June 26, 1956 C. F. ROBINSON 2,752,501

METHOD AND APPARATUS FOR MASS SEPARATION

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FIG. 1.

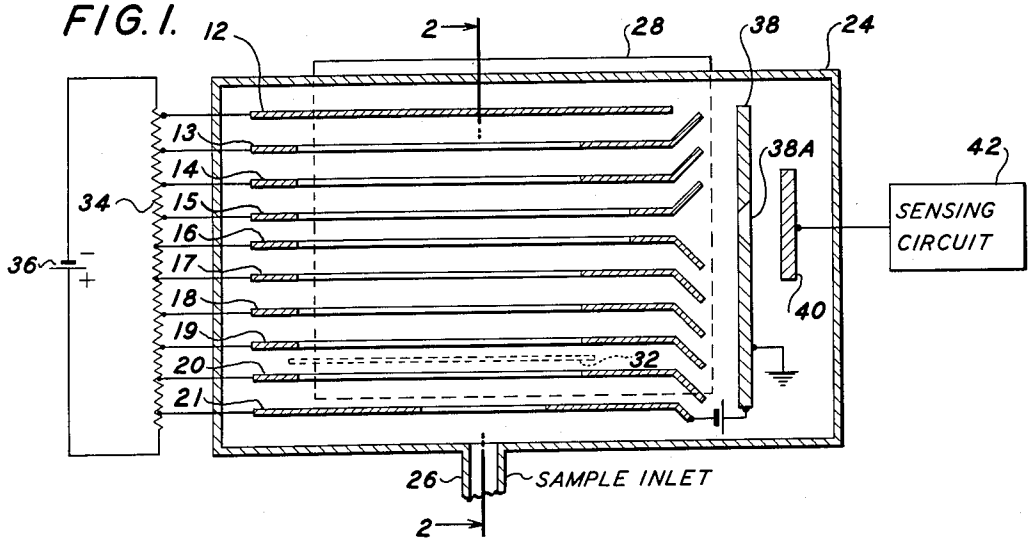


FIG. 2.

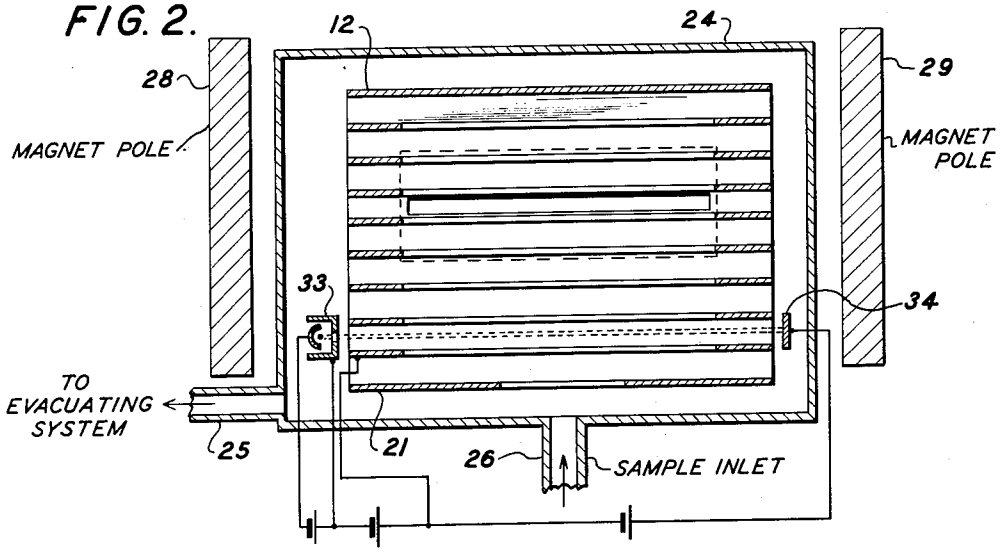
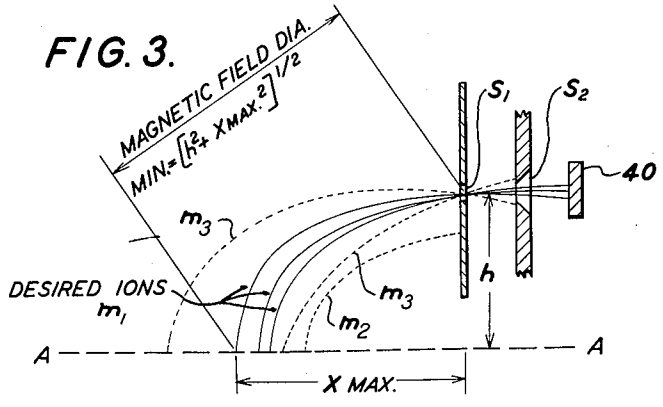


FIG. 3.



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FIG. 4.

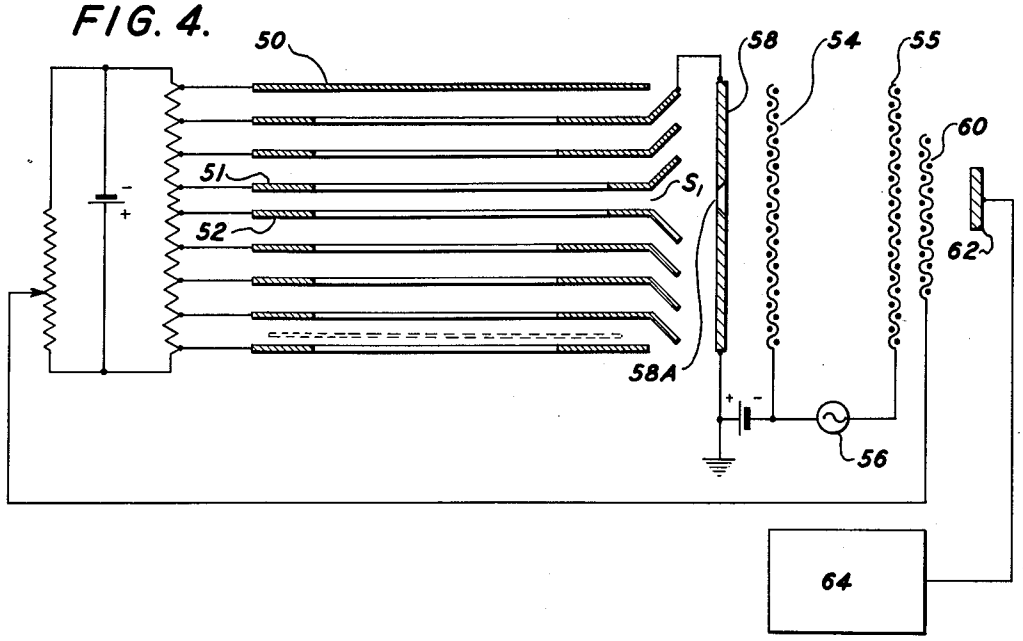
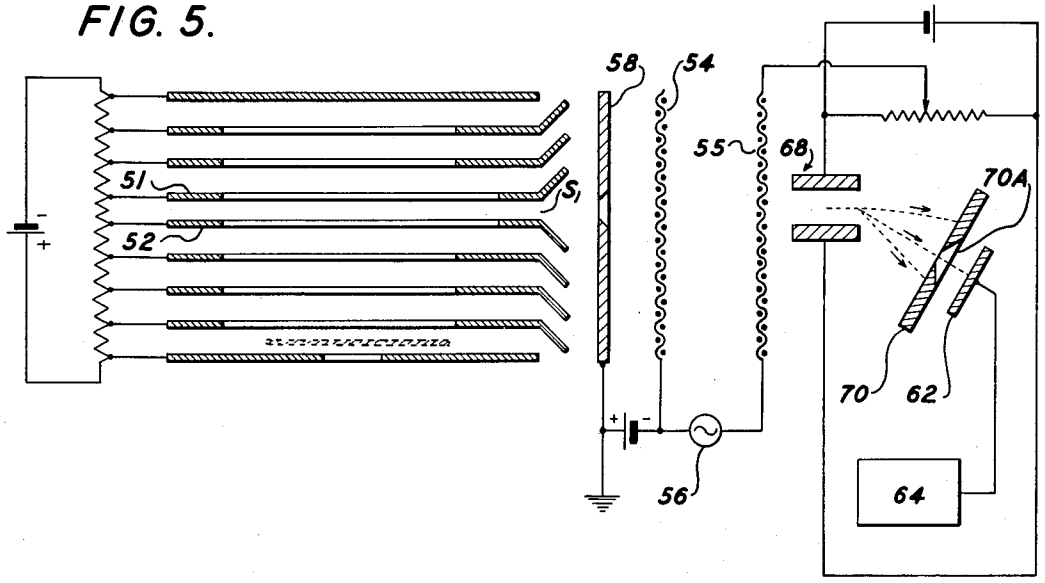


FIG. 5.



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METHOD AND APPARATUS FOR MASS SEPARATION

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Application March 21, 1952, Serial No. 277,773

9 Claims. (Cl. 250—41.9)

This invention relates to a method of mass separation and to a mass spectrometer and to a mass discriminating ion source embodying such method. The ion source may be used by itself to accomplish mass separation or may be used in conjunction with associated resolving systems.

Mass separation in general, as utilized in the practice of mass spectrometry, involves ionization of a sample under investigation, subjecting the ions to the effects of electrical or magnetic fields or both, to effectuate spatial or temporal separation thereof as a function of specific mass and selectively sensing the relative abundance of one or more given masses. Ions exhibit characteristic movement in electrical and magnetic fields as a function of ion mass and of the nature of the field. In the conventional 180° mass spectrometer resolving system ions are propelled through a transverse magnetic field and follow curved paths therein, the radii of which are determined by the strength of the magnetic field and the specific mass of the ions. In this method of mass separation ions of a given mass are focused through a so-called resolving slit for collection either by altering the strength of the magnetic field or by varying the velocity at which the heterogeneous beam of ions is introduced into the magnetic field.

In the so-called crossed field method of mass separation ions are subjected to mutually perpendicular electrical and magnetic fields under which stimulus the ions travel in cycloidal paths, again the pitch of which is a function of specific mass and field strengths. In all of the foregoing, selective collection of ions of a given mass is based upon separation of the ions in space under the influence of the applied field or fields.

I have now developed a method of mass separation wherein the direction of travel of ions, as they emerge from such a crossed field, is made use of to effectuate the desired selective mass separation. The invention in one aspect involves the method of mass separation which comprises ionizing a sample to be analyzed, orienting the ions in a common plane, developing an electrical field perpendicular to this plane and a magnetic field normal to the electrical field whereby the ions are set in motion with cycloidal trajectories, the pitches of which vary as a function of ion mass, and separating the ions by selectively collecting the ions traveling in a given direction at the moment of issuing from the influence of the electrical and magnetic fields. The term "plane" is used to designate planar, laminar or pencil-shaped beams.

In this method the ions are permitted to move in cycloidal trajectories through approximately one-quarter period of cycloidal motion, and discrimination of one mass from another is accomplished on the basis of the direction of travel of the various ions after such quarter period. In this respect the method of mass separation of the invention differs from any heretofore contemplated as being the first to utilize direction of movement as a critical factor rather than position in space.

The method enables the construction of an ion source in which mass discrimination is inherent, which ion source may be used as a highly sensitive, comparatively low

resolution mass spectrometer, or may be associated with an auxiliary resolving system to result in a high resolution system. In one aspect, the invention is directed to a mass discriminating ion source comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electric field, means for ionizing a sample to be analyzed in a region lying normal to the electric field whereby ions are propelled from this region under the influence of the electrical and magnetic fields in cycloidal trajectories and means forming an outlet aperture adjacent the boundary of the space and spaced from the region of ion origin whereby ions issue through said aperture with a direction of travel dependent upon the mass thereof.

In its simplest embodiment the mass discriminating source described above may be provided wtih a collector electrode and a resolving electrode intermediate the collector electrode and the referred to boundary aperture. In this way only ions traversing the boundary aperture with a direction of travel such as to carry them through the resolving aperture will reach the collector electrode. In the alternative, any one of the many present forms of resolving systems may be associated with the ion source so that the ions issuing from the boundary aperture are subjected to additional ion discriminating stimuli whereby high resolution is accomplished.

The ion source as described is highly sensitive, but at the same time is more sensitive to intial energies than presently conventional mass spectrometers of the same size and magnetic field strength magnitude. As a consequence, resolution in the ion source itself may not be as high as desired in the higher mass ranges because of initial energy spread in these ranges. In such a situation an auxiliary resolving system, as mentioned, is indicated. In lower mass ranges, as for example mass 4, where electric fields may readily be made large compared to initial energies, the ion source may be used as an integral unit to effectuate desired mass separation and is extremely sensitive in this use.

The invention will be more clearly understood by reference to the following detailed description thereof taken in conjunction with the accompanying drawing in which:

Fig. 1 is a diagram in sectional elevation of an ion source in accordance with the invention illustrating application of the source as a mass spectrometer;

Fig. 2 is a transverse section taken on the line 2—2 of Fig. 1;

Fig. 3 is a diagram illustrating the operation of the apparatus of Fig. 1;

Fig. 4 is a diagram of a mass spectrometer in accordance with the invention wherein the mass discriminating ion source is used in conjunction with an auxiliary resolving system, in this case a full-wave radio frequency gap system; and

Fig. 5 is a diagram of a modified form of the mass spectrometer of Fig. 4.

The apparatus of Figs. 1 and 2 includes a plurality of parallel spaced electrodes **12**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20** and **21** disposed in an enclosing envelope **24**. The envelope is provided with an exhaust line **25** connected to an evacuating system (not shown) and to a sample inlet line **26** providing means for introducing a sample to be analyzed into the ion source. A feature of the instrument is its suitability for use with solid samples whereby the sample inlet **26** is representative of means for introducing such a solid sample. The problem of ionizing a solid sample is discussed in considerable detail in my co-pending application Serial No. 277,772, filed March 21, 1952.

The several electrodes **13** through **21** are apertured to permit ion movement in the field and are at one end pro-

vided with baffles to prevent exit of the ions from the field, except between electrodes **15**, **16**. The opening between these electrodes, as shown at the right-hand end in Fig. 1, forms in effect an outlet aperture adjacent the boundary of the electrical field.

A transverse magnetic field is developed across the space by means of magnet poles **28**, **29** so that ions formed in the electrode system are subjected to transverse electrical and magnetic fields, whereby they move in the field in cycloidal trajectories.

Ions are formed in the source by means of a laminar electron beam **32** directed across the source by a conventional electron gun **33** to an electron-receiving target **34**. As an alternative, the ions may be formed exteriorly of the transverse field and propelled into the field as a laminar beam or may be produced in the field in the desired plane by impingement of a positive ion beam on a solid sample in the manner described in the aforementioned co-pending application. It is important to the invention that the ions be formed in a plane of minimum thickness so that all will be subjected to the same field forces at the moment of origin and their trajectories will hence originate in a given plane.

The several electrodes **12** through **21** are connected to a voltage divider **34** which is, in turn, connected across a voltage source **36** so that the region defined by the electrodes has a uniform electrical field impressed thereon.

A barrier or resolving electrode **38** is disposed exteriorly of the crossed fields and is provided with a resolving aperture **38A** substantially parallel to the so-called boundary aperture defined by the adjacent electrodes **15**, **16**. A collector electrode **40** is disposed to collect ions passing through the resolving aperture **38A** and is connected to a sensing circuit **42**, which may be any of the conventional types.

Operation of the instrument of Fig. 1 is best explained with relation to the diagram of Fig. 3 in which the dotted line AA represents the plane of ion formation corresponding to the laminar electron beam **32** of Fig. 1. Three types of cycloidal trajectories originating on the plane AA are shown in Fig. 1. The boundary aperture defined by the electrodes **15**, **16** in Fig. 1 is illustrated simply as a slit S_1 in the diagram of Fig. 3, the resolving aperture in the electrode **38** as the slit S_2 giving access to collector electrode **40**.

In the diagram, ions whose mass M_1 is such that their maximum y-coordinate is exactly equal to h will, if formed in the proper region of the plane AA, emerge from the boundary slit S_1 moving in a direction approximately parallel to AA, where the interrelationship between the various parameters is given by

$$h=\frac{2M_1EC^2}{qB^2}$$

where:

h=maximum ordinate of trajectory, cm.
M_1=ion mass, gm.
E=electric field strength, ESV/cm.
C=ratio of electromagnetic to electrostatic units, 3×10^{10}
q=ion charge ESU
B=magnetic field strength, gauss.

These are the ions which will pass through the resolving slit S_2 and discharge at the collector electrode. Particles of lighter mass M_2 having a trajectory with a maximum ordinate pitch less than h cannot emerge from the slit S_1 at all as will be seen from the Equation 1. Particles of heavier mass M_3 can emerge from the slit S_1 only in directions which make an angle with the plane AA greater than the maximum angle made by ions of mass M_1. These particles are eliminated from the beam by the resolving slit S_2 so that the only ions which can emerge from the crossed fields of the source at such an angle as to pass through the slit S_2 are those of a single well defined mass.

As explained above, this mass discriminating ion source as constituted with resolving and collector electrodes, is unconventional in that the resolution of one mass from another takes place on the basis of the angle at which ions of mixed mass pass from the influence of the crossed fields, i. e. through the boundary aperture, the angle being different for different masses. Focusing, as the term is usually understood in the art, does not occur and hence the normaliy objectionable space charge effects are minimized.

This so-called directionally sensitive mass spectrometer has an important advantage over the well known crossed field mass spectrometer. In the conventional instrument there is a region in the neighborhood of the resolving slit in which the ions are moving very slowly and hence are susceptible to disturbance by relatively small space charge effects. In the present instrument, ion movement can be maintained at a convenient velocity after leaving the boundary slit S_1 (Fig. 3) so as to minimize the sensitivity to space charge effects.

The instrument is very sensitive because of the large effective electron beam area, but is also very sensitive to initial energies. From the examination of Fig. 3 it is apparent that initial energy of ions formed in the plane AA may disturb their induced relationship to the boundary aperture S_1 so that a lighter ion, the trajectory of which is represented by the curve m_2 of the figure, may be displaced by such initial energies so as to pass through the boundary aperture. By the same token, a heavier ion, the trajectory of which would normally prevent it from passing through such an aperture may, as a result of initial energies, be caused to pass through the boundary aperture on an axis approximately parallel to the plane AA. The effects of initial energies are particularly noticeable when higher masses are involved and in such circumstances it is desirable to combine the mass discriminating ion source with an associated resolving system. In such a combination the ion source not only accomplishes a gross preliminary separation but also is highly efficient for the reason mentioned above and, when combined with any of several conventional resolving systems, results in a highly efficient mass spectrometer of high resolving power. The mass discriminating feature of this ion source is particularly convenient in such combinations where high intensities are desired, since the main resolving system has admitted to it only a limited fraction of the total ion current formed by the ion source. This feature serves to alleviate space charge effects in the main resolving system.

In Fig. 4 I have shown diagrammatically an ion source in accordance with the invention combined with a so-called full-wave R. F. gap system. The ion source itself does not differ appreciably from the source of Fig. 1, the difference in the apparatus of Fig. 4 lying in the associated resolving system. Referring to the figure, a source **50** similar to that of Fig. 1 is shown including electrodes **51**, **52** which define a boundary aperture S_1 as in the foregoing figures. A full-wave R. F. gap system is defined by the electrodes **54**, **55** connected across an oscillator **56**. A full-wave R. F. gap system functions to affect the energy of ions passing therethrough as a function of specific mass, the energy of all ions other than the so-called resonant ions being altered in traversing the gap system. The so-called resonant ions will traverse the gap system in exactly one cycle of oscillation and will emerge therefrom with exactly the same energy at which they were introduced. The principle of operation of a full-wave gap system is explained at some length in my co-pending application Serial No. 275,567, filed March 8, 1952. As described in this co-pending application a full-wave gap system is helpless to effectuate separation between ions of differing mass if they enter the system at the same velocity. Since the ions issuing from the boundary apertures S_1 and the preliminary resolving slit **58A**

may do so at essentially a uniform velocity, it is necessary to develop an accelerating field between this boundary aperture and the full-wave gap system to remove such velocity degeneracy. This is accomplished by application of a high negative bias to the first grid **54** of the full-wave gap system, the accelerating field thus established between electrode **58** and grid **54** overcoming any velocity degeneracy of the ions issued from the ion source.

In employing the ion source with a full-wave R. F. gap system, as shown in Fig. 4, it is necessary to modulate the ion beam to provide proper phasing and time duration of the ion pulses introduced to the gap system. Conveniently such modulation is accomplished by modulation of the ionizing electron beam by conventional and familiar means, such modulation being synchronized with the periods of alternation of the R. F. gap system itself.

As stated above, ions of non-resonant mass change energy in passing through the gap system. A bucking grid **60**, provided with a small positive bias, will reject all but the most energetic ions emerging from the gap system. This means that the so-called resonant ions will be rejected as well as less energetic ions, unless the resonant ions are, due to the characteristics of the sample and the band pass characteristics of the source, the lightest or the heaviest of the ions injected into the gap system. The most energetic ions will be either the lightest or the heaviest entering the gap system depending on the phasing of the system. A collector electrode **62** is disposed to collect ions traversing the bucking grid **60** and is connected to a sensing circuit **64** which may be of any conventional type. In this system, and as explained above, the most energetic ions issuing from the source are collected and sensed, and these may or may not be the resonant ions.

The mass spectrometer of Fig. 5 differs from that of Fig. 4 in being sensitive to resonant ions regardless of the band pass, characteristics of the source. In this embodiment, an electrostatic energy filter **68** replaces the bucking grid **60** of Fig. 4 and a resolving electrode **70** is interposed between the velocity filter and collector electrode. In all other respects the devices of the two figures are identical and common reference numerals are employed. Since all ions other than resonant changes energy in the full-wave gap system, the energy filter **68** can be operated to focus the resonant ions through an aperture **70A** in the resolving electrode **70** on the collector electrode **62**.

The apparatus of Figs 4 and 5 merely illustrate the possibility of combining the mass discriminating ion source of the invention with an auxiliary resolving system. There is no inherent limitation to combination with a full-wave R. F. gap system, it being also feasible to effectuate further resolution by means of a conventional 90° or 180° magnetic analyzer or by the other mass revolving means.

I claim:

1. An ion source for a mass spectrometer comprising an ionizing chamber having an ion outlet aperture, means for establishing a uniform electrical field across the chamber, means for establishing a magnetic field across the chamber normal to the electric field, means for ionizing a sample to be analyzed in a plane spaced from the aperture and normal to the electric field whereby ions are propelled from the plane of origin under the influence of the electrical and magnetic fields in cycloidal trajectories so that certain ions will be propelled through the aperture after approximately one-quarter cycle of cycloidal travel.

2. An ion source for a mass spectrometer comprising an ionizing chamber having an ion outlet aperture, means for establishing a uniform electrical field across the chamber, means for establishing a magnetic field across the chamber normal to the electric field, means for ionizing a sample to be analyzed, means for orienting the ions in a plane spaced from the aperture and normal to the electric field whereby ions are propelled from the plane under the influence of the electrical and magnetic fields

in cycloidal trajectories so that certain ions will be propelled through the aperture after approximately one-quarter cycle of cycloidal travel.

3. An ion source for a mass spectrometer comprising an ionizing chamber having an ion outlet aperture, means for establishing a uniform electrical field across the chamber, means for establishing a magnetic field across the chamber normal to the electric field, means for introducing a sample to be ionized into the chamber, means for directing a laminar electron beam across the chamber in a plane spaced from the aperture and normal to the electric field whereby ions are formed in said plane and are propelled therefrom under the influence of the electrical and magnetic fields in cycloidal trajectories so that certain ions will be propelled through the aperture after approximately one-quarter cycle of cycloidal travel.

4. A mass spectrometer comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electrical field, means forming an outlet aperture adjacent a boundary of said space, means for ionizing a sample to be analyzed in a plane normal to the electrical field and spaced from the outlet aperture, ion mass resolving means disposed exteriorly of said space and in the line of travel of at least part of the ions issuing from the aperture, and ion collection means disposed to collect ions traversing the resolving means.

5. A mass spectrometer comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electrical field, means forming an outlet aperture adjacent a boundary of said space, means for ionizing a sample to be analyzed, means for orienting the ions in a plane normal to the electrical field and spaced from the outlet aperture, from which plane they are propelled under the influence of the electrical and magnetic fields in cycloidal trajectories so that certain of the ions will reach the outlet aperture, ion mass resolving means disposed exteriorly of said space and in the line of travel of at least part of the ions issuing from the aperture, and ion collection means disposed to collect ions traversing the resolving means.

6. A mass spectrometer according to claim 5 wherein the resolving means comprises an apertured electrode positioned with the aperture therein being aligned with said outlet aperture so that only those ions traveling through the outlet aperture in a given direction with respect to the plane of ion orientation will pass through the apertured electrode.

7. A mass spectrometer comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electric field, means for ionizing a sample to be analyzed in a plane normal to the electric field whereby ions are propelled from said plane under the influence of the electrical and magnetic field in cycloidal trajectories, means forming an outlet aperture adjacent a boundary of said space and spaced from said plane, an apertured electrode disposed outside said space and adjacent the outlet aperture, and a collector electrode disposed adjacent the apertured electrode and on the side thereof opposite the outlet electrode.

8. A mass spectrometer comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electric field, means for ionizing a sample to be analyzed in a plane normal to the electric field whereby ions are propelled from said plane under the influence of the electrical and magnetic field in cycloidal trajectories, means forming an outlet aperture adjacent a boundary of said space and spaced from said plane, a full-wave R. F. gap system disposed outside said space and adjacent the outlet aperture, and an electrostatic energy filter, apertured resolving electrode and collector electrode arranged serially following the gap system.

9. A mass spectrometer comprising means for establishing a uniform electric field across a space, means for establishing a magnetic field across the space normal to the electric field, means for ionizing a sample to be analyzed in a plane normal to the electric field whereby ions are propelled from said plane under the influence of the electrical and magnetic field in cycloidal trajectories, means forming an outlet aperture adjacent a boundary of said space and spaced from said plane, a full-wave R. F. gap system disposed outside said space and adjacent the outlet aperture, an accelerating gap disposed in the region between the outlet aperture and the full-wave gap system, and an electrostatic energy filter, apertured resolving electrode and collector electrode arranged serially following the gap system.

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