United States Patent

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[54] **QUADRUPOLE MASS FILTER WITH ELECTRODE STRUCTURE FOR FRINGING-FIELD COMPENSATION**
10 Claims, 4 Drawing Figs.

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[51] **Int. Cl.** **H01j 39/34**
[50] **Field of Search** 250/41.9
SB, 41.9 SE, 41.9 (2); 313/230, 63

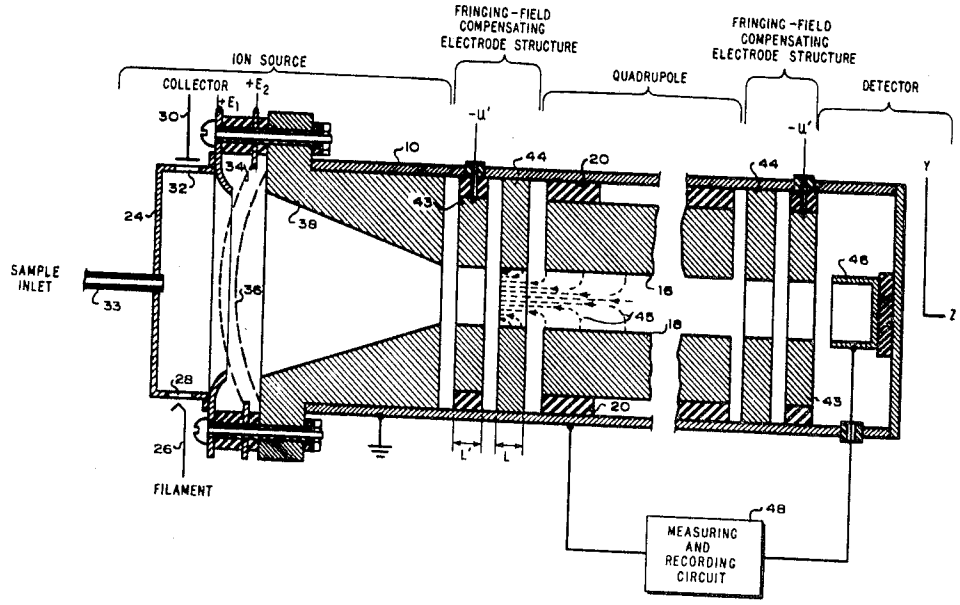
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ABSTRACT: Four parallel primary electrodes are symmetrically disposed about a central axis within an electrically conductive housing operated at a reference potential. These electrodes are driven by an excitation voltage comprising AC and DC components balanced with respect to the reference potential to provide a quadrupole mass filter. An ion source is positioned near the entrance of the quadrupole for transmitting ions generally along the central axis toward an ion detector positioned near the exit of the quadrupole. A pair of electrodes is symmetrically positioned about the central axis between the ion source and the entrance of the quadrupole. The electrode nearest the ion source is operated at a DC voltage referred to the reference potential and maintained directly proportional to the DC excitation voltage component applied to the quadrupole. The electrode nearest the quadrupole is operated at a fixed DC voltage referred to the reference potential. A similar pair of electrodes is also employed between the ion detector and the exit of the quadrupole.



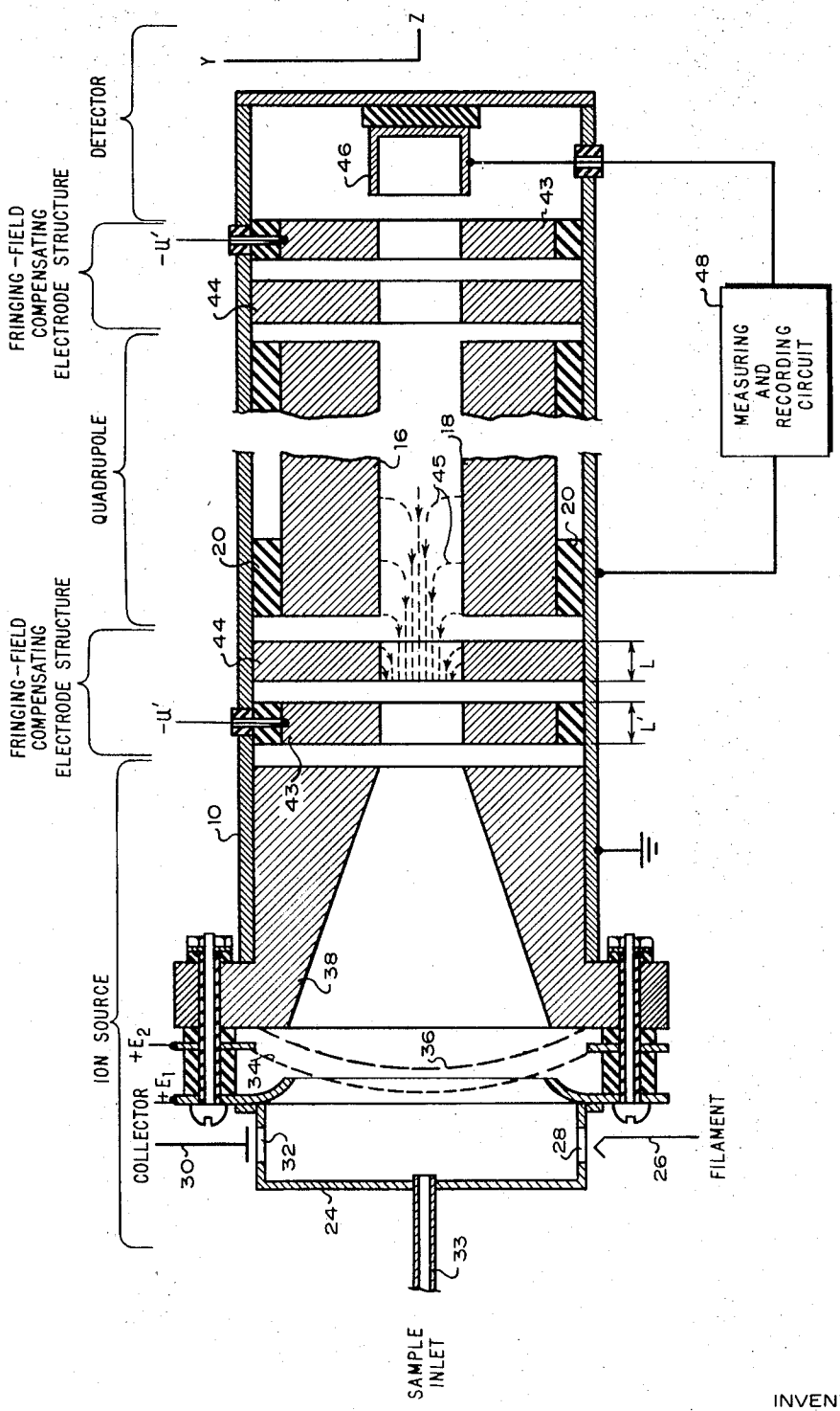


Figure 1

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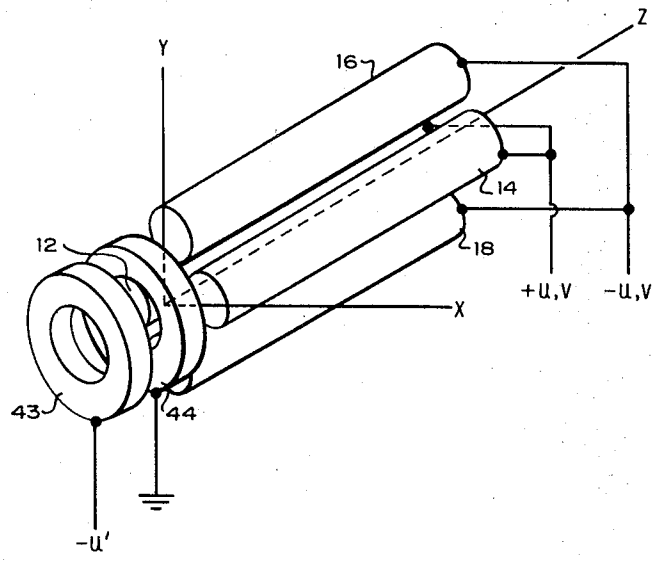


Figure 2

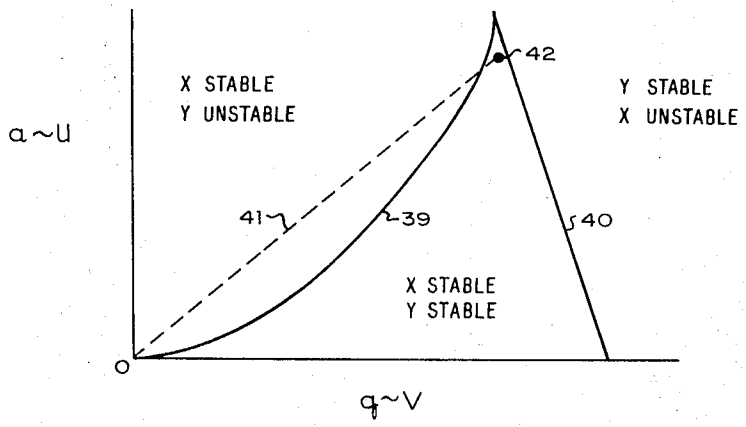


Figure 3

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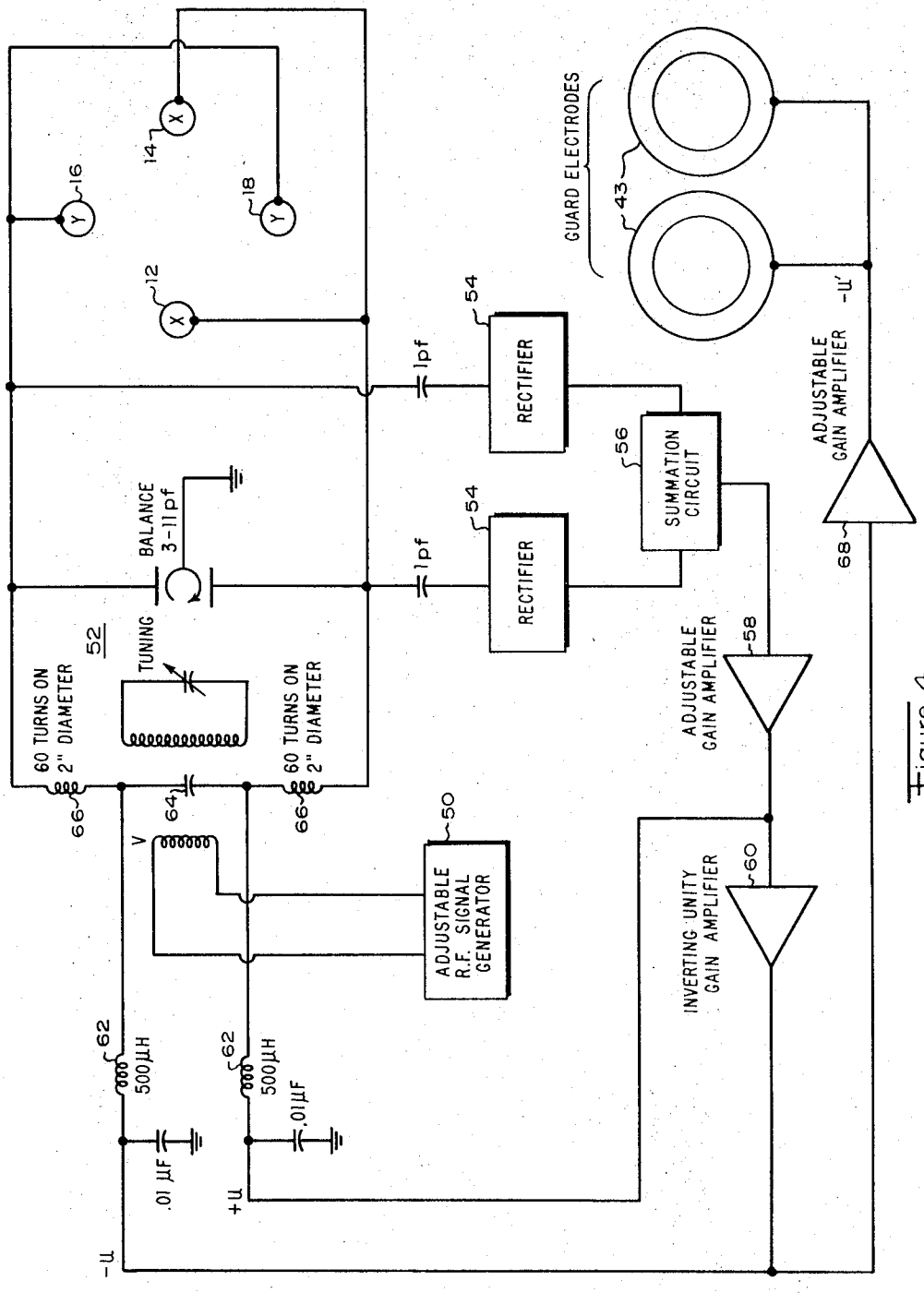


Figure 4

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QUADRUPOLE MASS FILTER WITH ELECTRODE STRUCTURE FOR FRINGING-FIELD COMPENSATION

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to quadrupole mass spectrometers and, more particularly, to the entrance and exit construction of quadrupole mass filters employed therein.

Fringing fields near the entrance of a quadrupole mass filter have a serious defocusing effect upon ions approaching and entering the quadrupole. Concomitantly, fringing fields near the exit of the quadrupole mass filter have a similar, though perhaps less serious, defocusing effect upon ions leaving the quadrupole. Auxiliary electrodes have been employed about the central axis of the quadrupole and partially around the opposite ends of the primary electrodes of the quadrupole to compensate for this defocusing effect by decreasing the ratio of the DC excitation voltage component to the peak AC excitation voltage component at the ends of the primary electrodes. See Wilson M. Brubaker's U.S. Pat. No. 3,129,327 entitled Auxiliary Electrodes for Quadrupole Mass Filters and issued on Apr. 14, 1964. Segmented primary electrodes have also been employed to compensate for this defocusing effect by similarly decreasing the ratio of the DC excitation voltage component to the peak AC excitation voltage component at the ends of the primary electrodes. See Wilson M. Brubaker's U.S. Pat. No. 3,371,204 entitled Mass Filter with one or more Rod Electrodes separated into a Plurality of Insulated Segments and issued on Feb. 27, 1968.

In accordance with the illustrated embodiment of this invention a pair of cylindrical electrodes is symmetrically positioned about the central axis of the quadrupole between an ion source and the entrance of the quadrupole. The cylindrical electrode nearest the ion source, hereinafter referred to as the guard electrode, is operated at a negative DC voltage referred to quadrupole ground and maintained directly proportional to the DC excitation voltage component applied to the quadrupole. Quadrupole ground is defined for purposes of this specification and the claims appended hereto as the mean potential of the primary electrodes of the quadrupole. The cylindrical electrode nearest the entrance of the quadrupole, hereinafter referred to as the intermediate electrode, is operated at a fixed DC voltage referred to quadrupole ground. Another pair of cylindrical guard and intermediate electrodes may be similarly employed between the exit of the quadrupole and an ion detector.

The overall effect of the guard and intermediate electrodes is to minimize the defocusing effect of the fringing fields both inside and outside the quadrupole and to thereby increase the ion transmission efficiency and hence the sensitivity of the quadrupole without impairing its resolution. This is accomplished in three ways. First, the guard electrodes provide a positive focusing effect to compensate for the defocusing effect of the fringing fields near the entrance and the exit of the quadrupole. Secondly, the guard electrodes cause ions to pass through the regions of fringing fields near the entrance and the exit of the quadrupole with a higher axial velocity than they have inside the quadrupole thereby reducing their exposure to the quadrupole fringing fields. Thirdly, the guard and the intermediate electrodes partially shield ions approaching the entrance of the quadrupole and leaving the exit of the quadrupole from the fringing fields outside the quadrupole.

DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic sectional view of a quadrupole mass spectrometer constructed in accordance with the preferred embodiment of this invention.

FIG. 2 is a fragmentary perspective view of the fringing field compensating structure at the entrance of the quadrupole mass filter of FIG. 1.

FIG. 3 is a stability diagram illustrating the operating characteristics of a quadrupole mass filter.

FIG. 4 is a schematic diagram of an electrical circuit for controlling the excitation voltage applied to the quadrupole and the voltage applied to the guard electrodes of FIGS. 1 and 2.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIGS. 1 and 2, there is shown a quadrupole mass spectrometer including a cylindrical electrically conductive housing **10** operated at ground potential and having four primary electrodes **12, 14, 16** and **18** mounted therein on electrically insulating supports **20**. Housing **10** is positioned within an evacuated enclosure when the quadrupole mass spectrometer is to be employed in the laboratory. However, this evacuated enclosure is unnecessary when the quadrupole mass spectrometer is to be employed for upper atmospheric research in the vacuum of space. The primary electrodes comprise coextensive, electrically conductive, cylindrical rods extending parallel to one another and symmetrically disposed about the central axis Z. Diametrically opposed rods **12** and **14** have their centers in the X–Z plane and are hereinafter referred to as the X-rods, whereas diametrically opposed rods **16** and **18** have their centers in the y–Z plane and are hereinafter referred to as the Y-rods. As shown in FIG. **2**, X-rods **12** and **14** are electrically connected together and Y-rods **16** and **18** are electrically connected together. An excitation voltage comprising both a balanced AC component V and a balanced DC component $\pm U$ is applied between the X-rods and the Y-rods to provide a quadrupole mass filter. All voltages are referred to quadrupole ground, which is maintained at the ground potential of housing **10**. The positive DC excitation voltage component $+U$ is applied to the X-rods, and the negative DC excitation voltage component $-U$ is applied to the Y-rods. This creates a quadrupole electric field having both AC and DC components between the X-rods and the Y-rods.

An ion source is mounted at one end of housing **10** and is symmetrically disposed about the central axis Z. The ion source may comprise, for example, an ionization chamber **24** operated at a positive voltage E_1 of about five volts. A filament **26** is mounted adjacent to an aperture **28** in one side of the ionization chamber, and a collector **30** is mounted adjacent to an aperture **32** in the opposite side of the ionization chamber. Positive ions are produced by operating the filament and the collector to provide an electron flow of about ten milliamperes through a gas sample injected into the ionization chamber by means of a sample inlet **33**. A beam of these ions is drawn out of the ionization chamber by a spherical-shaped mesh electrode **34** operated at a positive voltage E_2 of about three volts. A concentric spherical-shaped mesh electrode **36** operated at quadrupole ground and mounted on a conical shielding member **38** operated at quadrupole ground is positioned adjacent to drawout mesh electrode **34** to focus the beam of ions on the central axis Z near the entrance of quadrupole **12–18**.

The defocusing action of the quadrupole fringing fields upon positive ions from the ion source can be explained with reference to the stability diagram of FIG. **3**, where the abscissa q is proportional to the AC excitation voltage component V and the ordinate α is proportional to the DC excitation voltage component U. In this diagram, the triangularly shaped region defined by solid lines **39** and **40** represents stable ion motion in both the X and the Y directions. The region to the left of solid line **39** represents unstable ion motion in the Y direction, and the region to the right of solid line **40** represents unstable ion motion in the X direction. If the ratio of the DC excitation voltage component U to the AC excitation voltage component V is held constant, the locus of the operating point of an ion passing through the quadrupole fringing fields is the dashed straight line **41**. The ratio of U to V is adjusted so that this line passes just below the apex of the triangularly shaped region of stability to maximize the resolution of the quadrupole mass filter. Along dashed line **41** the ion motion is stable everywhere in the X direction and is unstable in the Y direction until nearly the final operating point **42** is reached.

This instability in the Y direction reduces the ion transmission efficiency and hence the sensitivity of the quadrupole mass filter.

A fringing-field compensating electrode structure is symmetrically disposed about the central axis Z between the ion source and the entrance of the quadrupole to increase the ion transmission efficiency and hence the sensitivity of the quadrupole mass filter. This structure includes a cylindrical or ring-shaped guard electrode **43** and a cylindrical or ring-shaped intermediate electrode **44** that is positioned between the guard electrode and the entrance of the quadrupole. Each of these electrodes has an inside diameter approximately equal to or slightly larger than the distance between the opposite rods of the quadrupole.

Guard electrode **43** is operated at a DC voltage $-U'$ directly proportional to the DC excitation voltage component U applied to Y-rods **16** and **18**, and intermediate electrode **44** is operated at quadrupole ground. Under these conditions, dashed lines **45** represent the DC electric field that would exist inside the intermediate electrode and extend into the quadrupole if the primary electrodes of the quadrupole were grounded. From the direction of this field, as indicated by the arrowheads, it is evident that positive ions in this region will experience a restoring force towards the central axis Z as well as a decelerating force in the direction of the central axis Z. The DC electric field resulting when the AC excitation voltage component V and the DC excitation voltage component $\pm U$ are applied to the quadrupole is a superposition of the electric field represented by dashed lines **45** and the usual DC quadrupole fringing fields. Thus, by applying a negative DC voltage $-U'$ of appropriate magnitude to guard electrode **43**, the operating point for motion in the Y direction of an ion passing through the quadrupole fringing fields may be shifted into the region of stability. The operating point for ion motion in the X direction is also shifted, but will remain in the region of stability provided the shift is not too large.

The length L of intermediate electrode **44** is made long enough to obtain compensation over the whole region where there is a significant amount of fringing-field defocusing. However, if it is made excessively long the optimum value of the ratio U'/U becomes inconveniently large. Our theoretical studies indicate that the intermediate electrode has an optimum value about equal to half the distance between the diametrically opposite quadrupole rods, hereinafter referred to as the field radius.

It appears from experimental results that for an intermediate electrode **44** having a length L approximately equal to the field radius, the effectiveness of the fringing-field compensating electrode structure is increased as the DC voltage $-U'$ applied to guard electrode **43** is decreased from ground to a negative voltage of about 2U to 2.5U. However, further decreasing the DC voltage $-U'U'$ applied to guard electrode **43** substantially below a negative voltage of 2.5U appears to decrease the effectiveness of the fringing-field compensating electrode structure because of an adverse effect upon the stability of ion motion in the X direction at such voltages. In order to obtain good fringing-field compensation over a wide range of mass numbers, it is necessary to scan the DC voltage $-U'$ applied to the guard electrode directly and uniformly proportional to the DC excitation voltage component U applied to the quadrupole.

Since a greater negative DC voltage is applied to guard electrode **43** than to the quadrupole, the guard electrode also causes the positive ions to pass through the region of fringing fields near the entrance of the quadrupole with a higher axial velocity than they have inside the quadrupole. This minimizes the exposure of the ions to the fringing fields near the entrance of the quadrupole. Furthermore, the guard and intermediate electrodes **43** and **44** partially shield ions approaching the entrance of the quadrupole from the fringing fields outside the quadrupole.

We have tested the effectiveness of the fringing-field compensating structure by using a quadrupole where the field radius was 0.254 inch, the length of rods **12–18** was 10 inches, the AC excitation voltage component V was swept from 0 to 1,800 volts peak at a frequency of 1 megahertz, and the DC excitation voltage component $\pm U$ was swept from 0 to ± 300 volts. An improvement in sensitivity of between one and two orders of magnitude was obtained by employing a guard electrode **43** having a length L' of 0.200 inch and an intermediate electrode **44** having a length L of 0.200 inch and by sweeping the voltage $-U'$ applied to the guard electrode from 0 to -600 volts directly and uniformly proportional to the DC excitation voltage component U applied to the quadrupole.

An ion detector **46** such as a conventional photomultiplier or Faraday cup is mounted at the other end of housing **10** and is symmetrically disposed about the central axis Z. Positive ions entering and traversing the quadrupole impinge upon ion detector **46** and thereby produce an electrical current that may be measured by a conventional measuring and recording circuit **48**. The DC excitation voltage component $-U$ applied to the Y-rods also has a defocusing effect in the Y–Z plane upon the positive ions approaching and leaving the exit of the quadrupole. Thus, another fringing-field compensating structure similar to that described above may be disposed along the central axis Z between the exit of the quadrupole and the detector **46** to compensate for this defocusing effect and thereby further increase the ion transmission efficiency and hence the sensitivity of the quadrupole mass spectrometer.

As shown in FIG. 4, the drive circuit for the quadrupole and the fringing-field compensating structures may comprise an RF signal generator **50** having an adjustable peak output voltage and an adjustable frequency. Signal generator **50** is inductively coupled to an RF tank circuit **52** for supplying an AC voltage V across the X- and Y-rods of the quadrupole. Rectifiers **54** are connected to the RF tank circuit **52** to provide rectification of the AC voltage supplied to the quadrupole. A summing circuit **56** supplies the resulting DC voltage to an adjustable gain amplifier **58** to provide the desired DC excitation voltage component $+U$. An inverting unity gain amplifier **60** is connected to the output of adjustable gain amplifier **58** to produce the desired DC excitation voltage component $-U$. The outputs of amplifiers **58** and **60** are connected by inductors **62** to the tank circuit **52** on opposite sides of capacitor **64** and between chokes **66** so that the DC excitation voltage component $+U$ is supplied to the X-rods and so that the DC excitation voltage component $-U$ is supplied to the Y-rods. Another adjustable gain amplifier **68** connected to the output of inverting unity gain amplifier **60** is connected for supplying the desired DC voltage $-U'$ to guard electrodes **43**. By varying the peak output voltage of adjustable signal generator **50** at a constant frequency, the AC excitation voltage component V and the DC excitation voltage component $\pm U$ may be swept to provide mass scanning. Concomitantly, the DC voltage $-U'$ applied to guard electrodes **43** is swept directly and uniformly proportional to the DC excitation voltage component U as required to counteract the defocusing effect of the fringing fields over the entire mass scanning range.

We claim:

1. A multipole mass spectrometer comprising:
   - a plurality of substantially parallel primary electrodes spaced symmetrically about a central axis;
   - means for applying to the primary electrodes an excitation voltage including AC and DC components balanced with respect to a reference potential to produce alternating and static multipole electric field components between the primary electrodes;
   - an ion source positioned along the central axis near an entrance end of the primary electrodes;
   - an ion detector positioned along the central axis near an exit end of the primary electrodes;
   - a first electrode positioned between one end of the primary electrodes and one of the ion source and detector for operating at a DC voltage referred to the reference potential;

means for varying the excitation voltage applied to the primary electrodes to scan ions having a range of masses; and

means for varying the DC voltage applied to the first electrode directly proportional to the DC component of the excitation voltage applied to the primary electrodes.

2. A multipole mass spectrometer as in claim 1 wherein said first electrode is positioned between the ion source and the entrance end of the primary electrodes.

3. A multipole mass spectrometer as in claim 2 including a second electrode positioned between the first electrode and the entrance end of the primary electrodes for operating at a DC voltage different from that of the first electrode.

4. A multipole mass spectrometer as in claim 3 wherein each of said first and second electrodes has an aperture symmetrically positioned about the line of intersection of two intersecting planes, one of said planes passing through the centers of one pair of the primary electrodes and the other of said planes passing through the centers of another pair of the primary electrodes.

5. A multipole mass spectrometer as in claim 1 wherein said first electrode is positioned between the ion detector and the exit end of the primary electrodes.

6. A multipole mass spectrometer as in claim 5 including a second electrode positioned between the first electrode and the exit end of the primary electrodes for operating at a DC voltage different from that of the first electrode.

7. A multipole mass spectrometer as in claim 6 wherein each of said first and second electrodes has an aperture symmetrically positioned about the line of intersection of two intersecting planes, one of said planes passing through the centers of one pair of the primary electrodes and the other of said planes passing through the centers of another pair of the primary electrodes.

8. A multipole mass spectrometer as in claim 4 including:

a third electrode positioned between the ion detector and the exit end of the primary electrodes for operating at a DC voltage referred to the reference potential;

means for varying the DC voltage applied to the third electrode directly proportional to the DC component of the excitation voltage applied to the primary electrodes; and

a fourth electrode positioned between the third electrode and the exit end of the primary electrodes for operating at a DC voltage different from that of the first electrode;

each of said third and fourth electrodes having an aperture symmetrically positioned about the line of intersection of said two intersecting planes.

9. A multipole mass spectrometer comprising:

a plurality of substantially parallel primary electrodes spaced symmetrically about a central axis;

means for applying to the primary electrodes an excitation voltage including AC and DC components balanced with respect to a reference potential to produce alternating and static multipole electric field components between the primary electrodes;

an ion source positioned along the central axis near one end of the primary electrodes;

an ion detector positioned along the central axis near the other end of the primary electrodes;

a first electrode positioned between the ion detector and said other end of the primary electrodes for operating at a DC voltage referred to the reference potential; and

a second electrode positioned between the first electrode and said other end of the primary electrodes for operating at a fixed DC voltage different from that of the first electrode.

10. A multipole mass spectrometer as in claim 9 including:

means for varying the excitation voltage applied to the primary electrodes to scan ions having a range of masses; and

means for varying the DC voltage applied to the first electrode directly proportional to the DC component of the excitation voltage applied to the primary electrodes.

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