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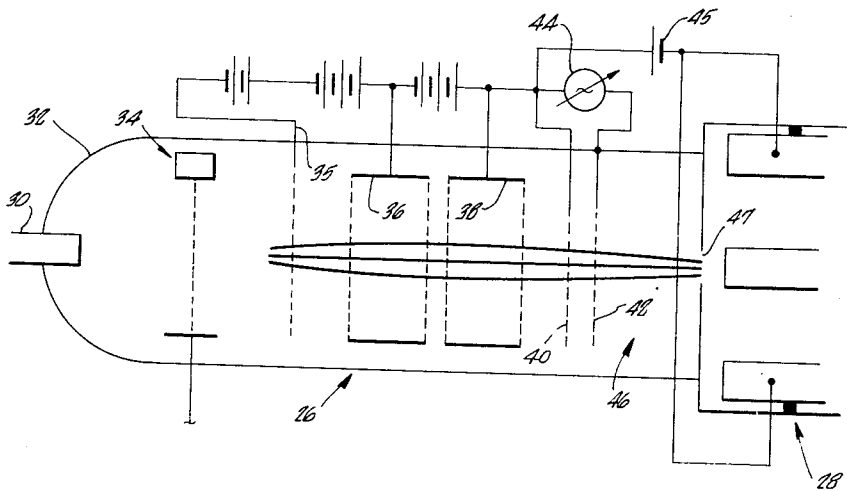
[54] RADIO FREQUENCY MASS ANALYZER OF THE
NONUNIFORM ELECTRIC FIELD TYPE
13 Claims, 4 Drawing Figs.

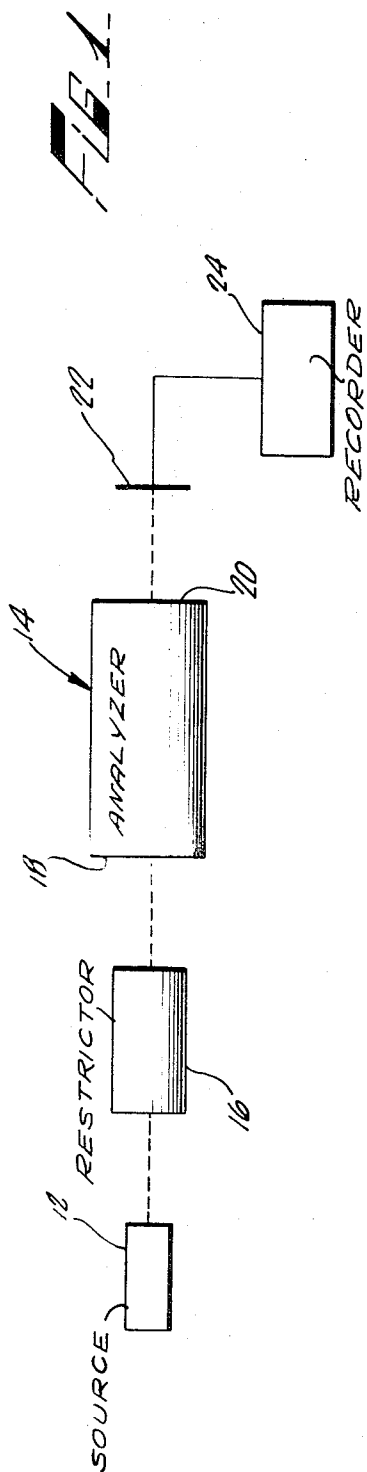
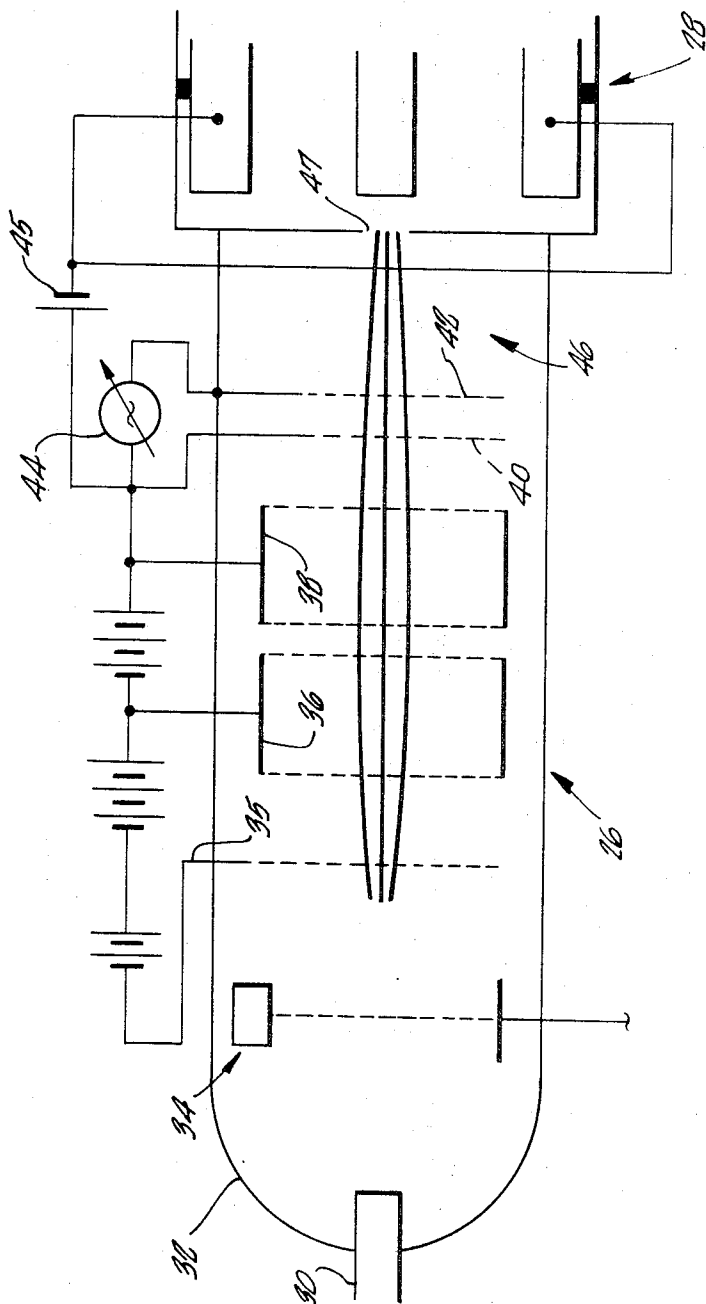
[52] U.S. Cl. 250/41.9
[51] Int. Cl. H01j 39/34
[50] Field of Search 250/41.9,
(2), (1), ISB

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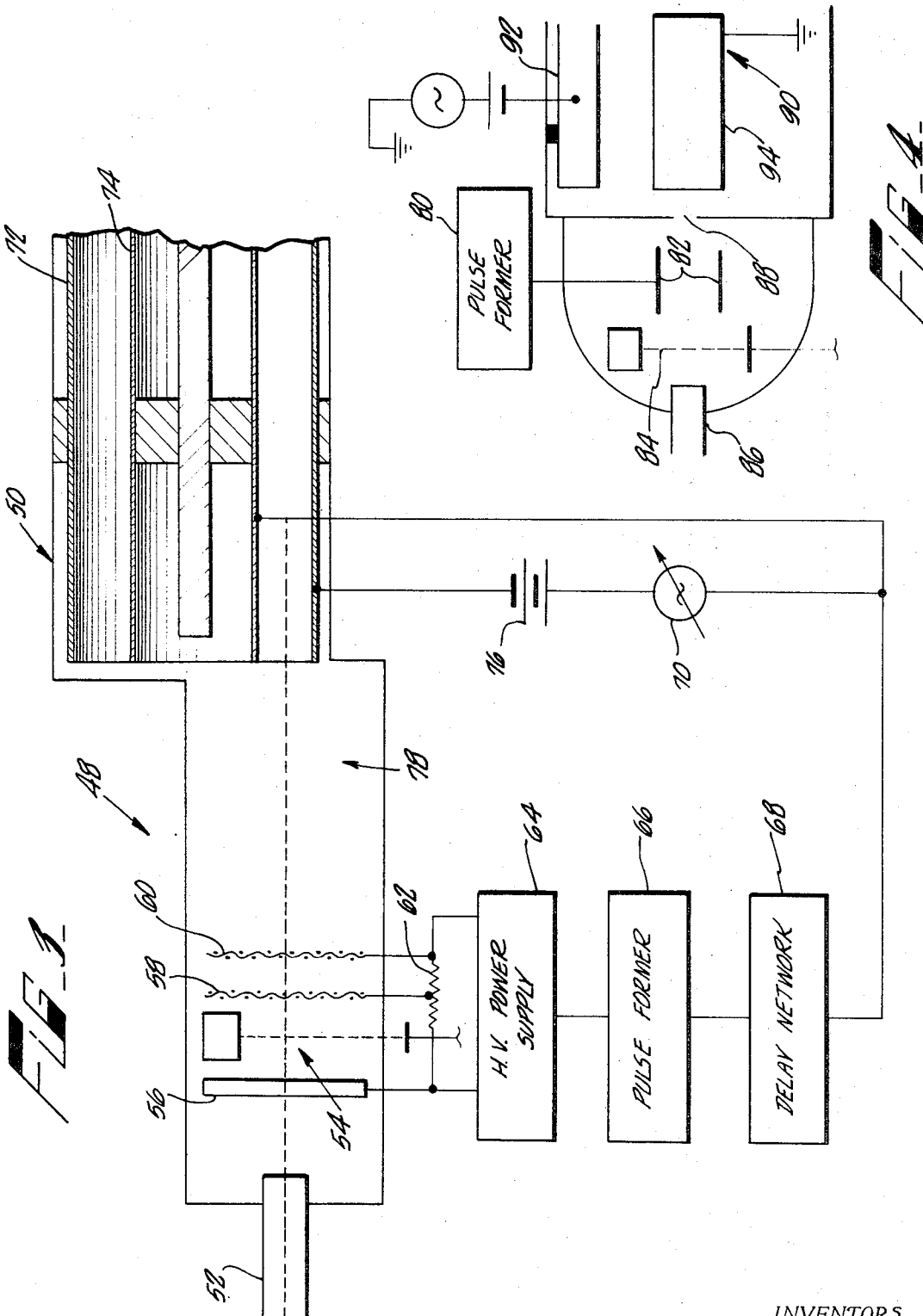
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ABSTRACT: Radio frequency mass analyzers of the nonuniform electric field type and a charged particle source for use therewith. The source provides means for ionizing particles and means for imparting energy pulses to charged particles emanating from the source. A drift tube is interposed between the source and analyzer in some embodiments to allow the pulsed particles to separate into discrete groups in space. The length of the drift tube and the frequency of the impulser are arranged such that charged particles of a predetermined mass are admitted to the mass analyzer during a specific phase angle of the AC voltage connected to the electrodes of the mass analyzer.





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RADIO FREQUENCY MASS ANALYZER OF THE NONUNIFORM ELECTRIC FIELD TYPE

BACKGROUND OF THE INVENTION

This invention relates to radio frequency mass analyzers of the nonuniform electric field type and in particular to ion sources for use with such analyzers.

By the term "radio frequency mass analyzers of the nonuniform electric field type" is meant analyzers referred to as monopole, duopole and quadrupole mass analyzers. In addition, this term is also intended to encompass a mass analyzer utilizing two coaxial cylinders to define an analyzing region in the space enclosed between the exterior of the smaller cylinder and the interior of the larger cylinder. Such a device is described in U.S. Pat. No. 3,473,018. In all of the above types of mass analyzers, charged particles introduced through the entrance aperture to these analyzers experience a transient impulse as they enter the strong electric fields within the analyzer.

Due to the impulse, particles which would normally be transmitted through the analyzer are caused to impinge upon and be discharged at the electrodes of the analyzer, creating an insulating layer at the entrance end of the analyzer which tends to degrade the efficiency of the analyzing fields. The impulse which particles experience in passing through the transition region may also result in the creation of a cloud of charged particles near the entrance end of the analyzer producing a space charge in this region which has a degrading effect on the efficiency and strength of the analyzing fields.

To combat these effects, the entrance aperture to the rod type of nonmagnetic analyzer is restricted to a relatively small size to confine the particles admitted into the analyzer to a region located relatively close to the axis of the instrument. Charged particles entering the analyzer are thereby confined to areas where the analyzing fields are zero or of a very low strength and thus the entering transient to which the particles are subjected is small thereby tending to prevent the occurrence of insulating and space charge effects referred to above.

In the coaxial type of analyzer the analyzing fields are of nearly uniform strength throughout the region bounded by the two cylinders. A majority of the charged particles entering this type of analyzer can traverse its length only if they are restrained from entering the analyzer except at very specific phase angle intervals. Where such particles are admitted on a continuous basis, along the median radius of the analyzer, the transmission efficiency is typically as low as 5 percent to 10 percent.

SUMMARY OF THE INVENTION

The present invention provides analyzers of the types described above with substantially improved transmission efficiency in comparison to the prior art devices. The invention provides a mass analyzer comprising a first elongated electrode, a second elongated electrode and sources of alternating and static voltage. Means for connecting the voltage sources to the electrodes to create combined alternating and static electric fields between the electrodes are provided and a source of charged particles is located at the entrance end of the two electrodes. Means are interposed between the source and the end of the electrodes for restricting the entry of the charged particles produced by the source into the analyzing field to a predetermined phase angle of the alternating voltage. Means are provided at the exit end of the electrodes opposite the charged particle source for detecting the particles transmitted by the analyzer.

By limiting the entrance of the charge particles into the analyzer to a time interval which is a small fraction of one cycle of the analyzing field alternating voltage, the entry of charged particles into the analyzer can be restricted to the most favorable phase angle of that voltage. It has been found that there are two such periods during each AC cycle, one each during the positive and negative portions of the cycle. More specifically, this preferred phase angle is a narrow range

of phase angles bracketing the 90° and 270° phase angle of the alternating voltage cycle where the alternating voltage is defined by the relation $V = V_a \sin \omega t$.

By limiting entry of charged particles into the analyzer to either or both of these two time intervals during each cycle, a substantial improvement in transmission efficiency (approaching 100 percent) is achieved. The improvement of the present invention is ideally suited to the coaxial type of analyzer because of its inherent phase angle dependence. With the rod type of nonmagnetic mass analyzer it is now possible to use a substantially larger charged particle entrance aperture to the analyzer. For example, a conventional quadrupole mass analyzer used at high resolution without the improvement of the present invention can tolerate an entrance aperture which is approximately 3 percent to 5 percent of the rod diameter. By providing the sources of the present invention, the area of the entrance aperture can be increased by more than an order of magnitude.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood by reference to the following FIGS. wherein:

FIG. 1 is a block diagram of a mass analyzer according to the present invention;

FIG. 2 is a sectional view of a quadrupole embodiment of the present invention;

FIG. 3 is an alternate embodiment of the invention utilizing an ion source operating on the time of flight principle in conjunction with a mass analyzer of the coaxial cylinder type; and

FIG. 4 is a monopole embodiment of the present invention.

In FIG. 1 a mass analyzer according to the present invention is shown in block form. The analyzer includes a source of charged particles 12, a radio frequency mass analyzer section 14, and a restricting apparatus 16 interposed between the ion source and the entrance end 18 of the analyzer section. Spaced from the exit end 20 of the analyzer section is a collector 22 for detecting charged particles transmitted by the analyzer, the signal detected at the collector being transmitted to a recording apparatus 24. In one embodiment restricting means 16 is an elongated device for providing a drift space to permit faster moving charged particles to overtake slower moving charged particles prior to entry into the analyzer section. As will be described in more detail below, by provision of a predetermined particle accelerating voltage, an impuler, and a predetermined length of drift space, charged particles of a predetermined mass can be bunched and the bunches spaced such that all bunches enter the analyzer section substantially at an instant when the alternating voltage applied to the electrodes of the analyzer is at such a phase angle as to ensure minimum disturbance due to end effects in the analyzer.

This concept may be more specifically illustrated by reference to FIG. 2 in which a pulsing means 26 operating on the klystron principle is located near the entrance end of a quadrupole mass analyzer 28. The quadrupole mass analyzer comprises four parallel elongated rod electrodes which are symmetrically disposed about and laterally spaced from a central axis.

Gas molecules to be analyzed are admitted through an inlet 30 to a tube 32. These molecules are ionized by an electron beam provided by electron gun 34 and are thereafter accelerated by electrodes 35, 36 and 38 toward the entrance end of the mass analyzer. A pair of closely spaced electrodes 40 and 42, located beyond the accelerating region, are connected to a source of high frequency alternating voltage 44. According to the well-known klystron theory, the particles are modulated, i.e., certain particles passing through the closely spaced grids 40 and 42 are accelerated and certain particles are decelerated depending upon the phase of the voltage from source 44.

In a drift space 46 between grid 42 and the entrance aperture 47 to the mass analyzer, the faster moving particles are allowed to overtake the slower moving particles such that after

passing through the distance to aperture 47 particles of the same mass are traveling in packets or bunches. At the entrance to the drift space, the pulsed particles pass a first given point in space in a first time interval (Δt). At the end of the drift space, these particles are now bunched and pass a second given point in space in a second time interval (δt), the second time interval being substantially smaller than the first time interval. By arranging the length of the drift space to have a distance dimension, d , and the amplitude of the accelerating voltage according to relationships to be defined more fully below, bunched ionized particles of a predetermined mass are brought to the entrance aperture 47 of the analyzer at a predetermined point in time.

The electrodes of the analyzer are connected to the source of alternating voltage 44 and to a source of static voltage 45 to create a combined alternating and static electric field (a nonuniform electric field) in the region defined by the electrodes of the analyzer. The ion source and pulsing apparatus are arranged and energized such that the predetermined point in time of admission of the bunched charged particles into the analyzer is restricted to predetermined phase angles of the alternating voltage applied to the electrodes of the analyzer.

The theory of operation of the analyzer of the present invention is as follows: If the distance which it takes an ion beam to converge and to "bunch" as it travels down a drift tube is designated S and the nominal velocity of the beam without modulation is v_0 , the time normally taken to travel this distance is t_0 or S/v_0 . According to a well-known relationship of particle physics, the accelerating voltage is related to the velocity of a charged particle by the expression:

$$V_0 = \frac{1}{2} mv^2$$

where V is the accelerating voltage, q is the charge on the particle, m is the mass of the particle and v is the velocity of the particle after it has moved through a potential difference equal to V .

In one embodiment of a drift tube it is specified that the transit time through the drift tube be limited to a time t which is equal to the period of an alternating voltage cycle used to energize the electrodes of the analyzer. With such a specification it can be shown that the length of the drift space (S) is defined by the following relationships

$$S = (2V_0)^{3/2} / dV f [m]^{1/2} \quad (1)$$

where V_0 is the nominal accelerating voltage, f is the frequency of the alternating voltage applied to the electrodes of the analyzer and dV is the modulating voltage superimposed on the nominal accelerating voltage to produce the bunching of particles.

If the transit times of the charged particles are to be independent of their mass, the nominal acceleration voltage V_0 is given a value proportional to the mass value. If this restriction is applied, then

$$dV/V_0 = \text{constant} \quad (2)$$

Equations (1) and (2) are the design equations for one embodiment of a source for use with the analyzer of the present invention. Utilization of an ion source conforming to these design equations will produce a bunching of charged particles which will arrive at the entrance aperture to the analyzer sector at time intervals corresponding to the 90° and 270° phase angles of the alternating voltage applied to the electrodes of the analyzer sector where the alternating voltage is defined by the relation $V = V_A \sin \omega t$ where V_A is the peak amplitude of the voltage. It has been found that if particles arrive at the entrance aperture at time intervals corresponding to a narrow band of phase angles ($\pm 10^\circ$) bracketing the 90° and 270° phase, the improved transmission efficiency of the invention will be achieved.

In another embodiment of the invention a module 48 analogous to a time of flight mass analyzer is interposed between a source of charged particles and a radio frequency mass analyzer of the nonuniform electric field type. Such an

embodiment is shown in FIG. 3. The time of flight sector 48 is located at the entrance end of a mass analyzer 50 of a coaxial type which comprises a pair of elongated coaxial cylinders, one having a smaller radius and being located interiorly of the other.

Sample molecules to be analyzed are admitted through inlet 52 and ionized by electrons from gun 54 and accelerated toward the analyzing region as a result of electric potentials being connected to electrode 56 and grids 58 and 60. Electrode 56 and grids 58 and 60 are connected by means of a suitable voltage dropping impedance 62 to a high voltage power supply 64 which is in turn connected to a pulse forming apparatus 66. The pulse forming apparatus 66 is connected by means of a suitable delay network 68 to a source of alternating voltage 70 which is also connected to the cylinders 72 and 74 of the analyzer. A DC source 76 connected in series with source 70 is also connected to the cylinders of the analyzer to cause the creation of a combined static and alternating electric field in the region between the two cylinders. Delay network 68 introduces the desired amount of time delay between the source 70 and the pulse former such that charged particles in a predetermined mass range are transmitted along the drift space 78 and arrive at the entrance end of the analyzing field when the phase angle of the alternating voltage applied to the electrodes of the analyzer is at its desired value or values. As before, this phase angle suitable for entry occurs in narrow range bracketing phase angles of 90° and 270° where the alternating voltage is defined by the relation $V = V_A \sin \omega t$.

Still another embodiment of the invention is shown in FIG. 4. In this embodiment a pulse forming apparatus 80 is connected to a pair of electrodes 82 in the region between the zone where electrons from gun 84 ionize molecules admitted through inlet 86 and the entrance aperture 88 to a mass analyzer 90. Mass analyzer 90 comprises an elongated rod electrode 92 and a right angle electrode 94 extending longitudinally of and laterally spaced from electrode 92 in the conventional monopole mass analyzer configuration. Since the fundamental frequency of the alternating voltages applied to the electrodes of this particular type of analyzer and the other types of analyzers of the nonuniform electric field type under consideration is in the megacycle range, and since the frequency at which ions may be introduced in the analyzer is double the fundamental frequency of the alternating voltage, the time duration of the most favored entry times is a small fraction of a microsecond. Thus ions created in the source may be collected in the ion source for this short time interval and projected into the analyzer in pulses spaced in time as required. Because a drift space is not provided, all of the charged particles in the sample are admitted to the analyzer. This causes the space charge admitted to the analyzer to be somewhat higher in this embodiment than in the embodiments of FIGS. 1-3, but this increased charge is substantially less than the space charge encountered in analyzers utilizing conventional ion sources. In all cases the transmission efficiency is further enhanced because the entrance aperture 88 can now be constructed substantially larger than was heretofore possible.

The arrangements illustrated in FIGS. 1-4 permit ions to be made in a source in a continuous manner and makes possible the analysis and sorting of these charged particles with high efficiency. Through concentration of ions entering the mass analyzer at times which favor their transmission probability, the sensitivity of the device is greatly enhanced. The bunching of charged particles and restriction of entry to specific phase angles is even more effective when the energy of the ions is high and they are caused to traverse the fringing field at the entrance end of a mass analyzer in less than two cycles of the applied alternating voltage.

In still another form of rod type mass analyzer, two rod electrodes are disposed about and parallel to a central axis. Spaced from the two rods is an electrode preferably in the form of a flat plate which is disposed relative to the two rod electrodes such that the plane of the plate is parallel to a plane

passed through the two rod electrodes. This type of analyzer is referred to as a duopole type of mass analyzer and is described in detail in U.S. Pat. No. 3,418,464. The various embodiments of the ion source described herein are equally applicable to the duopole type of mass analyzer.

Although specific embodiments of the ion source of the present invention have been described in conjunction with specific types of mass analyzers, such associations should not be regarded as limiting, but as illustrative only. The various embodiments of the ion sources shown herein can be interchangeably used with all of the various types of mass analyzers heretofore described.

We claim:

1. A mass analyzer comprising:
a first elongated electrode;
a second elongated electrode disposed in a parallel and substantially coextensive relation with respect to said first electrode, said first and second electrodes defining an entrance end and an exit end of the analyzer;
a source of alternating voltage;
a source of static voltage;
means for connecting the voltage sources to the electrodes to create a combined alternating and static analyzing electric field therebetween;
a source of charged particles located adjacent the entrance end of the two electrodes arranged to direct particles along a path generally parallel to the electrodes;
restricting means located between the source and the entrance end of the electrodes for limiting the transmission of charged particles past the entrance end of the electrodes to a predetermined phase angle of the alternating voltage connected to the electrodes of the analyzer; and
means for detecting the particles transmitted by the analyzer located at the exit end of the electrodes opposite the charged particle source.
2. A charged particle source according to claim 1 wherein the restricting means includes means for pulsing charged particles from the source to cause said particles to approach the entrance end of the electrodes in bunches.
3. A mass analyzer according to claim 2 wherein the restricting means includes a drift tube.
4. A mass analyzer according to claim 2 wherein the alternating voltage is defined by the relation $V = V_A \sin \omega t$ and the predetermined phase angle is approximately 90° and 270° .
5. A mass analyzer according to claim 1 wherein the first electrode is an elongated rod electrode and the second electrode is a right angle electrode laterally spaced and extending longitudinally of the first electrode, the two electrodes defining a monopole mass analyzer.
6. A mass analyzer according to claim 1 wherein the first electrode is an elongated rod, the second electrode is an elongated rod and including a third electrode comprising a flat plate laterally spaced and extending longitudinally of the first and second electrode in a parallel relationship with a plane passing through the first and second electrodes such that the three electrodes define a duopole mass analyzer.
7. A mass analyzer according to claim 1 wherein the first electrode is an elongated rod, the second electrode is an elongated rod and including two additional elongated rod electrodes laterally spaced from and extending longitudinally of the first and second electrodes, the four electrodes being symmetrically disposed about and laterally spaced from a central axis, the combination of the four electrodes defining an analyzer of the quadrupole type.
8. A mass analyzer according to claim 1 wherein the first electrode is an elongated cylinder having a first radius and the

second electrode is an elongated cylinder having a second smaller radius, the second electrode being located interiorly of and concentrically disposed with the first electrode such that the two electrodes define a coaxial mass analyzer having an analyzing field created between the two electrodes.

9. A mass analyzer comprising:
a first elongated electrode;
a second elongated electrode disposed in a parallel and substantially coextensive relation with respect to said first electrode, said first and second electrodes defining an entrance end and an exit end to the analyzer;
a source of alternating voltage;
a source of static voltage;
means for connecting the voltage sources to the electrodes to create a combined alternating and static electric field therebetween;
a source of ions located at a point removed from the entrance end of the two electrodes;
means for pulsing the ions produced by the source toward the entrance end of the electrodes; and
means for detecting the ions transmitted by the analyzer located at the exit end of the electrodes opposite the charged particle source.
10. A mass analyzer according to claim 9 wherein the pulsing means is a klystron device.
11. In a radio frequency mass analyzer of the nonuniform electric field type, the improvement comprising:
a source of ions located externally of the analyzing region of the analyzer;
grid means located in the ion source in the path of ion travel;
an electric pulse generator connected to the grid means; and
a drift tube interposed between the grid means and the exit end of the source whereby the ions from the source are bunched and the exit of ions therefrom is restricted to a predetermined phase angle of an alternating voltage applied to the electrodes of the analyzer.
12. An ion source according to claim 11 wherein the alternating voltage is defined by the relation $V = V_A \sin \omega t$ and the predetermined phase angle is approximately 90° and 270° .
13. A method of operating a radio frequency mass analyzer of the nonuniform electric field type including the steps of:
1. creating a plurality of charged particles at a source;
2. **directing the charged particles toward the entrance end of the analyzer;**
3. allowing the charged particles created by the source to pass a first predetermined point located between the source and the entrance end in a time $\frac{1}{2} t$;
4. causing the particles to accelerate through a distance, d , such that the particles bunch together in a pulse and pass a second predetermined point located between said first point and the entrance end in a time interval substantially smaller than $\frac{1}{2} t$;
5. restricting the transmission of the charged particles into the entrance end of the analyzer to a phase angle of approximately 90° and 270° of an alternating voltage defined by the relation $V = V_A \sin \omega t$ applied to the electrodes of the analyzer;
6. **transmitting particles of a predetermined mass through the analyzer by means of the discriminating effect of the analyzer electric field; and**
7. **collecting the particles transmitted through the analyzer subsequent to their emergence from the exit end of the analyzer.**

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,555,271 Dated January 12, 1971

Inventor(s) Wilson M. Brubaker and Charles F. Robinson

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

Col. 6, line 48, "1/3" should read --Δ--
line 54, "1/3" should read --Δ--

Signed and sealed this 25th day of May 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER,
Commissioner of Patent