June 4, 1968 J. C. HELMER 3,387,131

DUAL ORBIT MASS SPECTROMETER FOR ANALYZING IONS IN THE MASS RANGE OF 1 TO 100

Filed July 15, 1965 2 Sheets-Sheet 1

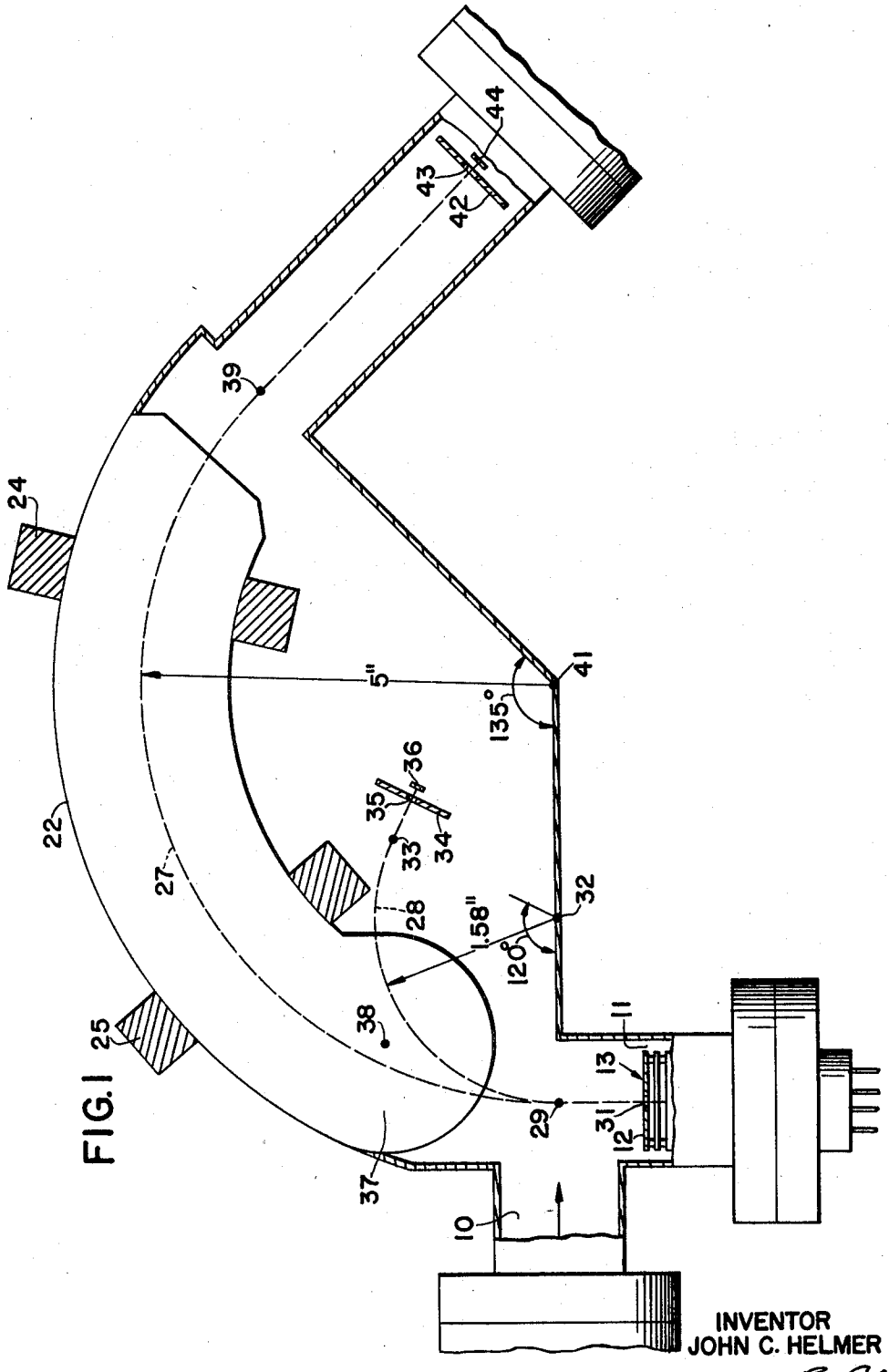

FIG. 1

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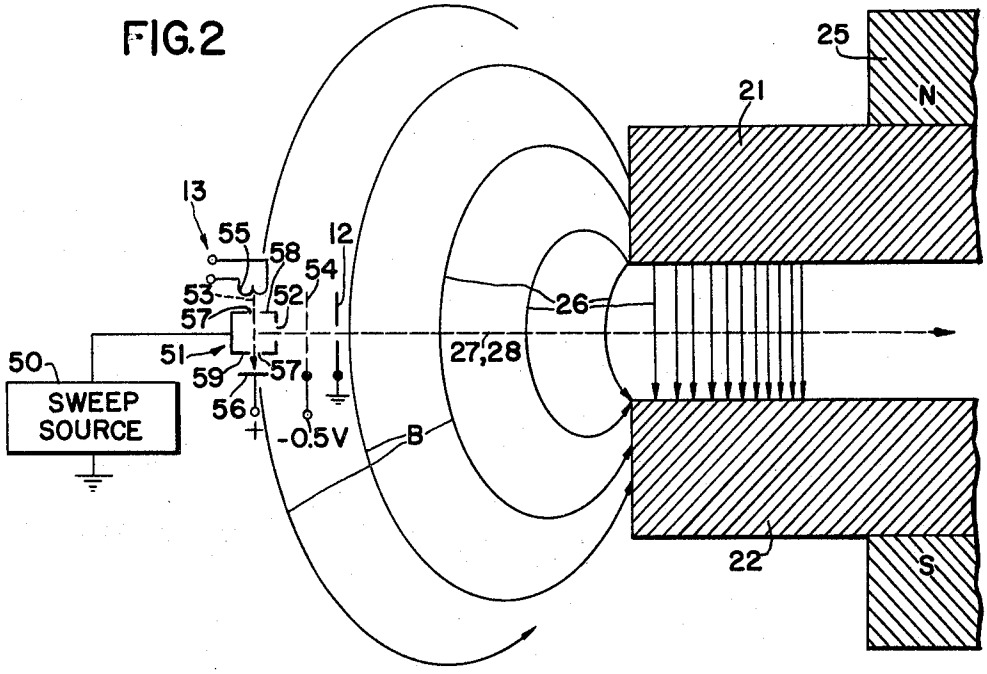
FIG.2



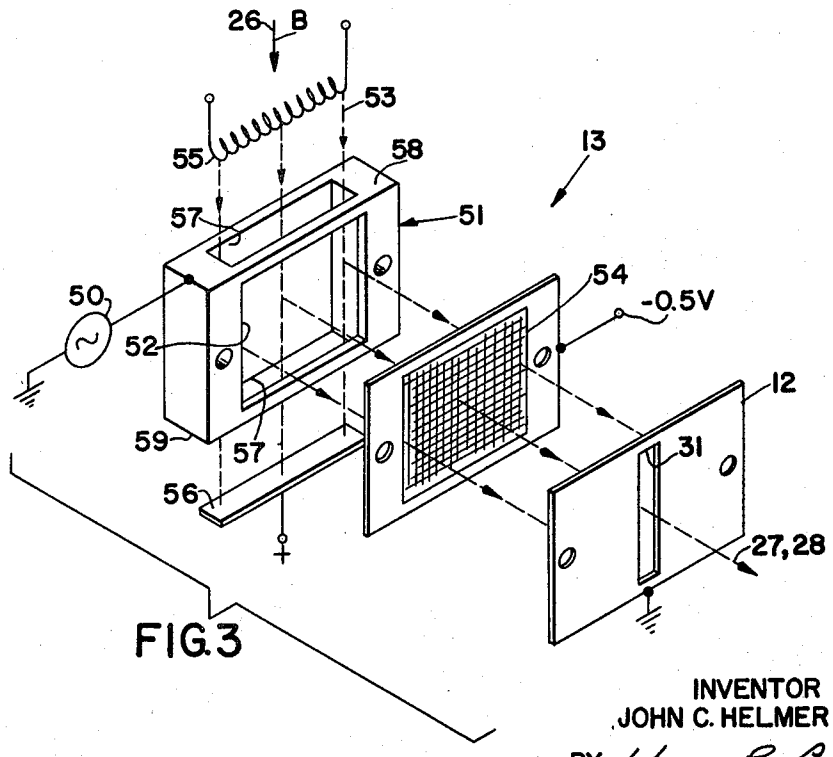


FIG.3

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DUAL ORBIT MASS SPECTROMETER FOR ANALYZING IONS IN THE MASS RANGE OF 1 TO 100

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11 Claims. (Cl. 250—41.9)

ABSTRACT OF THE DISCLOSURE

There is disclosed a dual orbit mass spectrometer which utilizes an arcuate ion trajectory of less than 180 degrees for purposes of reducing the magnet weight required heretofore in systems exhibiting equivalent performance. With the present device, a permanent magnet assembly providing a 1000 to 2000 gauss field is used in combination with an accelerating voltage swept from 100 to 1000 volts to provide the energy necessary to separate and monitor ion masses ranging from 1 to 100. Use of the fringing field of the permanent magnet to collimate the electrons in the ion source eliminates the need for a separate collimating magnet, eliminates a wider permanent magnet gap for accepting the ion source and in general permits a reduction in the size, weight and cost of magnets used in dual orbit spectrometers.

Mass spectrometers

The present invention relates generally to mass spectrometers and more particularly to a dual orbit mass spectrometer having a low mass collecting arrangement of relatively low resolution and an ion source wherein electrons are collimated by the fringing magnetic field from the pole pieces that establish the mass trajectories.

The design of mass spectrometers wherein a gas being analyzed is ionized and accelerated through a deflecting magnetic field is determined by the equation:

$$mV=\left(\frac{BR}{145}\right)^2 \quad (1)$$

where m equals the mass of the gas ion being analyzed; V equals the voltage necessary to accelerate the ion from the ion source into a deflecting magnetic field; B equals the density of the deflecting magnetic field in gauss; R equals the radius of curvature of the ion as it is deflected by the magnetic field, in centimeters. In mass spectrometers having a D.C. magnetic field, deflection of an ion having mass m_1 is determined solely by the accelerated potential V. Hence, the accelerating voltage required to deflect a singly charged ion of mass m_1 through a trajectory of radius R_1 and therefore through an aperture positioned to receive ions in said trajectory is given by:

$$mV=\text{constant} \quad (2)$$

Equation 2 indicates that the mass passing through the aperture to a collector is determined solely by the voltage necessary to accelerate ions from the ion source into the deflecting magnetic field.

To obtain a high degree of resolution (where resolution is defined as the ratio between the mass at a peak amplitude and the mass separation 50% below the peak amplitude), it is generally the practice with prior art mass spectrometers to select mV as approximately 10,000 over the entire mass range being analyzed. In consequence, to sweep from mass 1 to mass 100, an accelerating potential varying between 10,000 and 100 volts is required. In practical mass spectrometers, however, the upper and lower limits of the accelerating voltage are approximately 5,000 and 100 volts, respectively. If the upper limit is exceeded, high

voltage breakdown problems are encountered; because of these problems, it is actually preferable to limit the high voltage to approximately 2,000 volts. For accelerating potentials less than 100 volts, sensitivity is reduced and secondary electrons from the ionizing electron beam in the ion source are dispersed into the remainder of the system to prevent the derivation of an ion stream of uniform energy level.

Because of these factors, prior art mass spectrometers having fixed magnetic fields do not generally permit investigation of mass 1 and many have as their lower limit mass 10. Some attempts have been made to rectify the problem by employing deflecting magnetic fields that can be varied. The use of variable magnetic fields involves considerable difficulty; for example, inaccuracies in providing the correct field strength and down time requirements involved in adjusting the magnetic field strength are encountered.

The present invention avoids these difficulties of the prior art by providing a dual orbit mass spectrometer in which ions in mass range 1 to 10 are collected simultaneously with ions in the mass range 10 to 100 at two different collectors. The dual orbit operation is obtained by sweeping the accelerating potential from approximately 1,000 volts to 100 volts. Hence, the mV products for the low and high mass ranges are 1,000 and 10,000, respectively. I have found that high resolution for the low mass range is not required because of the relatively large percentage difference between adjacent masses in the range from mass 1 to mass 10. Hence, imprecise focusing and a wide collector slit can be tolerated in the low mass range of interest. Because of the 10 to 1 ratio of the mV products for the high and low mass ranges, the radius of the curvature of ions in the lower mass range is about 3.16 (square root of 10) smaller than those in the higher range. The different trajectory radii are arranged so that ions in both ranges enter and leave at right angles to the magnetic field boundary created by the pole pieces; the magnetic field boundary being defined as the area of the pole pieces plus the width of the gap through which the ions pass that is between the pole pieces. I have found that arcuate pole pieces having a generally semicircular protuberance at their ends proximate the ion source provide a very convenient arrangement for establishing the required field.

In the mass spectrometer of the present invention, the light ions are not deflected away from the gap between the pole pieces as is generally the case with many prior art devices. Deflection of the light ions does not occur because of the close proximity, about two inches, of the ion source outlet slit to the pole pieces. Because of the close proximity between the ion source and the magnetic field boundary, the heavy ions must be deflected through an angle greater than 90° so they can be focused. To obtain satisfactory resolution in the high mass range, the mass spectrometer of the present invention does not require 180° deflection as is the case with many prior art devices. I have found that 135° deflection is a suitable compromise between the field strength required and focusing necessary for relatively high resolution.

Because of these factors, the mass spectrometer of the present invention, in the high mass region, is characterized as having a relatively large resolution of approximately 100 as defined above despite having ion gun and collector slit widths of approximately 40 mils to provide great sensitivities, better than 2×10^{-4} amperes per torr. One of the factors whereby sensitivity is obtained without sacrificing resolution is in providing an ion stream wherein energy spread is minimized. The ion stream energy is uniformly maintained by collimating a sheet-like electron beam included in the ion source and arranging the source so gas molecules are mixed with the electron beam in a unipotential plane. Uniformity in the energy level of

the ions in both trajectories is attained with an open face ion box through which the electron beam passes. Since all ions are created at the same potential, the ions repelled from the box are of substantially uniform energy level. The ion stream accelerated between the pole pieces is defined by a 40 mil slit in an accelerating plate that forms the outlet of the ion source. To prevent coupling of the relatively large potential at the accelerating plate into the electron beam that can disturb the unipotential characteristics of the beam while it is in the ion box, an ion pervious grid is positioned between the box and accelerating plate.

The collimated electron beam is derived by placing the ion source in the fringing field of the pole pieces employed for ion deflection. By arranging the ion source about two inches from the pole pieces of a 1200 gauss magnet, having a one inch gap, a collimating magnetic field of approximately 100 to 200 gauss is coupled to the electron stream. The 100 to 200 gauss magnetic field is sufficiently straight and possesses enough field strength to prevent spread of the electron beam and maintain it collimated.

The use of the fringing field for electron beam collimation differs materially from prior art mass spectrometers with which I am familiar. Many mass spectrometers do not employ magnetic collimation of the electron stream, while those that do frequently utilize a separate source magnet that requires very critical adjustment. In still other spectrometers, the ion source is located directly between the pole pieces employed to establish the ion trajectory, an arrangement that is wasteful of the pole pieces because the electron beam does not require the strong magnetic field that exists directly between them. Placement of the ion source between the pole pieces requires a wider gap than would otherwise be used, and is therefore extremely wasteful of magnetic field energy. Furthermore, the relatively strong magnetic field in the gap tends to adversely affect the trajectory of the ions within the ion source. The use of the fringing field for electron beam collimation results in great improvement in operating procedures and reliability compared to all prior art devices with which I have familiarity.

It is, accordingly, an object of the present invention to provide a new and improved mass spectrometer.

An additional object of the present invention is to provide a new and improved dual orbit mass spectrometer.

Another object of the present invention is to provide a mass spectrometer capable of deriving spectral information over the mass range of 1 to 100 with a single sweep of the accelerating potential.

A further object of the present invention is to provide a dual orbit mass spectrometer for covering mass ranges of 1 to 10 and 10 to 100 simultaneously, wherein high resolution in the high mass range is attained but in which lower resolution in the low mass range is tolerable.

Still another object of the present invention is to provide a new and improved means for collimating the electron beam of a mass spectrometer.

A further object of the present invention is to provide a new and improved mass spectrometer in which ions having virtually no spread in energy level are derived.

An additional object of the present invention is to provide a new and improved mass spectrometer wherein ions originate from a unipotential area of an ionizing electron beam.

Still another object of the present invetnion is to provide a dual orbit mass spectrometer that is relatively sensitive, has a high resolution for ions of large mass, is reliable, easily operated and yet is relatively inexpensive.

The above and still further objects, features and advantages of the present invention will become apparent upon consideration of the following detailed description of one specific embodiment thereof, especially when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a top view of a preferred embodiment of the mass spectrometer of the present invention;

FIGURE 2 is a side sectional view of a portion of the pole pieces with a schematic showing of the ion source; and

FIGURE 3 is a persective view of the ion source employed in the present invention.

Reference is now made to FIGURE 1 of the drawings, wherein a gas containing molecules from mass 1 to mass 100 that is to be analyzed is introduced into the mass spectrometer of the present invention through conduit **10**. The gas molecules are admitted to an ion source **13** through gas access passageways **11** around the edges of the plate **12** having a central aperture **31** which defines the outlet of the ion source **13**. Ion source **13** ionizes the gas molecules coupled thereto with a positive charge. The positively charged ions are accelerated from source **13**, as is shown infra, into the magnetic deflecting field established between pole pieces **21** and **22**, that are fabricated of a material having a high magnetic permeability.

Pole pieces **21** and **22** are both of approximately the same generally arcuate shape and lie in parallel planes to provide a 1 inch magnetic field gap between them. In the gap between pole pieces **21** and **22**, there is established approximately a 1,000 to 1,200 gauss D.C. or steady magnetic field by permanent magnets **24** and **25**. The direction of the D.C. magnetic field established in the gap between pole pieces **21** and **22**, as well as the fringing magnetic field deriving from the pole pieces, is shown in FIGURE 2 by arrows **26**. The magnetic field boundary for establishing the trajectory of ions originating from source **13** is considered as extending 1 inch from pole pieces **21** and **22**, i.e., the length of the gap between the pole pieces. Ions deriving from source **13** traverse two different orbits **27** and **28**, the former for ions in the mass range 10 to 100 and the latter for ions in the mass range 1 to 10. In the region defined by the magnetic field boundaries of pole pieces **21** and **22**, orbits or trajectories **27** and **28** are both circular, having radii of curvature of approximately 5.00 and 1.58 inches, respectively. Both circular trajectories commence at magnetic field boundary point **29**, approximately 1 inch from slit **31** in disk **12**, where the ions emerge from source **13**. Both ion paths **27** and **28** define straight lines between slit **31** and point **29**.

To provide the necessary ion beam focusing, it is required for the ions in both orbits **27** and **28** to enter and leave the magnetic field boundary at right angles thereto. The shape of pole pieces **21** and **22** enables this result to be attained. By placing pole pieces **21** and **22** approximately 2 inches from outlet electrode **12** of source **13**, light ions in the mass range 1 to 10 have sufficient force to enter the gap between the pole pieces. This is in contrast with many prior art mass spectrometers with which I am familiar where the light ions are deflected by the fringing field before reaching the pole piece gap. Of course, the arrangement I employ enables the light ions to be focused so information relative thereto can be derived.

As shown infra, the ions in both ranges are accelerated by the same potential so that the mV product of the light ions is $\frac{1}{10}$ that of the heavy ions and the former turn on a circle having a radius of curvature smaller by a factor of 3.16 than that of the latter. From boundary point **29** of the magnetic deflecting field, the low mass ions define a circular path centered about point **32**. The circular path covers approximately 120° of arc from points **29** to **33**, at either end of the boundary of the magnetic deflecting field established by pole pieces **21** and **22**. After passing point **33**, the low mass ions assume a straight line trajectory, reaching a focal point at mask **34**, that is located approximately ½ inch from point **33**. At the focal point on mask **34**, slit **35**, of approximately 0.040 inch diameter, is provided so that the light ions can reach collector electrode **36**. The 1½ inch separation between mask **34** and pole pieces **21** and **22** is sufficiently great to enable

the mask and collector **36** to be placed at points that enable the mass spectrometer to be conveniently fabricated.

I have found that by providing pole pieces **21** and **22** with semicircular disk-like terminations **37** in a region proximate source **13** and collector **34**, that the requirement of the low mass trajectory to be perpendicular to the deflecting magnetic field is fulfilled. The semicircular termination **37** has approximately a 1.25 inch radius and a center at point **38**. The circumference of disk **37** forms a smooth intersection with one edge of pole piece **22** but extends considerably beyond the other edge of the pole piece. This enables the high mass trajectory **27** to be centered relative to the edges of the pole pieces **21** and **22** and establishes the required right angle relationship between the magnetic field boundary and both trajectories.

The remainder of pole pieces **21** and **22** are of generally arcuate shape, having a radius of curvature midway between their edges equal to the radius of curvature of high mass trajectory **27** to obtain the most efficient coupling between the deflecting magnetic field and the ions. Pole pieces **21** and **22** are shaped so that the circular trajectories between magnetic field boundary points **29** and **39** cover an arc of 135°, circumscribed from point **41**. After passing point **39**, the heavy ions assume a straight line path and are focused on mask **42**, 3⅜ inches from the magnetic field boundary. At the focal point of trajectory **27**, mask **42** is provided with a 0.040 inch diameter slit **43** through which the focussed, high mass ions pass so they can impinge on collector **44**. The relatively large slit width enables sensitivities on the order of 2 amperes per torr to be delivered.

At any instant, ions of masses m_1 and m_2 in trajectories **27** and **28**, respectively, have accelerating potentials of:

$$V=\frac{10{,}000}{m_1}=\frac{1{,}000}{m_2} \qquad (3)$$

applied thereto by voltage source **50** that is connected between ion box **51** and accelerating electrode **12** in ion gun **13**. The potential of source **50** is exponentially swept with respect to time from −1,000 to −100 volts so that ions from mass 10 to mass 100 are successively focused to assume trajectory **27** while simultaneously ions from mass 1 to mass 10 are successively focused to be projected through trajectory **28**. In consequence, m_1 identically equals $10m_2$.

The accelerated ions are derived in response to gas molecules from inlet **10** passing through apertures **11** in accelerating electrode **12**. From accelerating electrode **12**, the gas molecules pass through the relatively large, open face **52** of ion box **51** to interact with the uni-potential, collimated electron sheet **53** in the box. Electrons in sheet **53** interact with the gas molecules to ionize them with a positive charge, in a manner well known to those skilled in the art. Because the electrons in box **51** are at the same potential, ions repelled from the box by accelerating electrode **12** are at substantially the same energy level, whereby trajectories **27** and **28** are well defined. The ions that comprise trajectories **27** and **28** are repelled from box **51** by the accelerating field established by electrode **12** and pass through the relatively wide slit **31**, having a diameter of 0.040 inch, of the accelerator. To maintain electron sheet **53** at a single potential value while it is within box **51**, ion pervious 100-mesh tungsten grid or screen **54**, maintained at a D.C. potential of approximately −0.5 volt, is positioned between box **51** and accelerator electrode **12**. If grid **54** were not employed, the electrostatic accelerating field developed at electrode **12** would penetrate through the large, open face **52** of box **51** and cause potential gradients in electron stream **53** while it is within the box. The existence of potential gradients in electron stream **53** while it is in the interaction region defined by box **51** would prevent the derivation of ion streams having homogeneous energy levels, i.e., the ion streams would have energy spreads therein.

Electron sheet **53** is derived by thermionic emission from electron emitting cathode **55** to high voltage anode **56**, that are separated by approximately ½ inch. Sheet **53** is coupled into metallic box **51** through slit **57** in the top and bottom walls **58** and **59** of the box. Because walls **58** and **59** are maintained at the same potential, the voltage of source **50**, and the ion accelerating voltage of electrode **12** is not coupled into the interior of box **51**, electron sheet **53** remains at a constant potential while in the box.

Another important factor relating to the unipotential characteristic of electron sheet **53** and the homogeneous nature of ion streams **27** and **28** resides in the fact that the electron beam is collimated. Collimation of electron sheet **53** is derived by placing anode **56** and cathode **55** approximately 2 inches from the ends of pole pieces **21** and **22** and each equidistant from the plane bisecting the gap between pole pieces. In addition, electrodes **55** and **56** are arranged so that electron sheet **53** traverses a plane at right angles to the plane bisecting the magnetic field gap. Thereby, magnetic lines of force **26** from pole pieces **21** and **22** are coupled along electron path **53** between cathode **55** and anode **56**. The magnetic field in the plane coincident with electron sheet **53** is sufficiently removed from pole pieces **21** and **22** to have almost zero curvature. The field strength is on the order of 100 to 200 gauss where intersection with electron sheet **53** occurs. The 100 to 200 gauss field strength is an ample value for collimating electron sheet **53**. To enable coupling of an undistorted collimating fringing magnetic field from pole pieces **21** and **22** into electron stream **53**, each of electrodes **51**, **54**, **55** and **56** of ion source **13** is fabricated from a non-magnetically permeable metal. Thus, the fringing field between pole pieces **21** and **22** produces a substantially straight magnetic field in the plane of electron stream **53**. The field is of sufficient intensity to collimate stream **53** throughout its ½ inch travel. The fringing magnetic field beyond its boundary is not, however, sufficiently strong to affect trajectories **27** and **28** before the ions therein reach boundary point **29** so that straight line trajectories of both the high and low mass ions are achieved in the region between accelerator **12** and boundary point **29**.

While I have described and illustrated one specific embodiment of my invention, it is clear that variations of the details of construction that are specifically illustrated and described may be had without departing from the true spirit and scope of the invention as defined in the appended claims.

I claim:

1. A mass spectrometer for analyzing ions in the mass range of approximately 1 to 100 with a single sweep comprising a single slit source of said ions, a pair of pole pieces having a gap, the entrance to which is spaced apart from and in front of said slit, for providing a steady magnetic field for deflecting ions deriving from said source, said source and pole pieces being positioned so all ions deriving from said source have sufficient acceleration to reach the magnetic field boundary established by said field and be projected through said gap, said pole pieces being shaped so that ions with mass 1 to mass 10 define a first circular trajectory of less than 180° and ions with mass 10 to mass 100 define a second circular trajectory of less than 180° while within the magnetic field boundary established thereby, said pole pieces being shaped so that ions in both trajectories enter and exit at approximately 90° relative to said magnetic field boundary, whereby ions in said first trajectory have a radius of curvature approximately 3.16 times the radius of curvature of ions in said second trajectory, a first collector having a slit positioned to receive focused ions in said first trajectory, and a second collector having a slit positioned to receive focused ions in said second trajectory, wherein said ion source includes means for establishing a sheet of electrons to ionize molecules introduced into said mass spectrometer, said electron sheet being positioned relative to said pole pieces to be collimated only by the fringing magnetic field between said pole pieces.

2. The mass spectrometer of claim **1** wherein said

source further includes an ion box through which said electron sheet passes, said box having a relatively large open face and always being maintained at a uniform potential, an accelerating electrode including said slit through which said ions pass and are accelerated into the gap between the pole pieces, and an ion pervious grid positioned between said accelerating electrode in said box for preventing the forces from said accelerating electrode from affecting the potential of said electron sheet while said sheet is within said box, said box, grid and accelerating electrode being fabricated of non-magnetically permeable materials.

3. The mass spectrometer of claim 2 wherein said electron sheet is removed from the edges of said pole pieces by approximately twice the gap between the pole pieces and the magnetic field intensity coupled to the electron sheet is on the order of 100 to 200 gauss.

4. The mass spectrometer of claim 1 wherein said pole pieces are shaped to provide a high mass circular trajectory of approximately 135°.

5. The mass spectrometer of claim 4 wherein the radius of curvature of said high mass trajectory is approximately 5 inches.

6. The mass spectrometer of claim 1 wherein said pole pieces are of generally arcuate configuration and have protruding disks at the ends thereof proximate said ion source, said disks extending beyond one edge of the arcuate portions of said pole pieces to provide said magnetic field boundary for the second trajectory.

7. A mass spectrometer comprising an ion source, a pair of pole pieces having a gap for deflecting ions deriving from said source, said source and pole pieces being positioned so all ions deriving from said source have sufficient acceleration to reach the magnetic field boundary established by said pole pieces and be projected through said gap, said source including means for establishing a sheet of electrons to ionize molecules introduced into said mass spectrometer, magnetic means for collimating said sheet of electrons, said last-named means including only the fringing field between said pole pieces.

8. The mass spectrometer of claim 7 wherein said

source further includes an ion box through which said electron sheet passes, said box having a relatively large open face and always being maintained at a uniform potential, an accelerating electrode including a slit through which said ions pass and are accelerated into the gap between said pole pieces, and an ion pervious grid positioned between said accelerating electrode and said box for preventing the forces from said accelerating electrode from affecting the potential of said electron sheet, said box, grid and accelerating electrode being fabricated of non-magnetic permeable materials.

9. A mass spectrometer comprising an ion source, a pair of pole pieces having a gap for deflecting ions deriving from said source, said source including means for establishing a sheet of electrons to ionize molecules introduced into said mass spectrometer, said electron sheet being positioned relative to said pole pieces to be collimated only by the fringing magnetic field between said pole pieces.

10. The mass spectrometer of claim 9 wherein said electron sheet is removed from the edges of said pole pieces by approximately twice the gap between the pole pieces and the magnetic field intensity coupled to the electron sheet is on the order of 100 to 200 gauss.

11. The mass spectrometer of claim 10 wherein said gap is on the order of one inch and said electron stream is approximately two inches from the edge of said pole pieces.

References Cited

UNITED STATES PATENTS

2,355,658	8/1944	Lawlor	250—41.9
2,499,288	2/1950	Backus	250—41.9
2,710,354	6/1955	Inghram et al.	250—41.9
2,894,136	7/1959	Reinecke	250—41.9
2,911,531	11/1959	Rickard et al.	250—41.9
3,265,890	8/1966	Briggs	250—41.9

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