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[73] Assignee **The Bendix Corporation**

[54] **MONOPOLE/QUADRUPOLE MASS SPECTROMETER**
14 Claims, 12 Drawing Figs.

[52] U.S. Cl. **250/41.9 DS**
[51] Int. Cl. **H01j 39/36**
[50] Field of Search. **250/41.9 DS**

[56] **References Cited**
UNITED STATES PATENTS

3,555,271 1/1971 Brubaker..... 250/41.9 DS

3,560,734 2/1971 Barnett..... 250/41.9 DS

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Lever; *IMB Technical Discl. Bulletin*; Vol. 8, No. 1, June 1965; pp. 179, 180.

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ABSTRACT: This invention combines an auxiliary apertured electrode with a quadrupole type mass filter. The assembly comprises a quadrupole arrangement with at least one of the poles of the filter extending beyond the others. Beneath the extended electrode is a V-shaped electrode having an aperture therein for the passage of ions. The extended rod and the V-shaped electrode forms a monopole configuration so that ions to be analyzed are introduced through the aperture in the V-shaped electrode and into the analyzing region at an angle to the central axis (Z-axis) of the quadrupole structure thereby reducing the effect of the fringing field.

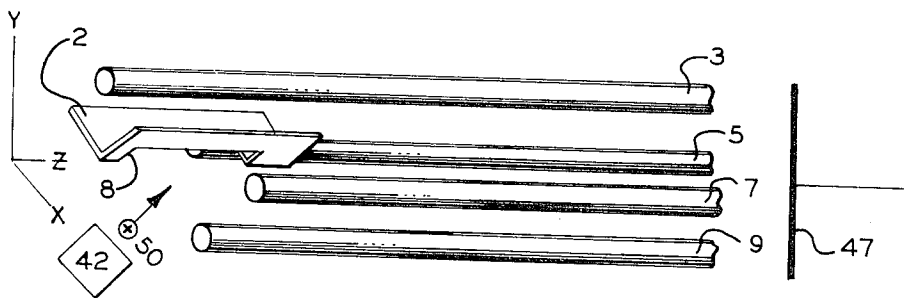


FIG. 1
(Prior Art)

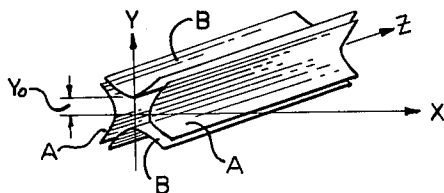


FIG. 2
(Prior Art)

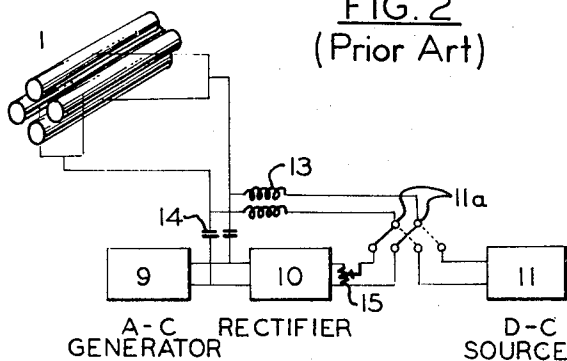
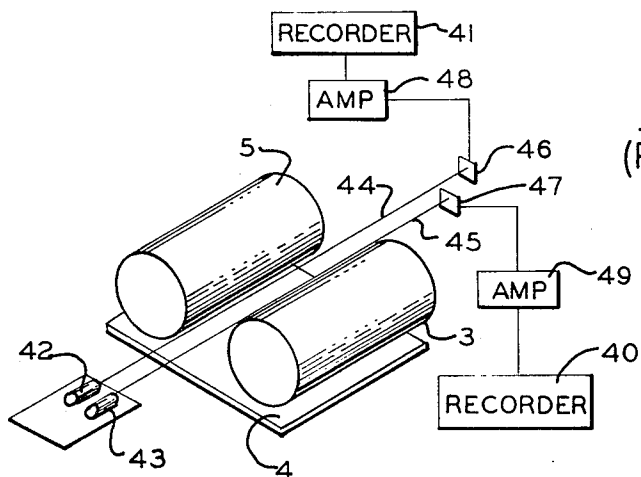


FIG. 3
(Prior Art)



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FIG. 4
(Prior Art)

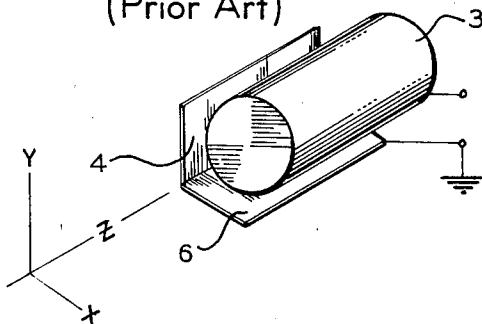
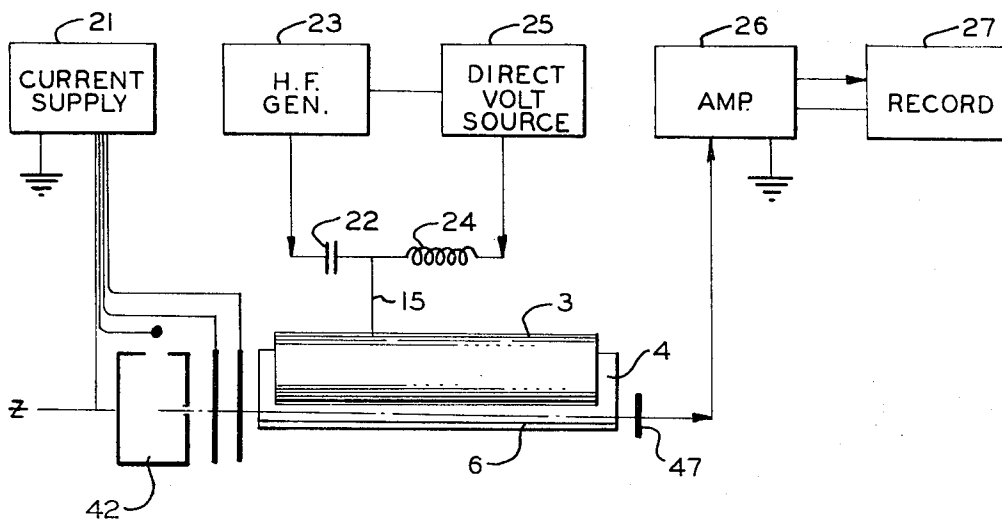


FIG. 5
(Prior Art)



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FIG. 7

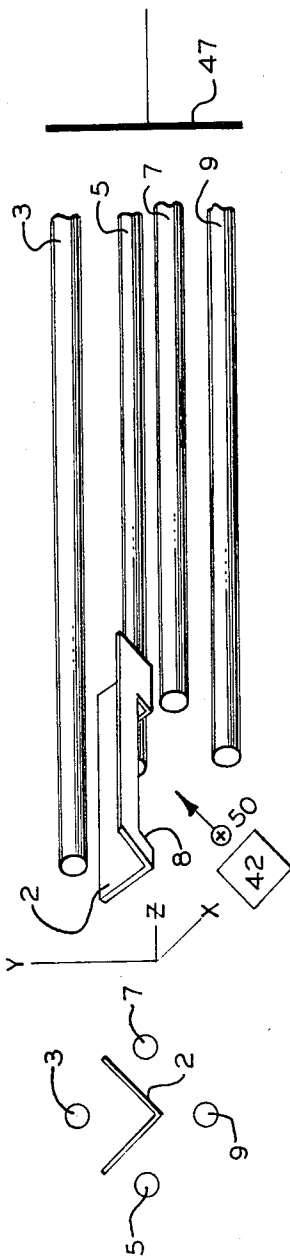


FIG. 6

FIG. 9

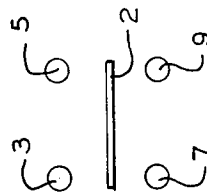
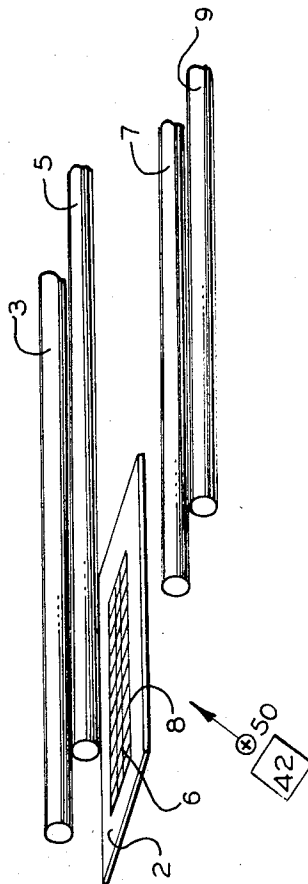


FIG. 8



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FIG. 10

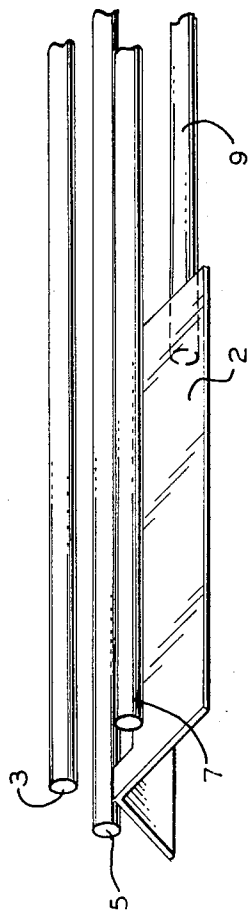


FIG. 11

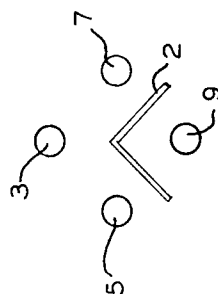
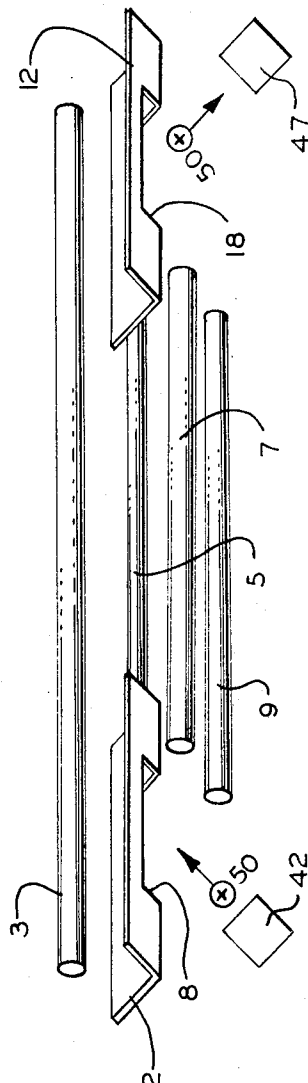


FIG. 12



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MONOPOLE/QUADRUPOLE MASS SPECTROMETER

BACKGROUND OF THE INVENTION

This invention relates to a nonmagnetic mass analyzer, and more specifically to a monopole-quadrupole mass filter apparatus for separating charged particles of different specific charges.

In the operation of a nonmagnetic mass analyzer, such as a quadrupole mass filter of the type described in U.S. Pat. No. 2,939,952 to W. Paul et al., it has been found that exposure of charged particles to be analyzed to the fringing electric fields existing at the entrance end of the analyzer for more than two or three cycles of the AC voltage applied to the field-forming electrodes results in an undesirable radial impulse being imparted to the particles. If the impulse is sufficiently high, the charged particles contact the electrodes where they are discharged, thereby reducing the quantity of charged particles which would otherwise be transmitted by the analyzer and creating several other undesirable side effects.

A first approach to reducing the undesirable impulse producing effects of the fringing field has been to impart a relatively high injection energy to particles as they are directed towards the entrance end of the filter so as to reduce the transient time of the particles through the fringing fields to a minimum. A high injection energy, however, limits the maximum power which can be obtained and imposes additional electric power requirements on the instrument. To restore some of the lost resolving power, an analyzer of increased length is often provided in order to permit the analyzing or resolving action of the electric fields within the analyzer to be exerted over a longer distance and particle transient time. Increased analyzer length is frequently undesirable especially when the analyzer is made part of the instrumentation in a space vehicle.

A second approach has been to provide auxiliary electrodes adjacent to the entrance end of the instrument. The ratio of the voltages connected to these electrodes is then arranged such that particles entering the analyzer encounter an intermediate ratio in the transition from the region of zero field outside the analyzer to the region of very strong electric fields in the center of the analyzer. This is done by reducing the amplitude of the DC voltage connected to the auxiliary electrodes while leaving the amplitude of the AC voltage unchanged. By this means, a substantial increase in the transmission efficiency of the analyzer is achieved. Such an approach is described in U.S. Pat. No. 3,129,327 to W. M. Brubaker.

In the preceding approaches, and in general, it has been common practice to inject ions into the analyzing region of a mass filter from a point parallel to the central axis (Z-axis) of the analyzing region. See U. VonZahn, review of Scientific Instruments 34, (1963). This practice subjected ions to the undesirable effects of the fringing electromagnetic field at the ends of the electrodes forming the analyzing region and reduced the sensitivity of the mass filter.

SUMMARY OF THE INVENTION

To increase the sensitivity of a nonmagnetic mass filter, especially a quadrupole type filter, ions are introduced into the filter through an aperture in an auxiliary electrode.

The invention is characterized by a mass filter which includes an auxiliary electrode having an aperture therein for the passage of ions. The auxiliary electrode is disposed in axial alignment with at least one of the electrodes of the mass filter so that ions passing through the aperture of the auxiliary electrode will become subject to a time periodical electric field between at least one of the mass filter electrodes and the auxiliary electrode. In one embodiment of the invention the auxiliary electrode is characterized by two axial elongated conductive and electrically interconnected surface members forming an angle with each other (V-shaped) and extending along and in spaced relationship to the central axis between the quadrupole electrodes. Located along a portion of at least

one surface member of the auxiliary electrode is an aperture for the passage of ions. This type of arrangement permits ions to be introduced into the quadrupole analyzer field without subjecting the ions to the adverse effects of the fringe-field associated with the ends of the mass filter electrodes.

Accordingly, it is an object of this invention to introduce ions into the quadrupole mass filter without subjecting them to the electric field associated with the end portions of the quadrupole electrodes.

It is another object of this invention to increase the sensitivity of a quadrupole mass filter.

It is a further object of this invention to combine the advantages of both a monopole and quadrupole structure in a single mass filter.

It is still a further object of this invention to combine the advantages of both a duopole and quadrupole structure in one mass filter.

It is still another object of this invention to reduce the fringing field scattering of ions at both the entrance and exit ends of a quadrupole filter by the use of an apertured auxiliary electrode for the passage of ions.

It is still a further object of this invention to improve the overall operation and performance of a quadrupole mass analyzer.

The above and other objects and features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings and claims which form a part of this specification.

BRIEF DESCRIPTION OF THE DRAWINGS

Prior Art

FIG. 1 illustrates an ideal shape for electrodes used in a quadrupole mass spectrometer.

FIG. 2 shows an arrangement of four cylindrical rod electrodes of circular cross section, which sufficiently approximate the field generated by the hyperbolic electrodes shown in FIG. 1.

FIG. 3 shows the arrangement and shape of the electrodes used in a duopole mass spectrometer.

FIG. 4 shows the arrangement and shape of electrodes used in a monopole mass spectrometer.

FIG. 5 is a block diagram of a mass analyzer of the type shown in FIG. 4.

Invention

FIG. 6 is a diagrammatic view of a preferred embodiment of the invention showing the monopole-quadrupole combination.

FIG. 7 is a side view of the electrodes shown in FIG. 6.

FIG. 8 is a diagrammatic view of a preferred embodiment of the invention showing a duopole-quadrupole combination.

FIG. 9 is a side view of the electrodes shown in FIG. 8.

FIG. 10 is a diagrammatic view of another preferred embodiment of the invention which shows an apertured auxiliary electrode in combination with quadrupole electrodes.

FIG. 11 is a side view of the electrodes shown in FIG. 10.

FIG. 12 is a diagrammatic view of another preferred embodiment of the invention which shows an additional apertured electrode at both the input (source) end and the detector end of a quadrupole mass filter.

DETAILED DESCRIPTION OF THE DRAWINGS

Prior Art

FIG. 1 illustrates four electrodes A,A,B,B of hyperboloidal shape arranged at a distance r_0 from the Z-axis of an X,Y,Z coordinate system. The electrodes receive a potential which creates a time varying symmetrical electric field between them. The potential of the field is periodic in time, symmetrical with respect to the Z-axis, and depends quadratically on x and y:

$$\Phi = (U + V f(t)) (ax^2 - by^2).$$

$f(t)$ is an arbitrary periodic function of time (t) and the field is assumed to be quasistatic, so that Laplace's equation $\Delta\Phi=0$ requires that the constants a and b should satisfy the condition $a=b$. The two electrodes A, A are electrically interconnected, and the electrodes B, B are electrically interconnected. A time-periodical voltage $U=U_0+V\cos\omega t$ is applied to electrodes A and $U=-U_0-V\cos\omega t$ to electrode B whereby an electric field is created between the electrodes. This field is independent of z , its center of symmetry being the Z-axis.

FIG. 2 shows a schematic diagram of how voltage sources are coupled to the electrodes 1 of a quadrupole filter. Four elongated or cylindrical rod-shaped electrodes 1, which sufficiently approximate the field generated by hyperboloidal electrodes, are arranged to make a quadrupole mass filter. An electric generator 9 creates a high-frequency voltage $V\cos\omega t$ which is applied to the electrodes 1 through two capacitors 14. In this arrangement, the high-frequency voltage is rectified and smoothed by a rectifier 10. The direct voltage so created is divided by a potentiometer 15 and coupled to the electrodes 1 through inductors 13 whereby the ratio (u) of the direct voltage U to the alternating voltage V is substantially independent of alterations of the alternating voltage. As an alternative, a direct current voltage may be supplied to the electrodes 1 by an independent voltage source 11 and an electric two-way switch 11A. This electrode arrangement establishes an electric field between the electrodes whereby ions brought into such a field have equations of motion that are differential equations with periodical coefficients, the equations being characterized by having ranges of stable and unstable solutions. Thus, there exists two different kinds of ion paths (stable and unstable); either the ions perform oscillations around the center of symmetry of the field (Z-axis) because the amplitudes of the oscillations remain smaller than a certain maximum value (stable paths) or the amplitudes of the oscillations increase until they exceed a certain maximum value (unstable paths) whereby the ions impinge upon the field generating electrodes and are removed.

FIG. 3 is a schematic and perspective view of a duopole mass filter. Sources of charged particles 42 and 43 are arranged at one end of a pair of rod-shaped electrodes 3 and 5 which are arranged in parallel relationship to a planar electrode 4. The electrodes 3, 4 and 5 are oriented so as to direct charged particles along axis 44 and 45 (in the Z-plane) toward collector 46 and 47. The collectors 46 and 47 are shown as planar electrodes which are of prime advantage with this type of apparatus because of the elimination of induced voltages in the collector. Ions emerging from the exit of the filter impinge on the collectors 46 and 47 whereby signals are conducted to amplifiers 48 and 49 and hence to recorders 40 and 41 such as strip chart recorders. As is typical of conventional quadrupole mass filters, this apparatus is also energized with symmetrical AC and DC potentials. A more detailed description of a duopole filter may be found in U.S. Pat. No. 3,418,464 to W. M. Brubaker et al.

FIG. 4 is a schematic and perspective representation of a monopole mass filter. The cylindrical rod-shaped electrode 3 is arranged in parallel and spaced relation from two axially elongated conductive and electrically interconnected surface members 4 and 6 forming an angle with each other and extending in parallel in spaced relation to an axis (Z) between an ion source (not shown) and an ion collector (not shown).

FIG. 5 is a schematic block diagram of the monopole mass filter shown in FIG. 4. An ion source 42 is connected to a current-supply unit 21 which is preferably energized from a utility line. The ion accelerating voltage, for example about 30 volts, is then connected between the ion source and the angle structure comprised of two surface members 4 and 6. The ions are produced by electron collision in the ion source 42. The field electrode 3 is connected to a high-frequency generator 23 and a direct voltage source 25 through a circuit containing a lead 15, a capacitor 22 and an inductance coil 24. The high-frequency generator 23 and the direct voltage source 25 are preferably energized by the same power source coupled to current supply 21. A collector 47 is grounded through an

input stage of an amplifier 26 whose output circuit is connected to a recording instrument 27. In this filter, as in the previously described filters, the ions are introduced into the filter from a position which is generally along the Z-axis and, therefore ions must pass the field at the ends of the electrodes (and the fringing field) when entering and leaving the mass filter. A more detailed description of a monopole mass filter may be found in U.S. Pat. No. 3,197,633 to U. VonZahn.

Preferred Embodiments

FIG. 6 illustrates a mass filter which utilizes the principles of the invention. Four elongated electrodes 3, 5, 7 and 9 are symmetrically arranged about a central axis. Preferably the elongated electrodes have hyperbolic surfaces but cylindrical rod-shaped electrodes are also acceptable. Disposed in axial alignment with at least one of the elongated electrodes 3 is an auxiliary electrode 2 having an aperture 8 therein. In this embodiment, the cylindrical rod-shaped electrodes 5, 7 and 9 are approximately the same length, whereas the fourth electrode 3 extends beyond the other electrodes so that the extended portion of electrode 3 and the auxiliary electrode 2 form a monopole configuration. Located on one side of the aperture of electrode 2 is an ion source 42 which injects ions 50 through the aperture 8 and into the space between electrodes 2 and 3. The ions thus injected have components of momentum both perpendicular and parallel to the Z axis. Once in this space, the ions 50 are subjected to an electric field, first between the monopole electrodes 2 and 3 and then between the quadrupole electrodes 3, 5, 7, 9. The ends of electrodes 5, 7, 9 overlap auxiliary electrode 2 so that ions 50, traveling into the quadrupole field, travel in the space between the auxiliary electrode 2 and quadrupole electrode 3 and, therefore, are not subjected to the fringing fields associated with the ends of electrodes 5, 7, 9 on the other side of the auxiliary electrode 2. The entrance end of the filter can be further modified by locating a plate perpendicular to the ends of the electrodes 5, 7, 9 to further shield ions entering the filter. Disposed at the other end of the quadrupole mass filter is a detector 47 which detects the ions which exit from the quadrupole filter. As an additional feature, the aperture 8 in the auxiliary electrode 2 may have a wire mesh or screen (not shown) placed over the opening so that ions passing through the aperture 8 will be more uniformly arranged. Further, the wire mesh may be grounded or biased to obtain other advantages.

FIG. 7 is a side view of the preferred embodiment illustrated in FIG. 6. From this view it can be seen that auxiliary electrode 2 is disposed in axial alignment with quadrupole electrode 3. The auxiliary electrode 2 comprises two axially elongated conductive and electrically interconnected surface members forming an angle with each other and having an aperture therein which extends along a portion of at least one surface member. Alternatively, the aperture 8 in the auxiliary electrode could extend along a portion of both surface members as is shown in FIG. 6.

FIG. 8 is a diagrammatic representation of a duopole mass filter and a quadrupole mass filter. Electrodes 3, 5, 7 and 9 are arranged about a central axis with electrodes 3 and 5 aligned in a plane that is in parallel relationship to electrodes 7 and 9. In this embodiment, the auxiliary electrode 2 has a wire screen 6 covering the aperture 8 therein. Ions from introduced from an ion source 42 so that the ions 50 enter the electric field between the auxiliary electrode 2 and the duopole electrodes 3 and 5 through aperture 8. The ions so entering then pass into the quadrupole mass filter defined by electrodes 3, 5, 7 and 9.

FIG. 9 is a side view of a preferred embodiment shown in FIG. 8. This figure illustrates the arrangement of the auxiliary electrode 2 with respect to the quadrupole electrodes 3, 5, 7 and 9. It is preferred that the planar electrode 2 be located in a plane that is parallel to a first plane located between the center axis of electrode 3 and 5 and parallel to a plane located between the center axis of electrodes 7 and 9.

FIG. 10 is an alternate embodiment of the invention. Four elongated electrodes 3, 5, 7 and 9 are symmetrically arranged about a central axis. In this embodiment, the cylindrical rod-shaped electrodes 5, 7 and 9 extend beyond electrode 3 and are in axial alignment and spaced relationship to auxiliary electrode 2. Ions introduced through the aperture 8 in the auxiliary electrode 2 will be subjected to the electric field established between auxiliary electrode 2 and quadrupole electrodes 5, 7 and 9.

FIG. 11 is a side view of the embodiment illustrated in FIG. 10.

FIG. 12 is an illustration of how auxiliary apertured electrodes 2 may be used at the entrance end and exit end of a quadrupole filter. In this embodiment, a potential is applied to electrodes 3, 5, 7 and 9 to create a time varying electric field. A first auxiliary electrode 2, having an aperture 8 therein, is arranged so that it forms generally a monopole configuration with one of the quadrupole electrodes 3. An ion source 42 accelerates ions 50 into the field between the first auxiliary electrode 2 and one of the quadrupole electrodes 3. This arrangement introduces ions into the electric field at an angle to the central (Z) axis of the quadrupole structure. Similarly, a second auxiliary electrode 12 having an aperture 18 therein is located at the exit end of the quadrupole filter. A detector 47 is located on one side of the second auxiliary electrode to detect ions that leave the quadrupole field by passing into the field between the second auxiliary electrode 12 and the quadrupole electrode 3 and then through the aperture 18 where they are detected by the detector 47. Although this embodiment uses V-shaped electrodes at both the input and output of the mass filter, planar electrodes or planar electrodes in combination with a V-shaped electrode may be used. Other modifications such as, biasing the detector 47 to draw ions 50 out of the filter and locating a plate over the ends of each electrode 5, 7 and 9 at the source and/or detector end may also be made to this embodiment.

Operation

Ideally, a quadrupole has a mass analyzing region that consists of four electrically conducting, parallel hyperbolic surfaces in which opposite pairs of surfaces are connected together. Applied to the two pairs of surfaces are equal but opposite polarity potentials (each potential having DC and RF voltage components) so that equipotential surfaces in the analyzing region between the four poles appear as oscillating hyperbolic potentials.

If an ion is now injected down the Z-axis of the four surfaces, it will undergo transverse motion in the X-Y plane in addition to its motion down the Z-axis. The exact trajectories of the ions are solutions of Mathieu's differential equation and contain either an oscillatory factor or an exponential factor, depending upon, among other factors, the charge-to-mass ratio of the ion in question.

For singly charged ions and a specific frequency and set of voltages, only one mass of ion will undergo oscillatory motion that allows transmission through the analyzing region. All other ions will be swept radially outward from the center Z-axis and be neutralized when they strike one of the surfaces. Thus, the apparatus functions as a mass filter by transmitting only one particular mass of ion from a collection of injected ions.

Referring now to FIG. 12 the advantages of the invention are as follows: To avoid the undesirable effect, e.g., rejection, in the fringe-fields at the entrance of the mass filter, ions 50 from ion source 42 are injected into the region between the V-shaped electrode 2 and the quadrupole electrode 3 through aperture 8. An ion in this region is subjected to forces similar to those in a monopole filter; the ion 50 having an oscillatory motion and traveling along Z-axis. As the ions 50 leave the monopole configuration, they enter the quadrupole filter where ions having unstable oscillation are neutralized when they strike one of the quadrupoles. The remaining ions, having

stable oscillations, travel in a direction along the Z-axis. To minimize the fringe-fields at the exit end of the mass filter, an arrangement similar to that at the entrance end is located at the exit end of the analyzer region. Here another apertured electrode 2 allows the ions to pass out of the quadrupole field without being affected by the fringing fields associated with the ends of the electrodes. A detector 47 disposed on one side of the aperture electrode receives the ions as they pass through the aperture 18. From this embodiment, it can be seen that the fringe-field effects on ions as they enter and leave the mass filter are eliminated.

While a preferred embodiment of the invention has been disclosed, it will be apparent to those skilled in the art that changes may be made to the invention as set forth in the appended claims, and, in some cases, certain features of the invention may be used to advantage without corresponding use of other features. For example, the auxiliary electrode having the aperture therein may be covered by a wire mesh which is either grounded or electrically biased to reflect or accelerate ions. Further, the rod electrodes and/or one electrode such as, electrode 3, may be comprised of a plurality of electrically separate electrodes for electrical biasing to achieve certain effects. Accordingly, it is intended that the illustrative and descriptive materials herein be used to illustrate the principles of the invention and not to limit the scope thereof.

Having described the invention, what is claimed is:

1. In combination with a mass filter of the type having four axially elongated electrodes having coextensive portions and arranged about a central axis for creating a time periodical electric field therebetween to separate ions having different mass-to-charge ratios by causing certain ions to perform oscillations of limited amplitudes and other ions to perform oscillations of increasing amplitudes depending on the mass-to-charge ratios of the ions, thereby separating certain ions from the others, the improvement comprising:

an auxiliary electrode having an aperture therein for the passage of ions, said auxiliary electrode aligned with and adjacent to at least one of said elongated electrodes which extends beyond the other three so that ions passing through said auxiliary electrode aperture enter said time periodical electric field.

2. The combination as recited in claim 1 wherein said auxiliary electrode comprises:

two axially elongated conductive and electrically interconnected surface members forming an angle with each other and extending along and in spaced relationship to said central axis between said elongated electrodes, said aperture therein extending along a portion of at least one surface member.

3. The combination as recited in claim 2 wherein said plurality of elongated electrodes arranged about the central axis for creating a time periodical electric field therebetween are cylindrically shaped electrodes.

4. The combination as recited in claim 2 wherein said auxiliary electrode includes a screen covering said aperture.

5. The combination as recited in claim 1 wherein said auxiliary electrode comprise a planar electrode having an aperture therein for the passage of ions.

6. In combination with a mass filter of the type having four axially elongated electrodes arranged about a central axis for creating a time periodical electric field therebetween to separate ions having different mass-to-charge ratios, the improvement wherein one of said electrodes extends beyond the ends of the other electrodes, and a fifth electrode having an aperture is disposed opposite the extended portion of said extended electrode on the side of said central axis so that ions may pass through the aperture in said fifth electrode and into said time periodical electric field between said electrodes.

7. The combination as recited in claim 6 wherein said fifth electrode comprises:

two axially elongated conductive and electrically interconnected surface members forming an angle with each other and extending along and in spaced relationship to said

central axis between said elongated electrodes, said aperture therein extending along a portion of at least one surface member.

8. The combination as recited in claim 7 wherein said elongated electrodes arranged about the central axis are cylindrically shaped electrodes.

9. The combination as recited in claim 6 wherein said auxiliary electrode includes a screen covering said aperture.

10. An apparatus for separating ions having different mass-to-charge ratios, comprising:

an evacuable enclosure;

four axially elongated electrodes located within said evacuable enclosure and arranged about a central axis, one electrode extending beyond the other three;

an auxiliary electrode having an aperture therein for the passage of ions, said auxiliary electrode disposed in parallel axial alignment with and adjacent to said one electrode extending beyond the other three on the side of the central axis;

means for holding said electrodes in spaced relation;

means for applying a voltage having a periodical function of time $f(t)$ to said elongated electrodes to create a time periodical electric field therebetween;

means for creating and introducing ions into said electric field through said aperture in said auxiliary electrode whereby said electric field causes certain ions to perform oscillations of limited amplitude and other ions to perform oscillations of increasing amplitude, depending upon the respective specific charges on the ions, thereby separating certain ions from others; and

means for detecting said ions having oscillations of limited amplitude said detecting means disposed at one of the ends of said elongated electrodes.

11. The apparatus as recited in claim 10 wherein said auxiliary electrode having an aperture therein comprises:

two axially elongated conductive and electrically interconnected surface members forming an angle with each other and extending along and in spaced relationship to said central axis between said elongated electrodes, said aperture therein extending along a portion of at least one surface member.

12. The apparatus as recited in claim 10 wherein said detecting means includes:

a second auxiliary electrode having an aperture therein for the passage of said ions having oscillations of limited amplitude, said second auxiliary electrode disposed in axial alignment with at least one of said elongated electrodes; and

means for collecting ions passing through said second auxiliary electrode aperture, said collecting means disposed adjacent the central axis of said elongated electrodes.

13. The apparatus as recited in claim 11 wherein said detecting means includes:

a second auxiliary electrode having an aperture therein for the passage of said ions having oscillations of limited amplitude, said second auxiliary electrode disposed in axial alignment with at least one of said elongated electrodes; and

means for collecting ions passing through said second auxiliary electrode aperture, said collecting means disposed adjacent the central axis of said elongated electrodes.

14. The combination as recited in claim 10 wherein said auxiliary electrode comprises a planar electrode having an aperture therein for the passage of ions.

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