March 17, 1953 C. E. BERRY 2,632,113

MASS SPECTROMETRY

Filed Aug. 7, 1950

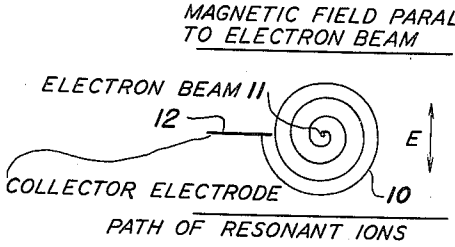


FIG. 1.

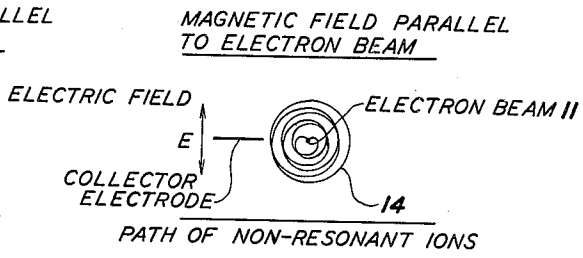


FIG. 1A.

FIG. 2.

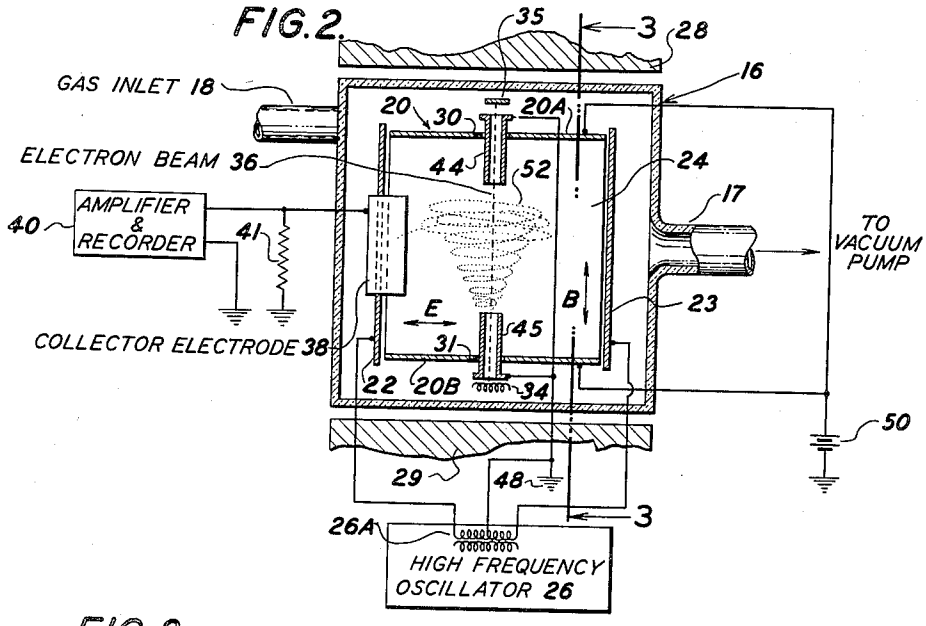
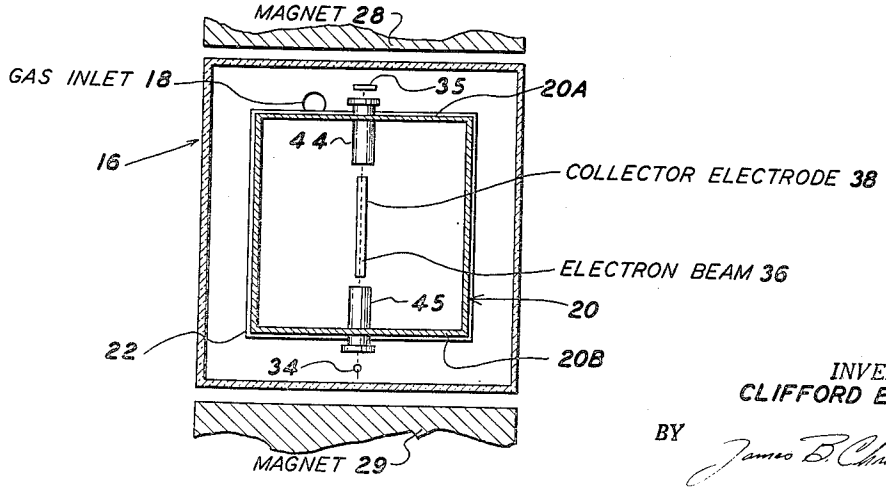


FIG. 3.



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MASS SPECTROMETRY

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This invention is directed to improvements in methods and apparatus for the analysis of mixtures by mass separation. More particularly the invention is concerned with that phase of mass spectrometry wherein mass separation is accomplished as a function of differences in the periodicity of motion of ions of different mass-to-charge ratio 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 mass-to-charge ratio of the ions, and selectively collecting the separated ions. Spatial separation of ions of differing mass-to-charge ratio may be accomplished in many ways usually involving application of magnetic or electrical fields to induce and take advantage of characteristic differences in movement of ions of differing mass-to-charge ratio in 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 impinge on and discharge at the collector electrode.

It has been found that ions subjected to a 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 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. 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. These ions are referred to as resonant ions.

All ions of mass-to-charge ratio different from the mass-to-charge ratio of the resonant ions will travel about the axis in 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 mass-to-charge ratio of the resonant ions 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.

To avoid anomalous ion paths within the field, ions are preferably formed at some point along the aforementioned axis. This is conveniently accomplished by projecting an electron beam

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through the crossed fields parallel to the magnetic field and in the plane of symmetry of the alternating field. The electron beam then coincides with the axis of rotation of the ions.

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

Since the non-resonant ions have a maximum radius of revolution about the axis, they tend to remain within the crossed field and theoretically will accumulate indefinitely therein. Accumulation of non-resonant ions may reach the point where the attendant build up of space charge interferes with the accuracy of analysis. The present invention is directed to a method of operation which avoids excessive accumulation of non-resonant ions and to a form of apparatus for carrying out the method.

In one aspect the invention contemplates in mass spectrometry involving the formation of ions, segregation thereof on the basis of their characteristic periodicity of motion in a magnetic field by means of an alternating electrical field established across a chamber in which the ions are confined and a magnetic field established across the chamber normal to the electrical field, and selectively collecting at a collector electrode disposed in the chamber those ions of a given mass-to-charge ratio having a resonant frequency corresponding to the frequency of the alternating field, the improvement which comprises collecting ions of resonant frequency differing from the frequency of the alternating field at least one point in the chamber which is not traversed by those ions of resonant frequency corresponding to the frequency of the alternating field.

Substantially all of the ions have a small component of velocity parallel to the axis of rotation due to the end effects of the electrical field and due to initial thermal energy. Moreover, such motion is frequently induced by a weak D. C. field established across the chamber parallel to the magnetic field and for the purpose of repelling ions from the chamber walls. While spiralling about the axis, the ions may move toward the extremities of the axis. It is this linear velocity component which makes the practice of the present invention possible. Resonant ions formed along the axis as by an electron beam, spiral away from the axis and do not return so that any of these ions formed intermediate the extremities of the axis will never intersect the axis adjacent its extremities even though they

may move in a lateral direction and revolve in a plane intersecting the extremities of the axis. However, non-resonant ions, since their spiral paths carry them away from and back to the axis, will periodically intersect the axis adjacent its extremities even though they may originate intermediate the extremities of the axis. I have found that these non-resonant ions may be selectively collected and discharged by an electrode mounted adjacent the extremities of the axis and projecting into the chamber substantially parallel thereto while resonant ions will, for the most part, not come in contact with these electrodes and hence will not be removed in any appreciable number from the analyzing region.

To carry out the foregoing method, the invention also provides in a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising an auxiliary collector electrode extending into the space parallel to the magnetic field and spaced from the collector electrode for collection and discharge of ions of non-resonant frequency.

In a preferred form of the apparatus, ions are formed in the analyzer chamber by means of an electron beam directed through the chamber on an axis parallel to the magnetic field and substantially centered on the plane of symmetry of the alternating electrical field. The electron beam thus becomes the axis of rotation of the ions traveling in spiral paths in the analyzer chamber. Two tubular electrodes are mounted to project into the chamber coaxially with the electron beam and spaced on opposite sides of the mid-point of the electron beam. These tubular electrodes shield the extremities of the beam so that ionization is substantially completely accomplished along the portion of the beam intermediate the two electrodes. Ions of resonant mass formed between the two electrodes will immediately spiral away from the electron beam never to return, and hence will not strike the two electrodes regardless of any lateral component of the spiral motion. Non-resonant ions, on the other hand, formed anywhere along the electron beam between the two tubular electrodes will likewise spiral away from the beam but will return to the beam after having achieved the maximum radius of spiral motion. In spiralling away and back to the beam, the non-resonant ions will also move linearly parallel to the beam and hence a portion of the non-resonant ions will at all times be striking on and discharging at the two tubular electrodes. By this means an undesirable accumulation of non-resonant ions in the analyzer region is avoided without in any way interrupting the analysis.

The invention will be more thoroughly understood by reference to the following detailed description thereof taken in relation to the accompanying drawing wherein:

Figs. 1 and 1A illustrate diagrammatically the characteristic paths of resonant and non-resonant ions respectively in the crossed magnetic and alternating fields and with relation to an axial electron beam;

Fig. 2 is a transverse sectional elevation through a preferred form of apparatus in accordance with the invention and capable of carrying out the method of the invention; and

Fig. 3 is a vertical sectional elevation taken on the line 3—3 of Fig. 2.

In Fig. 1 the spiral path 10 of resonant ions is shown in relation to an electron beam 11 extending perpendicularly to the plane of the drawing with the transverse electrical field E represented by a suitable arrow. The magnetic field is parallel to the electron beam and likewise perpendicular to the plane of the drawing. A collector electrode 12 spaced from the electron beam 11 is located in the spiral path 10 of the resonant ions. In Fig. 1A the electron beam 11 and also the magnetic field are again perpendicular to the plane of the paper and the electric field E is represented by an arrow as shown in Fig. 1. The path 14 of non-resonant ions shown in Fig. 1A illustrates the fact that they do not attain the radius attained by the resonant ions and that these ions spiral to a maximum radius and then collapse back to the origin, in this case the electron beam. These figures illustrate the basic principle of the type of mass spectrometry hereunder consideration wherein ions of a given mass-to-charge ratio are separated from ions of differing mass-to-charge ratio by reason of the fact that ions of any mass-to-charge ratio exhibit a characteristic periodicity of motion in a magnetic field. This characteristic may be exploited by means of an alternating electrical field transverse to the magnetic field whereby the ions in resonance with the electrical field will pursue a path of travel materially differing from the paths of travel of all ions not in resonance with the electrical field.

One form of apparatus for making use of this principle and incorporating a preferred embodiment of the invention is shown in transverse sectional elevation in Fig. 2 and in vertical sectional elevation in Fig. 3, the latter figure being taken on the line 3—3 of Fig. 2. The instrument there shown includes an envelope 16 having an evacuating line 17 for connection to an evacuating system (not shown) and a gas inlet line 18 for admitting a sample of gas to be analyzed to the interior of the envelope 16. A conductive open ended box 20 is disposed within the envelope, and a pair of plate electrodes 22, 23 are mounted adjacent the opposite open ends of box 20 and are insulated therefrom as by the illustrated gap. The box 20 and electrodes 22, 23 together define an analyzer region 24.

A high frequency oscillator 26 is connected across the electrodes 22, 23 to develop across the analyzer region 24 a high frequency alternating field in the direction of arrow E. Magnetic pole pieces 28, 29 are mounted adjacent envelope 16 and on opposite sides thereof to develop across the analyzer region 24 a magnetic field transverse to the alternating electrical field and in the direction represented by the arrow B.

Opposite walls 20A, 20B of the box 20 are provided with substantially centered apertures 30, 31 respectively. An electron emitting filament 34 is mounted adjacent the aperture 30 so that an electron beam 36 may be directed through the analyzer region 24 parallel to the magnetic field and substantially at the mid-point of the plane of symmetry of the alternating electrical field.

A collector electrode 38 is mounted through the electrode 22 and is insulated therefrom. The collector electrode is oriented to project into the analyzer region 24 in a plane transverse to the magnetic field and intersecting the electron beam.

The collector electrode is connected to an emplifying and recording network 40 across a grounded resistor 41. In the particular embodiment shown, the electrode 38 is at substantially ground potential although such arrangement does not constitute an operational or structural limitation.

Two conductive tubular members 44, 45 are mounted through the respective apertures 30, 31 in the sides 20A, 20B of the box 20 and extend into the analyzer region 24 coaxially with respect to the electron beam 36. Members 44, 45 are in the nature of electrodes and extend substantially equidistant into opposite sides of the analyzer region 24 with their inner ends spaced about the center point of the electron beam 36.

The oscillator 26 is connected across the electrodes 22, 23 through a transformer 26A. The mid-point of the secondary winding of the transformer 26A is grounded at 48 and is connected to the tubular members 44, 45 so that each of these members is at substantially ground potential as is the plane of symmetry of the alternating electrical field. The opposite sides 20A, 20B of the conductive box 20 are ground through a bias battery 50 which, according to preferred practice, places a small positive potential on the walls of the box 20. As mentioned above, ions formed in a magnetic field tend to drift in the direction of the magnetic field under the influence of distortions of the electrical field and because of small initial thermal energies. The small positive potential on the walls of the box 20 prevents ions from drifting into and discharging at the walls.

The operation of the apparatus illustrated in Figs. 2 and 3 is substantially as follows:

With the envelope evacuated, a gas sample is introduced through line 18 and finds its way into the analyzer chamber 24 by diffusion. Upon intersecting the electron beam 36 between the inner ends of the tubular electrodes 44, 45, molecules of the sample are ionized and are immediately set in motion under the influence of the crossed magnetic and high frequency alternating fields. The ions of mass-to-charge ratio in resonance with the frequency of the alternating field travel in a path 52 as illustrated and ultimately reach the collector electrode 38. Upon striking the collector electrode these ions discharge and the magnitude of the discharge current as amplified and recorded in the network 40 gives a measure of the partial pressure of the molecule or molecules in the original sample from which these particular ions are derived. As is shown by the path 52, an ion formed at any place along the electron beam between the inner ends of the tubular electrode 44, 45 will have a linear component of motion in addition to the spiral motion. Since the resonant ions do not return again to the origin (this being the electron beam) any such ions formed along this open region of the beam will not come into contact with the tubular electrode 44, 45. Non-resonant ions formed in the same manner as the resonant ions will also initially spiral away from the electron beam. As described above, these ions will return to the axis of origin and again spiral away, etc. Like the resonant ions, the non-resonant ions also have a linear component of motion which will eventually carry these ions into a plane intersecting either one or the other of tubular electrodes 44, 45. Any non-resonant ion, in the process of collapsing back to the origin, which finds itself in a plane intersecting

the tubular electrodes 44, 45, will strike and discharge at one or the other of these electrodes. A proportion of the total number of resonant ions will be continuously discharging at one or the other of the tubular electrodes 44, 45. This proportion depends upon the axial extension of these electrodes into the analyzer region and may be varied by varying the length of the electrodes.

Although the tubular electrodes illustrated in the drawing represent the preferred construction, it is apparent from the consideration of the factors involved that such is not the necessary limitation of the invention. A plate type electrode mounted through a wall of the box 20 on a plane parallel to the electron beam and preferably closely adjacent the electron beam serves the same purpose although with lower efficiency.

As previously discussed the invention provides means for preventing an undue accumulation of resonant ions and the space charge attendant thereon. In addition the electrodes projecting into the analyzer region adjacent the electron beam minimize the space charge developed by the electron beam. This space charge is a junction of the intensity of the beam and is inversely proportional to the magnitude of the capacitive coupling between the beam and the chamber walls. The projecting electrodes increase this capacitance materially and thereby reduce the space charge correspondingly.

An evident feature of the invention is the simplicity of operation whereby no complex electrical signals need be fed to any portion of the apparatus for sweeping non-resonant ions therefrom and analysis of ions of preselected mass-to-charge ratio may proceed uninterrupted by the continuous removal of the non-resonant ions.

I claim:

1. In a mass spectrometer having an analyzer chamber means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising an auxiliary electrode extending into the space parallel to the magnetic field and spaced from the collector electrode for collection and discharge of ions of non-resonant frequency.

2. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising auxiliary electrodes extending into the space from opposite sides of the chamber and parallel to the magnetic field for collection and discharge of ions of non-resonant frequency.

3. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode projecting into said space transversely of the magnetic field and in

the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising a pair of auxiliary electrodes extending into the space from opposite sides of the chamber adjacent the plane of symmetry of the alternating field and parallel to the magnetic field for collection and discharge of ions of non-resonant frequency.

4. Apparatus according to claim 3 wherein said auxiliary electrodes are aligned on a line paralleling the magnetic field.

5. In a mass spectrometer having an analyzer chamber, means for propelling an electron beam axially through the chamber to ionize gas admitted to the chamber, means for producing a magnetic field across the chamber parallel to the electron beam, means for establishing an alternating electrical field across the chamber normal to the magnetic field, and a collector electrode projecting into the chamber normal to the electron beam and spaced therefrom to collect ions which travel about the electron beam in orbits of ever increasing radius, the improvement comprising auxiliary collector means projecting into the chamber parallel to and in region of the electron beam for discharging ions which travel about the electron beam in orbits which increase in radius to a maximum and collapse back to the electron beam.

6. In a mass spectrometer having an analyzer chamber, means for propelling an electron beam axially through the chamber to ionize gas admitted to the chamber, means for producing a magnetic field across the chamber parallel to the electron beam, means for establishing an alternating electrical field across the chamber normal to the magnetic field, and a collector electrode projecting into the chamber normal to the electron beam and spaced therefrom to collect ions which travel about the electron beam in orbits of ever increasing radius, the improvement comprising separate auxiliary collector means projecting into opposite sides of the chamber parallel to and in the region of the electron beam for discharging ions which travel about the electron beam in orbits which increase in radius to a maximum and collapse back to the electron beam.

7. In a mass spectrometer having an analyzer chamber, means for propelling an electron beam axially through the chamber to ionize gas admitted to the chamber, means for producing a magnetic field across the chamber parallel to the electron beam, means for establishing an alternating electrical field across the chamber normal to the magnetic field, and a collector electrode projecting into the chamber normal to the electron beam and spaced therefrom to collect ions which travel about the electron beam in orbits of ever increasing radius, the improvement comprising a tubular electrode projecting into the chamber coaxially with the electron beam to shield a portion of the electron beam and for discharging ions which travel about the electron beam in orbits which increase in radius to a maximum and collapse back to the electron beam.

8. In a mass spectrometer having an analyzer chamber, means for propelling an electron beam axially through the chamber to ionize gas admitted to the chamber, means for producing a magnetic field across the chamber parallel to the electron beam, means for establishing an alternating electrical field across the chamber normal to the magnetic field, and a collector electrode projecting into the chamber normal to the electron beam and spaced therefrom to collect ions which travel about the electron beam in orbits of ever increasing radius, the improvement comprising a pair of tubular electrodes projecting into opposite sides of the chamber coaxially with the electron beam and terminating in the chamber in opposite sides of the midpoint of the electron beam.

9. In a mass spectrometer having an analyzer chamber, means for projecting an ionizing electron beam across the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field and parallel to the electron beam, and a collector electrode disposed in said space and spaced from the electron beam in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising an auxiliary electrode disposed in the chamber adjacent an extremity of an axis of the chamber lying parallel to the magnetic field and in the path of ions having a resonant frequency differing from the frequency of the alternating field.

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