Feb. 15, 1966 W. M. BRUBAKER 3,235,724

QUADRUPOLE MASS FILTERS WITH INTRODUCTORY ION ACCELERATING FIELD PROPORTIONAL TO THE QUADRUPOLE ELECTRIC FIELD

Filed Oct. 2, 1962 2 Sheets-Sheet 1

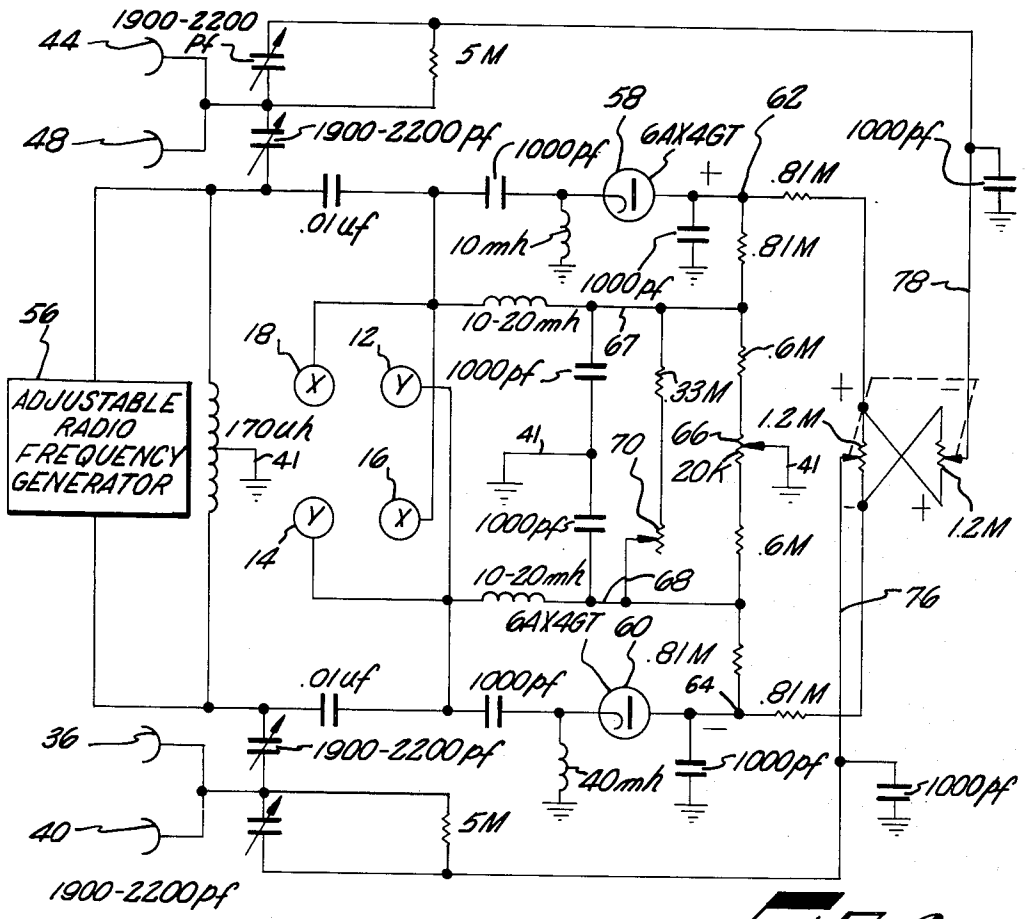


FIG. 3

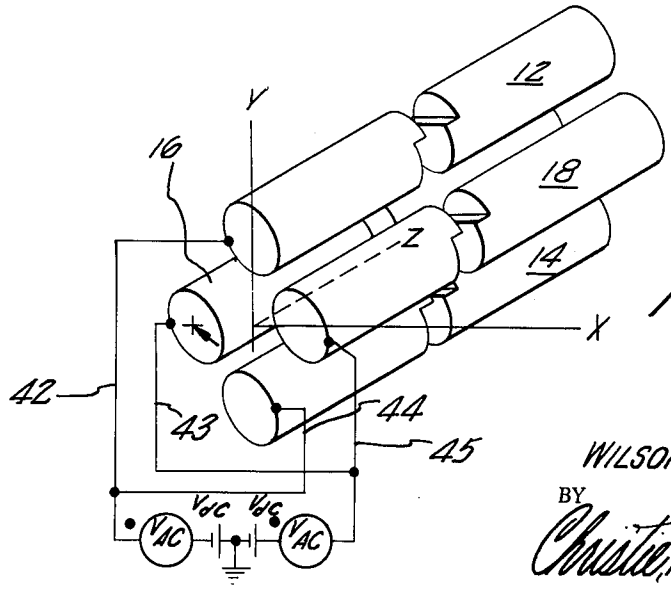


FIG. 1

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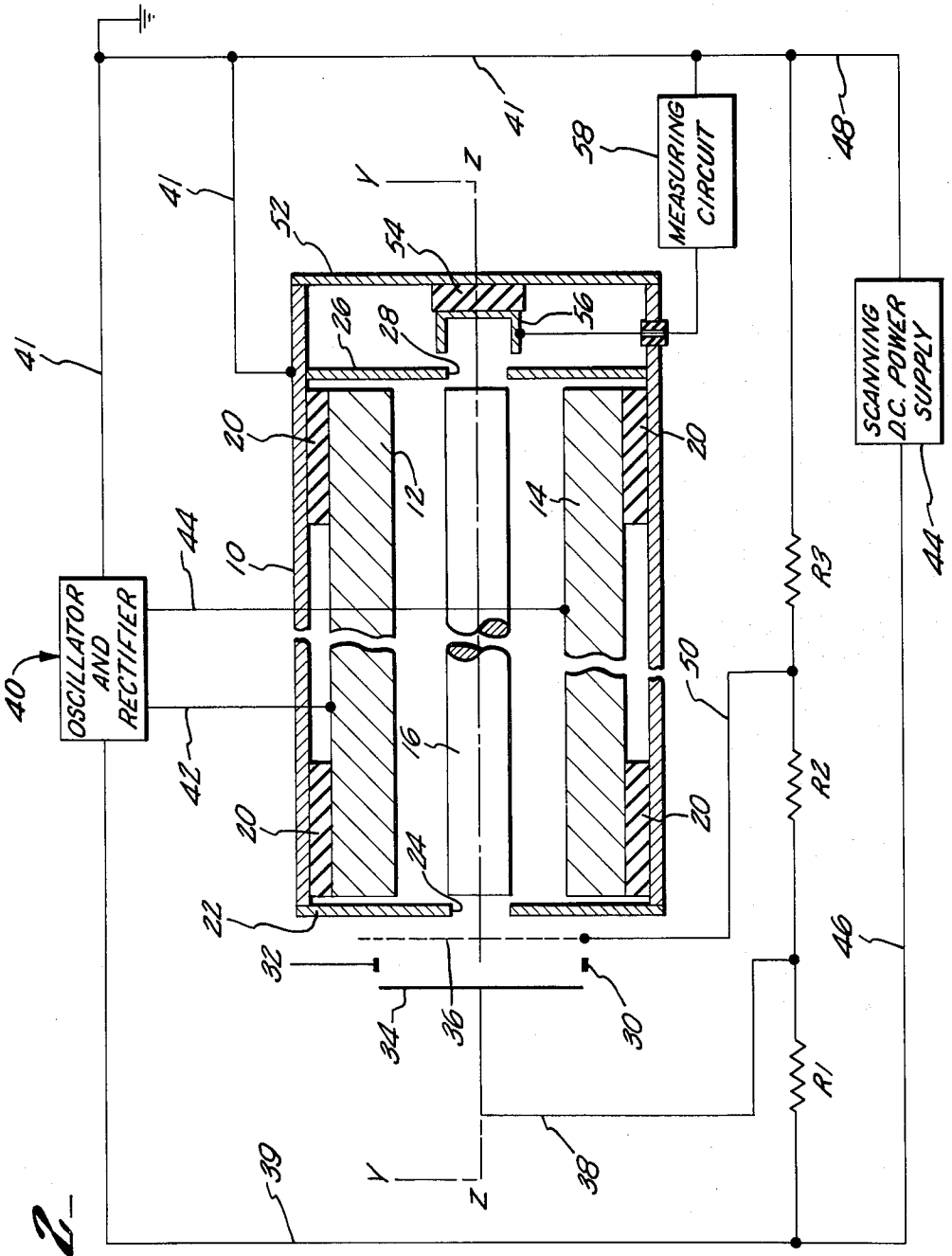


FIG 2

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QUADRUPOLE MASS FILTERS WITH INTRODUCTORY ION ACCELERATING FIELD PROPORTIONAL TO THE QUADRUPOLE ELECTRIC FIELD

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3 Claims. (Cl. 250—41.9)

This invention relates to a quadrupole mass filter and more particularly, to a quadrupole mass filter wherein the energy of the entering ions to the filter is proportional to the voltage of excitation thereon.

Mass filters present a means of investigating a beam of ions by sorting the ions into a spectrum according to their mass to charge ratio (M/e) and recording the relative abundance of those under investigation. This principle is well known as adapted to mass spectrometers which employ a magnetic and an electrostatic field to sort the ions according to their mass to charge ratio. A variation of this apparatus for separating ions is known as a quadrupole mass filter.

Quadrupole mass filters present a means of separating or selectively detecting ions having particular mass to charge ratios much in the same manner as more conventional mass spectrometers. However, the quadrupole filter accomplishes detection or separation in a unique way, without a magnetic field, by utilizing the motion of charge particles through an electric field having both alternating and static components.

A quadrupole mass filter consists primarily of four electrodes connected symmetrically about a central axis. The electrodes ideally consist of four identical hyperbolae, but practically shaped as cylindrical rods, with the potential of neighboring electrodes being equal in amount but opposite in sign. The potential consists of a D.C. component and a superimposed radio frequency voltage such that an ion entering along the axis of the electrodes may either strike an electrode or pass through the filter. Generally, the path the ion will take depends on its mass and on the frequency and the amplitude of the voltages applied to the quadrupole electrodes. When the electrical fields are, as previously described, an ion having a stable trajectory moves in bounded volume about the axis to a receiving collector located near the exit portion of the electrodes. Ions with unstable trajectories will normally divert from the axis and eventually strike the electrodes thereby being separated from the desired stable ions.

A theoretical explanation for the operation of quadrupole mass filters is clearly set forth in co-pending application serial No. 158,697, now U.S. Patent No. 3,129,327, by Wilson M. Brubaker, filed December 12, 1961.

One of the necessary conditions for separating ions of mass m from ions of mass $(m+\Delta m)$ is that the ions experience a minimum number of radio frequency cycles as they pass through the filter. In particular, it has been found that

$$n \geq 5(m/\Delta m)^{1/2} \quad (1)$$

where n is the number of cycles impressed on the assembly during the passage of the ions, and

$$(n=(l/v)f \quad (2)$$

where l is the length of the filter, v is the axial velocity of the ion, and f is the frequency of excitation of the unit.

The y-component of the velocity of the ions is given by:

$$v_y=(2V_i e/m)^{1/2} \quad (3)$$

where $V_i e$ is the energy associated with the radial component of the velocity, V_i is proportional to the potential V_0 through which the ions are accelerated. At constant frequency the conditions of operation of the filter are:

$$V_{ac}/m=\text{constant} \quad (V_{ac}=\text{quadrupole excitation voltage}) \quad (4)$$

combining Equations 1, 2, and 3, the axial relations conducive to constant resolution are given by:

$$n=1f/v=1f(m/2V_i e)^{1/2}=\text{constant} \quad (5)$$

and comparison with Equation 4 yields the result that V_i/V_{ac} is constant and analysis of the operation of the filter shows that the condition necessary for successful operation is when:

$$V_i/V_{ac} \geq 0.064(dm/m) \quad (6)$$

Accordingly, it has now been realized that if mass scanning is by voltage variation, at constant frequency, and in proportion to the energy of entering ions, a quadrupole mass filter results in which the transmission efficiency remains approximately similar for ions of all masses.

Generally described, this invention provides a quadrupole mass filter having means for providing entering ions with equal energy, and means for proportionalizing the entering energy of the ions with the voltage of excitation applied to the primary electrodes of the mass filter.

More particularly, this invention provides a multi-pole mass filter having a plurality of primary electrodes spaced about a central axis, and having means for applying a D.C. voltage to said electrodes to produce a static multipole electric field component between the primary electrodes and means for applying an A.C. voltage to the primary electrodes to produce an alternating multipole electric field component between the primary electrodes. In combination with this filter structure is a means for providing energy to entering ions proportional to the voltage of excitation applied to the primary electrodes such that the transmission efficiency of ions of all masses will be approximately similar.

This invention will be further described with reference to the drawings in which:

FIG. 1 is a general perspective view of a quadrupole mass filter;

FIG. 2 is a more detailed schematic side elevation taken along the Y–Z plane of FIG. 1 and including the circuit according to this invention; and

FIG. 3 is a schematic diagram indicating the general manner in which voltages are applied to quadrupole electrodes.

Referring to FIGS. 1 and 2, the quadrupole mass filter includes a cylindrical metallic housing **10** having four primary electrodes **12**, **14**, **16** and **18**, mounted therein on electrical insulating supports **20**. The primary electrodes are in the form of coextensive conductive cylindrical rods extending parallel to one another and disposed symmetrically about the central axis Z of the filter. One pair of diametrically opposed rods **12** and **14** lie with their centers in the Y–Z plane and will hereinafter be referred to as Y poles; and the other pair of opposed rods designated **16** and **18** lie with their centers in the X–Z plane and will be referred to hereinafter as X rods. A conductive plate **22** is mounted across one end of the housing and has a centrally located circular aperture **24** forming the entrance of the filter and called the ion entrance aperture. At the opposite end of the filter is mounted a conductive plate **26** having a central circular aperture **28**

therein which serves as the ion exit aperture for the filter.

An ion source is provided near the aperture **24**. It consists of an electron beam between a repeller **34** and an ion accelerator grid **36**. The electron flows from the filament **30** to the anode **32**, approximately equidistant from the repeller and the ion accelerator. The repeller is connected by lead wire **38** to resistor R_1 which is further connected by line **39** to an oscillator and rectifier system **40**, shown in greater detail in FIG. 3, which provides voltage to quadrupole electrodes **12** and **14** by lines **42** and **44** and to electrodes **16** and **18** by lines **43** and **45**. The system is grounded by lines **41**. A scanning D.C. power supply **44** is also included for energizing the oscillator and providing the accelerating potential for the ions.

The ion accelerating grid **36** located near the aperture **24** is connected by line **50** to one end of a resistor R_2, the other end of which is connected to the ion repeller plate by line **38**. A third resistor R_3 is included which connects the ion accelerator line **50** to ground line **42**.

The housing **10** is enclosed by a conductive rear wall **52** on which an electrical insulating support **54** is mounted. An ion collector **56** is mounted on support **54** opposite the ion exit aperture **28**. Ions entering the entrance aperture **24** from the source and traversing the filter impinge upon collector **56** and thereby produce an electrical charge which is measured by any conventional measuring circuit **58** connected between the collector and a ground.

When used in the laboratory the housing **10** is evacuated and the ion source is mounted over the entrance aperture. When the mass filter is employed for upper atmosphere research, the ion entrance aperture may be exposed and the vacuum inside is provided by the vacuum of space.

In an actual device fabricated according to the illustrations in FIGS. 1 and 2, the interior of the housing and its contents are gold plated, including the primary electrodes, but not including the insulating supports for these electrodes.

The electrical connections are indicated in general fashion in FIGS. 1 and 2. Diametrically opposed rods are connected together in pairs, and both A.C. and D.C. voltages ($V_{ac}+V_{dc}$) are applied between the two rod pairs. The X-rods **16**, **18** are D.C. positive, and the Y-rods **12**, **14** are D.C. negative. This creates a quadrupole electric field having both A.C. and D.C. components between the rods.

A more detailed circuit for applying and controlling the voltages on the primary electrodes, particularly as to the apparatus illustrated in FIGS. 1 and 2, is shown in the circuit diagram of FIG. 3. In this circuit a radio frequency generator **56**, the peak output voltage of which and the frequency of which is adjustable, supplies an A.C. signal through capacitive coupling across the pairs of primary electrodes **12**, **14** and **16**, **18**.

Full wave rectification of the A.C. signal from the radio frequency generator is provided by a pair of diodes **58**, **60**, and the resulting D.C. voltage is applied across the terminals **62**, **64** of a voltage divider network. At terminal **62** the D.C. voltage is maintained positive with respect to ground. At terminal **64** the voltage is maintained negative with respect to ground. A balance adjustment is provided by a resistor **66** having an adjustable grounded tap.

The D.C. potential to be applied across the pairs of primary electrodes is derived over a pair of leads **67**, **68** from a first arm of the divider network. This D.C. potential may be adjusted by a variable shunt resistor **70**.

The other two arms of the divider network each contain crossed potentiometers with ganged taps **76** and **78**, respectively, the taps being coupled to the electrodes for maintaining a D.C. voltage across electrode pairs.

Typical values for the circuit components are indicated on the drawing. Typical operating frequencies and voltages are as follows:

Frequency	kc	781
Primary electrodes:		
V_{dc}	v	48.2
V_{ac}	v	282

In the X–Z plane, the D.C. potential on the X-rods repel positive ions toward the filter axis; whereas, the A.C. potential causes positive ions to oscillate about the filter axis, analogous to a resonant system. If the amplitude of the oscillation becomes too large, the ion will be lost. It should be noted that while in the usual resonant sytsem the amplitude is bounded for excitation frequencies on either side of resonance, in the quadrupole system, the ions appear to oscillate with a bounded amplitude only when their mass is above the resonant mass. For the resonant mass and all lighter masses, the amplitude appears to increase without limit.

In the Y–Z plane, the positive ion is pulled outwardly from the axis by the negative D.C. potential on the Y-rods. If the trajectory of the ion is to be stable, it must result from the A.C. field whereby the motion of the ion in a non-uniform electric field causes the net momentum impulse toward the axis to equal or exceed that directed away from the axis when the ion approaches the outer limits of a stable trajectory. This condition will obtain only when the ion has a sufficient low mass so that it moves enough. For higher masses, the ion will not move enough responsive to the A.C. field to achieve stability, and will be lost from the beam.

Thus, in the X direction positive ions are stable in the D.C. fields and the influence of the A.C. field is to make them unstable. The lighter ions tend to be unstable. In the Y direction, stability results solely from the motion of the ions in the non-uniform A.C. field, and the heavier ions tend to be unstable.

According to the theory of operation of the present invention, the transmission efficiency for those ions within the pass band of the filter is the same regardless of the mass of the ions.

This may be accomplished by providing an accelerating force for the ions (in the source) which is proportional to the excitation potential of the rods. By further providing a scanning means by the voltage of excitation, at constant frequency, a quadrupole mass filter may be realized having the transmission efficiency independent of mass.

In operation of a quadrupole mass filter, it is desirable that the transmission and resolving power remain independent of mass. When mass scanning is by voltage variation and at constant frequency, mass independency may be accomplished by causing the energy with which the ions enter the filter to be proportional to the voltage of excitation of the filter.

After examination of the axial and radial conditions influencing the transmission and resolution of a mass filter, the desirability of having the injection energy of ions proportional to the voltage of excitation of the mass filter may be readily realized. This is accomplished by having the injection voltage proportional to the mass of the ions which reach the collector.

Numerous variations will readily be apparent to those skilled in the art. Accordingly, it is intended that the invention be not limited to that specifically shown, and that the appended claims are contemplated to cover all modifications falling within the scope and spirit of the invention.

What is claimed is:

1. In a multi-pole mass filter having a plurality of substantially parallel primary electrodes spaced symmetically about a central axis, means for imposing an excitation voltage on the primary electrodes including means

for applying a D.C. voltage to produce a static multi-pole electric field component between the primary electrodes and means for applying an A.C. voltage to produce an alternating multi-pole electric field component between the primary electrodes, a source of ions located outside the multi-pole field, and propelling electrode means located in the region of the source of ions, the improvement which comprises means for applying a potential to the propelling electrode means for injecting ions from the source into the mass filter and means for maintaining the potential applied to the propelling electrode means uniformly proportional to the multi-pole electric field to cause the energy with which the ions are injected into the mass filter to be uniformly proportional to the excitation voltage.

2. In a multi-pole mass filter having at least four approximately parallel primary electrodes spaced diametrically opposite one another in pairs about a central axis, means for applying an excitation voltage to the primary electrodes including means for applying a D.C. voltage of one polarity to one pair of diametrically opposite primary electrodes and a D.C. voltage of opposite polarity to another pair of diametrically opposite primary electrodes so as to produce a static multi-pole electric field component between the primary electrodes and means for applying an A.C. voltage to the primary electrodes to produce an alternating multi-pole electric field component between the primary electrodes and an entrance aperture and an outlet aperture for the mass filter, an ion source located adjacent the entrance aperture, the source having an ion repeller electrode and an ion accelerating electrode, means for introducing ions into a space between the repeller and accelerating electrodes, the improvement comprising means for imposing an accelerating electric potential between the repeller and accelerating electrodes to inject the ions through the entrance aperture along the central axis toward the outlet aperture and means for causing the accelerating potential to vary directly and uniformly proportional to the excitation voltage whereby the transmission efficiency of ions

passing through the filter are similar and independent of ion mass.

3. In a multi-pole mass filter having at least four approximately parallel primary electrodes spaced diametrically opposite one another in pairs about a central axis, means for applying an excitation voltage to the primary electrodes including means for applying a D.C. voltage of one polarity to one pair of diametrically opposite primary electrodes and a D.C. voltage of opposite polarity to another pair of diametrically opposite primary electrodes to produce a static multi-pole electric field component between the primary electrodes and means for applying an A.C. voltage to the primary electrodes to produce an alternating multi-pole electric field component between the primary electrodes, and an entrance aperture and an outlet aperture for the mass filter, and an ion source located adjacent the entrance aperture, the source having an ion repeller electrode and an ion accelerating electrode, and means for introducing ions into a space between the repeller and accelerating electrodes, the improvement comprising first impedance means connecting the accelerating electrode to the excitation voltage, second impedence means connecting the repeller electrode to the excitation voltage, the first and second impedence means being chosen such that the electric potential imposed between the repeller and accelerating electrodes is maintained uniformly proportional to the excitation voltage whereby the transmission efficiencies of ions passing through the filter are similar and independent of ion mass.

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RALPH G. NILSON, *Primary Examiner.*