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This invention relates to mass spectrometry and, in particular, to novel methods and apparatus for separating ions according to their mass-to-charge ratios.

One form of mass spectrometer apparatus employed heretofore comprises means for accelerating a plurality of ions having heterogeneous mass-to-charge ratios through an electrostatic field into a direct current magnetic field wherein they are separated into a plurality of spatially distributed ion beams, each of which is homogeneous with respect to mass-to-charge ratio. In order to secure desired high resolution with such apparatus, however, it is necessary to employ collimating slits and apertured focusing plates which, while they serve their purpose, tend to restrict the amount of output current which may be obtained from a given ion beam. Accordingly, it is a principal object of the present invention to provide a method and apparatus for separating ions according to their mass-to-charge ratios with which it is unnecessary to arrange beam constricting structure along the ion paths to obtain high resolution.

Another form of mass spectrometer apparatus involves the successive application of a plurality of radio frequency and direct current electric fields whereby separation of ions is accomplished by permitting only ions having a given mass-to-charge ratio to pass completely through the succession of fields. This apparatus, however, is not easily adaptable to the production of high beam currents inasmuch as the ultimate passage of ions through the successive fields depends not only upon the mass-to-charge ratio, but also upon the time of origination of the ions with respect to the phase of the radio frequency field. Therefore, it is another principal object of this invention to provide a mass spectrometer method and apparatus in which the separation of ions having a given mass-to-charge ratio does not depend upon the time of their origination.

According to one important aspect of the invention, which is more fully described hereinafter, ions having heterogeneous mass-to-charge ratios are accelerated by means of an alternating or R. F. electric field against the force of an electrostatic or direct current electric field having a linear space distribution. Thereupon, the ions having a given mass-to-charge ratio, properly correlated with the frequency of the alternating or R. F. field, execute simple harmonic motion to and fro through and in phase with the alternating or R. F. electric field whereby they become separated in space from ions having other mass-to-charge ratios. The ions thus separated are then collected and measured to determine the amount present in the sample being studied.

The features of the invention desired to be protected are set forth in the appended claims. The invention itself, together with further objects and advantages thereof, may best be understood by reference to the following specification taken in connection with the accompanying drawings in which Fig. 1 is a graph illustrating the direct current voltage distribution which obtains in devices constructed in accordance with the present invention; Fig. 2 is a sectional view presenting one embodiment of the invention; Fig. 3 is a sectional view illustrating a second embodiment of the invention; Fig. 4 represents in section a third embodiment of the invention; Fig. 5 is a second graph illustrating direct current voltage distribution pertinent to an explanation of the invention; Fig. 6 is a graph illustrating of operational characteristics pertinent to an adequate explanation of portions of the invention; and Figs. 7 and 8 illustrate in sectional manner respectively fourth and fifth embodiments of the invention.

If it is assumed that a parabolically distributed voltage, as indicated by the solid line in Fig. 1 wherein the voltage V is plotted as a function of distance x, is arranged to have its apex positioned upon the y-axis or median plane, then, since by definition the electrostatic or direct current electric field is the negative of the first derivative with respect to x of the voltage, a linear electrostatic field increasing in both directions from the plane will be created. If it is also assumed that a confined alternating electric or R. F. field is arranged to have a component parallel to the direction of the x-axis at the apex of the voltage or potential distribution curve, ions injected into the alternating or R. F. field will continuously extract energy therefrom, providing the period of oscillation of the ions about the alternating or R. F. field is equal to the period of the field. The requirements of ion mass-to-charge ratio and R. F. field frequency may be derived as follows:

From Newton’s laws of motion,
Since it has been stipulated that $V$ has a parabolic space distribution,

$$ V(x) = \frac{1}{2} K x^2 $$

(2)

where $K$ is a proportionality constant. Differentiating Equation 2 to obtain the first partial derivative with respect to $x$ and substituting in Equation 1, we have

$$ \frac{d^2 x}{dx^2} = -\frac{e}{m} K x $$

Integrating Equation 3, we obtain

$$ x(t) = A \sin \left( \sqrt{\frac{e K t}{m}} + C \right) $$

where $A$ and $C$ are constants.

But it has been specified that, to obtain continuous acceleration of the ions to and fro through the R. F. field, the period of the ions, $T$, must be equal to the period of the R. F. field, $T_{nr}$, therefore, from Equation 4, we may state

$$ T = 2\pi \sqrt{\frac{m}{e K}} T_{nr} $$

And from Equation 5, it follows that

$$ f = \frac{e}{4 \pi^2 f^2} $$

where $f$ is the frequency of the R. F. or alternating electric field.

From the above analysis, culminating in Equation 6, it may be seen that the mass-to-charge ratio of the ions which receive continuous acceleration by the R. F. electric field is a function of the frequency of the R. F. field alone. Thus, ions having a given mass-to-charge ratio, or resonant ions, are accelerated in simple harmonic motion by the R. F. field until they have sufficient energy to overcome the opposing force of the electrostatic field. Despite the fact that the resonant ions travel different distances from the median plane up the potential "bowl" each time they traverse the R. F. field, they always have the same period and remain in phase with the R. F. field. Non-resonant ions of other mass-to-charge ratios will also have a constant period, but their period will not be equal to the period of the R. F. field. Hence, non-resonant ions will fall to remain in phase with the R. F. field where their acceleration will be limited in space.

Referring now to Fig. 2, there is shown in cross-section a mass spectrometer according to the invention which comprises an evauable envelope 10 having re-entrant seal portions 11 and 12 disposed respectively at opposite ends thereof. Opposed cup-shaped collector electrodes 13 and 14 are supported within envelope 10 by means of rigid leads 15 and 16 hermetically introduced through seal portions 11 and 12 respectively.

Along the median plane, indicated by the broken line 17, there is positioned a source of electrons 18 which may comprise a thermionically emissive filament 19, supported by conductive leads 20 and 21 hermetically introduced through a sealing boss 22 suitably located upon the periphery of envelope 16. To supply heating current for the production of electrons from filament 19, a source of direct current, indicated conventionally by battery 23, may be connected between leads 20 and 21. A hollow cylindrical shield 24 of metallic material may be supported upon lead 20 to partially enclose filament 19, as indicated, for the purpose of reducing the amount of light transmitted into the mass spectrometer apparatus wherein undesirable photoelectric effects may be created. Electrons emanating from heated filament 19 are accelerated, as indicated by the dotted lines 25, through an aperture 26 within an annular member which may be termed an electron trap. Trap 27 is supported by means of a rigid conductive lead 28, hermetically introduced through sealing boss 22 and connected as shown to a source of direct current 29 whereby accelerating potential is applied between trap 27 and filament 18.

To produce an R. F. or alternating electric field having a component parallel to the common axis of collector electrodes 13 and 14, there are provided opposed, cup-shaped, annular electrodes 30 and 31 having apertures 32 and 33 positioned respectively therein. Electrodes 30 and 31 are supported respectively by means of rigid conductive leads 34 and 35 between which is connected the secondary winding 36 of a transformer 37. Alternating or R. F. voltage may be supplied to electrodes 30 and 31 through transformer 37 by means of an oscillator 38 connected to the primary winding 39 of transformer 37. Oscillator 38 preferably has a variable frequency output, the reason for which will be more fully appreciated in the light of the following discussion. An electrostatic or direct current electric field may be produced between collector electrodes 13 and 14 by means of a plurality of annular grading rings 40-43 and 44-47. All the grading rings 40-47, along with electrodes 30 and 31, may be insulatingly supported in coaxial alignment by means of spacer members 40 and may be positioned as a unit within envelope 10 by means of bolts 48, spring fingers 50 and nuts 51. Direct current potential may be applied to the grading rings 40-47 and electrodes 30 and 31, which are interconnected by resistors 52-55, by means of a rigid conductive lead 56, hermetically introduced through sealing boss 22 and connected to the positive terminal of a source of direct current voltage indicated conventionally by battery 61. The negative terminal of battery 61 is connected, as shown, to the center tap 62 upon secondary winding 36 of transformer 37, which will now be appreciated, resistors 52-55 and 56-59 constitute potential dividers which, if the resistances have the proper values, will provide a parabolic voltage distribution increasing positively in both directions from median plane 17 between terminal grading rings 43 and 47. Terminal grading rings 43 and 47 are interconnected by lead 63 to assure that the extremities of the parabolically distributed voltage are at the same potential.

In the operation of the device of Fig. 2, if it is assumed that envelope 10 has been evacuated through a pump lead 64 and a suitable gas sample or ionizable medium introduced therein in a manner well known to those skilled in the art, it will be realized that a plurality of ions are formed by impact when electrons, emanating from filament 19 and traveling within 17, strike the gas molecules. The ions thus generated are accelerated to the left or to the right from the median plane, indicated by line 17, depending upon whether electrodes 30 and 31 are respectively positive and negative or vice versa at the time of their generation. The ions move according to the impetus of the kinetic energy imparted to them by the R. F. field toward either collector electrode 13 or 14 against the force of the linear electrostatic field heretofore mentioned until all their kinetic energy has been transformed into potential energy, whereupon they come to rest.
and travel in the opposite direction under the impetus of the electrostatic field. If, however, a particular ion has a mass-to-charge ratio such that the above-stated Equation 6 is satisfied, it will execute simple harmonic motion and arrive back in the region of influence of the R. F. field exactly one-half cycle later when the polarity of the R. F. field has reversed. Consequently, such an ion will receive an additional increment of kinetic energy from the R. F. field in the opposite direction and travels even further toward the opposite collector electrode against the force of the electrostatic field. This process, with the particular resonant ion executing simple harmonic motion and from the R. F. field and remaining in phase therewith, continues until the ion has extracted enough energy from the R. F. field to overcome the potential barrier of the electrostatic field.

When the ions having the correct or resonant mass as above described receive enough energy from the R. F. field to overcome the force of the opposing linearly distributed electrostatic field, they emerge from the aperture in terminal grading ring 43 or 47, as the case may be, with substantially zero kinetic energy or velocity and impact, conventionally represented by a battery 71. Collector electrodes 13 and 14 are connected in parallel such that the total ion current thus generated flows through resistor 65 to the ground connection indicated at 69. The voltage generated by the ion current flowing through resistor 65 may be supplied to an amplifier 66 and hence to a recorder 67 whereby a permanent record of the concentration of such ions may be obtained. To insure that ions emerging from either terminal grading ring 43 or 47 reach the respective collector electrodes, a small negative potential may be provided therebetween, as is indicated by the connection of battery 68 in circuit with resistor 65.

In some instances it may be found desirable to discourage premature impingement of ions upon the various electrodes comprising the device of the invention. Consequently, solenoidal windings 69 and 70 may be positioned about envelope 19 to provide a paraxial magnetic field which tends to retain the ions along the axis of the device. Windings 69 and 70 may be connected in series, as shown, and energized by a source of direct current conventionally represented by a battery 71.

Ions having mass-to-charge ratios other than that which satisfies Equation 6 do not remain in phase with the R. F. field; consequently they never receive enough energy therefrom to overcome the force of the opposing electrostatic field and to reach one of the collector electrodes. However, more general expression of the relationship stated in Equation 6 is

$$\frac{m}{e} = \frac{nK}{4\pi f^2}$$

where \( n \) is an odd integer. This means that, in addition to the ions having the fundamental mass-to-charge ratio (where \( n = 1 \)), ions having harmonics of the fundamental

$$\left( \frac{9m}{25m}, \frac{25m}{e}, \frac{e}{e}, \text{etc.} \right)$$

will be resonant or will be continuously in phase with the R. F. field and receive energy therefrom during each traversal thereof. Upon first consideration, this appears to be a disadvantage but, as a practical matter, such harmonics are very seldom found coincidentally, particularly where ions having mass-to-charge ratios of the order of 100 are concerned.

From the above relations, the resolution of the device illustrated in Fig. 2 may be shown to be given by the following relation.

$$R = \frac{m}{de} \approx \frac{2}{2} V E$$

(8)

where \( E \) is the peak of value of the R. F. voltage of oscillator 38. If the voltage of battery 61 is selected at 1000 volts, the peak voltage of oscillator 38 chosen to be 1 volt, the frequency of oscillator 38 set at 0.07 megacycle, and the device constructed such that the distance between terminal grading rings 43 and 47 is 30 centimeters; then ions having an atomic mass number of about 100 will be collected upon collectors 13 and 14.

In such event the resolution, as defined in Equation 6, is of the order of 1600.

With particular reference now to Fig. 3, wherein numerals used hereinbefore are utilized to designate like elements, there is shown an embodiment of the invention in which the aforementioned electrostatic or direct current electric field having a linear space distribution may be obtained without the use of grading rings. As illustrated, opposed between electrodes 75 and 76 serve as collector electrodes and also as means of establishing the desired linearly distributed electrostatic field. Electrode 75 is supported by a stud 78 sealed into envelope 16 while electrode 76 is supported by lead 66 as shown. It may be proved that, if electrodes 75 and 78 have bent surfaces which correspond in shape to that of hyperboloids of revolution, then with the indicated exterior circuit connections the desired parabolically distributed voltage or linearly distributed electrostatic field will exist between the electrodes. Consequently, if it is so desired, electrodes 75 and 76, shaped as hyperboloids of revolution, may be employed to replace the plurality of grading rings and interconnecting resistors illustrated in Fig. 2. It should be observed, however, that the collimating solenoids 69 and 70 are more nearly essential when electrodes 75 and 76 are utilized, because vertical components of the electrostatic field, existing between the electrodes except along the axis thereof, tend to withdraw the ions from the field.

Referring now to Fig. 4 wherein parts corresponding to those shown in Fig. 2 are designated by like numerals, there is shown a modification of the invention in which the R. F. or alternating electric field, rather than being generated along the median plane 17 between collector electrodes 13 and 14, is generated in series with the electrostatic or direct current electric field existing between terminal grading rings 43 and 47. As shown, the secondary winding 38 of transformer 37, to which oscillator 38 is connected, is now connected through battery 68 to the positive terminal of battery 61 whereby the potentials of the voltage dividers comprising resistors 52—59 vary in accordance with the alternating or R. F. voltage of oscillator 38. To assure maintenance of the linear electrostatic field distribution adjacent median plane 17 with these altered connections, electrodes 30 and 31 are connected together by means of shorting bar 32 and electrode 31 is joined with lead 35 through resistor 81.

An understanding of the effect of the modification illustrated in Fig. 4 may be obtained from Fig. 5 wherein Fig. 1 is duplicated. Added curves 82 and 83 illustrate the voltage distribution be-
tween terminal grading rings 43 and 47 at two separate instants of time when the R. F. field supplied by oscillator 38 is other than zero. Curve 1 of course, represents the voltage distribution when the R. F. field is zero. Therefore, it may be considered that the R. F. voltage generated by oscillator 38 modulates the direct current voltage between terminal grading rings 43 and 47 or, in other words, that it alters the rate of change of slope of the parabolically-shaped voltage distribution and, hence, the value of the electrostatic field.

If the voltage $v$ of oscillator 38 in the modification shown in Fig. 4 is defined as

$$v = -E \cos (wt + \phi)$$  \hspace{1cm} (9)

then the potential function $V_1$ between terminal grading rings 43 and 47 may be written as

$$V_1(x,t) = (V - E \cos (wt + \phi)) \frac{1}{2}RZ^2$$  \hspace{1cm} (10)

where $V$ is the direct current potential as herefore defined and $R$ is a constant. It may now be shown that the equation of motion of ions formed by bombardment of electrons from filament 19 is as follows:

$$\frac{d^2x}{dt^2} + \frac{eV}{m} - \frac{eE}{m} \cos (wt + \phi) = 0$$  \hspace{1cm} (11)

Which, with proper substitutions, becomes:

$$\frac{d^2x}{dt^2} + \left[ \frac{a - 2q \cos 2\phi}{m} \right] x = 0$$  \hspace{1cm} (12)

where $B = \frac{1}{2} (wt + \phi)$ and

$$a = \frac{eV}{m}$$  \hspace{1cm} (13)

$$q = \frac{2qE}{m}$$  \hspace{1cm} (14)

Equation 12 is known as Mathieu's equation, and for present purposes, the essential consideration is that for certain values of "a" and "q" resonance occurs. This means that ions having certain mass-to-charge ratios continue to gain energy from oscillator 38 and hence finally reach either collector electrode 13 or collector electrode 14, as the case may be. Ions having mass-to-charge ratios other than the resonant ones do not continue to gain energy from oscillator 38 and therefore do not reach the collector electrodes.

In Fig. 6, there is shown a stability chart for Mathieu functions of integral order wherein "q" is plotted upon the $x$-axis while "a" is plotted upon the $y$-axis. Now, if Equation 13 is divided by Equation 14, the following is obtained:

$$\frac{a}{q} = \left( \frac{2V}{E} \right)$$  \hspace{1cm} (15)

And, if $V$ and $E$ are both held constant by maintaining the voltage of battery 61 and oscillator 38 at constant values, then the equation of a straight line having a slope

$$\frac{2V}{E}$$

results. Lines satisfying Equation 15 at the two different values of slope are represented by broken line 84 and solid line 85. If the voltage of battery 61 and oscillator 38 are maintained at constant values such that operation of the device occurs along dotted line 84, then, at a particular value of frequency of oscillator 38, ions having mass-to-charge ratios which will give values of "a" and "q" falling within the shaded regions marked "unstable" in Fig. 6 will continue to gain energy from oscillator 38 and ultimately reach either collector electrode 13 or 14. Those ions having mass-to-charge ratios such that "a" and "q" have values falling within the unshaded regions of Fig. 6, marked "stable," will not continue to gain energy and hence will not reach the collector electrodes. Consequently, to obtain the best discrimination between ions having heterogeneous mass-to-charge ratios values of $V$ and $E$ should be selected so that operation of the device will occur along a line such as line 85. Since line 85 traverses essentially only one unstable region, only ions having mass-to-charge ratios such as to cause "a" and "q" to fall within this region will receive energy continuously from the R. F. field. In addition, the operating line, such as line 85, should be kept as near the vertical axis of Fig. 6 as possible in order that ions having mass-to-charge ratios immediately adjacent the desired resonant mass-to-charge ratio will not also receive continuous acceleration.

As will appear from the above, it is preferred that the voltage of battery 61 and the voltage of oscillator 38 in the device of Fig. 4 be maintained constant at a desired value. To obtain a mass spectrum, the frequency of oscillator 38 is varied. With frequency as the independent variable, the following equation may be employed for the determination of the particular ion mass-to-charge ratio being collected upon electrodes 13 and 14:

$$\frac{m}{e} = \left( \frac{f_1}{f} \right)^2 \frac{m_1}{e}$$  \hspace{1cm} (16)

Now, if

$$\frac{m_1}{e} = \frac{f_1}{f}$$

and $f_1$ are so selected that the operating point of the device of Fig. 4 falls within a region of instability, as discussed in connection with Fig. 6, then, when the frequency of oscillator 38 is changed to another value, ions having a mass-to-charge ratio as determined by Equation 16 will be collected upon electrodes 13 and 14.

In Fig. 7, there is shown a modification of the invention wherein structure similar to that discussed heretofore in Fig. 3 is utilized in connection with circuitry similar to that disclosed in Fig. 4. As will be observed from the employment of identical reference characters, used hereinbefore in the designation of similar elements, amplifier input resistor 65 is connected to the secondary winding 38 of transformer 37 which, in turn, is connected to battery 61. Bent surface electrodes 55 and 56 have the shape of hyperboloids of revolution to obtain the desired electrostatic or direct current field distribution therebetween as discussed in connection with Fig. 3. The equation of motion of ions generated within envelope 10 is determined by Equation 12 in a manner similar to that discussed heretofore in connection with Fig. 4.

In the above described modifications of the invention shown in Figs. 2 and 3, the ions should pass through the R. F. field in a time short compared with the period of the R. F. field in order to insure that they receive an increase of kinetic energy during each traversal thereof. Accordingly, electrodes 30 and 31 should be as closely spaced as possible with respect to each other commensurate with the positioning therebetween of annular trap 21. It should also be noted that, when ions are first formed by impingement of
the electrons emanating from filament 19 upon gas molecules, the only means for their escape from the region of trap 21 is by acceleration due to the R. F. field, and therefore some ions may fail to receive a sufficient net increment of kinetic energy to enable the inception of the desired to and fro movement through the R. F. field. In the modification of the invention shown in Fig. 8, these difficulties are obviated by displacing the bombarding electron stream from median plane 17.

As illustrated in Fig. 8, wherein portions here-inbefore shown and described are identified by like numerals, the requisite linearly distributed electrostatic field, or parabolically distributed voltage, is provided by means of a plurality of spaced, plate-shaped, grading rings 106-109 and potential dividing resistors 110-117 connected as shown. A source of electrons 118 is positioned adjacent median plane 17 and comprises a thermionically emissive filament 119, hollow cylindrical shield 120 and supporting leads 121 and 122. Heating current for filament 119 is supplied by a source of direct current, indicated conventionally by battery 123 connected between leads 121 and 122. An electron trap 124 is supported by means of a rigid conductive layer 125 in the space between grading rings 106 and 106. Accelerating voltage is supplied between filament 119 and trap 124 by a unidirectional voltage source 126. Trap 124 is maintained at approximately the average potential of rings 106 and 106 by means of a suitably placed source of unidirectional voltage 127 connected between the positive terminal of battery 126 and the center-tap 62 of transformer 36. As indicated, rings or electrodes 104 and 105, supported by leads 128 and 129, are spaced as closely as possible with respect to each other to minimize the axial extent of the R. F. field generated therebetween by oscillator 38.

As will now be observed, ions generated by bombardment within trap 124 are at once subjected to the force of the electrostatic field whereby they are propelled through the R. F. field between rings 104 and 105 with a considerable velocity on their first traversal thereof. In addition, displacement of trap 124 and electron source 118 from median plane 17 permits the closer spacing of electrodes 104 and 105 to reduce the axial extent of the R. F. field. It will be realized, of course, that trap 124 and source 118 may be positioned between any of the plurality of grading rings to achieve the above described purposes. Also, the same expedients are equally applicable to the modifications shown in Figs. 3 and 7 wherein hyperbolically-shaped electrodes 15 and 16 render unnecessary the employment of grading rings.

In the embodiments of the invention utilizing grading rings and resistors constituting potential dividers to provide a linearly distributed electrostatic field, the grading rings may be evenly spaced and the desired parabolic voltage distribution obtained by selecting suitable values for the resistors. However, other arrangements having unequally spaced grading rings may be employed for this purpose, as will appear to those skilled in the art from the foregoing considerations.

While the invention has been described with reference to particular embodiments thereof, it will be understood that numerous changes may be made without departing from the invention. I therefore aim in the appended claims to cover these and all such equivalent variations of application and structure as are within the true spirit and scope of the foregoing disclosure.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A mass spectrometer comprising an evacuable envelope, a pair of electrodes mounted in spaced apart relationship within said envelope, means for producing in the space between said electrodes an electrostatic field having a linear space distribution, the voltage creating said field having a parabolic space distribution with the apex lying substantially upon the median plane between said electrodes and increasing from the median plane toward each of said electrodes, means for generating an alternating electric field between said electrodes, means for introducing ions into the space between said electrodes, and means for introducing an ionizable medium into said envelope.

2. A mass spectrometer comprising an evacuable envelope, a pair of electrodes mounted in spaced apart relationship within said envelope, means for producing in the space between said electrodes an electrostatic field having a linear space distribution, the axial component of said field being substantially zero upon the median plane between said electrodes and increasing from the median plane toward each of said electrodes, means for generating an alternating electric field between said electrodes, means for directing a magnetic field along the common axis of said electrodes, means for injecting ions into the space between said electrodes, and means for introducing an ionizable medium into said envelope.

3. A mass spectrometer comprising an evacuable envelope, a pair of electrodes mounted in spaced apart relationship within said envelope, means for introducing ions into the space between said electrodes, means for introducing an ionizable medium into said envelope whereby said medium may be ionized by said electrons to form ions having a plurality of mass-to-charge ratios, means for producing in the space between said electrodes a direct current voltage having a parabolic space distribution, said parabolic voltage having its apex lying substantially upon the median plane between said electrodes and increasing positively from the median plane toward each of said electrodes, means for generating an alternating electric field between said electrodes, the combined effect of said direct current voltage and said alternating electric field being to cause resonant ions to be continuously accelerated by said alternating electric field during successive passages therethrough while non-resonant ions are accelerated to only a limited extent, and means for collecting and measuring said resonant ions.

4. A mass spectrometer comprising an evacuable envelope, a pair of electrodes mounted in spaced apart relationship within said envelope, means for injecting electrons into the space between said electrodes, means for generating an alternating electric field between said electrodes, the combined effect of said direct current voltage and said alternating electric field being to cause resonant ions to be continuously accelerated by said alternating electric field during successive passages therethrough while non-resonant ions are accelerated to only a limited extent, said direct current voltage and said alternating electric field both being of a polarity such as to cause said resonant ions to be continuously accelerated by said alternating electric field during successive passages therethrough while non-resonant ions are accelerated to only a limited extent, and means for collecting and measuring said resonant ions.
erating an alternating electric field between said electrodes, the combined effect of said direct current voltage and said alternating electric field being to cause resonant ions to be continuously accelerated by said alternating electric field during successive passages therethrough while non-resonant ions are accelerated to only a limited extent, means for directing a magnetic field along the common axis of said electrodes, and means for collecting and measuring said resonant ions.

6. A mass spectrometer comprising an evacuable envelope, a pair of electrodes mounted in spaced apart relationship within said envelope, means for injecting electrons into the space between said electrodes, means for introducing an ionizable medium into said envelope whereby said medium may be ionized by said electrons to form ions having a plurality of mass-to-charge ratios, means for producing in the space between said electrodes a direct current electric field with voltage increasing positively in both directions from the median plane between said electrodes substantially proportional to the square of distance from said plane, means for generating an alternating electric field between said electrodes, the combined effect of said direct current and alternating electric fields being to cause resonant ions to be continuously accelerated by said alternating electric field during successive passages therethrough while non-resonant ions are accelerated to only a limited extent, and means for collecting and measuring said resonant ions.

7. In mass spectrometry involving the formation of ions and the separation thereof, the improvement which comprises accelerating the ions by means of an alternating electric field against the force of a direct current electric field having a linear space distribution whereby the ions of a given mass-to-charge ratio execute simple harmonic motion through said alternating electric field and become separated from those of other mass-to-charge ratios in space, and selectively collecting the ions thus separated.

8. In mass spectrometry involving the formation of ions and the separation thereof, the improvement which comprises accelerating the ions by means of an alternating electric field against the force of an electrostatic field having a linear space distribution to cause the ions of a given mass-to-charge ratio to execute simple harmonic motion in time phase with the alternations of said alternating electric field and ultimately to overcome the opposing force of said electrostatic field while ions having other mass-to-charge ratios fail to execute such motion to overcome said electrostatic field, and selectively collecting the ions which overcome the opposing force of said electrostatic field.

9. In mass spectrometry involving the formation of ions and the separation thereof, the improvement which comprises accelerating the ions by means of an alternating electric field against the force of a direct current voltage having a parabolic space distribution to cause ions of a given mass-to-charge ratio to execute to and fro motion through said alternating electric field in time phase with the alternations thereof and ultimately to overcome the opposing force of said electrostatic field while ions having other mass-to-charge ratios fail to overcome said opposing force, and selectively collecting the ions which overcome said opposing force.

10. In mass spectrometry involving the formation of ions and the separation thereof, the improvement which comprises accelerating the ions by means of a radio frequency field against the force of a direct current voltage having a space distribution which varies as the square of distance from said plane and a radio frequency field to cause ions of a given mass-to-charge ratio to execute to and fro motion through said radio frequency field in time phase therewith and ultimately to overcome the opposing force of said direct current voltage while ions having other mass-to-charge ratios fail to overcome said opposing force, and selectively collecting the ions which overcome said opposing force.

11. A mass spectrometer comprising an evacuable envelope, a first plurality of coaxially aligned potential grading rings disposed within said envelope on one side of a plane traversing said envelope, a second plurality of coaxially aligned potential grading rings disposed within said envelope on the opposite side of said plane, a source of direct current voltage connected to said first and second pluralities of grading rings for establishing therealong a parabolic potential distribution having its apex lying upon said plane and increasing positively in both directions from said plane, means for establishing a radio frequency field parallel to said grading rings and along said plane, and means for generating ions within said envelope whereby ions having a given mass-to-charge ratio will be accelerated to and fro by said radio frequency field against the opposing force of said parabolic potential distribution to ultimately overcome said opposing force while ions having other mass-to-charge ratios will fail to overcome said opposing force, and means for collecting said ions having a given mass-to-charge ratio.

12. A magnetic field against comprising an evacuable envelope, a first plurality of coaxially aligned potential grading rings disposed on one side of a plane traversing said envelope, a second plurality of coaxially aligned potential grading rings disposed within said envelope on the opposite side of said plane, a potential divider connected to said pluralities of grading rings, means for energizing said potential divider to establish along said pluralities of grading rings a parabolic potential distribution having its apex lying upon said plane and increasing positively in both directions from said plane, means for establishing a radio frequency field between said pluralities of grading rings and along said plane, and means for generating ions within said envelope whereby ions having a given
mass-to-charge ratio are accelerated to and fro by said radio frequency field against the opposing force of said parabolic potential distribution to ultimately overcome said opposing force, and means for collecting said ions having a given mass-to-charge ratio.

13. A mass spectrometer comprising an evacuable envelope, a first plurality of coaxially aligned potential grading rings disposed on one side of a plane traversing said envelope, a second plurality of coaxially aligned potential grading rings disposed within said envelope on the opposite side of said plane, the grading rings terminating each of said pluralities of grading rings adjacent said plane being adapted to serve also as electrodes for the establishment of a radio frequency field, means constituting a potential divider connected to said pluralities of grading rings, means for energizing said potential divider to establish along said pluralities of grading rings a parabolic potential distribution having its apex lying upon said plane and increasing positively in both directions from said plane, means for establishing a radio frequency field between said grading rings serving also as electrodes, and means for generating ions within said envelope whereby ions having a given mass-to-charge ratio are accelerated to and fro by said radio frequency field against the opposing force of said parabolic potential distribution to overcome ultimately said opposing force, and means for collecting said ions having a given mass-to-charge ratio.

14. A mass spectrometer comprising an evacuable envelope, a pair of opposed electrodes supported within said envelope, said electrodes having the shape of hyperboloids of revolution, a source of direct current voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, means for generating a radio frequency field between said electrodes and along said plane whereby ions having a given mass-to-charge ratio will be accelerated to and fro by said radio frequency field against the opposing force of said parabolically distributed voltage to overcome ultimately said opposing force while ions having other mass-to-charge ratios will fail to overcome said opposing force, and means for collecting said ions having a given mass-to-charge ratio.

15. A mass spectrometer comprising an evacuable envelope, a first pair of spaced electrodes supported within said envelope, said electrodes having the shape of hyperboloids of revolution, a source of direct current voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, and a source of radio frequency voltage connected to said first pair of electrodes, said electrodes in said second pair being positioned on opposite sides of said plane between said first pair of electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, and a source of radio frequency voltage applied to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, a second pair of spaced electrodes supported between said first pair of electrodes, said electrodes in said second pair being positioned on opposite sides of said plane between said first pair of electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, and a source of radio frequency voltage applied to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, means for generating ions having a given mass-to-charge ratio.

16. A mass spectrometer comprising an evacuable envelope, a first pair of spaced electrodes supported within said envelope, said electrodes having the shape of hyperboloids of revolution, a source of direct current voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, a second pair of spaced electrodes supported between said first pair of electrodes, said electrodes in said second pair being positioned on opposite sides of said plane between said first pair of electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, and a source of radio frequency voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, means for generating ions having a given mass-to-charge ratio.

17. A mass spectrometer comprising an evacuable envelope, a first plurality of coaxially aligned potential grading rings disposed within said envelope on one side of a plane traversing said envelope, a second plurality of coaxially aligned potential grading rings disposed within said envelope on the opposite side of said plane, a source of direct current voltage connected to said first and second pluralities of grading rings for establishing therealong a parabolically distributed voltage having its apex lying upon said plane and increasing positively in both directions from said plane, a source of radio frequency voltage connected in circuit with said source of direct current voltage for varying the rate of change of slope of said parabolic potential distribution, means for generating ions within said envelope whereby ions having a given mass-to-charge ratio will be accelerated to and fro by said varying potential distribution to emerge ultimately from the region of influence thereof while ions having other mass-to-charge ratios will fail to so emerge, and means for collecting said ions having a given mass-to-charge ratio.

18. A mass spectrometer comprising an evacuable envelope, a first plurality of coaxially aligned potential grading rings disposed on one side of a plane traversing said envelope, a second plurality of coaxially aligned potential grading rings disposed within said envelope on the opposite side of said plane, means for generating ions having a given mass-to-charge ratio to establish along said pluralities of grading rings a parabolic potential distribution having its apex lying upon said plane and increasing positively in both directions from said plane, a source of radio frequency voltage connected in circuit with said source of direct current voltage for varying the rate of change of slope of said parabolic potential distribution,
means for generating ions within said envelope whereby ions having a given mass-to-charge ratio will be accelerated to and fro by said varying potential distribution to emerge ultimately from the region of influence thereof while ions having other mass-to-charge ratios will fail to so emerge, and means for collecting said ions having a given mass-to-charge ratio.

19. A mass spectrometer comprising an evacuable envelope, a pair of opposed electrodes supported within said envelope, said electrodes having the shape of hyperboloids of revolution, a source of direct current voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, a source of radio frequency voltage connected in circuit with said source of direct current voltage for varying with time the rate of change of slope of said parabolically distributed voltage whereby ions having a given mass-to-charge ratio will be accelerated to and fro between said electrodes until they ultimately reach a desired axial displacement while ions having other mass-to-charge ratios will fail to reach such displacement, and means for collecting said ions having a given mass-to-charge ratio.

20. A mass spectrometer comprising an evacuable envelope, a pair of opposed electrodes supported within said envelope, said electrodes having the shape of hyperboloids of revolution, a source of direct current voltage connected to said electrodes to establish therebetween a parabolically distributed voltage the apex of which lies upon the median plane between said electrodes, means for generating ions having a plurality of mass-to-charge ratios between said electrodes, a source of radio frequency voltage connected with said source of direct current voltage for varying with time the rate of change of slope of said parabolically distributed voltage whereby ions having a given mass-to-charge ratio will be accelerated to and fro between said electrodes until they ultimately impinge thereupon while ions having other mass-to-charge ratios will not receive sufficient acceleration to reach said electrodes, and means in circuit with said electrodes for measuring the ion current generated by the impingement thereupon of said ions having a given mass-to-charge ratio.

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No references cited.