Sept. 20, 1955 C. F. ROBINSON 2,718,595

MASS SPECTROMETRY

Filed Aug. 29, 1952 2 Sheets-Sheet 1

FIG. 1.

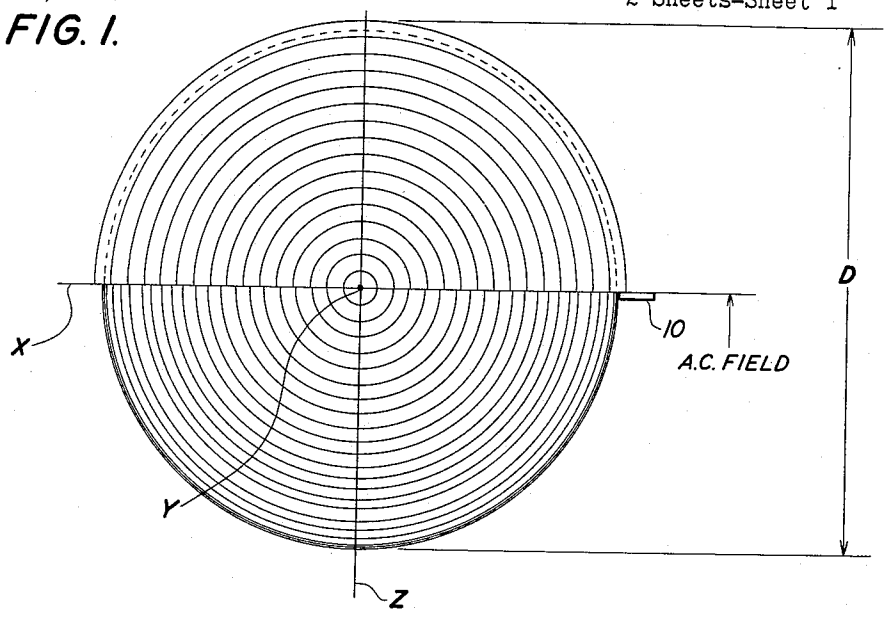
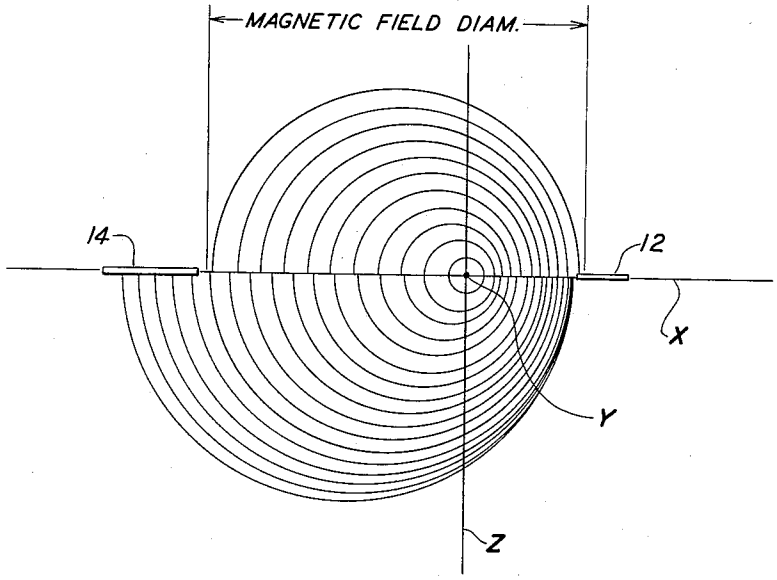


FIG. 2.



INVENTOR.
CHARLES F. ROBINSON

BY James D. Christie

ATTORNEY

Sept. 20, 1955 C. F. ROBINSON 2,718,595

MASS SPECTROMETRY

Filed Aug. 29, 1952 2 Sheets-Sheet 2

FIG. 3.

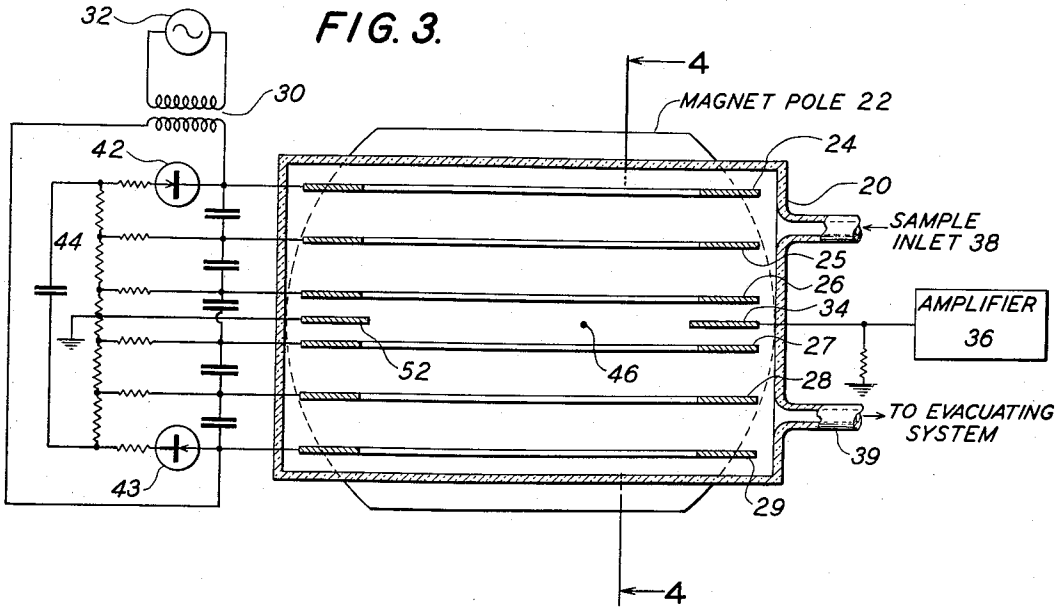
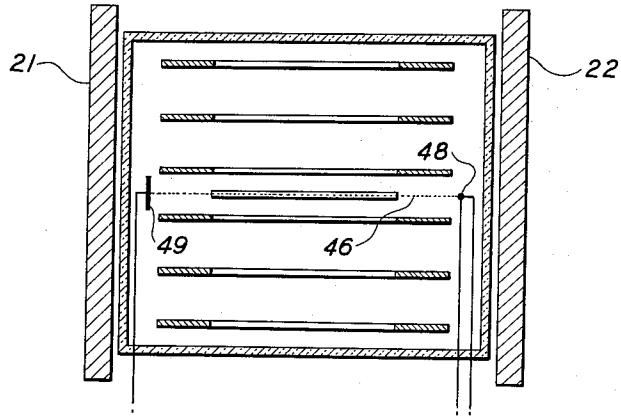


FIG. 4.



INVENTOR.
CHARLES F. ROBINSON

BY James B. Christie

ATTORNEY

United States Patent Office 2,718,595 Patented Sept. 20, 1955

2,718,595

MASS SPECTROMETRY

Charles F. Robinson, Pasadena, Calif., assignor to Consolidated Engineering Corporation, Pasadena, Calif., a corporation of California

Application August 29, 1952, Serial No. 307,087

8 Claims. (Cl. 250—41.9)

This invention is in the field of mass spectrometry and relates particularly to that phase of analytical mass separation which makes use of the inherent differences in the periodicity of motion of ions of different mass-to-charge ratio (specific mass) in a magnetic field.

The principle of mass spectrometry is, in general, one of spatially separating ions produced from a sample to be analyzed as a function of the specific mass of the ions and selectively collecting the separated ions. Spatial separation of ions of differing specific mass may be accomplished in many ways, usually involving application of magnetic or electrical fields to induce and take advantage of characteristics and differences in movement of ions in such fields, which differences are a function of their specific mass. A collector electrode may be disposed in space so that under any given set of conditions only those ions of a given specific mass will impinge on and discharge at the collector electrode.

It has been found that ions subjected to a magnetic field and a high frequency alternating electrical field oriented transversely of the magnetic field will move in spiral orbits about axes parallel to the magnetic field. It is also known that in such a field arrangement, ions of differing specific mass will exhibit different and characteristic periods of movement about the axes of gyration as a function of the magnetic field strength. In the use of this characteristic motion to accomplish analytical mass separation, it is the practice to develop or form ions on a line traversing the crossed fields in a direction parallel to the magnetic field so that all the ions will gyrate about a common axis. This is conveniently accomplished by ionizing the sample to be analyzed in the field by means of an electron beam directed across the field parallel to the magnetic field. Alternatively, a stream of ions may be propelled into the field from a point exteriorly thereof and again along a line paralleling the magnetic field.

Ions of a given specific mass having a periodicity of motion corresponding to the frequency of the alternating field will travel about the common axis in orbits of ever increasing radius. These ions are referred to as "resonant ions." All ions of specific mass differing from that of the resonant ions will travel about the axis in orbits, the radii of which increase at a decreasing rate to a maximum, and thereafter decrease at an increasing rate until the ion returns to the axis and so on in successive cycles. Ions of this behavior pattern are referred to as "non-resonant ions." The non-resonant ions of differing specific mass will travel in different orbits and will attain different maximum radii with those ions most closely approaching the specific mass of the resonant ions, frequently referred to as "adjacent ion masses," attaining the greatest radial displacement from the axis.

By locating a collector electrode at a distance from the axis of rotation exceeding the maximum orbital radius of the non-resonant ions as established by the strength of the crossed fields, the resonant ions can be selectively collected and measured. By introducing or forming the ions along a common axis as mentioned above, anomalous

ion paths within the field are avoided. If ionization is accomplished by means of an electron beam directed across the field, the beam will define the axis of rotation of all of the ions.

The designation of ions of any particular specific mass as resonant or non-resonant is relative only to the environment, since any change in the magnetic field strength or in the frequency of the alternating electrical field will result in ions of different specific mass becoming resonant with the alternating field. For this reason, all or any portion of the total mass spectrum of a particular sample may be scanned by varying the frequency of the alternating field or the strength of the magnetic field so as to bring ions of differing specific mass successively into resonance with the alternating field.

The resolution achieved in this form of mass separation is a function of the strength and geometric magnitude of the magnetic field and of the magnitude of the alternating electric field. The resolution is impaired by any space charge that may be present. If the size of the magnetic field is increased, resolution is improved since the collector electrode may be displaced radially from the axis of rotation. This displacement permits the use of stronger electric fields to overcome the effects of space charge, or for the same alternating electric field strength, permits ions to describe a larger number of turns in reaching the collector electrode, thus increasing the numerical resolution. However, an increase in size of the magnetic field greatly increases the cost of the instrument and any reduction in size is economically desirable. Moreover, space charges developed within the field by the non-resonant ions effect variations in the pattern of rotation from the theoretical conditions discussed above with a consequent impairment of resolution.

I have now developed an improved mass spectrometer of the character discussed which is characterized by the attainment of a given degree of resolution with a smaller magnetic field than has heretofore been possible and in which objectionable space charge may be substantially and readily eliminated. The reduction in the size of the required magnetic field to achieve a given resolution is realized in the instrument of the invention by reason of the fact that a given orbital separation between resonant and non-resonant ions of adjacent mass is obtained in a lesser number of cycles of revolution about the axis of origin than in conventional embodiments of this principle. The term "axis of origin" is used herein in reference to the axis of ion formation along an ionizing electron beam or the axis of an ion beam directed into the region of the crossed fields.

I have found that by establishing a direct current electrical field across the region encompassing the transversely oriented magnetic and alternating fields the axes of gyration of the ions are caused to move transversely of the axis of origin and at a constant velocity. In this manner the ion orbits are distorted so that they are no longer symmetrical with respect to the point of origin. Specifically, the distortion has the result that the maximum departure of the ions along an axis perpendicular to both the electric and magnetic fields is less in a certain direction than it is in the absence of the direct current electrical field. As a consequence the non-resonant ions achieve their maximum departure along this axis in an appreciably lesser number of cycles than in the absence of the D. C. electrical field and resonant ions can be collected with a given resolution on a shorter radius than in the absence of the D. C. electric field.

The invention therefore contemplates in a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for developing a magnetic field

across the chamber paralleling this axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field and a collector electrode disposed in the chamber remote from the line along which ions are developed.

As mentioned above, development of ions along a line paralleling an axis of the chamber may be accomplished by means of an electron beam directed across the chamber and defining this line or by means of an ion beam propelling into the chamber along this line. Conveniently, the line is defined by an electron beam along which ions are originated within the chamber, and although this is not a limitation of the invention the following description is based upon this method of ion development. As will be more clearly explained hereinafter, the practice of the present invention involves ion development on a line preferably spaced from a central axis of the magnetic field and in this preferred embodiment differs from conventional instruments of this type in which ion development, as by means of an ionizing electron beam, is accomplished along the central axis of the magnetic field. The reasons for this variant from conventional procedure will become apparent.

The invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a graphical portrayal of the orbital paths of resonant ions of a given mass and non-resonant ions of an adjacent mass as developed in a conventional mutually perpendicular magnetic and alternating high frequency electrical field;

Fig. 2 is a graphical portrayal of the orbital paths of ions of the same mass in a moving coordinate system in accordance with the present invention;

Fig. 3 is a longitudinal sectional elevation through one form of mass spectrometer embodying the principles of the invention; and

Fig. 4 is a transverse sectional elevation taken on the line 4—4 of Fig. 3.

Referring to Fig. 1, the axis of rotation of the ions and hence the axis of origin is designated by the letter Y, this axis being oriented perpendicularly to the plane of the drawing. The transverse axis defining the radial dimension of the orbital envelope is designated by the letter X. The alternating electrical field is parallel to the Z axis and the magnetic field of indicated diameter D is in the direction of the Y axis.

In the region above the X axis in Fig. 1, succeeding half cycles in the orbital path of a resonant ion of mass **50** is illustrated and in the region below the X axis in Fig. 1 succeeding half cycles in the orbital path of the adjacent ion mass **51** is illustrated, only one-half of the pattern of each of the ion masses being shown for purposes of clarity. The ion paths shown in Fig. 1 are characteristic in a so-called stationary coordinate system, this terminology being definitive of a system in which ion gyration is uniformly about the Y axis, that is, where the axis of rotation always coincides with the axis of origin. It can be shown mathematically that the minimum magnetic field diameter D at which resolution can be accomplished between ion masses **50** and **51** is that in which the non-resonant mass **51** will achieve 25 complete cycles of rotation (n_0) to attain its maximum orbital radius before commencing its return or collapse to the Y axis. It can also be shown that the resonant mass **50** will accomplish 15.9 cycles of gyration (n_0') to achieve the same radial displacement from the Y axis and that this mass may be collected on the collector electrode **10** in the next succeeding cycle of rotation.

Referring now to Fig. 2 the relationship of the consecutive orbits of rotation of a resonant mass **50** as compared to the consecutive orbits of rotation of the non-resonant mass **51** under the conditions imposed in accordance with the present invention is illustrated in the same manner. The letter Y is again used to designate the axis of origin of ions in the system and the letter X again denotes the transverse axis definitive of the radial displacement of the gyrating ions from the axis of origin. Characteristic consecutive half cycles in the orbital paths of the non-resonant ions of mass **51** are shown below the X axis. The field imposed on the ions developed along the Y axis in Fig. 2 is similar to that in Fig. 1 as including a magnetic field parallel to the Y axis and a high frequency alternating electrical field in the direction of the Z axis, and in addition includes a D. C. electrical field in the direction of the Z axis. In this regard both the A. C. and D. C. electrical fields must be perpendicular to the magnetic field, but it is not necessary that the two electrical fields be mutually parallel.

This type of field is herein referred to as a moving coordinate system as distinguished from the stationary coordinate system considered with relation to Fig. 1 and is characterized by the fact that the axis of rotation of the ions formed along the Y axis moves at a constant velocity (v) along the X axis so that the axis of origin (Y) is in this instance the axis of rotation only at the moment of formation.

In the moving coordinate system, as will be shown more clearly in the mathematical analysis below, ions of mass **51** will achieve their maximum X axis displacement from the axis of origin Y in 17 cycles of revolution as contrasted to 25 cylcles of revolution as required in the stationary coordinate system illustrated in Fig. 1, and the resonant ions (mass **50**) may be selectively collected on a collector electrode **12** after 10.5 cycles of revolution instead of 15.9 cycles of revolution as required in the stationary coordinate system. This means that the same degree of resolution is achieved in the moving coordinate system with a magnetic field diameter approximately equal to 0.7 D where D is the magnetic field diameter in the stationary coordinate system.

A further advantage is realized in the moving coordinate system of the invention by reason of the fact that non-resonant ions may be collected simultaneously with resonant ions on a so-called wiper plate **14** extending into the orbital envelope at a point spaced from the resonant ion collector **12** and preferably diametrically opposite the resonant ion collector **12** on the X axis. This provides a very simple and effective means of avoiding the accumulated space charge attendant upon the presence of uncollected non-resonant ions in the system. Such space charge is of major significance in the stationary coordinate system illustrated schematically in Fig. 1 where non-resonant ion collection cannot be accomplished by the simple expedient of a non-resonant ion wiper plate.

The following mathematical analysis will clarify the significance of the diagrams of Figs. 1 and 2. It has previously been shown by several workers in the field that the radius of gyration (r) of non-resonant ions in crossed magnetic and high frequency alternating electrical fields is bounded. It can also be shown that the radius of gyration of a non-resonant ion at the end of its nth complete gyration in such a crossed field and where the electrical field is uniformly distributed is given approximately by the expression:

$$r = r_0 \sin \frac{\pi n}{2n_0} \qquad (1)$$

where

r_0=upper limit of radius;

n=cycle number; and

n_0=number of complete gyrations required for the ion to achieve maximum radius.

The number of gyrations (n_0') required for an adja-

cent resonant particle to achieve radius r_0 is approximately

$$n_0' = \frac{2n_0}{\pi} \quad (2)$$

so that at the end of this number of cycles the resonant particles will have achieved a radius r_0, and the non-resonant particles will have achieved a radius r' given by the expression:

$$r' = r_0 \sin 1 \text{ (radian)} \quad (3a)$$
$$= 0.842\ r_0 \quad (3b)$$

If the alternating electrical field is parallel to the Z axis and a D. C. field of strength E (*esu/cm*) is superimposed on the A. C. field in accordance with the invention, it will have the effect, as mentioned above, of moving all of the trajectories parallel to the X axis in one direction or another dependent upon the polarity of the D. C. field, with a constant velocity (v) and without changing the shape as referred to the moving coordinate system, where

$$v = \frac{CE}{B} \quad (4)$$

and

v=velocity cm./sec.
C=a constant=3×10^{10}
E= D. C. field strength (*esu/cm*)
and
B=magnetic field, Gauss

Under these conditions the maximum radial displacement of the resonant ions referred to as the X position of the resonant ions during the nth cycle of gyration is given by:

$$X_{res} = \frac{r_0 \pi n}{2n_0} - vt \quad (5a)$$

in which expression

t=time, sec.

and the maximum X position of non-resonant ions at the same time can be given by:

$$X_{non\text{-}res} = r_0 \sin \frac{\pi n}{2n_0} - vt \quad (5b)$$

Differentiating (*5a*) and (*5b*) with substitution of

$$t = \frac{2\pi n}{\omega}$$

$$\left(\frac{dx}{dt}\right)_{res} = \frac{r_0\omega}{4n_0} - v \quad (6a)$$

$$\left(\frac{dx}{dt}\right)_{non\text{-}res} = \frac{r_0\omega}{4n_0} \cos \frac{\omega t}{4n_0} - v \quad (6b)$$

where ω=angular frequency of applied field.

If the magnitude (E) of the D. C. field is established so that (for example)

$$v = 0.42 \frac{r_0\omega}{4n_0} \quad (7)$$

then

$$\left(\frac{dx}{dt}\right)_{non\text{-}res} = 0$$

for

$$\frac{\omega t}{4n_0} = 65.2° = 1.138 \text{ rad.} \quad (8)$$

and the maximum X displacement of the non-resonant ions is given by

$$x_{non\text{-}res}\ (max) = 0.432\ r_0 \quad (9)$$

Referring back to the Expression *6b*, it can be shown that

$$\left(\frac{dx}{dt}\right)_{res}$$

is constant and that under the same conditions the number of turns required for a resonant particle to reach the maximum X position of the non-resonant particles as given by the Expression 9 is equal to 0.745 n_0' where n_0' is the number of turns required to reac an orbital radius in excess or beyond the maximum radius achievable by non-resonant particles in a stationary coordinate system. In other words, the foregoing analysis establishes that by virtue of the imposition of the D. C. field in accordance with the invention, the minimum transit time of resonant ions is reduced by 25% for constant resolution, or, for the same transit time, resolution is increased by 25%.

It is noted that the D. C. field and the A. C. field can both be regarded as determining the scale of the system, so that any desired behavior can be preserved through a range of masses by maintaining the A. C. and D. C. fields in fixed proportionality, and accordingly it is preferred practice to maintain such fixed relationship. This may be conveniently achieved by rectifying a fixed portion of the A. C. voltage employed to develop the A. C. field as a means of providing the D. C. field.

It has been shown that there are two very important advantages in operation in accordance with the principle of the invention. First, the magnetic field diameter required is reduced in proportion to the reduction of number of cycles of revolution required for a given resolution so that this method permits smaller magnetic fields for the same A. C. field strength and resolution. The second important advantage is in the fact that non-resonant ions can be removed from the influence of the fields by a plate, such as the wiper plate **14** in Fig. 2, and that this removal may be accomplished when these ions have undergone less than n_0 gyrations. In other words, the moving coordinate system of the invention can discriminate between resonant and non-resonant ions and remove the latter before the conventional stationary coordinate system can even sense the difference. This results in a very desirable reduction in space charge effects.

A mass spectrum may be scanned or predetermined ion masses may be brought into "focus" for collection at the collector electrode **12** by suitable variation in magnetic field strength or A. C. field frequency, or by a combination of both expedients. Further, the instrument may be used as an ionization gauge either by adjustment of the A. C. or D. C. fields so as to drive all ions, resonant as well as non-resonant, to the wiper or non-resonant ion collector **14**, or by reversing the polarity of the D. C. field so that all ions are driven to the resonant ion collector **12**. This facility of the system can be a great convenience to accomplish periodic checks of the system pressure.

In terms of apparatus for carrying out the invention, Figs. 3 and 4 show diagrammatically in longitudinal and sectional elevation respectively, one form of suitable instrumentation. Referring to these figures, the instrument comprises an envelope **20** having magnetic pole pieces **21**, **22** disposed adjacent opposite end walls of the envelope. In some cases the pole pieces themselves may form the end walls of the envelope if desired. A plurality of electrodes **24**, **25**, **26**, **27**, **28** and **29** are uniformly arranged in the envelope and are connected through a transformer **30** to an oscillator **32** or other source of high frequency alternating voltage. The electrodes **24**, **25**, etc. develop across the region defined thereby a high frequency alternating field transversely of the magnetic field developed by the pole pieces **21**, **22**. A resonant ion collector electrode **34** is mounted in the space adjacent the boundaries thereof and is connected to a conventional amplification system **36**. A sample inlet line **38** provides means for introducing a sample to be analyzed to the system and an exhaust line **39** is adapted for connection to an evacuating system for evacuating the chamber **20**. To this extent the instrument is similar to presently conventional mass spectrometers of this type.

In the present instrument, however, means are provided

for developing a D. C. field transversely of the magnetic field and preferably paralleling the high frequency alternating field. As mentioned above it is preferable that this D. C. field bear a fixed proportionality to the A. C. field. One convenient means of accomplishing this is illustrated in the drawing as including rectifiers **42**, **43** and a voltage divider **44** connected to rectify a portion of the A. C. voltage delivered to the system through transformer **30** to distribute this voltage across the several electrodes **24**, **25**, **26**, etc.

Another peculiarity of the instrument as illustrated is the orientation of the ionizing electron beam **46** with respect to the axis of the transverse fields. Conventional practice in this form of mass separation dictates the orientation of the electron beam or the injected ion beam at the axis of symmetry of the field and paralleling the magnetic field. The electron beam **46**, as in prior instruments, parallels the magnetic field but is displaced from the axis of symmetry toward the collector electrode **34** for reasons which are apparent from the previous discussion and from the diagram of Fig. 2.

The ionizing electron beam may be developed in a conventional manner by means of a filament **48** disposed adjacent one boundary of the electrical field directing the beam **46** toward a target electrode **49** disposed adjacent an opposite boundary of the electrical field. The filament **48** and the target **49** are connected to suitable and conventional circuitry which forms no part of the present invention. Alternatively, and as mentioned above, an ion beam derived from the sample to be analyzed may be propelled across the instrument in the same region as the illustrated electron beam, in such case the ion being originated outside the influence of the crossed fields.

In preferred practice, a non-resonant ion collector or wiper plate is included to remove non-resonant ions from the system prior to the accumulation of any undesirable space charge. This removal is made possible by the moving coordinate system of the invention and permits the inclusion of a non-resonant ion wiper plate **52** projecting into the envelope of the field at a point spaced from the resonant ion collector **34** and on a radius with respect to the electron beam **46** greater than the radius of separation between the electron beam **46** and the collector electrode **34**.

Obviously many refinements in instrumentation may be and generally will be included in a mass spectrometer embodying the principles of the invention, the illustrated instrument being sufficient to explain the principle of operation of a moving coordinate system as herein described.

The operation of the illustrated instrument is plain from the preceding discussion, and involves simply the introduction of a sample to be analyzed through the inlet line **38**, ionization thereof along the electron beam **46**, ion motion within the space defined by the fields in accordance with the pattern illustrated in Fig. 2, collection of resonant ions at the ion collector **34**, measurement of the discharge signal developed by resonant ion collection in the conventional amplification and sensing circuit **36**, and, in preferred practice, simultaneous collection of non-resonant ions at the wiper plate **52**. The discharge signal produced by collection of the non-resonant ions can also be sensed and measured if desired.

Non-resonant ions may be removed from the influence of the fields in an alternative manner, as for example by arrangement of the shape of the magnetic field so as to exclude an area roughly corresponding to the illustrated location of the wiper plate. In this event, non-resonant ions, upon reaching the region of no magnetic field or considerably lesser magnetic field, will simply be "dumped" from the envelope of the fields not to return.

Many ways may be employed to develop the D. C. field which effectuates the moving coordinate system other than the rectifier means as illustrated. Simple batteries may be used to replace the rectifiers, in which event the magnitudes of the A. C. and D. C. fields are preferably controlled to adhere to a fixed proportionality as is automatically achieved in the illustrated circuit.

I claim:

1. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for developing a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, and a collector electrode disposed in the chamber remote from the line along which ions are developed.

2. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for developing a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a unidirectional direct current electrical field across the chamber transversely of the magnetic field, and a collector electrode disposed in the chamber remote from the line along which ions are developed.

3. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for developing a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, and a collector electrode disposed in the chamber remote from the line along which ions are developed and in a direction perpendicular to both the magnetic field and the direct current electrical field.

4. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber and offset therefrom, means for developing a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, and a collector electrode disposed in the chamber remote from the line along which ions are developed.

5. Apparatus according to claim 4 wherein the means developing ions of a sample to be analyzed comprises means developing an ionizing electron beam and directing it across the chamber in a direction parallel to the magnetic field and offset from the corresponding axis of symmetry of the chamber.

6. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for developing a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, a first collector electrode disposed in the chamber remote from the line along which ions are developed, and a second remote collector electrode disposed in the chamber, the first and second electrodes being spaced different distances from the line along which ions are developed.

7. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber, means for de-

veloping a magnetic field across the chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, a first collector electrode disposed in the chamber remote from the line along which ions are developed, a second collector electrode spaced in the chamber diametrically opposite the first electrode and at a greater distance from the line along which ions are developed.

8. In a mass spectrometer the combination comprising an analyzer chamber, means for developing ions of a sample to be analyzed within the chamber and along a line paralleling one axis of the chamber and offset therefrom, means for developing a magnetic field across the

chamber paralleling said one axis, means for establishing a high frequency alternating electrical field across the chamber transversely of the magnetic field, means for establishing a direct current electrical field across the chamber transversely of the magnetic field, a first collector electrode disposed in the chamber remote from the line along which ions are developed and on the side thereof opposite said one axis, and a second collector electrode disposed in the chamber diametrically opposite the first collector and spaced a greater distance from said line along which ions are developed than said first collector.

References Cited in the file of this patent

UNITED STATES PATENTS

2,627,034 Washburn et al. ---------- Jan. 27, 1953