positive potential; means for supplying negative pulses to a first electrode which is situated at said second point of relatively positive potential, said pulses being synchronized with said high frequency voltage and occurring when said accelerated ions are approaching said second point of relatively positive potential to transfer them past the last-mentioned point; means for retarding the transferred ions to prevent them from returning by oscillation back to the area between said first and second points of relatively positive potential; a secondary electron multiplier provided adjacent said third point of relatively positive potential at the opposite site thereof as said second point of relatively positive potential; and means for applying negative pulses to a further electrode situated at said third point of relatively positive potential, said pulses occurring periodically when the transferred ions approach said third point of relatively positive potential.

6. Mass spectrometer in accordance with claim 5, characterized in that the source of high frequency voltage furnishes pulses with a mark-space ratio of less than 30° of an operating cycle.

7. A mass spectrometer according to claim 5, characterized in that said first electrode is coupled to said source of high frequency voltage by a phase-shifting network.

8. A mass spectrometer according to claim 7 characterized in that said phase shifting network is adjustable.

9. A mass spectrometer according to claim 8, characterized in that the intensity of one electron beam produced by said gun is modulated with a frequency which is equivalent or a sub-multiple of the oscillation frequency of the ions which are to be transferred over said second point of relatively positive potential.

10. A mass spectrometer according to claim 9 characterized by a pulse source for supplying pulses to an electrode of said gun adapted to modulate the intensity of said electron beam.

11. A mass spectrometer according to claim 10 characterized by means for deriving said pulses from said source of high frequency voltage.

12. Mass spectrometer according to claim 11 characterized by an electrode inserted between the beam modulating electrode and the point at which the ions are produced, which is fed with a voltage approximately 180°

out of phase with the voltage applied to the beam modulating electrode.

13. Mass spectrometer in accordance with claim 12, characterized in that between the electrodes to which a high frequency accelerating voltage is applied and the electrodes producing the region of said potential distribution between said second and third points of relatively positive potential an electrode is provided which during operation has a high frequency voltage applied to it which is substantially 180° out of phase with the high frequency voltage applied to the next adjacent electrode supplied with the high frequency accelerating voltage.

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