Feb. 17, 1953 C. F. ROBINSON 2,629,055

MASS SPECTROMETRY

Filed June 22, 1950

FIG. 1.

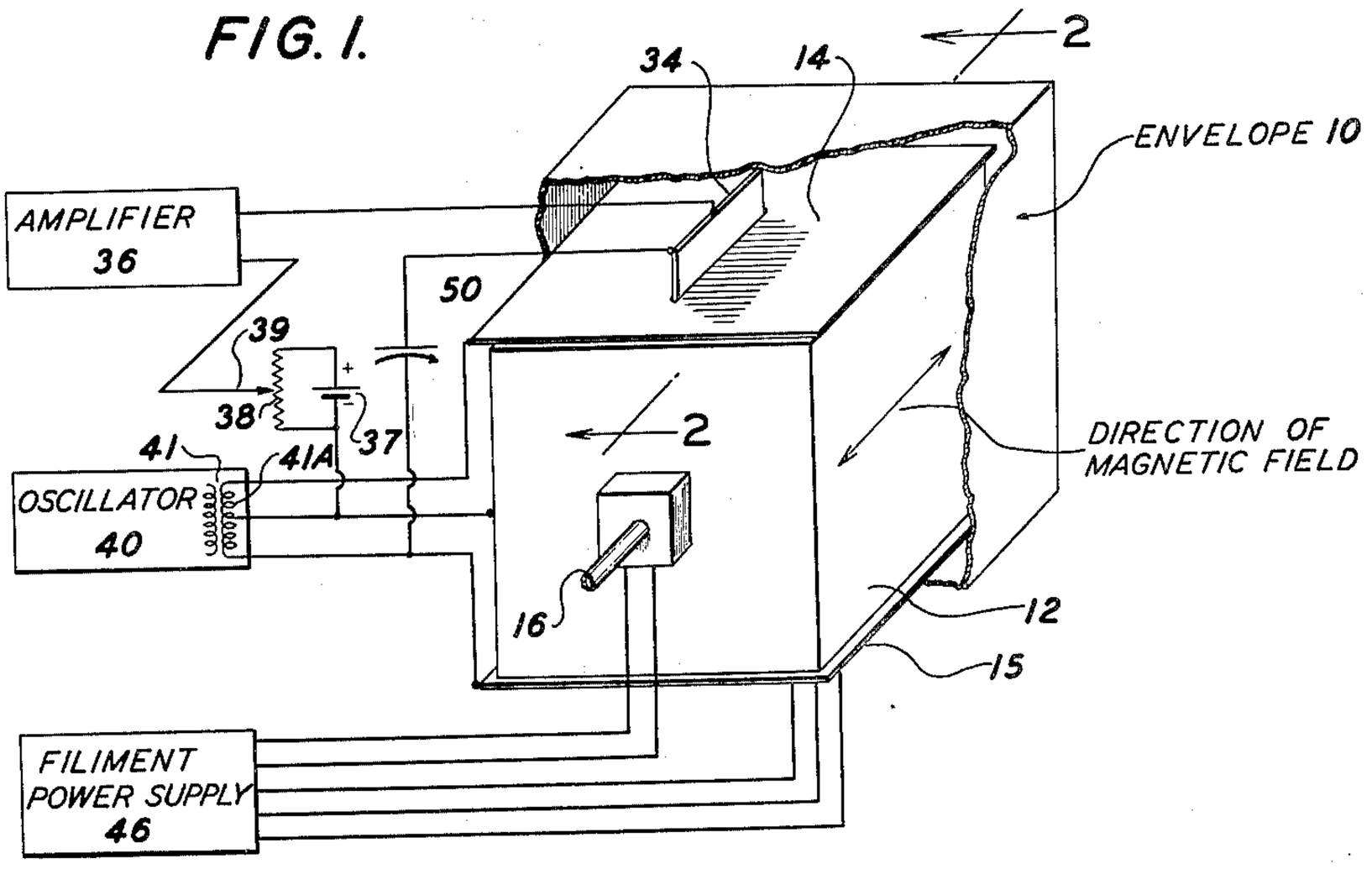
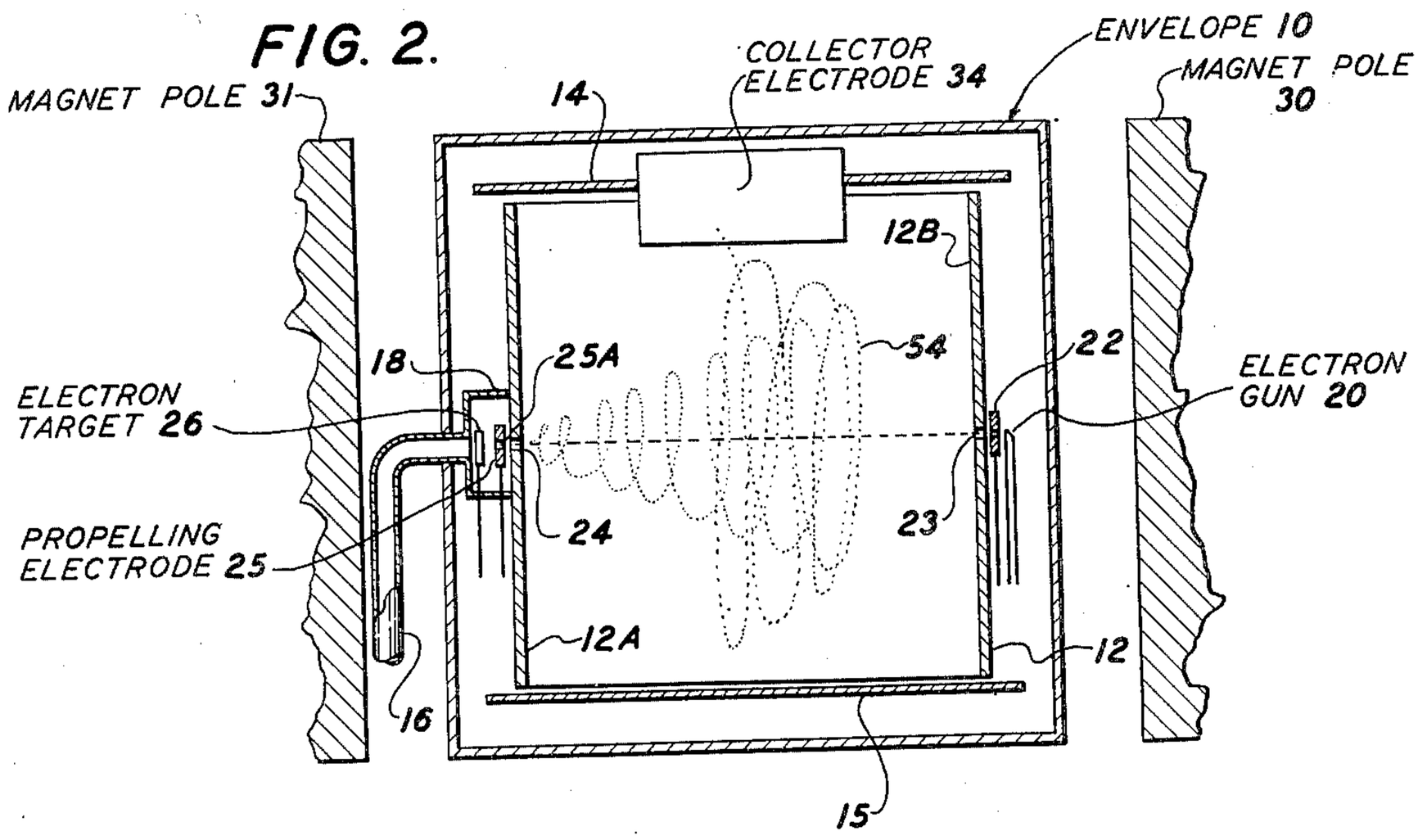


FIG. 2.



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MASS SPECTROMETRY

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6 Claims. (Cl. 250—41.9)

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This invention is directed to improvements in mass spectrometry, and more particularly relates to mass spectrometry wherein ions are separated on the basis of characteristic periodicity of motion in a magnetic field.

In mass spectrometry a sample to be analyzed is ionized, as for example by bombardment with an electron beam, and the various ions formed from the sample are separated from each other on the basis of some function of their mass-to-charge radio. In one type of operation this separation is brought about by propelling the ions under the influence of suitable electrical potentials from the point of their formation toward a target or collector electrode and in a path which carries them through a magnetic field. This method of mass spectrometry takes advantage of the fact that with a given initial kinetic energy, ions of differing mass-to-charge ratio will exhibit different radii of curvature under the influence of a magnetic field. A collector electrode is positioned to receive ions of a given mass-to-charge ratio. By varying the potential applied to propel the ions through the magnetic field or by varying the strength of the magnetic field through which the ions pass, ions of different mass-to-charge ratio can be selectively caused to impinge on and discharge at the collector electrode. The magnitude of the discharged current developed at the collector electrode by ions of a given mass-to-charge ratio is a function of the partial pressure of the parent particles in the gas sample.

A more recent development in the field of mass spectrometry involves the segregation of ions of differing mass-to-charge ratio on the basis of differences in the resonant frequency of the ions, this property also being a function of the mass-to-charge ratio. This separation may be accomplished by forming the ions in a space traversed by an alternating electrical field and a magnetic field normal to the electrical field. The crossed fields excite the ions to motion, those ions having a resonant frequency corresponding to the frequency of the alternating field assuming a characteristic movement from the point of origin in the form of an expanding spiral path. A collector or target electrode disposed in the path of the resonant ions will collect these ions while the non-resonant ions will travel in different paths which theoretically will not carry them to the target electrode.

By altering the frequency of the alternating field, ions of different mass-to-charge ratio in resonance with the altered frequency will be

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caused to follow the uniformly expanding spiral path which will carry them to the collector electrode. A mass spectrometer designed to operate on the foregoing principles is described and illustrated in co-pending application Serial No. 736,758, filed March 24, 1947, by Harold W. Washburn.

A charged particle in a magnetic field travels in a path of radius such that the centrifugal and magnetic forces are equal. Hence:

$$\frac{mv^2}{r}=qvB \tag{1}$$

where

m=the mass of the particle
v=velocity of travel
r=radius of curvature of path
q=particle charge, and
B=magnetic field strength

The angular frequency W in radians per second is represented by the following expression:

$$W=\frac{v}{r}=\frac{qB}{m} \tag{2}$$

If a particle of mass and charge m and q is placed in an AC field of frequency Wo such that

$$\frac{q}{m}=\frac{Wo}{B} \tag{3}$$

the particle will be uniformly accelerated by the field and will gain energy at each half cycle. Since the radius of the particle's path is related to the energy $q\gamma$ where γ is the potential through which the particle has been accelerated, by

$$r=\frac{1}{B}\sqrt{\frac{2m\gamma}{q}} \tag{4}$$

the particle will ultimately attain any preassigned radius r_o and do so with energy γ in accordance with the function

$$\gamma=\frac{q}{m}\left(\frac{B^2r^2}{2}\right) \tag{5}$$

Under certain types of electrical field, as for example where the particle is accelerated only across a narrow gap (as for example in a cyclotron) particles of mass $3m$, $5m$ . . . will also acquire energy at every half turn and will also attain any preassigned radius. Equation 5 shows that such particles will have only ⅓, ⅕ . . . of the energy possessed by a resonant particle of mass (m) of low initial energy.

Ions of anomalous initial energies although

not in resonance with the alternating field may also reach the preassigned radius. Such ions pursue paths differing from the theoretical path and carrying them to the collector electrode. Such ions will reach the collector over a much wider range of frequencies than will ions of lower initial kinetic energy. The high kinetic energy of these ions in effect distorts their path of travel to spread over several mass units and thus reduces the resolution of the instrument.

I have now developed a method of operation whereby the harmonically related ions and the ions of anomalous initial kinetic energy will not interfere with the linear superposition of the resonant mass.

The invention contemplates, in mass spectrometry involving the formation of ions, separation thereof on the basis of their resonant frequencies by means of an alternating electrical field established across a space in which the ions are confined and a magnetic field normal to the electric field, and selectively collecting at a collector electrode those ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement which comprises impressing on the collector electrode a positive potential of such magnitude as to repel therefrom ions having less than a predetermined minimum kinetic energy.

As explained above, ions having a high initial kinetic energy or non-resonant ions of harmonically related mass may achieve the collector electrode even though not in resonance with the alternating field. However, the resonant ions which are caused to pursue an ever expanding spiral path under the influence of the established field will approach the collector with appreciably greater energy than will those ions which reach the collector only by reason of initial energy distortion of their normal paths. It is possible, therefore, to impress on the collector a potential of sufficient magnitude to repel all but the resonant ions.

The invention also contemplates apparatus for carrying out the foregoing method which comprises in a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space normal to the electrical field, means for establishing a magnetic field across the space normal to the electric field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising means for impressing on the collector electrode a positive potential, and means for varying said positive potential to repel from the collector electrode ions having less than a predetermined energy.

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

Fig. 1 is a perspective diagrammatic view of one form of the apparatus; and

Fig. 2 is a sectional elevation taken on the line 2—2 of Fig. 1.

Referring to the drawing, the embodiment of the invention there shown comprises an envelope 10 with a rectangular conductive box or shell 12 disposed therein. A pair of plate electrodes 14, 15 are mounted adjacent to and substantially enclosing the open ends of the box 12 within the envelope and are insulated from the box as by the illustrated small gap.

A gas inlet tube 16 is carried through a wall of the envelope and opens into an inlet chamber 18 conveniently mounted on a side 12A of the box 12. An electron gun 20 and a propelling electrode 22 are mounted adjacent an opposite side 12B of the box to direct an electron beam axially through the box, the beam passing through apertures 23, 24 in the box walls 12B, 12A respectively, to impinge on an electron target 26 mounted in the inlet chamber 18. A propelling electrode 25 is mounted in the chamber 18 and has an aperture 25A. Any ions formed in the inlet chamber are propelled into the shell by a propelling potential established between the chamber and electrode 25.

The arrangement is such that an electron beam generated at the gun 20 is directed through electrode 22 and through the shell 12 along a central axis thereof and roughly midway between electrodes 14, 15 to the target electrode 26. The gas molecules introduced through the inlet tube 16 migrate into the box 12 by diffusion and are ionized therein. Since the electron beam travels axially through the shell, gas contained therein will be ionized as it is impacted by this beam, and hence all ions originate along the axis defined by the electron beam.

Magnetic pole pieces 30, 31 are mounted outside the envelope 10 and are oriented to develop a magnetic field in the box parallel to the electron beam and normal to the alternating field developed between the electrodes 14, 15. The magnetic pole pieces may be mounted within the envelope or may form a part of the envelope with equal facility, as will be obvious to anyone familiar with the art. A collector electrode 34 extends into the space defined by the box 12 conveniently through one of the electrodes 14, 15 and with its collecting face lying parallel to the electron beam.

An amplifier 36 is connected to the collector electrode and to a bias battery 37 through a slidewire 38 and adjustable tap 39. A high frequency oscillator 40 is connected across the electrodes 14, 15 through a transformer 41 with the electrodes being connected to opposite ends of the secondary winding 41A of the transformer. The oscillator supplies a high frequency alternating voltage to the electrodes so that a high frequency A. C. field is developed across the space defined by the shell 12. The negative side of the bias battery is connected to the midpoint of transformer secondary 41A and to the case 12. The collector is thus always at a positive potential with respect to the electrodes 14, 15 and case 12. In this manner the minimum kinetic energy required to drive ions through the repelling field to the collector can be varied as desired.

A filament power supply 46 is connected by appropriate leads to the electron gun 20, inlet chamber 18, electrode 22, electron target 26 and electrode 25 to supply the necessary voltages to these various elements.

The operation of the instrument is as follows. With the envelope 10 evacuated, as is standard practice in mass spectrometry, a gas sample is introduced through inlet 16 and is ionized within the shell 12 whenever molecules of the same intersect the electron beam. Under the influence of the high frequency alternating field and the magnetic field normal thereto, the ions are set in motion within the confines of the shell 12 with the ions of varying mass-to-charge ratio follow-

ing different paths of travel. The resonant ions, that is, the ions of a given mass-to-charge ratio which have a resonant frequency corresponding to the frequency of alternation of the A. C. field, travel in a uniformly expanding spiral path illustrated at 54 in Fig. 2. With the shell 12 at a slight positive potential with respect to the electrodes 14, 15, the ions are repelled from the walls 12A and 12B of the shell. Thus ions formed at the midpoint of the electron beam, i. e. midway between walls 12A, 12B, will remain in a plane transverse to the beam and intersecting the midpoint, while ions formed elsewhere along the beam will oscillate across the midpoint. When the radius of travel of the resonant ions is such as to reach the collector electrode 34, these ions will be discharged. The non-resonant ions which do not attain a radius of travel equal to the spacing between the collector electrode and the axis of origin along the electron beam, travel back and forth within the shell, as for example in spiral paths which expand to a maximum and collapse back to the origin. These non-resonant ions, therefore, accumulate in the box. It may be desirable to provide for periodic removal of the accumulated ions, but such provision is outside the scope of this invention.

As indicated above, certain non-resonant ions will have a mass harmonically related to the mass of resonant ions and these harmonic ions may reach the collector electrode. Also some such non-resonant ions are possessed of anomalous initial energy which will result in an anomalous center of curvature of their spiral paths so that they may reach the collector electrode before collapsing back to their origin. In either of these cases, erroneous discharge current values will be obtained. In the illustrated apparatus, this problem is overcome by biasing the collector electrode so that it is always slightly positive with respect to the shell 12 and the electrodes 14, 15. This positive bias may be adjusted by means of slidewire 38 so that any ions having less kinetic energy than the resonant ions will be repelled from the collector electrode. It is possible to provide that regardless of the magnitude of initial kinetic energy of the non-resonant ions they will not, as they approach the collector electrode, have kinetic energies of the order of magnitude of the resonant ions to which kinetic energy is imparted by the driving field. If the bias of the collector electrode is properly adjusted, only those ions which are in resonance with the fundamental frequency of the A. C. field will be capable of striking and discharging at the collector electrode while the non-resonant harmonically related ions or the non-resonant or resonant ions of anomalous initial energies will be repelled.

As illustrated, the output of the collector electrode will be in the nature of a pulsating current, the frequency of which will depend upon the frequency of alternation of the alternating electric field. This pulse type output current may be amplified in an A. C. amplifier having suitable frequency response or in a D. C. amplifier since the frequency is so high as to appear as a steady current in such amplifier.

If an A. C. amplifier is used, spurious signals may result from electrostatic coupling between collector electrode 34 and electrode 14, an A. C. signal being induced in collector 34 by the A. C. accelerating field. This can be neutralized by placing a small capacity such as "trimmer" capacitor 50 between collector electrode 34 and electrode 15. Such a capacitor, properly adjusted, will maintain the collector 34 at zero potential for R. F. signals. If A. C. amplification at lower frequency is desired, the discharge current may be pulsed by other means, as for example modulation of the electron beam. The present invention is independent of any special provision for pulsing the discharge current at a frequency other than the frequency of the A. C. field or for removing non-resonant ions from the analyzer chamber.

I claim:

1. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising means for biasing said collector electrode, and means for varying said bias to repel from the collector electrode ions having less than a predetermined minimum kinetic energy.

2. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising means for maintaining said collector electrode at a positive potential with respect to the chamber and means for varying said potential to repel from the collector electrode ions having less than a predetermined minimum kinetic energy.

3. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the spaced defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising a source of D. C. voltage, means connecting the collector electrode to the positive side of said source, and means for connecting the chamber to the negative side of said source.

4. In a mass spectrometer having an analyzer chamber, means for ionizing a gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and a collector electrode disposed in said space in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising a source of D. C. voltage, means connecting the collector electrode to the positive side of said source, means for connecting the chamber to the negative side of said source, and means for varying the potential impressed across the collector electrode and chamber by said source.

5. In a mass spectrometer having an analyzer chamber with conductive walls, an electron gun for propelling an electron beam axially through the chamber to ionize gas admitted to the chamber, a pair of electrodes disposed at opposite ends of the chamber and insulated from the chamber

walls, means for impressing a high frequency alternating potential between said electrodes to establish an A. C. field in said chamber transverse to the electron beam, means for producing a magnetic field across the chamber normal to the A. C. field and parallel to the electron beam and a collector electrode disposed in said chamber in the path of ions having a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising an A. C. amplifier connected to receive the discharge current developed at the collector electrode, a source of D. C. voltage, variable means connecting the positive side of said source to the collector electrode, means connecting the negative side of said source to said pair of electrodes and the walls of said chamber, and a variable capacitor

connected between the collector electrode and one of said pair of electrodes.

6. In a mass spectrometer having an analyzer chamber, means for ionizing gas admitted to the chamber, means for establishing an alternating electrical field across the space defined by the chamber, means for producing a magnetic field across the space normal to the electrical field, and an electrode disposed in the path of ions having a resonant frequency corresponding to the frequency of the alternating field for collecting such ions, the improvement comprising means for biasing said electrode to repel therefrom ions having less than a predetermined kinetic energy.

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No references cited.