Feb. 21, 1956 W. M. BRUBAKER 2,735,942

MASS SPECTROMETER

Filed June 1, 1954

FIG. 1.

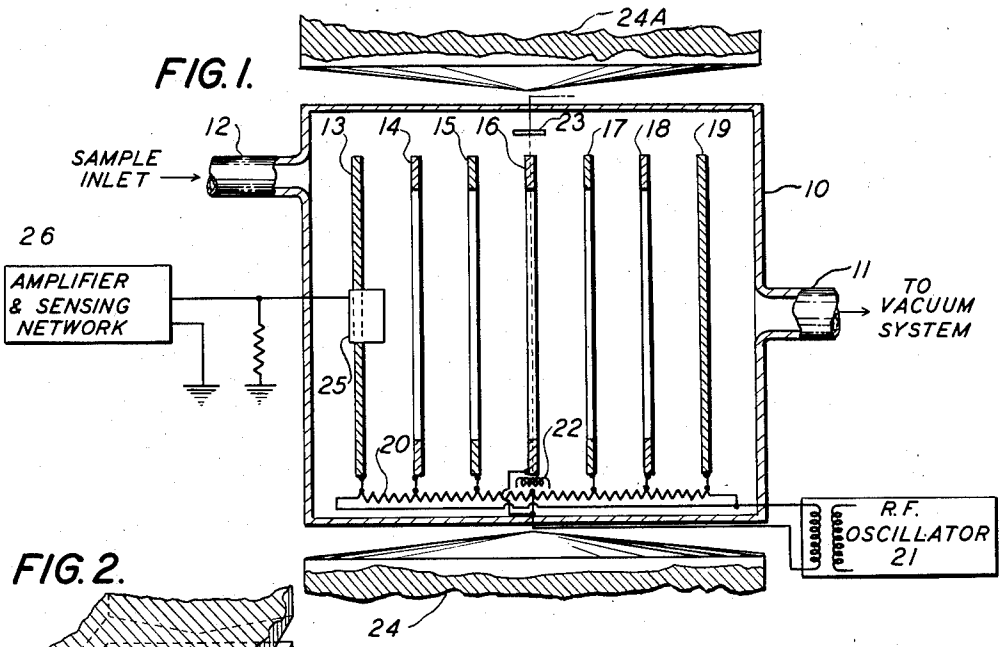


FIG. 2.

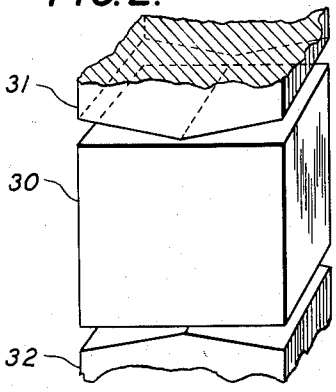


FIG. 4.

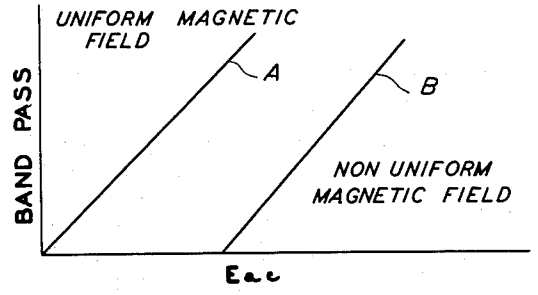
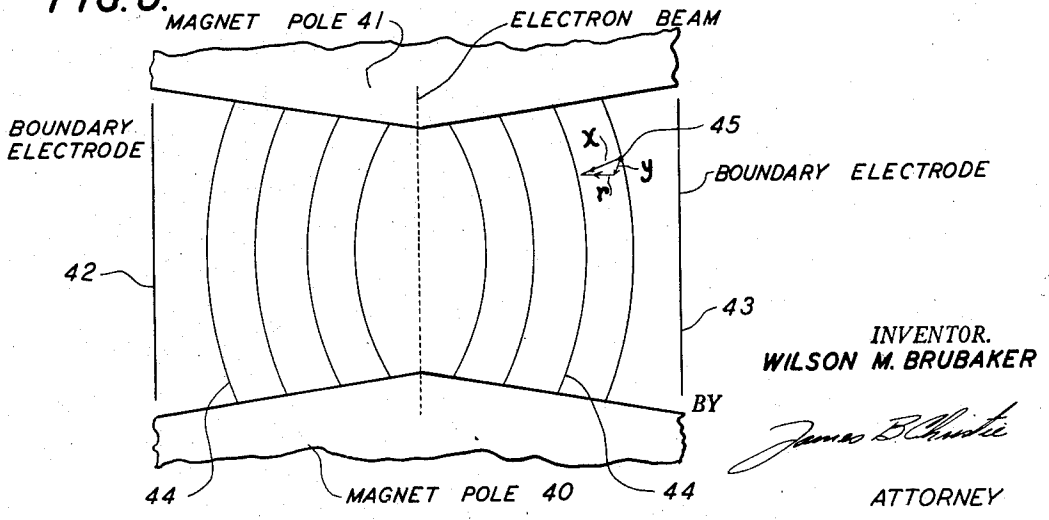


FIG. 3.



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MASS SPECTROMETER

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7 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometry and particularly to improvements in that form of mass spectrometry in which mass separation is accomplished as a function of differences in the periodicity of motion of ions of differing mass to charge ratio.

The principle of mass spectrometry is, in general, one of separating ions produced from a sample to be analyzed as a function of the mass to charge ratio of the ions and selectively collecting the separated ions. Ion separation may be accomplished in many ways, usually involving application of magnetic or electrical fields, or both, to induce and take advantage of characteristic differences in the movement of ions of differing mass to charge ratio under the influence of such fields. A collector electrode may be disposed in space so that under any given set of conditions only ions of a given mass to charge ratio will focus on and discharge at the collector electrode.

It has been found that ions subject to a uniform magnetic field and an alternating electrical field normal to the magnetic field will move in spiral orbits about an axis parallel to the magnetic field. It is also known that in such crossed magnetic and A. C. electrical fields, ions of differing mass to charge ratio will exhibit different and characteristic periods of movement about the axis as a function of the magnetic field strength and the frequency of the alternating electrical field. Ions of a given mass to charge ratio having a periodicity of motion corresponding to the frequency of the alternating field will travel about the axis in orbits of ever increasing radius. Ions of this given mass to charge ratio are referred to as "resonant ions."

All ions of mass to charge ratio different from the resonant mass will travel about the axis in spiral orbits, the radii of which increase to a maximum, collapse back to the axis, etc. in successive cycles. These ions are referred to as "non-resonant ions." Non-resonant ions of different mass to charge ratio will travel in different orbits and will attain different maximum radii with those ions most closely approaching the resonant mass attaining the greatest radial displacement from the axis. By locating a collector electrode at a distance from the axis exceeding the maximum orbital radius of the non-resonant ions, the resonant ions can be selectively collected and measured. The maximum radius obtained by an off-resonant ion is proportional to the magnitude of the applied R. F. voltage and inversely proportioned to the extent to which the ion is off resonance.

By varying the frequency of the alternating field or the strength of the magnetic field, ions of differing mass to charge ratio will come into resonance with the alternating field and all or a portion of the mass spectrum may be scanned.

To avoid anomalous ion paths within the field, ions are preferably formed along an axis of the chamber parallel to the magnetic field and preferably in the central region of the electrical field. This is conveniently accomplished by projecting an electron beam through the crossed fields

parallel to the magnetic field. The electron beam then coincides with the axis of rotation of the ions.

The conventional practice in the operation of a mass spectrometer of the type described is to develop a magnetic field of maximum uniformity. I have now found that many improvements in the operations of the mass spectrometer result from a deliberate distortion of the magnetic field so that it decreases in intensity at increasing radii from the axis of ion formation.

The invention contemplates in a mass spectrometer the combination comprising an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the chamber, means for producing a non-uniform magnetic field across the chamber transverse to the electrical field, the strength of the magnetic field being at a maximum at a central region of the analyzer chamber and decreasing outwardly thereof along any radius from the axis of ion formation, and a collector electrode disposed adjacent the boundary of the electrical field.

The improved operation of a mass spectrometer in accordance with the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawing in which:

Fig. 1 is a schematic sectional elevation of a mass spectrometer in accordance with the invention, showing one form of magnet means for developing the desired non-uniform magnetic field;

Fig. 2 is a schematic perspective of another embodiment of the invention showing a different form of magnet means;

Fig. 3 is a diagram illustrating the effect of a non-uniform magnetic field on ions immersed therein; and

Fig. 4 is a graphical portrayal of another effect of the non-uniform magnetic field on the operation of the mass spectrometer.

The mass spectrometer shown in Fig. 1 comprises an envelope **10** having an exhaust outlet **11** for connection to a vacuum system (not shown) and a sample inlet **12** for admitting a sample of gas to be analyzed into the envelope. A plurality of electrodes **13, 14, 15, 16, 17, 18, 19** are disposed in the envelope in spaced parallel relation. The outer electrodes **13** and **19** may be solid plates and the inner electrodes **14, 15, 16, 17** and **18** of ring type to provide a space for ion motion within the region defined by the electrodes. The several field-forming electrodes are connected across a voltage divider **20**, which is in turn connected to an R. F. oscillator **21** by means of which an alternating voltage is impressed on the several electrodes so as to establish within the envelope a substantially uniform alternating electrical field which is of symmetrical configuration about the center electrode **16**.

A conventional electron gun **22** and an electron target **23** are disposed adjacent opposite sides of the envelope to direct an electron beam across the envelope transversely of the electrical field and substantially at the midpoint thereof. The beam may be directed through collimating apertures in the median electrode **16**.

The entire envelope is immersed in a magnetic field established between magnet pole pieces **24, 24A**. These magnet poles are of unique configuration for this type of mass spectrometry in the provision of conical pole faces with the apex of the pole faces being in line with the axis of symmetry of the envelope and the electron beam. As a consequence of this configuration of the pole pieces the magnetic field across the envelope normal to the direction of the electrical field is at a maximum at the axis of symmetry of the system and decreases with increasing radii outwardly of the axis of symmetry. A collector electrode **25** is mounted adjacent a boundary of the electrical field and is connected to a conventional amplifying and sensing network **26**.

The operation of the mass spectrometer shown in Fig. 1 is, in general, similar to that of other conventional mass spectrometers of this type. A gas sample introduced to the envelope through inlet **12** is ionized by the electron beam established between the gun **22** and the target **23**. Under the influence of the transverse magnetic and electrical fields, the ions move in the fields in essentially spiral paths about an axis which, in this instance, coincides with the electron beam and thus the origin of the ions. As mentioned above, ions of a given mass may be made spiral outwardly from the axis of rotation until they are collected at the collector electrode **25**. Ions of other than the given mass follow spiral paths, the radii of which increase to a maximum for each such other mass and then collapse back to the origin in successive cycles. By varying the frequency of the alternating field different ion masses may be caused to reach the collector electrode.

Fig. 2 shows schematically another form of mass spectrometer in which envelope **30** is immersed in a magnetic field established by pole pieces **31**, **32**. The envelope 33, although not apparent from the drawing, is provided with field-forming electrodes, collector electrode, evacuating outlet, and sample inlet identical to the system shown in Fig. 1. The only difference in the mass spectrometer of Fig. 2 is that the magnet poles **31** and **32** are of peaked configuration, so that the magnetic field established thereby decreased with increasing radius along only one axis of the envelope, this axis being parallel to the direction of the electrical field. The operation of the mass spectrometer of Fig. 2 is the same as that of Fig. 1 and as described above.

Satisfactory resolution can be accomplished in this conventional type of mass spectrometer having a uniform magnetic field only by causing the ions to make a large number of turns about the point of ion formation. As a consequence some means must be provided for accelerating the ions toward the median plane. The median plane is defined for this purpose as a plane lying midway between the magnetic pole pieces and parallel to the direction of the electric field. Without some such means for accelerating the ions toward the median plane, their initial velocity in a direction parallel to the magnetic field will tend to carry them outside the influence of the electric field in the time required to make the large number of turns necessary for good mass resolution. The term "trapping" is applied to the phenomenon of accelerating ions which are not on the median plane toward the median plane.

When a mass spectrometer of this type is operated in a uniform magnetic field as is presently the conventional practice, trapping must be induced by electrostatic action since the lens action of the alternating field has been found to be inadequate for this purpose. Although highly effective trapping action can be obtained by means of an electrostatic field, it has been found in practice that such a field is difficult to control at optimum values which are dependent and complicated in unpredictable ways upon the parameters of the frequency and magnitude of the alternating field, the mass of the ions, pressure within the envelope, anode current, etc.

I have now found that trapping can be accomplished by means of the non-uniform magnetic field established by shaping the magnet poles, as for example in the manner illustrated in Figs. 1 and 2. The manner in which such a non-uniform magnetic field accomplishes the desired trapping action is illustrated schematically in Fig. 3. In the figure, magnet poles **40** and **41** and boundary electrodes **42** and **43** define a region of crossed magnetic and electrical fields of the type developed in the instrument illustrated in Fig. 1. The lines of force of the magnetic field developed by magnet poles of this type are normal to the pole faces and hence assume the configuration shown in the drawing at 44. If an ion **45** is moving perpendicularly to the plane of the drawing,

the instantaneous force exerted on the ion by the magnetic field at the position shown is represented by the arrow X. This force resolves into vectors r and y, r being the normal radial force to which the ion would be subjected in a uniform magnetic field and q being the trapping force which is unique to the non-uniform magnetic field established by the conical or peaked pole pieces **40** and **41**.

From the foregoing description it is apparent that the non-uniform magnetic field results in a simplification of the instrument by eliminating the requirement of an electrostatic trapping field and also improves the sensitivity of the instrument by preventing motion of ions along the axis of the magnetic field. A further advantage of the non-uniform field is realized in improved resolution.

When the magnetic field varies with radius there is only one radius at which a given ion is strictly resonant, that is, at which the natural frequency of rotation in the magnetic field is equal to the frequency of the applied alternating field. At this given radius the phase angle between the position vector of the ion relative to the electric vector is constant. At smaller radii the ion rotates faster than the electric vector and at larger radii it rotates slower. The pulsating electrical field is really the combination of two rotating electrical vectors each of half the peak voltage intensity and each rotating in opposite directions. A positive ion near resonance rotates with one of these vectors insensitive to the other while a negative ion is oppositely responsive. For this reason the energy gained by an ion each revolution can be expressed as follows:

$$e=E_0 q \rho \pi \sin \varphi$$

where

e is the energy;
q is the charge on the ion;
E_0 is the maximum field magnitude;
ρ is the radius of the nearly circular path of the ion; and
φ is the phase angle between ρ and E_0

From this equation it is apparent that the ion gains energy so long as $\pi>\varphi>0$. If the resonant radius for a given ion is less than the collector radius, the ion will at first rotate faster than the electric vector. Provided the ion reaches the resonant radius before $\varphi=\pi$ it will continue to gain energy and radius and so will enter a region where φ will decrease. When $\varphi=\pi/2$ the ion will be in the proper phase relation to gain energy at a maximum rate for that radius. However, it now will be in a region where it rotates slower than the electric vector and unless it reaches the collector before φ becomes 0 it will start losing energy and return toward the origin.

As a consequence of the foregoing relationships, when the magnetic field is non-uniform is accordance with the invention there is a threshold of R. F. voltage below which the ion will not reach the collector, even when the applied voltage is of the most favorable frequency. For voltages just above this threshold, the band of frequency through which the ion can be accelerated to reach the target is quite narrow. Thus, the non-uniform magnetic field results in narrow peaks as the frequency is scanned, while at the same time the level of radio frequency voltage is high and the total number of turns is moderate. This is desirable since the smaller the number of turns required for resonant ions to reach the collector the smaller the adverse effect of space and surface charges. With the uniform magnetic field, on the other hand, narrow peaks are obtainable only by reducing the R. F. voltage to a relatively low value and correlatively increasing the number of turns required by the resonant ion to reach the target. Under this circumstance an unfavorable relationship between spurious gradients due to space or

surface charges and the gradients due to the applied R. F. voltages is encountered.

Another important property of the non-uniform magnetic field is illustrated graphically in Fig. 4 in which the band pass of the instrument is plotted against the magnitude of the R. F. voltage. In the figure, curve A shows the relationship of band pass to R. F. voltage with a uniform magnetic field, and curve B shows this relationship in a non-uniform magnetic field. From this figure it is apparent that for a given R. F. voltage operation with a non-uniform magnetic field of the configuration disclosed will result in a relatively narrower band pass characteristic. The band pass characteristic of the type of mass spectrometer is proportional to peak width obtained as frequency is scanned.

The use of a non-uniform magnetic field in a mass spectrometer of the type involving crossed magnetic and alternating electrical fields thus improves the operation of this type of instrument with respect to improved sensitivity, the formation of narrow and well defined ion peaks as a consequence of characteristic of threshold voltage, with resulting high resolution. Moreover, the instrument is simplified by the elimination of complex control circuitry normally required for an electrostatic trapping field at the same time the foregoing advantages accrue.

Two forms of magnetic means have been shown for developing a desired non-uniform field. It is important in accordance with the invention that the magnetic field decrease from a maximum at the axis of ionization to a minimum at the boundary of the electrical field. With conically shaped magnet means, as shown in Fig. 1, the maximum magnetic field is developed along a line coinciding with the ionizing electron beam and the magnetic field decreases along any radius from this line. With the peaked magnetic poles shown in Fig. 2, the maximum magnetic field is established in a plane intersecting the electron beam and lying transverse to the electrical field and the magnetic field decreases along radii extending from this plane toward the boundary of the electrical field. Other magnet shapes may be employed to accomplish these results. As for example the conical surfaces of the magnet means shown in Fig. 1 and the sloping surfaces of the magnet shown in Fig. 2 may be either convex or concave. It is important only that the magnetic field decrease symmetrically about the point of maximum magnetic field.

I claim:

1. In a mass spectrometer the combination comprising an analyzer chamber, means for ionizing a gas admitted to the chamber within a restricted region of the chamber, means for producing a high frequency electrical field across the chamber, means for producing a non-uniform magnetic field across the chamber transverse to the electrical field, the strength of the magnetic field being at a maximum in a central region of the analyzer chamber and decreasing outwardly thereof in the direction of the electrical field, and a collector electrode disposed in the chamber and spaced from the region of ion formation.

2. In a mass spectrometer the combination comprising an analyzer chamber, means for ionizing a gas admitted to the chamber within a restricted region of the chamber, means for producing a high frequency electrical field across the chamber, a pair of magnet poles disposed on opposite sides of the chamber and having substantially

conical pole faces for producing a non-uniform magnetic field across the chamber transverse to the electrical field, and a collector electrode disposed in the chamber and spaced from the region of ion formation.

3. In a mass spectrometer the combination comprising an analyzer chamber, means for ionizing a gas admitted to the chamber within a restricted region of the chamber, means for producing a high frequency electrical field across the chamber, a pair of magnet poles disposed on opposite sides of the chamber and having pole faces which taper outwardly from a central portion for producing a non-uniform magnetic field across the chamber transverse to the electrical field, and a collector electrode disposed in the chamber and spaced from the region of ion formation.

4. In a mass spectrometer the combination comprising an analyzer chamber, means for directing the ionizing electron beam across the chamber, means for producing an R. F. electrical field across the chamber transverse to the electron beam, means for producing a non-uniform magnetic field across the chamber parallel to the electron beam in the region of the beam, the strength of the magnetic field being at a maximum along the electron beam and decreasing outwardly thereof along radii extending in the direction of the electrical field, and a collector electrode disposed in the chamber and spaced from the electron beam.

5. In a mass spectrometer the combination comprising an analyzer chamber, means for directing an ionizing electron beam across the chamber, means for producing an R. F. electrical field across the chamber transverse to the electron beam, means for producing a non-uniform magnetic field across the chamber parallel to the electron beam in the region of the beam, the strength of the magnetic field being at a maximum along the electron beam and uniformly decreasing outwardly thereof along radii extending in the direction of the electrical field, and a collector electrode disposed in the chamber and spaced from the electron beam.

6. In a mass spectrometer the combination comprising an analyzer chamber, means for directing an ionizing electron beam across the chamber, means for producing an R. F. electrical field across the chamber transverse to the electron beam, means for producing a non-uniform magnetic field across the chamber parallel to the electron beam in the region of the beam, the strength of the magnetic field being at a maximum at the electron beam and decreasing along any radii outwardly of the beam, and a collector electrode disposed in the chamber and spaced from the electron beam.

7. In a mass spectrometer the combination comprising an analyzer chamber, means for directing an ionizing electron beam across the chamber, means for producing an R. F. electrical field across the chamber transverse to the electron beam, means for producing a non-uniform magnetic field across the chamber parallel to the electron beam in the region of the beam, the strength of the magnetic field being at a maximum in a plane intersecting the electron beam transverse to the electrical field and decreasing outwardly of this plane in opposite directions, and a collector electrode disposed in the chamber and spaced from the electron beam.

No references cited.