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Janes

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[54] **TIME OF FLIGHT MASS SPECTROMETER COMPRISING A REFLECTING MEANS WHICH EQUALIZES TIME OF FLIGHT OF IONS HAVING SAME MASS TO CHARGE RATIO**

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[52] **U.S. Cl.** ..... **250/41.9 TF**

[51] **Int. Cl.** **B01d 59/44**

[58] **Field of Search** ..... 250/41.9 TF

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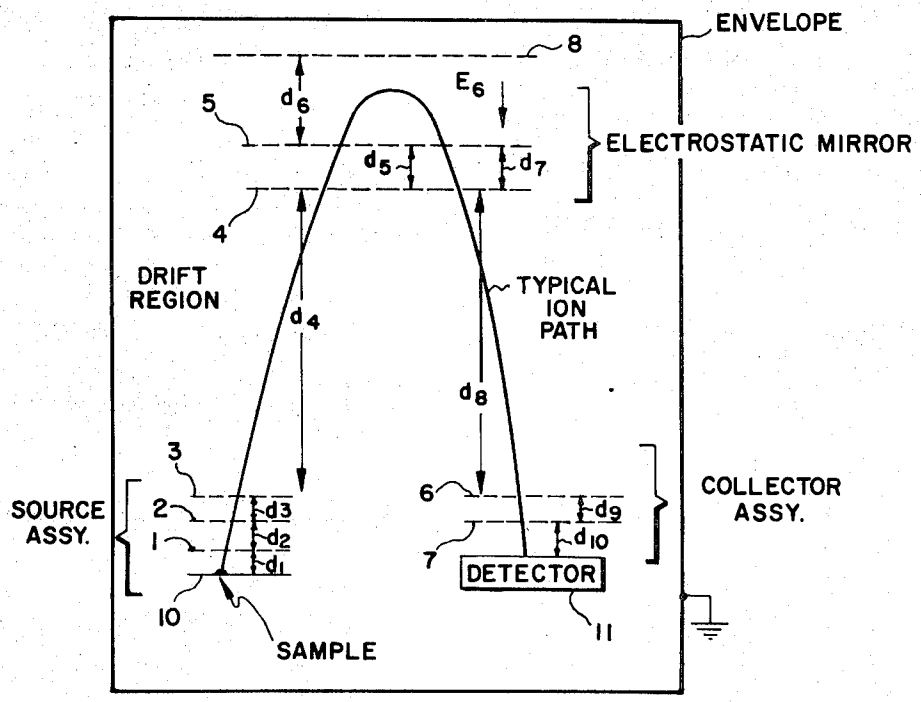
[57] **ABSTRACT**

In a time of flight mass spectrometer ions accelerated from the source are reflected by a soft reflection field toward the detector, the magnitude and direction of the reflection field being such as to lengthen the time of flight of ions of relatively high initial kinetic energy more than ions of relatively low initial kinetic energy so that ions of the same mass to charge ratio, but of different initial velocity will have the same total time of flight from the source to the detector. Thus, ions of a given charge to mass ratio which enter the system at different initial energies at a given time will all arrive at the detector at the same time.

27 Claims, 4 Drawing Figures



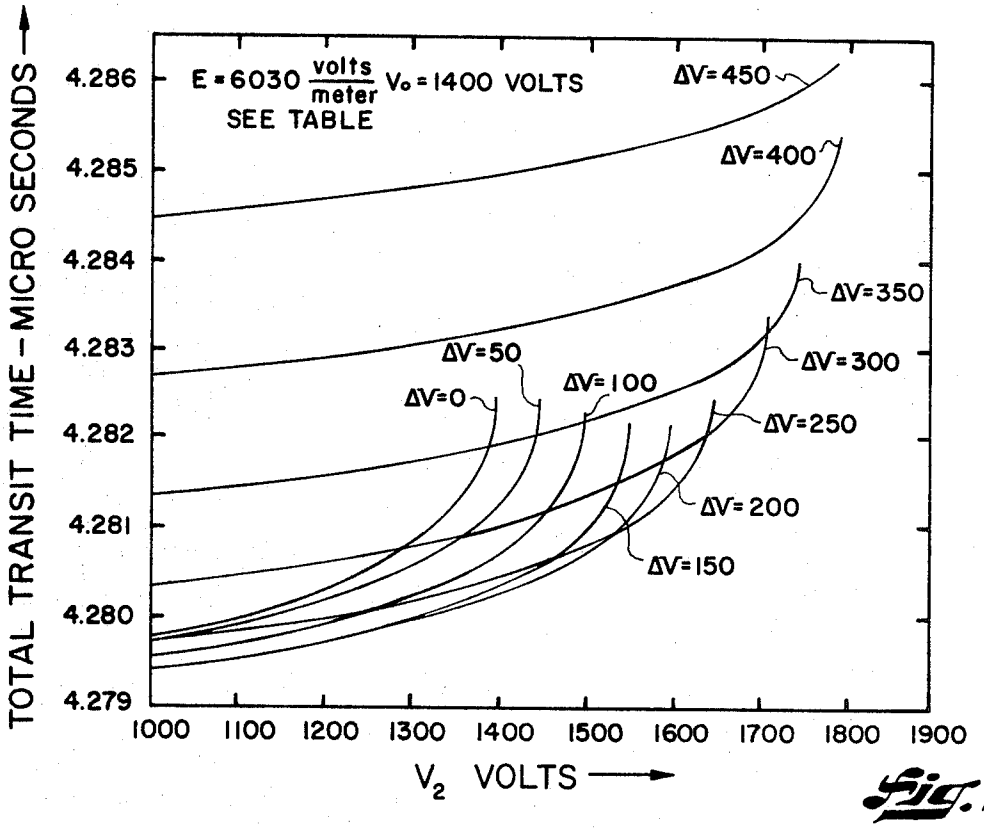


Fig. 2

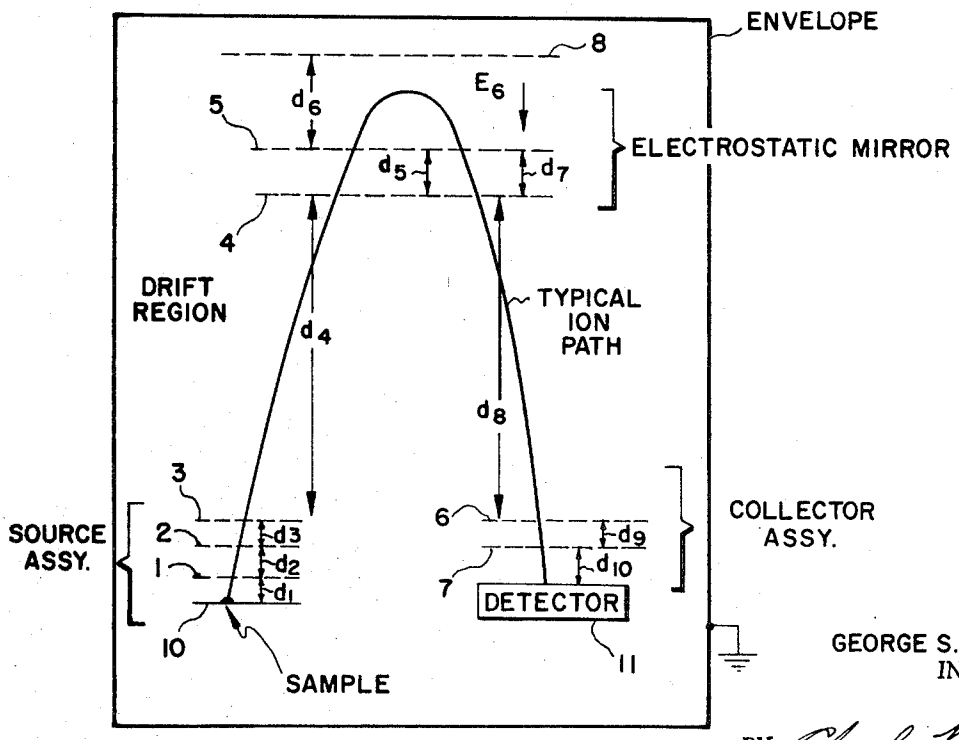


Fig. 1

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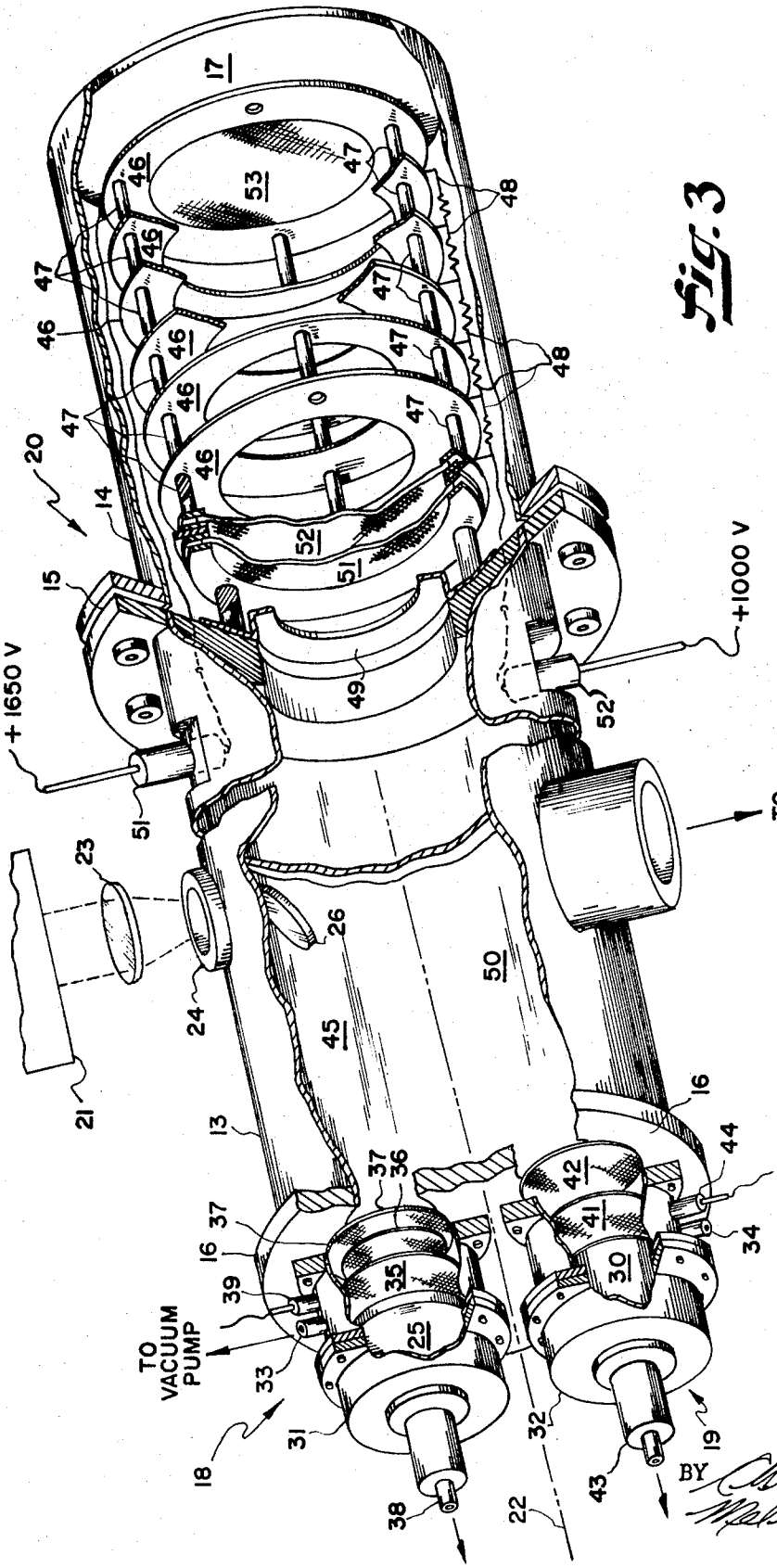

Fig. 3

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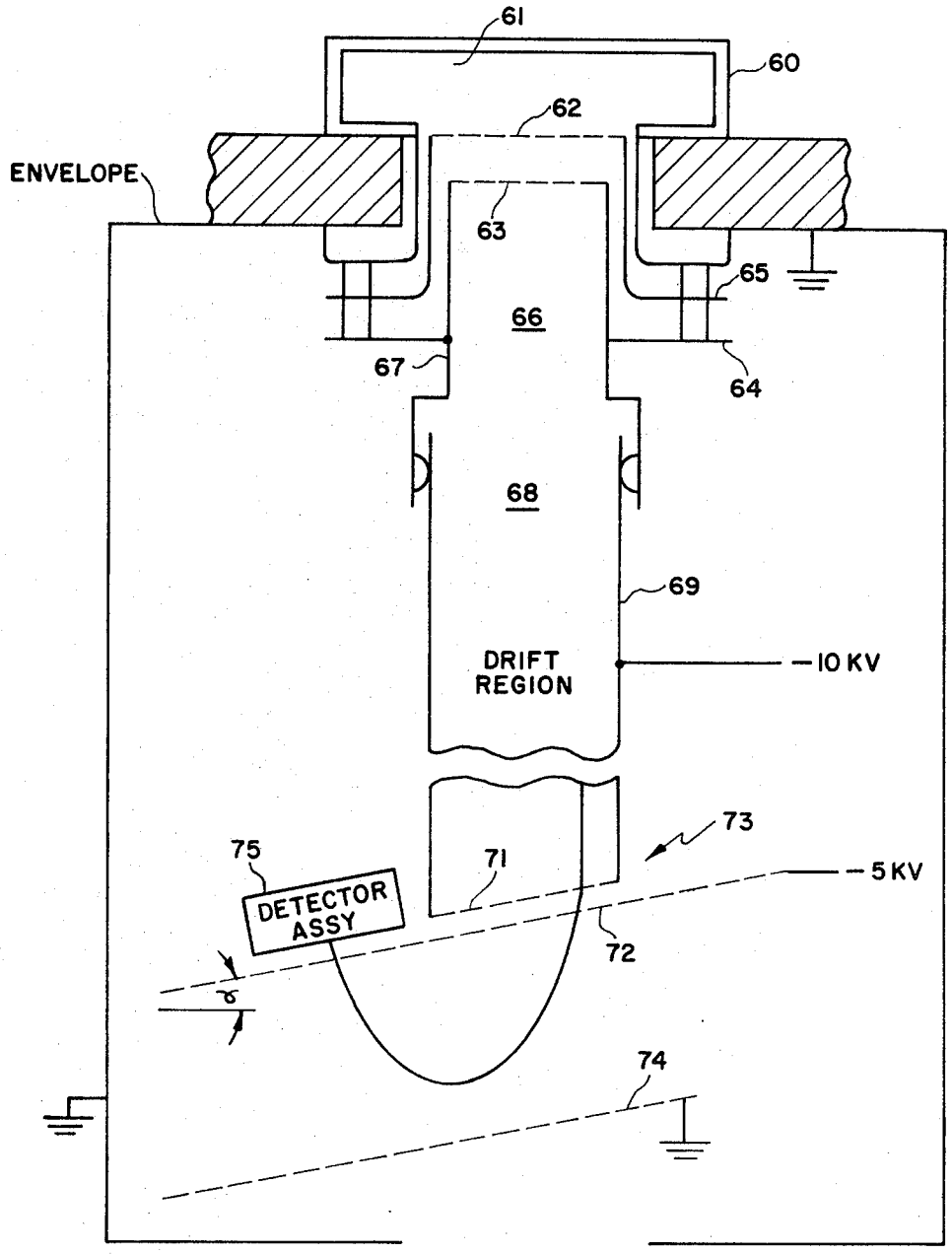

Fig. 4

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TIME OF FLIGHT MASS SPECTROMETER COMPRISING A REFLECTING MEANS WHICH EQUALIZES TIME OF FLIGHT OF IONS HAVING SAME MASS TO CHARGE RATIO

This invention relates to mass spectrometery and more particularly to method and apparatus for providing improved sensitivity and resolution in a time of flight mass spectrometer.

In mass spectrometery, the time of flight technique has advantages over position detecting techniques. The latter require expensive and heavy magnets and do not yield information about all mass species at each test. The time of flight spectrometers on the other hand do not require magnetic fields and do yield information about all mass species essentially simultaneously at each test. In these, a charged particle is accelerated through an electric potential and so it acquires a velocity equal to its initial velocity, due to initial kinetic energy, plus the square root of twice the voltage times the ratio of charge to mass. Thus, if one assumes that the initial velocity is negligible, then the time required for the ion or particle so accelerated to travel a fixed distance will be a measurement of the mass to charge ratio of the particle. Assuming that all the ions are created at the same instance of time, and commence acceleration in the voltage field at the same instance of time, then the lighter ions will arrive at the detector first and heavy ions will arrive at later times. In fact, the ions arrive at the detector in bunches spaced in time, each bunch being indicative of mass to charge ratio. Since the charge on each ion is known, depending upon the formula of the ion, it is then quite easy to determine the mass represented by the bunch and so the signal produced at the detector representative of each bunch which arrives at the detector is indicative of the relative quantity as well as quality of the ions. In this manner, a sample of material can be analyzed as to the constituent elements and the relative quantities of each constituent.

Certain difficulties are experienced with time of flight mass spectrometers. For example, where the ions are created by the bombardment of residual gas atoms with an electron beam of finite size, the fact that the ions are created at different points in space will result in different path lengths, which in turn produce differences in transit time even for ions of the same mass to charge ratio. This specific source of error is less pronounced where the ions are discharged from a solid body by the action of an electron beam or laser beam or a spark directed to the body. In that case, the source point is well localized and so the path for all ions is substantially the same. Another problem arises particularly where the ions are generated from a solid material. Such ions exhibit a wide range of initial energies as they are emitted from the material. Thus, the ions of a given mass to charge ratio emitted from the solid material and then accelerated through a given potential field will have a resulting velocity which is the sum of the initial velocity plus the velocity imparted by the accelerating field and so high initial energy ions of the given charge to mass ratio will transit to the detector in a shorter time than low energy ions. This causes a degradation in the resolution of the device.

It is one object of the present invention to provide a method and apparatus in time of flight mass spectrometery wherein the degradation in resolution due to varying amounts of initial energies of ions emitted from the source is substantially reduced.

It is another object to provide such method and apparatus suitable for the analysis of solid materials.

It is another object to provide a time of flight mass spectrometer of reduced overall length.

It is a further object to provide a time of flight mass spectrometer for the analysis of solid materials in which the initial energy of ion particles is spread substantially greater than possible heretofore without degradation in resolution, whereby a greater latitude is offered in the technique for vaporizing and energizing and ionizing material from the surface of the solid material under analysis.

These and other objects of the present invention can be achieved with apparatus included within an evacuated envelope including a source of ions and an ion collector wherein ions from the source are accelerated into a drift space and from there to a soft reflector. The reflector directs the ions to another draft space terminating at the collector, and so the total time of flight which is indicative of mass to charge ratio of the ions is the time of ion drift from the source to the reflector, plus the time of reflection, plus the time of drift from the reflector to the detector. These three intervals are of the same order of magnitude. An electric field causes the reflection. The direction and magnitude of this field is such that for ions of given mass to charge ratio, the reflection time varies directly with incident velocity. Thus, of these ions, those which have the higher initial energy before acceleration spend more time in the reflection area and the total time of flight of such ions is increased. The amount of the increase is calculated to exactly offset their higher initial velocity due to the higher initial energies at which they are generated from the material under analysis.

In one specific embodiment of the present invention described herein, the drift lengths from source to reflector and reflector to detector are substantially equal and so time of flight of ions is obtained with apparatus which is substantially half the length of equivalent apparatus used heretofore. This configuration of structure not only reduces the total overall length necessary, but permits the detector to be shielded from direct radiation from the source. This protects the detector from fast neutral atoms, ultraviolet light, and X-ray radiation likely to be generated at the source. The structural features of this embodiment are described with respect to arrangement, dimensions, and voltages. With this embodiment, the objects of the invention are achieved in the analysis of a range of materials. In the design, certain compromises and approximations are made which are described. The principles of the invention however are applicable in any time of flight mass spectrometer regardless of the materials under analysis and the techniques used to generate the ions and detect the ions.

These and other aspects of the invention will be understood more clearly in view of the following detailed description of features of the invention taken in conjunction with the accompanying figures in which:

FIG. 1 is a diagram illustrating the path of flight of an ion from the source to the detector through various field regions produced by energized grid structures and

aids to understand the principle features in the method and apparatus contemplated by the present invention;

FIG. 2 is a plot of a family of curves for ions of a given mass to charge ratio, each curve representing an initial energy for such ions, versus total transit time from grid 2 to the detector as a function of the potential V_2 on grid 2. Grid 2 is the cutoff grid which limits the time duration of the initial pulse of ions which enter the drift space toward the reflector. The incremental voltage ΔV shown is the equivalent excess ion energy above the initial accelerating voltage V_0 present at the ion sample source **10**;

FIG. 3 is a three quarter partially broken away view of structure incorporating the principle features and other features of the present invention; and

FIG. 4 is a schematic representation of another embodiment wherein the reflecting grid structure is tilted at an angle to the tube axis in order to produce an orbit in the reflection region, and the detector is immediately adjacent the reflection region.

A device incorporating the principle features of the present invention is shown schematically in FIG. 1. It utilizes a standard ion beam source denoted **10** evaporating ions from the surface of the sample. The energy for evaporation and ionization may derive from a laser beam or an electron beam directed to a point on the surface of the sample. Immediately adjacent the ion source are grid **1**, **2**, and **3** which act to accelerate the ions to their drift velocities and also act as a gating mechanism to gate out extraneous ions which may have been generated at the wrong time. This is accomplished, for example, by pulsing grid **2** with a voltage V_2 while holding the voltages applied to the source and grids **1** and **3** constant at V_0, V_1, and V_3 respectively. The grids **1**, **3**, **4**, and **6** are preferably set at zero potential as is the wall structure enclosing these grids all within an evacuated envelope. Thus, the region from grid **3** to grid **4** and the region from grid **4** to grid **6** are drift regions through which the ions move without accelerating. There is no potential gradient in these regions.

Grids **4**, **5**, and **8** form an electrostatic mirror or a soft reflector. The electrostatic fields bounded by these grids serve to decelerate the incident ions and reaccelerate them directing them to the detector **11**. The deflected ions move at constant velocity through the second drift region through grids **4** and **6** and pass through grids **6** and **7** to the detector which is preferably at a relatively high negative voltage. Electrical signals produced in the detector reveal the nature of the ions in terms of the ion mass to charge ratio. The amplitude and time interval of these electrical signals with respect to the voltage pulses applied to grid **2** reveal the mass to charge ratio of ions evaporated from the sample and the relative numbers of these.

In the region between each pair of grids the ions path constitutes a segment of a parabola. This is the case in the regions between grids where the ions have a velocity component in one direction which is constant while at the same time experiencing an accelerating electrostatic field orthogonal thereto. This is particularly evident in the drift region between grids **4** and **5**, and in the reflection region between grids **5** and **8**.

In an idealized case in which all times of flight or transit times other than those spent in the two drift regions between grids **3** and **4** and **4** and **6** and in the deflection region between grids **5** and **8**, can be neglected, it can be shown by analytic techniques that the choice of design parameters is given as follows:

$$0 < V_0$$

$$V_1 < V_0$$

$$V_2 < V_0$$

$$V_5 < V_7 < V_0$$

$$V_3 = V_4 = V_6 = 0$$

$$V_{11} < V_0$$

$$V_5 = \tfrac{2}{3} V_0$$

$$E_6 = 4\sqrt{3}(V_0/d_4 + d_8)$$

Among the above parameters, the V represents voltage and the subscript is the reference number of the grid. V_0 represents voltage at the ion source **10** and E is the electric field between grids **5** and **8**.

$$\text{i.e. } E_6 = V_0 - V_5/d_6$$

The total transit time of an ion from the source **10** to the detector **11** is denoted τ and is the sum of all transit times between all grids. If the initial excessive kinetic energy of an ion as it is evaporated from the surface of the sample at the source **10** parallel to the accelerating electric field is given by ΔV, then the total transit time can be expanded as a Taylor series around its value τ_0 for $\Delta V = 0$. The Taylor series is as follows:

$$\tau = \tau_0 + \Delta V \left(\frac{\partial \tau}{\partial \Delta V}\right)_{\Delta V=0} + \frac{1}{2}\Delta V^2 \left(\frac{\partial^2 \tau}{\partial \Delta V^2}\right)_{\Delta V=0} + \frac{1}{6}\Delta V^3 \left(\frac{\partial^3 \tau}{\partial \Delta V^3}\right)_{\Delta V=0} + \cdots$$

The first term in the Taylor series τ_0, is the total transit time for an ion of the given mass to charge ratio which has zero initial excess kinetic energy and so the subsequent terms in the series which are of progressively smaller magnitude add to the transit time τ_0 depending upon the initial excess kinetic energy of the ion.

The values of V_5 and E above constitute two parameters which can be used to establish a condition wherein the first two derivatives in the above Taylor series vanish. Substituting the preceeding appropriate values for the parameters, the following mathematical relations are obtained:

$$\tau_0 = (4/3)(l_1 + l_3)\,(m/2eV_0)^{1/2}$$

$$\delta\tau/\delta\Delta V = 0;\ \delta^2\tau/\delta\Delta V^2 = 0;$$

$$\frac{\partial^3 \tau}{\partial \Delta V^3} = \frac{3/2}{V_0^3}(l_1 + l_3)\left(\frac{m}{2eV_0}\right)^{1/2} = \frac{9}{8}\frac{\tau_0}{V_0^3}$$

Thus, in this case, ions of a given mass to charge ratio having a range of initial excess kinetic energies will have transit times that deviate only by the third order term in ΔV which all subsequent terms in the Taylor series are negligible. Thus, a close approximation for the resolution of the instrument for ions of different initial

excess kinetic energy can be had by substitution in the Taylor series expansion. In this case, the Taylor series reduces to the following:

$$\tau=\tau_0\left[1+\left(\frac{\Delta V}{V_0}\right)^3\frac{3}{16}\right]=\tau_0\left[1+\left(\frac{\Delta\tau}{\tau_0}\right)\right]$$

If the resolution R is defined in terms of the quantity $\Delta\tau/\tau_0$ as follows:

$$\Delta\tau/\tau_0 \equiv 1/2R$$

Then the resolution R is given by:

$$R=\frac{1}{2}\left(\frac{16}{3}\right)\frac{V^3}{\Delta V}=\left(\frac{8}{3}\right)\left(\frac{V}{\Delta V}\right)^3$$

For example, if a resolution of 1,000 is desired then $\Delta V/V$ can be as large as plus or minus 17 per cent or 34 per cent total span. In other words, the initial excess kinetic energy of the ion can vary 34 per cent and still yield a resolution of 1,000. A further step can be taken to improve resolution by intentionally making the second term in the Taylor series slightly negative and so that it cancels the third order term over a small range of values.

The precise optimization of dimensions and voltages for the arrangement of grids shown in FIG. **1** is readily done with a computer. Such a calculation done for a typical case resulted in the values given in Table I wherein the distance d_1—d_n are as shown and the voltages V_0, V_1, ---V_{10} are the value present at the source and grids **1** through **10**.

TABLE I

TYPICAL PARAMETERS

$d_1 = 5 \times 10^{-3}$m	$V_2 = 1300 \leq V_2 < 1700$
$d_2 = 5 \times 10^{-3}$m	$V_3 = 0$
$d_3 = 5 \times 10^{-3}$m	$V_4 = 0$
$d_4 = .85$m	$V_5 = 1000$v
$d_5 = 1 \times 10^{-2}$m	$V_6 = 0$v
$d_6 = 10.75 \times 10^{-2}$m	$V_7 = 1050$v
$d_7 = d_5$	$V_8 = 1650$v
$d_8 = .85$m	$V_{10} = 3000$v
$d_9 = 5 \times 10^{-3}$m	$E_8 = 60.30$ volts/cm
$d_{10} = 1 \times 10^{-2}$m	$\Delta = O - 250$ volts
$V_0 = 1400$v	$\Delta\tau/\tau = .00245/4.280 = 5.7 \times 10^{-4}$
$V_1 = 0$v	$\Delta m/m = 1.1 \times 10^{-3}$

Active mirror dia $= 4.14 - 1.05 = 3.10$ cm

A family of curves for ions of unit charge to mass ratio but of different initial excess kinetic energy is shown in FIG. **2**. These curves are derived from the typical parameters above in Table I. The ordinate in FIG. **2** is the transit time for an ion of unit charge to mass ratio and the abscissa is the potential V_2. It may be noted that for affixed value of V_2 at approximately 1,000 volts, the fractional spread in transit time is only about 1 part in 10^4. Thus, if the initial ion pulses are short enough, the resolution can approach 5,000. On the other hand, if grid **2** is not used to control the length of the ion pulse, then the resolution is about 1,000 providing V_8, the potential on grid **8** of the electrostatic mirror is set at about 1,650 volts in order to exclude ions with ΔV more than 250 volts. It should be noted that the total drift length $d_4 + d_8$ appear only in combination as the sum. This suggests that d_4 and d_8 need not be equal. If $d_4 < d_8$, it can be shown that a smaller mirror dimension is possible although the overall instrument length is greater.

A detailed specific embodiment of the present invention can be seen in FIG. **3**. The tube shown incorporates all the features discussed with relation to FIGS. **1** and **2** and discloses many other features as well. The structure is generally cylindrical in shape and many of the parts therein are figures of revolution about the cylinder axis **22**. The cylinder walls are of strength sufficient to withstand the structural forces produced by a vacuum inside the entire space wherein is contained the ion source and detector structures and the electrostatic mirror. The cylinder or envelope wall is in two sections **13** and **14** joined by a flange structure **15** and capped at one end by the plate **16** which carries the ion source and the detector assembly and capped at the other end by the closure **17**. The ion source assembly and detector assembly carried by the plate **16** and the electrostatic mirror assembly all within the evacuated envelope are denoted generally by the numerals **18**, **19**, and **20**, respectively.

External to the structure is a laser source of radiation **21**. The laser radiation is focused by a lens **23** through a window port **24** in wall **13**. Within the envelope, the laser radiation is reflected by mirror **26** to the surface of source plate **25**. The laser has sufficient energy to vaporize and ionize a small portion of the sample of material mounted on the source plate **25**. This illustrates but one technique for vaporizing and ionizing material from the source plate. Clearly, other effective techniques can be used such as, electron beam bombardment, spark discharged, etc.

The source plate **25** in the ion source assembly **18** and the detector plate **30** in the detector assembly **19** are positioned at one end of the structure on opposite sides of the structure axis. The source and detector plates are placed in individual trap door cylinder vacuum chambers which form the ion source and detector assemblies. These vacuum chambers denoted **31** and **32** allow the source material and the detector to be removed for service or replaced without the necessity of reevacuating the whole assembly. For this purpose, vacuum pump connections **33** and **34** are provided.

Within the ion source housing **31**, is the source plate **25** and three grid structures **35**, **36**, and **37** which correspond to the grids **1**, **2**, and **3**, respectively, shown in FIG. **1**. Potential is applied to the source plate **25** through electrical connection **38** and to grid **36** through electrical connection **39** which are insulated from the housing. The grids **35** and **37** however connect to the housing and are at ground potential.

In the detector assembly **19**, the housing **32** encloses the detector **30** insulated from the housing, grid **41** also insulated from the housing and grid **42** connected to the housing and at ground potential. The grids **41** and **42** correspond to grids **7** and **6**, respectively, in FIG. **1**. A voltage is applied to the detector via the terminal **43** and a voltage is applied to grid **41** via terminal **44**.

In operation, a potential of about 1,400 volts is applied via terminal **38** to the source plate **25** and a high negative voltage on the order of −3,000 volts is applied via terminal **43** to the detector **30**. The ions created by the impinging photon energy from the laser beam will be accelerated by the local electric field through grid

35 which is at ground potential and will be gated by the control voltage on grid 36. During the interval of electrical pulses applied via the terminal 39 to the grid 36, ions will be accelerated to a high velocity into the drift space 45.

The electrostatic mirror 20 is contained within the cylinder 14 that removably seals at flange 15 to the tube 13. This mirror functions as the electrostatic mirror shown in FIG. 1. It repels and deflects ions in a manner calculated to direct the ions to detector assembly 19 and to add to the transit time of ions of high initial kinetic energy in compensation for their high initial energy as already described above with respect to FIG. 1. The electrostatic mirror consists of grids 51, 52, and 53 which correspond to the grids 4, 5, and 8 in FIG. 1. Electrical equipotential baffle plates denoted generally 46 between the grids 52 and 53 define the region there between and insure the presence of a uniform electric field gradient between the grids. The baffle plates are separated by insulating standoffs denoted 47 and uniformly matched resistors 48 are inserted between the plates to further insure the presence of uniform electric field gradient. The uniform field gradient between the grids 52 and 53 is necessary in order to have precise control of the reflection time of ions which enter tiie electro-static mirror at different velocities. The aperture to the electrostatic mirror provided by a ring 49 which is part of the flange structure 15 is at ground potential.

In operation, the ions accelerated into the drift region 45 experience no electric field in traveling through this region between the grids 37 and 51. Likewise, the ions upon reflection from the electrostatic mirror experience no electric field in traveling through the drift region 50 between grid 51 and 42. Electrostatic shielding structures (not shown) are provided surrounding the interior of input terminals 51 and 52. Generally 51 connects electrically to grid 53 and terminal 52 provides a voltage at one end of the matched resistors which in turn space the potentials on the baffle plates 46 in such a manner that the uniform gradient between grids 52 and 53 is insured.

In operation, the control grid 36 in initially biased off at a potential somewhat in excess of that applied to grid 53, i.e., $V_2 > 1{,}650$ volts. Under these circumstances, most of the ions vaporized from the surface of the source 25 will not reach grid 36 and those that do pass through grid 36 will be lost in the system either on a wall or at grid 53. In order to select out a time resolved group of ions, the potential of grid 36 is temporarily lowered to some value such as 1,300 volts thereby permitting a group of ions to pass through into the drift space 45. This is the pulse control on grid 36. The precise selection of the gating time is based upon consideration of resolution, mass numbers, and sensitivity. However, for general use, gating times on the order of 10 to 15 nanoseconds will yield excellent resolutions characteristics for a device such as shown in FIG. 3 having an overall length of about 1 meter. Clearly there are other methods for gating the ion pulses. For example, the pulse interval may be determined by the interval of a burst of radiation from the laser 21 which vaporizes the ions from the surface of the sample under test. Alternatively, one might substitute a set (or sets) of small deflection plates for grid 36 (or grid 2 in FIG. 1) which would deflect ions from reaching the mirror for other than a very small time interval.

The electric field in the electrostatic mirror will determine the upper cutoff of the initial excess kinetic energy for the ions. For example, in the embodiment shown in FIG. 3, grid 53 is at 1,650 volts while the source plate 25 is at 1,400 volts. Thus, any ion with a Δvin excess of 250 volts will not be reflected by the electrostatic mirror and therefore will not return to the detector. Such ions will travel through grid 53 and be collected there or on the walls of the tube. As the potential V_2 on grid 36 is varied between, for example, 1,300 and 1,650 volts all particles having excess energy, $\Delta v$from 0 to 250 will be allowed to pass through grid 36 and will be accelerated into the drift region 45. The electrostatic mirror 20 will in turn decelerate and focus these high energy ions back onto the detector which will measure the effective mass of the particle on the basis of the total time of flight.

The operating voltages and sequences of operation of the mass spectrometer shown in FIG. 3 and described above are suitable for testing a wide variety of materials as the sample on the source plate 25. The entire range of ions can be detected and measured in this manner.

Turning next to FIG. 4, there is shown in schematic form another embodiment of the present invention incorporating some of the principle features. As already noted in the description of the embodiment represented in FIGS. 1 and 3, the length of the drift regions from the source to the electrostatic mirror and from the mirror to the detector (denoted d_4 and d_8 in FIG. 1) need not be equal. The optimum reduction in tube length is obtained when they are equal. However, the full effect and benefit of the delay added to the transit time for the relatively high energy ions by the electrostatic mirror can be taken full advantage of even when the drift lengths are not equal. Moreover, one of the drift regions (either d_4 or d_8) may be eliminated, for example, the drift region from the electrostatic mirror to the detector (d_8) can be eliminated as shown by the structure in FIG. 4. Here the detector assembly is located immediately adjacent the electrostatic mirror so that ions reflected by the mirror immediately enter the detector assembly and do not pass through another region. Of course, the overall tube length is greater, but probably no greater than in a conventional tube (for the same transit time) where the source and detector are at opposite ends of the tube and facing each other.

In FIG. 4, the source of ions is from a plasma device 60. The ions are extracted from the plasma cloud 61 in the device by the extraction grid 62 and accelerated by the field between grid 62 and grid 63 which is at a constant potential applied through lead 64. The extraction grid 62 is electrically pulsed through lead 65 so that it extracts ions from the cloud in bunches. These ions are accelerated by the field between grid 62 and grid 63. The extracted ions pass through grid 63 and move through the equipotential spaces 66 and 68 defined by the cylindrical extensions 67 from grid 63 and 69 from grid 71.

At the other end of the drift tube 69, the grid 71 is electrically connected to the tube 69 and disposed at a skew angle with respect to the axis of the tube. This grid 71 bounds an electrical field in conjunction with

the electrostatic mirror grid 72 which is parallel therewith. The grid 71 does not bound any field with other voltage surfaces inside the device because it is substantially shielded from them by the drift tubes 67 and 69. These drift tubes are at about −10 Kv.

The electrostatic mirror denoted generally by the numeral 73 consists substantially of grids 72 and 74. Grid 72 is at a high negative potential (about −5 Kv) and grid 74 is at ground potential. This provides a decelerating field between the grids 72 and 73. The angle that the ions turn, in leaving the drift tube 69 depends upon the skew angle of the grid 72 and 73 (denoted α) and the field strength and dimension between these grids. The field between grid 72 and 74 serves principally to extend the transit time of the relatively higher velocity ions which arrive from the drift tube as compared with the relatively slower ions. This field also turns the ions directing them to the detector 75 located immediately adjacent grid 72. This detector may be constructed similar to detector 19 shown in FIG. 3.

It can be shown that all ions which enter the electrostatic mirror at the same point and at the same angle of incidence will also emerge from the same point at an angle equal to the angle of incidence regardless of the mass to charge ratio of the ions. Clearly, the electrostatic field strength in the space between grids 72 and 74 is adjusted to add to the transit time of high speed ions in view of the considerations described above with respect to FIG. 1 and pertaining to the Taylor expansion equation representing the total transit time of ions in terms of certain voltages and initial excess energy.

The embodiments of the present invention described herein include, with respect to FIGS. 1, 2, and 3 the best known use and application of the invention. The invention is deemed to be the structure as described and the method of testing described whereby the mass to charge ratio of ions of a sample material are determined. In these methods, electrical equipment used in conjunction with the detector to examine the electrical signals from the detector and determine from those electrical signals the mass to charge ratios and the relative quantities of the ions are not described herein. Such equipments are deemed to be well known to those in the art and have been used in the past in conjunction with time of flight type mass spectrometers. The spirit and scope of the invention is set forth in the accompanying claims.

What is claimed is:

1. In a time of flight mass spectrometer, the combination comprising:

a. ion producing means for producing ions and accelerating said ions in a predetermined direction;

b. detecting means for detecting impinging ions;

c. means defining a linear drift region providing an ion time dispersion according to the mass to charge ratio; and

d. reflecting means including a plurality of grids for reflecting ions toward the detecting means after passing through at least one of said grids, said grids providing an ion reflecting and decelerating field the direction and magnitude of which lengthens the time of flight of ions of relatively high velocity more than ions of relatively low velocity, whereby ions of the same mass to charge ratio but different velocities have the same total time of flight from the instant of injection to detection.

2. Apparatus as in claim 1 wherein said reflecting means precedes said linear drift region.

3. Apparatus as in claim 1 wherein said linear drift region precedes said reflecting means.

4. Apparatus as in claim 1 wherein said linear drift region is divided into first and second portions, said first portion preceding said reflecting means and said second portion following said reflecting means.

5. Apparatus as in claim 3 wherein the ions move through the drift region toward the reflecting means at substantially constant velocity.

6. Apparatus as in claim 5 wherein the time of flight for an ion is substantially the total time of drift between injection and detection plus the total time of deceleration in the reflecting means.

7. Apparatus as in claim 4 wherein the time of flight of ions is substantially the total drift time through both said drift region portions from injection to collection plus total time of deceleration in the reflecting means.

8. Apparatus as in claim 4 wherein the drift path of the ions through the second drift region portion is substantially equal in length to the drift path through the first mentioned drift region portion thereby shortening the overall dimension of said spectrometer.

9. Apparatus as in claim 1 wherein said grids are planar and positioned substantially transverse to the direction of drift whereby the path of each ion in said reflecting field is parabolic.

10. Apparatus as in claim 9 wherein the path of the ions entering the reflecting means is at an angle to the grids of said reflecting means.

11. Apparatus as in claim 1 wherein said ion producing means includes further means for producing a beam of energy for evaporation and ionization of a test specimen.

12. Apparatus as in claim 6 wherein the detecting means is immediately adjacent the reflecting means whereby the drift time is substantially the drift time from injection to the reflecting means plus total time of deceleration in the reflecting means.

13. Apparatus as in claim 12 wherein ions drift through the drift region along a substantially straight line and the reflecting means decelerating field is defined by two parallel grids which are inclined at a skew angle to the ion drift path whereby the ions enter the deceleration field at an acute angle of incidence.

14. Apparatus as in claim 13 wherein the angle of reflection of the ions from the reflecting means is equal to said angle of incidence, all ions enter the reflecting means at substantially the same point and all ions leave the reflecting means at substantially the same point, and said detecting means is located at said point of exit of said ions.

15. Apparatus as in claim 1 wherein said reflecting means comprises first, second, and third parallel grids adapted to be coupled to a source of voltage, said first and second grids providing a first electric field and said second and third grids providing a second electric field, said first electric field being insufficient to reflect said ions and said second electric field being sufficient to reflect said ions, said first and second electric fields providing a transit time of ions therein whereby the total transit time of ions from said ion producing means

to said ion detecting means is invarient in both first and second order variations in the initial kinetic energy of ions produced by said ion producing means.

16. Apparatus as in claim 15 wherein the spacing between first and second grids being less than the spacing between said second and third grids.

17. Apparatus as in claim 15 and additionally including a source of voltage coupled to said third grid for preventing ions having energy greater than a predetermined amount from re-entering said first electric field.

18. Apparatus as in claim 1 wherein said detecting means includes fourth planar grid means coupled to a source of voltage for providing a voltage on said fourth grid means for preventing ions reflected from the reflecting means and having energy less than a predetermined amount from being detected.

19. In a method for determining the mass to charge ratio of ions by measuring the time of flight of said ions the steps comprising:

a. accelerating bunches of said ions at intervals through a controlled first electric field;
b. causing said bunches of accelerated ions to sequentially pass through a field free region wherein said ions travel at a constant velocity;
c. providing a second electric field having a direction and magnitude for receiving and reflecting said accelerated ions;
d. causing said accelerated ions to enter said second field at an acute angle of incidence measured between the direction of motion of said ions and the direction of said second electric field;
e. providing a direction and magnitude of said second electric field causing said ions to be reflected back out at an acute angle of reflection substantially equal to the said angle of incidence and to travel a distance within said field substantially proportional to ion velocity upon entering said second field whereby said ions of the same charge to mass ratio but of different velocities have the same total time of flight; and
f. collecting and detecting said ions reflected by said second field, whereby the total time of flight of an ion is substantially the time of drift plus the time of reflection.

20. A method as in claim 19 in which said accelerated ions pass through said field free drift region prior to entering said second electric field.

21. A method as in claim 19 in which said accelerated ions pass through said second electric field prior to entering said field free drift region.

22. A method as in claim 20 in which said accelerated ions pass through a second field free drift region after passing through said second electric field and prior to said collection and detection whereby the total time of flight of an ion is substantially the total time of drift before and after reflection plus the time of reflection.

23. A method as in claim 22 and in which the drift times before and after reflection are substantially equal.

24. A method as in claim 19 and additionally including the step of passing said accelerated ions through a third electric field for absorbing ions having energy greater than a predetermined amount.

25. A method as in claim 24 and additionally including the step of passing said reflected ions through a fourth electric field rejecting ions having energy less than a predetermined amount.

26. A method as in claim 19 wherein said second electric field is adjusted to absorb ions having energy greater than a predetermined amount whereby only ions of less than a predetermined energy level are reflected, collected, and detected.

27. A method as in claim 19 wherein said collector is adjusted to absorb ions having energy less than a predetermined amount whereby only ions of greater than a predetermined energy level are detected.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,727,047 Dated April 10, 1973

Inventor(s) George Sargent Janes

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 55, for " $\delta\tau / \delta \Delta V=0; \delta^2\tau / \delta \Delta V^2=0;$" read -- $\partial\tau / \partial \Delta V=0; \partial^2\tau / \partial \Delta V^2=0;$--; and Column 5, line 45, for "$d_{10}=1 \times 10^{-2}$m Δ=0 - 250 volts" read--$d_{10}=1 \times 10^{-2}$m ΔV=0 - 250 volts--.

Signed and sealed this 19th day of February 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents