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Turner

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[54] **MULTIPOLE MASS FILTER WITH ARTIFACT-REDUCING ELECTRODE STRUCTURE**

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[21] Appl. No.: **113,312**

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

[51] **Int. Cl.** **H01j 39/34**

[58] **Field of Search** .....250/41.9 DS, 49.5 C; 313/81, 313/83; 330/4.7

[56] **References Cited**

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Primary Examiner—William F. Lindquist

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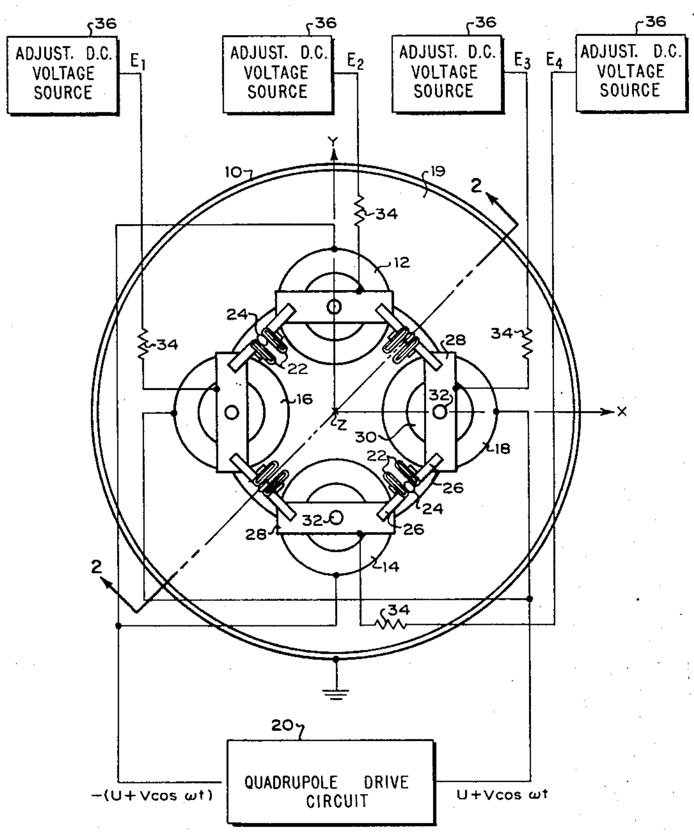
[57] **ABSTRACT**

Parallel primary electrodes are symmetrically disposed about a central axis within an electrically conductive housing operated at a reference potential. These primary electrodes are driven by an excitation voltage comprising A.C. and D.C. components balanced with respect to the reference potential to provide a multipole mass filter. An ion source is positioned adjacent to the entrance end of the multipole mass filter for transmitting ions generally along the central axis to an ion detector positioned adjacent to the exit end of the multipole mass filter. Auxiliary electrodes, at least some of which may be operated at different potentials, are disposed between adjacent pairs of the primary electrodes along the length thereof outside the central region defined by a cylinder inscribed between the primary electrodes. These auxiliary electrodes are driven by a plurality of independently adjustable D.C. control voltages to reduce artifacts in the mass spectra obtained from the multipole mass filter.

12 Claims, 12 Drawing Figures



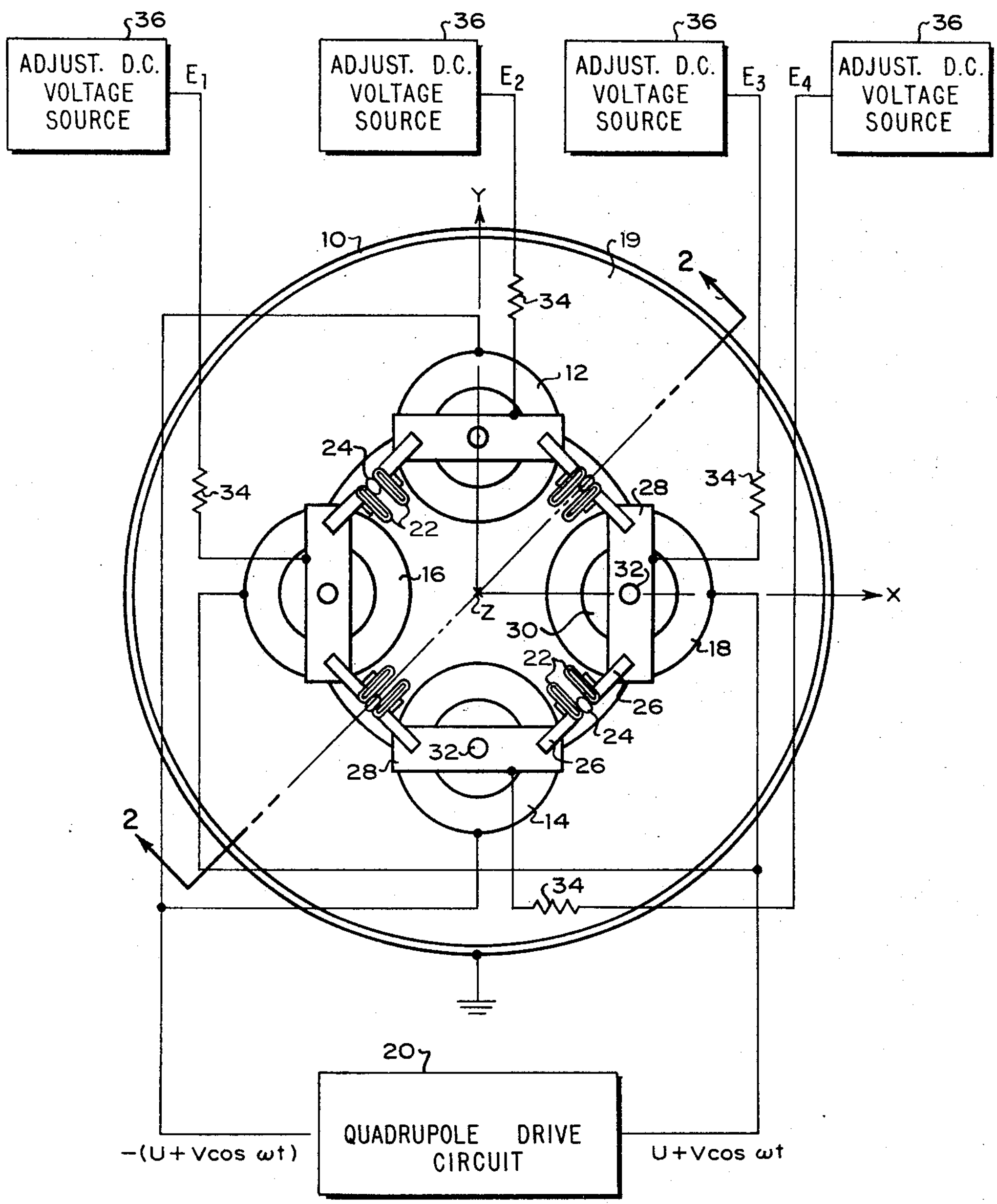


Figure 1

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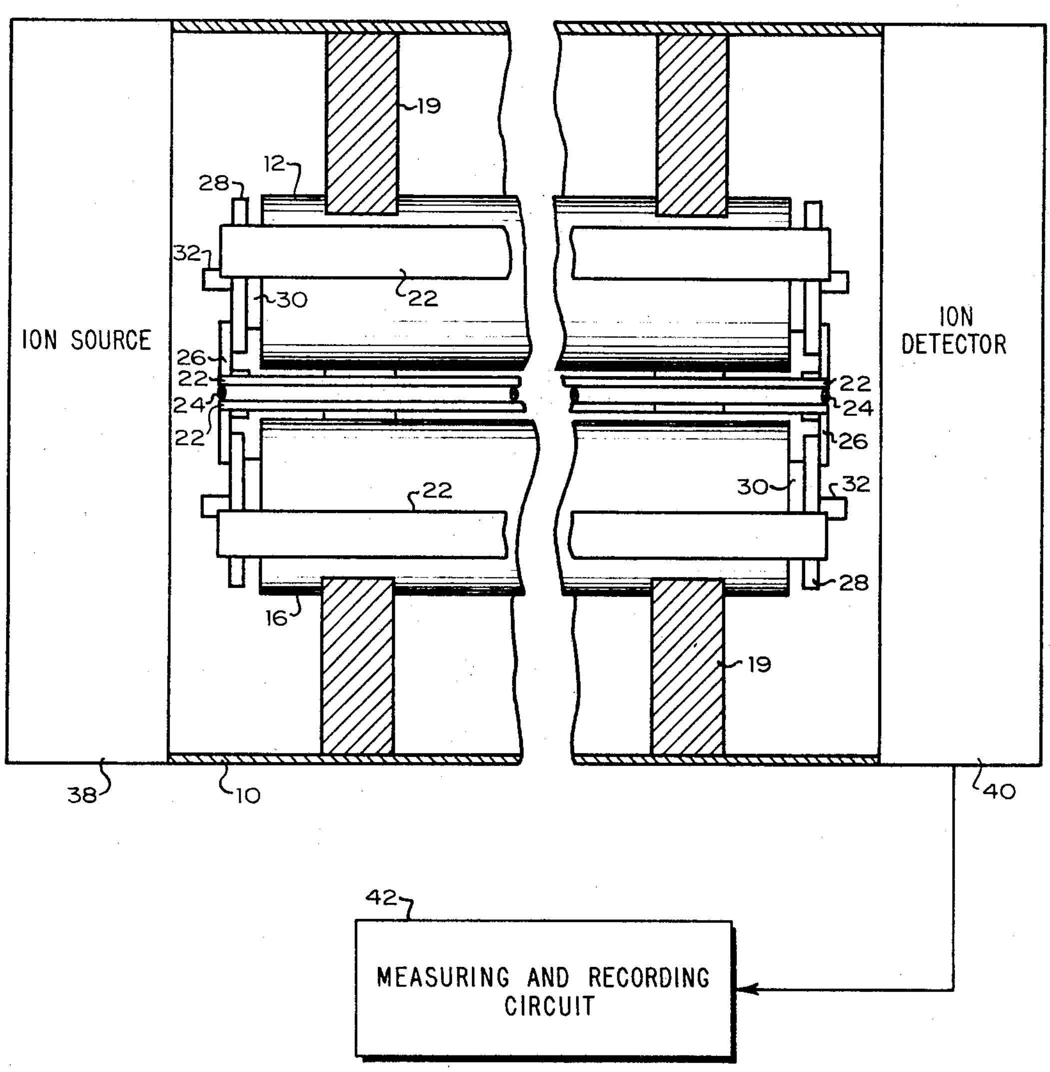

Figure 2

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ION PEAKS 69 AND 70 FROM PERFLUOROTRIBUTYLAMINE MASS SPECTRUM

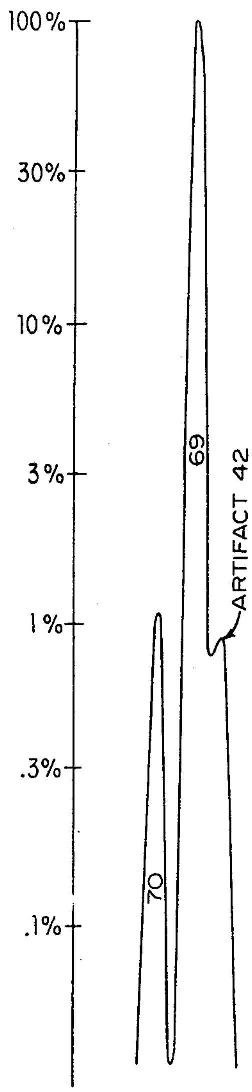

Figure 3

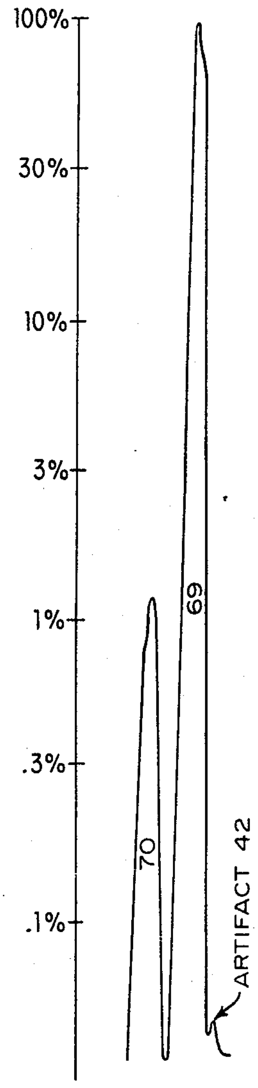

Figure 4

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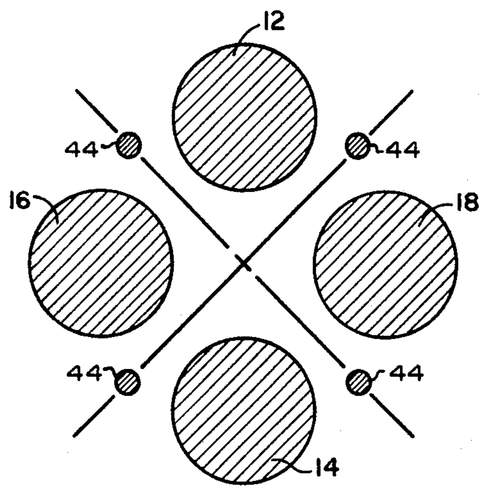

Figure 5

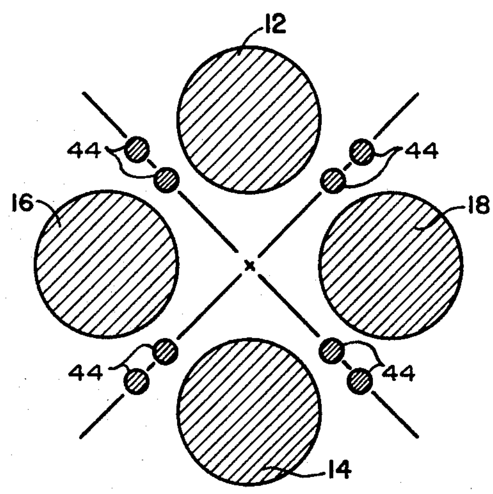

Figure 6

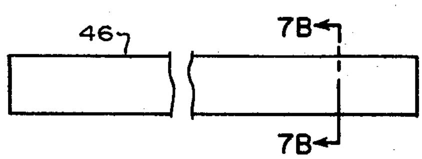

Figure 7A

Figure 7B

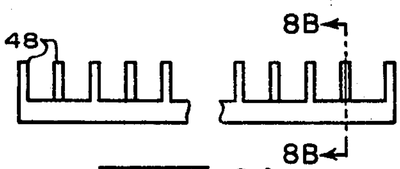

Figure 8A

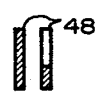

Figure 8B

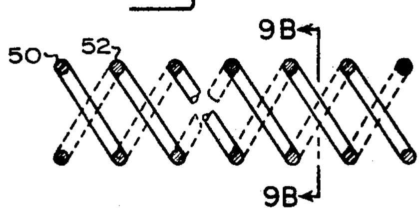

Figure 9A

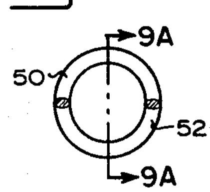

Figure 9B

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MULTIPOLE MASS FILTER WITH ARTIFACT-REDUCING ELECTRODE STRUCTURE

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates generally to multipole mass spectrometers and more particularly to an improved multipole mass filter structure that may be employed therein.

Ideally, the mass spectrum obtained from a multipole mass filter should comprise a series of sharply defined ion peaks. In practice, however, ion peaks in the mass spectrum typically exhibit tailing, cursors, or other artifacts that may either obscure other ion peaks present in the mass spectrum or be mistaken for ion peaks not present in the mass spectrum. This seriously impairs the resolution of the multipole mass filter. Another problem commonly associated with a multipole mass filter is that both the ion peak shape and the sensitivity change with time due at least in part to ion build-up on the electrodes of the multipole mass filter.

Accordingly, it is the principal object of this invention to provide an improved multipole mass filter structure that significantly reduces artifacts, improves the resolution to the point where measurement of C^{13} in natural abundance can be made, and permits changes with time in ion peak shape and sensitivity to be compensated.

This object is accomplished in accordance with the preferred embodiments of this invention by employing a plurality of parallel primary electrodes that are symmetrically disposed about a central axis and by further employing a plurality of auxiliary electrodes that may be operated at different potentials and that are disposed between adjacent pairs of the primary electrodes along the length thereof and outside the central region defined by a cylinder inscribed between the primary electrodes. According to different ones of the preferred embodiments, either a single auxiliary electrode or a pair of auxiliary electrodes positioned side by side or one outside the other are disposed between each adjacent pair of the primary electrodes along the full length thereof. These auxiliary electrodes may comprise, for example, electrically conductive tubes, rods, bars, combs, or bifilar helices. They are driven by a plurality of independently adjustable D.C. voltage sources, and two or more of them may be operated at the same potential or at different potentials as required for optimum performance of the multipole mass filter. Moreover, the potentials at which the auxiliary electrodes are operated may be readjusted from time to time as may be required for optimum performance over different mass ranges and as required to compensate for changes in ion peak shape and sensitivity with time.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is an end view of a multipole mass filter according to one of the preferred embodiments of the invention.

FIG. 2 is a sectional side view of the multipole mass filter of FIG. 1 taken along line 2—2.

FIG. 3 is a logarithmic plot of the intensities of ion peaks **69** and **70** from a perfluorotributylamine mass spectrum that was obtained by employing a multipole mass filter like that of FIGS. **1** and **2** without the auxiliary electrodes.

FIG. **4** is a logarithmic plot of the intensities of the same ion peaks that was obtained by employing the multipole mass filter of FIGS. **1** and **2** with the auxiliary electrodes.

FIGS. **5** and **6** are simplified cross-sectional views of multipole mass filters according to others of the preferred embodiments of this invention.

FIGS. **7A** through **9B** are side and cross-sectional views of various auxiliary electrodes that may be employed in the multipole mass filters of FIGS. **1** and **2**, **5**, and **6** in lieu of the auxiliary electrodes illustrated therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIGS. **1** and **2**, there is shown a quadrupole mass filter including a cylindrical and electrically-conductive housing **10** made, for example, of stainless steel. Housing **10** is operated at a reference potential, such as ground potential, and is positioned within an evacuated enclosure when the quadrupole mass filter is to be employed in the laboratory. This evacuated enclosure is unnecessary when the quadrupole mass filter is to be employed for upper atmospheric research in the vacuum of outer space.

Four parallel, coextensive, electrically-conductive, cylindrical primary electrodes **12**, **14**, **16**, and **18** electrically insulated from one another are fixedly mounted within housing **10** by, for example, a pair of electrically-insulating annular ceramic supports **19** fixedly secured to housing **10**, provided with aligned, symmetrically-spaced, generally-semicircular indentations in their inner peripheries for receiving the primary electrodes, and metallized and brazed along these generally semicircular indentations to the primary electrodes. The primary electrodes are symmetrically disposed about the central axis Z of the quadrupole mass filter with the central axes of primary electrodes **12** and **14** being diametrically opposed and lying in the Y—Z plane and with the central axes of primary electrodes **16** and **18** being diametrically opposed and lying in the orthogonal X—Z plane.

As shown in FIG. **1**, diametrically-opposed primary electrodes **12** and **14** are electrically connected in common to one terminal of a quadrupole drive circuit **20** such as that shown and described in copending U.S. Patent application Ser. No. 738,142 entitled QUADRUPOLE MASS FILTER WITH ELECTRODE STRUCTURE FOR FRINGING-FIELD COMPENSATION, filed on June 19, 1968, by Edward F. Barnett, Donald L. Hammond, and William S. W. Tandler and issued on Nov. 2, 1971, as U.S. Pat. No. 3,617,736. Diametrically-opposed primary electrodes **16** and **18** are similarly connected in common to another terminal of quadrupole drive circuit **20**. An excitation voltage comprising both a balanced D.C. component $\pm U$ and a balanced A.C. component $\pm V\cos \omega t$ is applied between diametrically-opposed primary electrodes **12** and **14** and diametrically-opposed primary electrodes **16** and **18** to provide a quadrupolar electric field having both A.C. and D.C. components between the diametrically-opposed primary electrodes. The positive D.C. component $+U$ of the excitation voltage is applied to diametrically-opposed primary electrodes **16** and **18**, and the negative D.C. component $-U$ is applied to diametrically-opposed primary electrodes 12 and 14. All voltages are referred to quadrupole ground, which is maintained at the reference potential of housing 10.

A separate pair of parallel, coextensive, electrically-conductive, flattened, tubular, kovar auxiliary electrodes 22 electrically insulated from one another is fixedly mounted within housing 10 between and substantially parallel to each adjacent pair of primary electrodes 12 and 18, 18 and 14, 14 and 16, and 16 and 12. The auxiliary electrodes are substantially symmetrically disposed about the central axis Z and between the primary electrodes outside the central region defined by a cylinder inscribed between the primary electrodes. Each pair of auxiliary electrodes 22 is bonded together at spaced intervals by electrically-insulating glass beads 24 and is mounted in place, for example, by spot welding the auxiliary electrodes at each end to electrically-conductive kovar studs 26 that are in turn spot welded to electrically-conductive stainless steel supports 28. These stainless steel supports are fixedly mounted adjacent to the ends of the primary electrodes by electrically insulating ceramic spacers 30 secured to the ends of the primary electrodes and provided with circular projections 32 for engaging mating holes in the stainless steel supports.

The two auxiliary electrodes 22 supported by each stainless steel support 28 are electrically insulated from the other auxiliary electrodes by the glass beads 24 and are electrically connected in common by the stainless steel support and associated kovar studs 26 and by a separate resistor 34 of about 5 megohms to an associated different one of four independently adjustable sources 36 of D.C. control voltages E_1 through E_4. This provides four independently controllable parameters E_1 through E_4 that may be adjusted for altering the quadrupolar electric field between primary electrodes 12 through 18 to reduce artifacts in the mass spectra obtained from the quadrupole mass filter and thereby improve the resolution of the quadrupole mass filter, to compensate for changes with time in ion peak shape and sensitivity due to ion build-up on the primary electrodes or other factors, and to otherwise control ion peak shape and optimize the performance of the quadrupole mass filter over different mass ranges. For values of the A.C. and D.C. excitation voltage components V and U ranging from −2,000 to +2,000 volts and from −325 to +325 volts, respectively, the optimum D.C. control voltages E_1 through E_4 may range in value from −40 to +40 volts. Moreover, in some applications involving scanning over large mass ranges it may be desirable to vary one or more of the parameters E_1 through E_4 with the D.C. component U of the excitation voltage.

The effectiveness of auxiliary electrodes 22 may be demonstrated with the aid of FIGS. 3 and 4. In FIG. 3, there are shown ion peaks 69 and 70 from a perfluorotributylamine mass spectrum that was obtained by employing a mass spectrometer including an ion source 38 such as that shown and described in a copending U. S. patent application entitled IONIZATION CHAMBER and filed on or about Feb. 1, 1971, by William P. Kruger and Wilson R. Turner, a quadrupole mass filter like that of FIGS. 1 and 2 without auxiliary electrodes 22, a fringing field penetrating structure like that shown and described in U.S. Pat. No. 3,560,734 entitled QUADRUPOLE MASS FILTER WITH FRINGING-FIELD PENETRATING STRUCTURE and issued on Feb. 2, 1971, to Edward F. Barnett, William S. W. Tandler, and Wilson R. Turner, an ion detector 40 such as an electron multiplier, and a measuring and recording circuit 42. It may be seen that the most significant ion peak 69 has an artifact 42 equal to 1 percent of its own magnitude and about equal in magnitude to the next most significant ion peak 70. This artifact may either obscure another ion peak in this mass spectrum or be mistaken for an ion peak not present in this mass spectrum. In any event, it seriously impairs resolution. For comparison, the same ion peaks obtained by employing the same mass spectrometer with auxiliary electrodes 22 is shown in FIG. 4. It may be seen that artifact 42 has been reduced by more than a factor of 10 to about 0.04 percent of the magnitude of the most significant ion peak 69 and to substantially less than 10 percent of the magnitude of the next most significant ion peak 70. This represents a significant improvement in resolution. In obtaining the ion peaks of FIGS. 3 and 4, a D.C. excitation voltage component U of approximately ±35 volts and an A.C. excitation voltage component V of approximately ±210 volts were employed, and in obtaining the ion peaks of FIG. 4 D.C. control voltages E_1, E_2, and E_4 of 0 volts and a D.C. control voltage E_3 of 2 volts were employed.

The auxiliary electrodes may be arranged in configurations other than that shown in FIGS. 1 and 2. For example, a single auxiliary electrode 44 may be fixedly mounted between each adjacent pair of primary electrodes 12 and 18, 18 and 14, 14 and 16, and 16 and 12 as shown in FIG. 5. Alternatively, a pair of auxiliary electrodes 44 positioned one outside the other and electrically insulated from each other may be fixedly mounted between each of these pairs of primary electrodes as shown in FIG. 6. The auxiliary electrodes may comprise electrically-conductive flattened tubes 22 as shown in FIGS. 1 and 2, circular rods 44 as shown in FIGS. 5 and 6, rectangular bars 46 as shown in FIGS. 7A and 7B, pairs of spaced combs 48 as shown in FIGS. 8A and 8B, or bifilar helices 50 and 52 as shown in FIGS. 9A and 9B. Any two or more of the auxiliary electrodes of whatever configuration or type may be operated at the same or different potentials as required for optimum performance of the quadrupole mass filter.

I claim:

1. A multipole mass filter comprising:

a plurality of substantially parallel primary electrodes for separating charged particles on the bases of their mass to charge ratio, said primary electrodes being spaced symmetrically about a central axis for receiving an excitation voltage including A.C. and D.C. components balanced with respect to a reference potential to produce alternating and static multipole electric field components in the central region between the primary electrodes; and

a plurality of auxiliary electrodes for altering the multipole electric field components in the central region between the primary electrodes to reduce artifacts in a mass spectrum obtained from the mass filter, at least two of said auxiliary electrodes being independently operable at different potentials and at least one of said auxiliary electrodes being positioned between each adjacent pair of the primary electrodes along the length thereof outside the central region between the primary electrodes.

2. A multipole mass filter as in claim 1 wherein at least one auxiliary electrode positioned between each adjacent pair of the primary electrodes may be operated at a different potential from at least one auxiliary electrode positioned between each of the other adjacent pairs of the primary electrodes.

3. A multipole mass filter as in claim 2 wherein said auxiliary electrodes are symmetrically positioned about the central axis along the full length of the primary electrodes.

4. A multipole mass filter as in claim 3 wherein said auxiliary electrodes comprise a single auxiliary electrode positioned between each of the adjacent pairs of the primary electrodes.

5. A multipole mass filter as in claim 4 wherein each of said auxiliary electrodes comprises an electrically conductive rod or tube.

6. A multipole mass filter as in claim 3 wherein said auxiliary electrodes comprise a pair of auxiliary electrodes positioned between each of the adjacent pairs of the primary electrodes.

7. A multipole mass filter as in claim 6 wherein each of said pairs of auxiliary electrodes comprises a pair of electrically conductive rods or tubes that may be operated at different potentials.

8. A multipole mass filter as in claim 7 wherein the electrically conductive rods or tubes of each of said pairs of auxiliary electrodes are positioned side by side.

9. A multipole mass filter as in claim 7 wherein the electrically conductive rods or tubes of each of said pairs of auxiliary electrodes are positioned one outside the other.

10. A multipole mass filter as in claim 6 wherein each of said pairs of auxiliary electrodes comprises a pair of electrically conductive combs that may be operated at different potentials.

11. A multipole mass filter as in claim 6 wherein each of said pairs of auxiliary electrodes comprises a pair of electrically conductive bifilar helices that may be operated at different potentials.

12. A quadrupole mass filter as in claim 3 wherein:

said primary electrodes comprise four substantially parallel, coextensive, electrically-conductive cylindrical rods;

said auxiliary electrodes comprise electrically conductive members supported from the ends of the primary electrodes;

an ion source is positioned adjacent to one end of the central region between the primary electrodes for focusing ions along the central axis; and

an ion detector is positioned adjacent to the other end of the central region between the primary electrodes for detecting ions passing therethrough.

* * * * *