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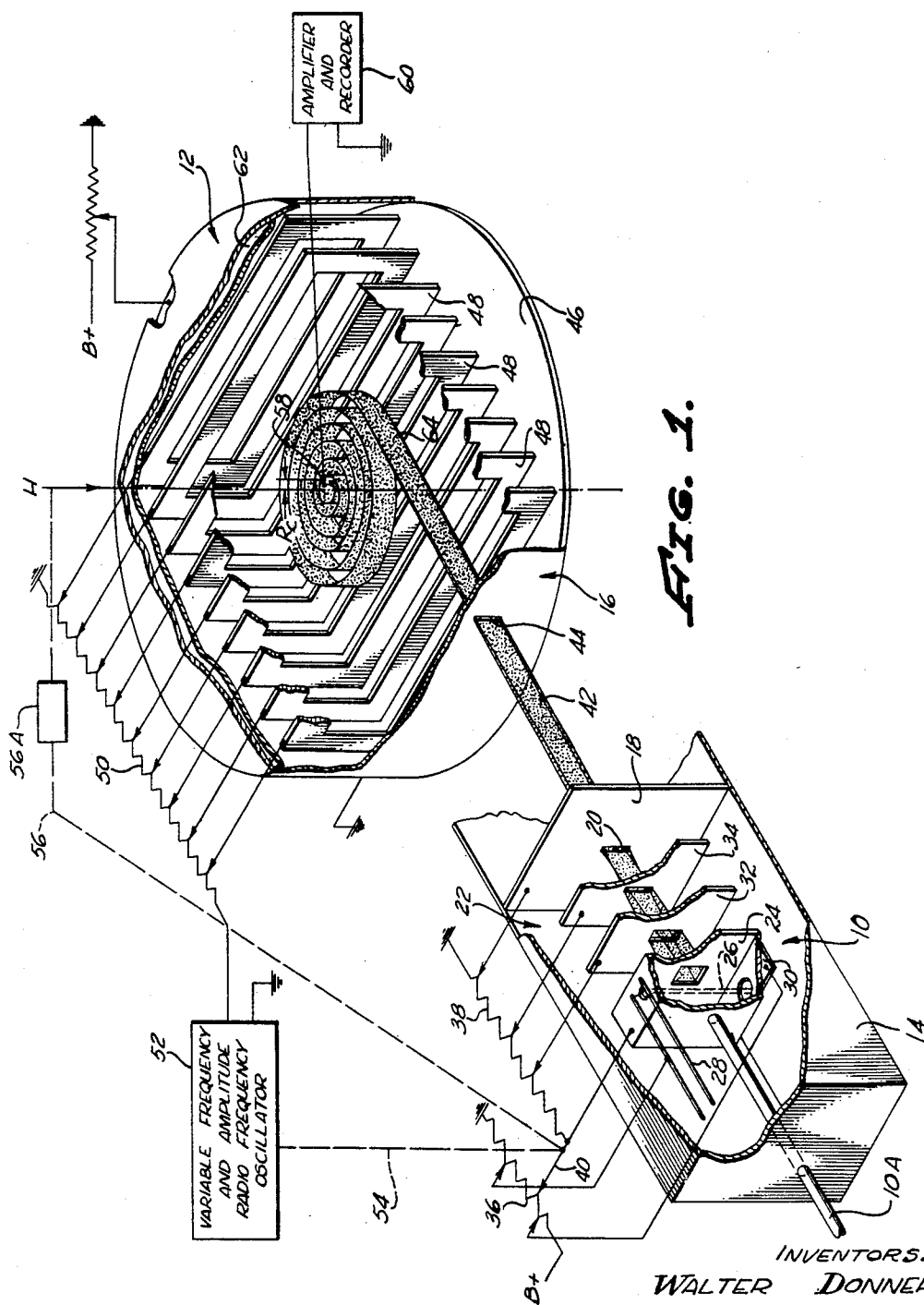
W. DONNER ET AL

2,829,260

MASS SPECTROMETER

Filed Nov. 19, 1954

2 Sheets-Sheet 1



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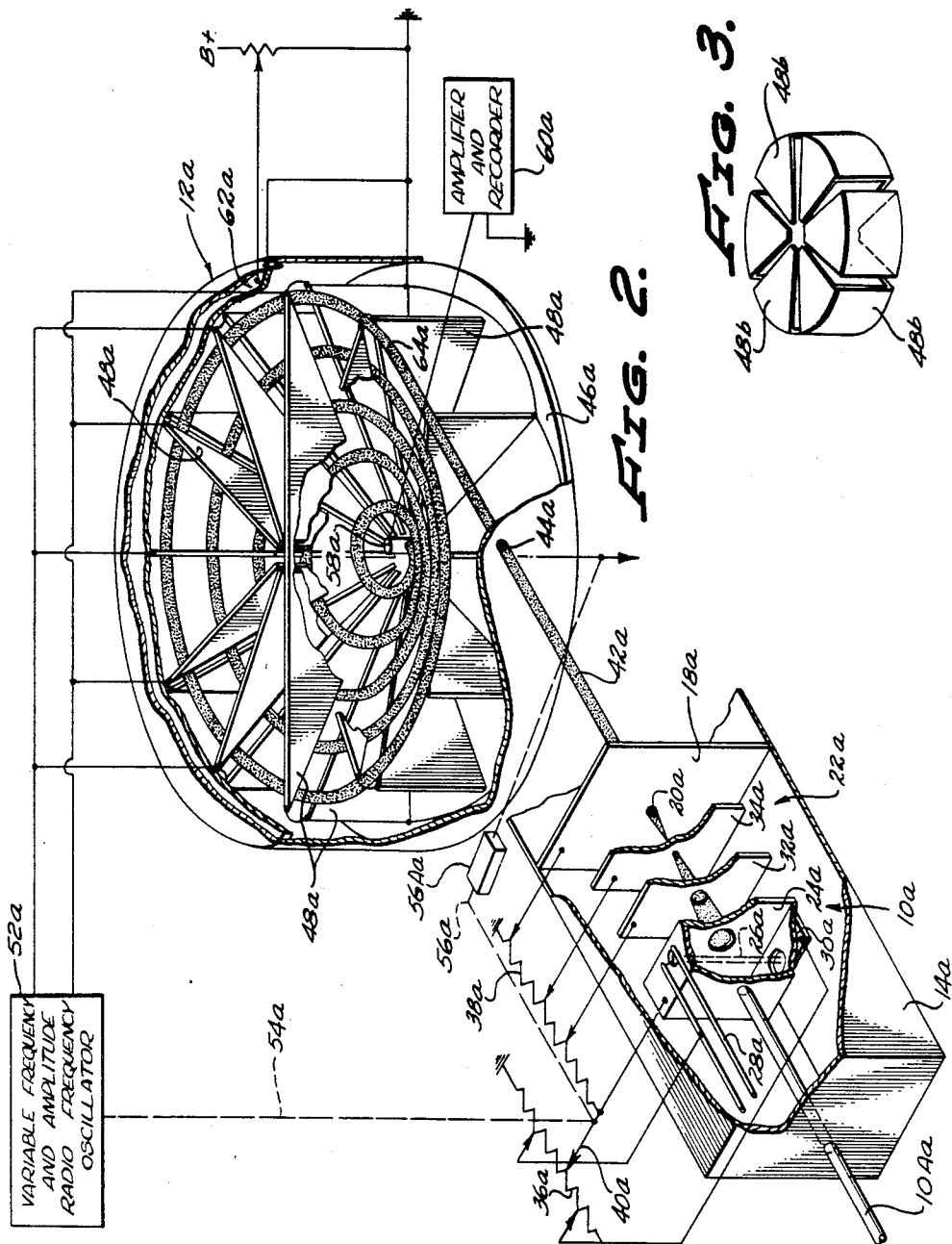
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MASS SPECTROMETER

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The present invention relates in general to the mass analysis of charged particles and, more particularly to an ion sorting device or mass spectrometer of the cyclotron resonance type in which ions are acted upon by crossed magnetic and alternating electric fields so as to execute spiral trajectories in the field space. In the classic cyclotron, and in certain previously known mass spectrometers of the cyclotron-resonance type, the ions are introduced at a central position in the superimposed magnetic and alternating electric field space and are cyclically accelerated by the alternating electric field to describe outwardly directed spirals. The electric field frequency is adjusted to be resonant for the selected or "preferred" ion mass (or, more exactly, the selected ion mass-to-charge ratio) at the given magnetic field strength, these preferred, resonant ions being collected and sensed at the periphery of the superimposed field region.

Mass spectrometers of the cyclotron resonance type have differed from the classic cyclotron in substituting for the narrow accelerating gap of the cyclotron a substantially uniform, parallel, alternating electric field extending over substantially the entire trajectory space. Thus, the ions are accelerated substantially continuously during the A. C. cycle, whereas in the classic cyclotron, the alternating electric field accelerates the particle only during the relatively small interval when the particle is crossing the gap. The advantage of the extended field is that harmonic effects are eliminated and all particles are "bunched" regardless of wide variations in starting phase angle. These advantages are of great importance in adapting the cyclotron-resonance principle to mass spectrometry, since they improve resolution and eliminate spurious signals when a mixture of ions of various masses occurs in the instrument.

In these well-known resonance-type mass spectrometers only ions of the selected mass attain sufficient energy to reach the peripheral ion collector. Ions of other mass oscillate within the crossed field or "analyzer" space on paths of alternately larger and smaller radius, but always of insufficient maximum radius to reach the collector. To scan a mass spectrum with such a mass spectrometer, operating conditions are varied to make successive ion masses, in the mass range of interest, the selected or resonant mass. This may be accomplished by varying the frequency of the alternating electric field, or the strength of the magnetic field, or both.

The resonance-type mass spectrometers described above have a number of serious disadvantages which are eliminated by the present invention, as more fully discussed hereinafter. For example, in the prior mass spectrometers of this type, the ions are formed within the analyzer space at the center thereof, at a point where they have nearly zero initial energy. Ions thus congregate at the starting position, rapidly building up space charge and blurring the starting locus, with the result that resolution is impaired.

Another disadvantage of prior mass spectrometers of the resonance type is that the selected or resonant ions do not all take the same path initially because they have some initial random thermal energy while having no initial kinetic energy due to the alternating electric field.

Still another disadvantage of prior mass spectrometers

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of this type is that the sample substance to be ionized, such as a gas or vapor, completely fills the analyzer means, thereby creating a mean-free-path problem and reducing the ratio of the desired signal to the residual background signal. If sample pressure within the analyzer means is reduced, in order to increase the mean free path, then ultimate sensitivity and useful signal range are impaired.

Another disadvantage of these prior spectrometers is that ions of other than the selected or resonant mass tend to remain in the analyzer space, oscillating back and forth across the path of the preferred ions, thereby further increasing the space charge and the mean-free-path problems.

Other disadvantages of these prior mass spectrometers are that they are sensitive to variations in pumping speed of the diffusion pump which controls pressure in the analyzer, and that they require temperature control of the entire analyzer means lying within the magnetic gap space.

As a feature of the present invention, the foregoing and various other disadvantages of prior resonance-type mass spectrometers are overcome by reversing the path of ion movement through the superimposed magnetic and alternating electric fields. The ions are thus injected into the analyzer means peripherally at relatively high energy levels and are decelerated along inwardly directed spiral paths to a central ion-sensing or collecting means. It will be apparent that only the ions of the selected or resonant mass are fully in resonance with the alternating electric field and thus only such resonant ions are decelerated sufficiently to reach the central ion sensing or ion collecting means. All other ions are either deflected inwardly to oscillate on spiral paths of relatively large radius, or are not deflected inwardly at all.

Another object of the invention is to provide a mass spectrometer of the resonance type which includes an ionizing means or ion source located externally of the analyzer means, the invention also providing means for initially accelerating the ions produced by the ion source to relatively high energy levels and for injecting such initially accelerated ions peripherally into the analyzer means.

It will be apparent that the present invention thus attains a number of important advantages over prior mass spectrometers of the resonance type, and eliminates many of the disadvantages of these earlier instruments.

For example, an important advantage of the present invention is a reduction of space charge effects, since the ions enter upon their path in the analyzer means at relatively high energy levels.

Another advantage is that the mean-free-path problem is minimized since pressure in the ionizing means may be maintained at a relatively high level to attain high ion production rate, while pressure in the analyzer means may be maintained at relatively low level to minimize the mean-free-path problem. This results in a much higher ratio of desired signal to residual background and results in a more nearly relationship between signal and the pressure applied to the sample substance, usually a gas or vapor.

Another important advantage of the present invention is that there is less interference by non-preferred particles, i. e., particles of mass other than the selected mass, existing in the preferred trajectory space, since such non-preferred particles will either spiral inwardly only to a limited extent relative to the preferred ion path, or will not be deflected inwardly at all, or may even spiral outwardly if they are sufficiently off resonance.

Another important result of the present invention is improved sensitivity stability since random thermal en-

ergy of the ions produced by the ionizing means is but a small fraction of the energy with which the ions are injected into the analyzer means, and is preferably a small fraction even of the energy possessed by preferred ions when they reach the central ion sensing or collecting means.

Another advantage of the present invention is improved fractionation stability since the ionizing means is external to the analyzer means and can be independently and therefore more effectively temperature controlled. Such temperature control also reduces variations in random thermal energy of the ions formed by the ionizing means, and so improves reproducibility of instrument performance.

Another advantage of the present invention is that the signal obtained is less dependent on the speed of the pump utilized to evacuate the analyzer means. With the present invention, the pressure in the analyzer means may be maintained at a very low level as compared to the pressure in the ionizing means and, thus, pressure variations in the analyzer means due to variations in pumping speed have negligible effects on the pressure in the ionizing means, and thus on the level of the wanted signal.

Another advantage of the present invention is that, since only the analyzer means is in the magnetic field, higher flux densities may be attained with an equivalent magnet since the gap between the magnet poles may be reduced. Also, the magnet poles may be of smaller diameter because of the removal of the ionizing means from the center of the analyzer means.

An important object of the present invention, applicable either to a resonant mass spectrometer of decelerating type described above wherein preferred ions spiral inwardly to a central collecting means, or to a mass spectrometer of the resonant accelerating type wherein preferred ions spiral outwardly from a central ion source, is to provide an analyzer means which produces a circular alternating electric field instead of a parallel alternating electric field. In this embodiment of the invention, the analyzer means includes electrode means comprising a radial array of electrodes angularly spaced about a common axis. Preferably, the electrodes are alternately connected to opposite terminals of an alternating potential source. Alternatively, however, it will be understood that in any given circular array of electrodes, only selected electrodes, uniformly spaced in the array, need be alternately connected to the opposite terminals of the alternating potential source, while electrodes positioned between these selected electrodes are connected to suitable points on a voltage divider spanning the source of potential. Such electrodes provide fields in the interelectrode spaces in the array for applying incremental forces to ions of selected mass to change the velocity thereof generally in the direction of motion in each interelectrode space. With this embodiment of the invention, the analyzer means possesses an inherent geometric center and corrective forces are applied to the preferred ions to counteract any tendency to deviate from the desired spiral path, whether such spiral path be inwardly or outwardly directed. With a parallel or uniform alternating electric field, on the other hand, the analyzer means possesses no inherent geometric center, so that the spiral path may be influenced by factors such as the point of entry of the ions into the magnetic field, magnetic edge effects, deviations from uniformity of the alternating electric field, and, to some extent, the entrant phase of the preferred ions relative to the phase of the alternating electric field. By providing an inherent geometric center with a circular alternating field, such difficulties are overcome to provide improved resolution.

Another object of the invention is to provide an alternative electrode means for producing a circular alternating electric field in which radial electric field spaces,

or interelectrode spaces, are provided between electrodes having the shape of hollow sectors.

Other objects of the invention in connection with any of the embodiments hereinbefore discussed are to provide means for varying the selected ion mass, so as to derive a mass spectrum covering a desired range of ion masses, this means including means for varying the frequency of the alternating electric field, or for varying the intensity of the magnetic field.

In those embodiments of the invention wherein the preferred ions spiral inwardly, objects are to derive mass spectra either by maintaining a constant ratio between the frequency of the alternating electric field and the initial accelerating potential while varying the field frequency, or by maintaining a constant ratio between the intensity of the magnetic field and the initial accelerating potential, as the magnetic field intensity is varied.

The foregoing objects, advantages and features of the present invention, together with various other objects, advantages and features thereof, may be attained, in a manner which will be apparent, with the exemplary embodiments of the invention illustrated in the accompanying drawings and described in detail hereinafter.

Referring to the drawings:

Fig. 1 is a diagrammatic perspective view of a mass spectrometer of the invention of the cyclotron resonance type wherein the preferred ions are decelerated along an inwardly spiralling path in a uniform alternating electric field;

Fig. 2 is a diagrammatic perspective view of a mass spectrometer of the invention of the cyclotron resonance type wherein the preferred ions are decelerated along an inwardly spiralling path in a circular alternating electric field, it being understood that such circular alternating electric field may also be utilized for accelerating preferred ions along an outwardly spiralling path; and

Fig. 3 is a diagrammatic perspective view illustrating an alternative electrode means for producing a circular alternating electric field.

Referring first to Fig. 1 of the drawings, the mass spectrometer of the invention illustrated therein includes an ion source or ionizing means 10 external to an analyzer or analyzer means 12, the ionizing means and the analyzer means both being enclosed in an evacuable chamber which is fragmentarily shown. The evacuable chamber includes a section 14 enclosing the ion source 10 and a section 16 enclosing the analyzer 12, the chamber sections 14 and 16 being separated by a partition 18 which is provided with a relatively small aperture 20 therethrough and which also serves as a terminal electrode of an ion accelerating means 22 as hereinafter described. The aperture 20 provides the primary means of communication between the chamber section 14 and 16 so that, when evacuating the chamber section 16 in any suitable manner, not shown, a relatively large pressure differential between the chamber sections 14 and 16 is maintained. Thus, the chamber section 14 containing the ion source, and in particular the space within the ionization chamber 24, may be maintained at a relatively high pressure to attain a high ion production rate from a sample substance, such as a gas or vapor, introduced thereto and, at the same time, the pressure in the chamber section 16 containing the analyzer 12 may be maintained at a relatively low value to minimize mean-free-path problems, as hereinbefore discussed in greater detail.

As hereinbefore suggested, any suitable evacuating means, such as a vacuum pump, not shown, is connected to the vacuum tight space including the ion source 10 and the analyzer chamber section 16. The chamber section 14 is provided with inlet means 10A, for introducing the sample substance thereto, and in particular into the space within the ionization chamber 24. The sample is generally in the form of a gas or vapor, the sample substance being introduced into the ion source 10 at a relatively low pressure as is well known in the art. Similarly, the

chamber sections 14 and 16 are provided with suitable means, not shown, for bringing out electrical connections therefrom through the vacuum tight enclosure. Also, the analyzer 12 includes means, such as a permanent magnet or electromagnet for producing a magnetic field therein, the magnetic field being designated by the vector H . Since the foregoing components are all conventional, it is considered unnecessary to illustrate and describe them in detail.

Considering the ion source 10 now in more detail, the sample substance, introduced into the ion chamber 24 at relatively low pressure via the sample inlet 10A, is bombarded by an electron stream 26 emitted by an electrically heated filament 28 and accelerated and collected by a positively charged collector plate 30. The ion accelerating means 22 includes apertured electrodes 32 and 34 and the previously mentioned apertured electrode 18, the various elements of the ion source 10 and the ion accelerating means 22 having external electrical connections as shown. More particularly, the ion chamber 24, the filament 28 and the collector 30 are connected to suitable points on a potential divider 36 to make the ion chamber and collector positive with respect to the filament, and the electrodes 32, 34 and 18 are connected to suitable points on a potential divider 38. One end of the potential divider 38 is adjustably connected to the potential divider 36 by a movable contact 40 so as to vary the accelerating potential applied to ions produced in the ion chamber 24 while maintaining proper focussing conditions for the ion beam.

Positive ions formed in the ion chamber 24 are accelerated and collimated by the electrodes 32, 34 and 18 and are projected from the ion source through the aperture 20 as a beam or ray 42, the beam here being shown as ribbon-like in cross-section. The beam 42 is projected into the chamber section 16 housing the analyzer 12 through an aperture 44 which may act to define further the beam 42.

The analyzer 12 is enclosed by a grounded shell or shield 46 shown as forming part of the evacuable chamber section 16. Within the chamber section 16 is a series of parallel, apertured plates or electrodes 48 connected to separate points on a potential divider 50, the latter being connected across a radio-frequency oscillator 52 of adjustable or continuously variable frequency and amplitude. Suitable frequency and amplitude controls, not shown, are provided. Preferably, the frequency and amplitude controls are coupled together so that, as the frequency of the oscillator 52 is increased or decreased, the amplitude is also simultaneously increased or decreased. Also, means are provided for coupling the oscillator frequency control to the means for varying the accelerating potential provided by the ion accelerating means 22, as by connecting the oscillator frequency control to the movable contact 40, as indicated diagrammatically by the broken line 54. This coupling is designed to maintain a constant ratio between the ion accelerating potential and oscillator frequency as the latter is varied to derive a mass spectrum, as hereinafter discussed in detail. Similarly, alternative means for deriving a mass spectrum may be provided which maintains a constant ratio between the ion accelerating potential and the magnetic field H as the latter is varied to derive a mass spectrum, as hereinafter discussed in detail, such constant ratio being maintained by a coupling indicated by the broken line 56 extending between the movable contact 40 and the magnetic field H and including magnetic field varying means 56A.

The magnetic field H traverses the central portion or core area of the array of electrodes 48, these electrodes producing a substantially parallel, uniform alternating electric field perpendicular to the magnetic field. The superimposed fields cause the preferred ions of selected mass in the beam 42 to spiral inwardly as shown to an ion sensing or ion collecting means shown as including a vertically positioned collector electrode 58 which is either centrally located, or offset from the center of the

electrode array by a relatively small distance R_0 , as shown. The electrode 58 is shown as connected to a signal amplifier and recorder 60, although it will be understood that other devices may be substituted for the amplifier and recorder, such as means for performing a control function, or the like.

The analyzer 12 also includes electrode means for applying a relatively weak unidirectional electric field, which may be a D. C. field, to the region traversed by the preferred ion trajectory, this being applied in a direction perpendicular to the alternating electric field so as to remove nonpreferred ions tending to accumulate in such region. This electrode means is shown as including an electrode 62, which is positively charged by means of the external electrical connection shown.

Considering the operation of the mass spectrometer illustrated in Fig. 1 of the drawings, it will be assumed that upon admitting a sample via the inlet 10A, a mixture of ions of different masses is produced in the ion chamber 24. After acceleration by the ion accelerating means 22, i. e., upon reaching the electrode 18, all ions of unit charge have been accelerated to the same energy $K. E.$, in accordance with the equation

$$K. E. = eV \quad (1)$$

wherein e is the particle charge and V is the total accelerating potential (in Fig. 1, the potential difference between electrode 18 and chamber 24). However, the ion velocity v , upon reaching electrode 18, varies with ion mass m , according to the equation

$$K. E. = mv^2/2 \quad (2)$$

When the ions enter the magnetic field H , at 64, they assume a curved trajectory. Considering only the effect of the magnetic field H and ignoring for the time being the effect of the alternating electric field, the magnetic field tends to cause the ions to describe circles at constant tangential velocities v , due to the balance between centrifugal force mv^2/R , wherein R is the path radius, and the centripetal, magnetic force Bev , where B is the magnetic field strength. This balance of forces may be expressed as

$$Bev = mv^2/R \quad (3)$$

Rewriting Equation 3, the resulting equation is

$$R = mv/Be \quad (4)$$

Now, the angular velocity w of the ions equals v/R radians. Substituting in Equation 4, the resulting equation for w is

$$w = Be/m \quad (5)$$

The cyclical frequency f of the ions may then be expressed by the equation

$$f = Be/2\pi m \quad (6)$$

Thus, the cyclical frequency f of each ion in the magnetic field H is, for a particular magnetic field strength and particle charge, independent of trajectory radius, and dependent only on the particle mass. Since in most analytical mass spectrometry the ions dealt with are largely singly charged, the variable of charge is substantially eliminated.

Considering now the effect of the alternating electric field, if the frequency of such field is made equal to the resonant frequency of a selected ion, then, assuming for the moment that the selected ion is injected into the alternating electric field in phase therewith, it will be resonantly decelerated. Thus, when the motion of the selected ion has a component directed toward one end of the alternating electric field, the polarity of the field is such as to decelerate it. The moment the particle subsequently acquires a component of motion in the opposite direction, the alternating electric field reverses polarity, with the result that the particle is again decelerated. The selected or preferred, resonant particle thus suffers a uniform decrement of energy with each transit across the alternating electric field. On first entering the magnetic field, the particle velocity is

$$v = (2eV/m)^{1/2} \quad (7)$$

Substituting Equation 7 in Equation 4, the resulting equation is

$$R = (1/B)(2Vm/e)^{1/2} \quad (8)$$

which is the initial radius of the path of a particle of mass m accelerated in the ion source 10 to a potential V . Each revolution of such particle will cause it to lose $2E$ volts where E is the "effective" or averaged value of the alternating electric potential acting on the particle through one-half cycle. Accordingly, the equation for the radius of path curvature after N complete revolutions is

$$R = (1/B)[2(m/e)(V - 2EN)]^{1/2} \quad (9)$$

Thus, the selected ions spiral inwardly toward a position of zero radius or, in practice, to a position, at the moment of collection, of a few volts residual energy, due to the finite radius of the collector electrode 58, or due to its displacement from the center of the analyzer 12. As hereinbefore indicated, the collection point is preferably slightly displaced from the center, or from the zero energy position, in order to prevent excessive space charge effects at the collection point. Also, better resolution is obtained if the particle energy at the collection point is appreciably higher than the initial random thermal energy.

The discussion thus far has been concerned with ions of the selected mass which enter in phase with the alternating electric field. However, ions of the preferred mass which depart within relatively wide limits from the optimum or resonant entrance phase angle will nevertheless ultimately fall into synchronism after a number of revolutions along the inwardly spiralling path. This is a significant advantage of an extended alternating electric field as compared with the narrow, gap-field of the classic cyclotron.

Since the preferred ions must always be made to spiral about the same collection point, irrespective of the mass to which the mass spectrometer is tuned either by varying the oscillator frequency or the magnetic field, as hereinbefore discussed, it is necessary to vary the entrant energy inversely as the mass so that R is constant in Equation 8. In one of the modes of operation illustrated by Fig. 1, this condition is met by varying the total accelerating potential applied to the ions in such a manner as to maintain a constant ratio between the accelerating potential and the oscillator frequency as the latter is varied, this being accomplished by coupling the oscillator frequency control and the accelerating potential control together as described earlier. In the alternative mode of operation shown in Fig. 1, the selected mass is varied by varying the magnetic field, and the required condition of constant initial radius is met by varying the accelerating potential to maintain a constant ratio between the accelerating potential and the magnetic field strength as the latter is varied. This is indicated by the broken line connection 56 hereinbefore mentioned. In either instance, during the mass "scanning" operation, different masses are successively made the preferred, resonant ion mass, whereby a mass spectrum may be derived.

Since resolution is ordinarily inversely proportional to mass, it is desirable, when increasing or decreasing oscillator frequency to derive a mass spectrum, to likewise simultaneously increase or decrease the amplitude of the applied radio frequency voltage. This causes heavier ions to make more revolutions before reaching the collector, so that resolution for such masses is increased.

Preferably, the central collector electrode 58 is of uniform circular cross section. Alternatively, however, the collector electrode 58 may be tapered to a smaller diameter in a direction away from the electrode 62. As will be further explained later, such an arrangement may supplement the procedure, discussed above, of varying the amplitude of the radio frequency voltage for increased resolution at high mass numbers.

The discussion thus far has been limited to preferred

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particles of the selected mass to which the mass spectrometer is, at any given moment, tuned. Considering now the nonpreferred particles, these may first be decelerated in the analyzer 12 for a few cycles, so that they spiral inwardly to some extent, but subsequently they will be alternately accelerated and decelerated as they fall into and out of phase with the alternating electric field. Thus, such particles are unable to lose any substantial portion of their energy, and, accordingly, either spiral outwardly to collect on the peripheries of the electrodes 48, or the shield 46, or oscillate back and forth at some relatively large radius. Other nonpreferred particles may not be deflected inwardly at all, but may spiral outwardly from the outset.

It is desirable to include a positively charged electrode 62 as shown in Fig. 1 to clean out such unwanted ions from the analyzer 12. While the preferred ions remain in the analyzer fields only a short time, the nonpreferred ions, unless immediately rejected at the periphery of the fields, remain longer, and are therefore deflected slowly out of the way of the preferred ion trajectory, to be collected either on the electrodes 48 or the shield 46.

It will be noted that while the spiral trajectory of preferred particles of the lightest mass may be substantially in a plane, as shown in Fig. 1, the heavier particles, caused to execute more revolutions before being collected and hence remaining in the field longer, will show the effect of the vertical "cleanout" field more strongly. Thus, heavier ions will have a more marked downward component of motion, i. e., will execute a slightly helical path. Accordingly, if as mentioned earlier, the vertical collector electrode 58 is tapered downward from electrode 62 to a smaller diameter the heavier particles will describe a further number of revolutions before being collected and resolution for such particles will be further increased.

As an alternative to the use of the positively charged electrode 62 for cleaning out the unwanted ions, the apertures in the electrodes 32, 34 and 18 may be so oriented as to give to the ions entering the analyzer 12 a small component of motion parallel to the magnetic field H . This imparts to all of the ions a small upward or downward motion which is maintained throughout the trajectory. Accordingly, nonpreferred ions which would otherwise persist in the analyzer are ultimately eliminated by collection on the electrodes 48, or the shield 46.

One problem encountered with the mass spectrometer embodiment illustrated in Fig. 1 of the drawings is that, since a substantially uniform, parallel alternating electric field is employed, the analyzer 12 possesses no inherent geometric center. Consequently, the collection point ultimately reached by preferred ions may be affected by factors such as the point of entry into the magnetic field, magnetic edge effects, deviations from uniformity of the alternating electric field, and, to some extent, the entrant phase of the particles. The point of entry may be accurately defined by the slits or apertures in the electrodes 32, 34 and 18, but the other factors mentioned will still cause trajectory deviations which may impair resolution.

The foregoing problem is overcome with the mass spectrometer embodiment of Fig. 2 of the drawings, in which a circumferential alternating electric field, rather than a parallel alternating electric field, is employed. Thus, the analyzer in the embodiment of Fig. 2 possesses an inherent geometric center and corrective forces are applied to the preferred ions to counter any tendency thereof to deviate from the desired spiral path. While a circular alternating electric field will be considered in connection with an embodiment in which the preferred ions spiral inwardly, this being an embodiment in which this type of field serves to particular advantage, it will be understood that such a field may be also used in a mass spectrometer wherein the ions spiral outwardly from an ion source at the center of the superimposed fields.

Turning now to Fig. 2 of the drawings, the mass spectrometer illustrated therein is generally similar to that il-

illustrated in Fig. 1 of the drawings and corresponding reference numerals, differing only by the addition of the suffix "a," are employed for corresponding components. The principal difference between the mass spectrometers of Figs. 1 and 2 is that, in the mass spectrometer of Fig. 2, the analyzer 12a includes an electrode means which comprises a radial array of apertured electrodes 48a uniformly circumferentially spaced about a common axis, which axis lies near the center of the superimposed field space. Alternate ones of the electrodes 48a are connected to opposite terminals of the oscillator 52a. As previously mentioned, the electrodes 48a are apertured to provide an ion trajectory region. In the particular construction shown, each electrode 48a is formed by electrically interconnected upper and lower plates lying in the same plane. However, it will be understood that each electrode 48a may be a single plate with an aperture therein.

A slight helical component is given to the preferred ion trajectory, either by the positively charged plate 62a, or by initially imparting a component of motion parallel to the magnetic field H, as hereinbefore discussed in connection with Fig. 1 of the drawings. The apertures in the electrodes 48a are inclined to accommodate such helical component for the preferred trajectory.

With the radial array of electrodes 48a described, wherein alternate electrodes are connected to opposite terminals of the oscillator 52a, there is set up an alternating electric field of radial symmetry, the field having a radial standing wave configuration. Thus, the alternating electric field acts circularly in the direction of motion of the preferred ions. In other words, the electrodes 48a provide fields in the interelectrode spaces for applying incremental forces to the preferred ions in directions such as to change the velocity thereof generally in their direction of motion in each interelectrode space. In the particular embodiment under consideration, the changing velocity is a decreasing velocity, so that the preferred particle describes a spiral path of diminishing radius, it being understood that such changing velocity will be an increasing velocity in a mass spectrometer in which the circularly acting alternating electric field is utilized to accelerate ions along an outwardly spiralling path from an ion source at the center of the fields.

Considering the operation of the mass spectrometer of Fig. 2 of the drawings in more detail, the ions injected into the analyzer 12a assume a curved trajectory at the point 64a of entry into the magnetic field H, as in the embodiment of Fig. 1 of the drawings. However, since the force lines of the alternating electric field are now substantially circular, there is always a corrective component of force acting on ions tending to stray from the desired path. Moreover, a resonant ion now suffers an energy decrement of E volts each time it crosses one of the interelectrode spaces. Accordingly, the analysis previously given in connection with the embodiment of Fig. 1 of the drawings remains generally valid, but where, in the embodiment of Fig. 1, the resonant frequency for a given particle is w , in the embodiment of Fig. 2 of the drawings, it will be $nw/2$, where n is the number of interelectrode spaces traversed during each cycle. Furthermore, the equation defining radius of path curvature after N complete revolutions may now be written as

$$R = (1/B) [2m/e] (V_{-n} EN)^{1/2} \quad (10)$$

In Equation 10, E is the effective radio frequency potential operative across each interelectrode space during one-half cycle.

In Fig. 3 of the drawings is illustrated an alternative electrode means for obtaining the desired circumferentially acting alternating electric field. In this embodiment, only electrodes 48b are shown, these electrodes corresponding to the electrodes 48a in the embodiment of Fig. 2 of the drawings and being connected in the external circuit in the same manner. In the embodiment of Fig. 3 of the drawings, the radial electric field spaces, or inter-

electrode spaces, are provided in the gaps between the electrodes, the electrodes being sectors of a hollow cylinder as shown, or, more generally speaking, radial sectors of a radially symmetrical hollow body. In other words, each electrode 48b includes upper and lower portions providing inwardly tapered electrode surfaces and a peripheral portion joining the upper and lower portions. In alternative designs to that shown, the upper and lower portions may, for example, be substantially triangular and may be joined by a peripheral plane sheet. Preferably, the interelectrode gaps are themselves tapered inwardly toward the center of the electrode means to some extent as shown, thereby providing curved force lines in the interelectrode spaces to provide the corrective action hereinbefore described.

Although we have described various exemplary embodiments of our invention herein for purposes of illustration, it will be understood that various changes, modifications and substitutions may be incorporated in such embodiments without departing from the spirit of the invention as defined by the claims hereinafter appearing.

We claim as our invention:

1. In an apparatus of the character described, the combination of: an ion source; accelerating means for accelerating ions from said source; analyzer means for decelerating ions of a selected mass among said accelerated ions along an inwardly spiralling path to a position of minimum radius while decelerating ions of other masses in said beam to positions of larger radius than said minimum; and ion sensing means at said position of minimum radius for sensing said ions of selected mass.

2. In an apparatus of the character described, the combination of: an ion source; accelerating and focusing means for accelerating and focusing ions from said source into a beam; analyzer means for decelerating ions of a selected mass in said beam along an inwardly spiralling path to a position of minimum radius while decelerating ions of other masses in said beam to positions of radii larger than said minimum; and ion sensing means at said position of minimum radius for sensing said ions of selected mass.

3. In an apparatus of the character described, the combination of: an ion source; accelerating means for accelerating ions from said source into a beam; analyzer means for decelerating ions of a selected mass in said beam along an inwardly spiralling path to a position of minimum radius while decelerating ions of other masses in said beam to positions of radii larger than said minimum; and ion collecting means at said position of minimum radius for collecting said ions of selected mass.

4. An apparatus as defined in claim 1 wherein said analyzer means includes means for producing a magnetic field in a position to intercept said beam, and includes means for producing an alternating electric field superimposed on said magnetic field and acting in a direction to apply a decelerating force to the ions in said beam perpendicular to the direction of said magnetic field.

5. In an apparatus of the character described, the combination of: an ion source; means for producing a magnetic field; means for superimposing on said magnetic field an alternating electric field perpendicular to said magnetic field; means for accelerating ions from said source and for injecting such ions into said fields peripherally thereof, whereby ions of a selected mass injected into said fields are decelerated along an inwardly spiralling path to a position of minimum radius while ions of other masses injected into said fields are decelerated to positions of radii larger than said minimum; and ion collecting means at said position of minimum radius for collecting said ions of selected mass.

6. In an apparatus of the character described, the combination of: means for producing a magnetic field; means for producing ions; means for accelerating ions from said ion-producing means to a predetermined potential; means for injecting such accelerated ions into said magnetic field

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peripherally thereof; a source of alternating potential; electrode means connected to said source of alternating potential for superimposing on said magnetic field an alternating electric field in a direction perpendicular thereto so as to apply decelerating forces to said injected ions perpendicular to said magnetic field, whereby ions of a selected mass are decelerated along an inwardly spiralling path to a position of minimum radius while ions of other masses are decelerated to positions of radii larger than said minimum; and collecting electrode means at said position of minimum radius for collecting said ions of selected mass.

7. An apparatus as defined in claim 6 including electrode means for applying a unidirectional electric field to the region traversed by said injected ions so as to remove ions of masses other than said selected mass tending to accumulate in said region.

8. An apparatus as defined in claim 6 in which said electric field is a substantially parallel, uniform field.

9. In an apparatus of the character described, the combination of: means for producing a magnetic field; means for producing ions; means for accelerating ions from said ion-producing means to a predetermined potential; means for injecting such accelerated ions into said magnetic field peripherally thereof; a source of alternating potential; electrode means connected to said source of alternating potential for superimposing on said magnetic field an alternating electric field in a direction perpendicular thereto so as to apply decelerating forces to said injected ions perpendicular to said magnetic field, whereby ions of a selected mass are decelerated along an inwardly spiralling path to a position of minimum radius while ions of other masses are decelerated to positions of radii larger than said minimum, said electrode means including a radial array of spaced electrodes connected to said source of alternating potential for producing a circular alternating electric field and for decelerating said ions of selected mass in each interelectrode space in said array in a direction generally parallel to the direction of movement of said ions of selected mass through each of said spaces; and collecting electrode means at said position of minimum radius for collecting said ions of selected mass.

10. An apparatus as defined in claim 6 wherein said electrode means includes an array of parallel, apertured electrodes for producing a substantially parallel, uniform alternating electric field, said mass spectrometer including a voltage divider spanning and connected to said source of alternating potential, said electrodes being connected to said voltage divider at different points thereon.

11. In an apparatus of the character described, the combination of: means for producing a magnetic field; means for producing ions; means for positioning said ions at a trajectory starting position in said magnetic field; a source of alternating potential having opposite terminals; electrode means for superimposing on said magnetic field a circular alternating electric field, including a radial array of spaced electrodes alternately connected to said opposite terminals of said alternating potential source, said electrodes providing fields in the interelectrode spaces in said array for applying to ions of a selected mass incremental forces generally parallel to the direction of motion of said selected ions in each interelectrode space whereby the velocity of said selected ions is changed and whereby they describe a spiral path of changing radius in accordance with their changing velocity; and collector means for collecting said ions of selected mass, said collector means being positioned at a radius corresponding to the velocity attained by said ions of selected mass after a predetermined number of revolutions.

12. An apparatus as defined in claim 11 including means for applying a unidirectional electric field to the region traversed by said ions of selected mass so as to remove from said region ions of other masses tending to accumulate therein.

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13. An apparatus as defined in claim 9 wherein said electrodes are flat, apertured plates lying in planes intersecting a common axis, said plates being uniformly angularly spaced about said axis.

14. An apparatus as defined in claim 13 in which said apertured plates are provided with elongated slots obliquely positioned with respect to said axis.

15. An apparatus as defined in claim 11 wherein said electrodes are flat, apertured plates lying in planes intersecting a common axis, said plates being uniformly angularly spaced about said axis.

16. An apparatus as defined in claim 15 in which said apertured plates are provided with elongated slots obliquely positioned with respect to said axis.

17. An apparatus as defined in claim 9 in which said electrodes comprise spaced radial sectors of a radially symmetrical hollow body, each sector including upper and lower portions providing surfaces tapered inwardly of said body and a peripheral portion joining said upper and lower portions.

18. An apparatus as defined in claim 11 in which said electrodes comprise spaced radial sectors of a radially symmetrical hollow body, each sector including upper and lower portions providing surfaces tapered inwardly of said body and a peripheral portion joining said upper and lower portions.

19. An apparatus as defined in claim 6 wherein said means for producing ions includes ion chamber means external to said fields for ionizing a substance to produce ions thereof, and wherein said ion injecting means includes electrode means for accelerating and collimating at least some of the ions produced in said ion chamber means into an ion beam and for injecting said ion beam peripherally into said fields.

20. An apparatus as defined in claim 19 including means for introducing said substance into said ion chamber means, and including means for producing a narrow electron beam traversing said ion chamber means to ionize said substance.

21. An apparatus as defined in claim 11 wherein said ion producing means includes ion chamber means external to said fields for ionizing a substance to produce ions thereof, and wherein said ion positioning means includes electrode means for accelerating and collimating at least some of the ions produced in said ion chamber means into an ion beam and for injecting said ion beam peripherally into said fields.

22. An apparatus as defined in claim 6, including: means for varying the output frequency of said alternating potential source; and means coupled to said frequency varying means for varying said accelerating potential so as to maintain a constant ratio between said output frequency and said accelerating potential, whereby to vary said selected mass so as to derive a mass spectrum.

23. An apparatus as defined in claim 22 including means coupled to said frequency varying means for simultaneously reducing the amplitude of said alternating electric field when said output frequency is reduced, whereby to increase resolution with respect to heavy ions.

24. An apparatus as defined in claim 6, including: means for varying said magnetic field; and means coupled to said field varying means for varying said accelerating potential so as to maintain a constant ratio between said magnetic field and said accelerating potential, whereby to vary said selected mass so as to derive a mass spectrum.

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,829,260

April 1, 1958

Walter Donner et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 60, after "nearly" insert --linear--.

Signed and sealed this 3rd day of June 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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