March 17, 1953 H. W. WASHBURN 2,632,111

MASS SPECTROMETRY

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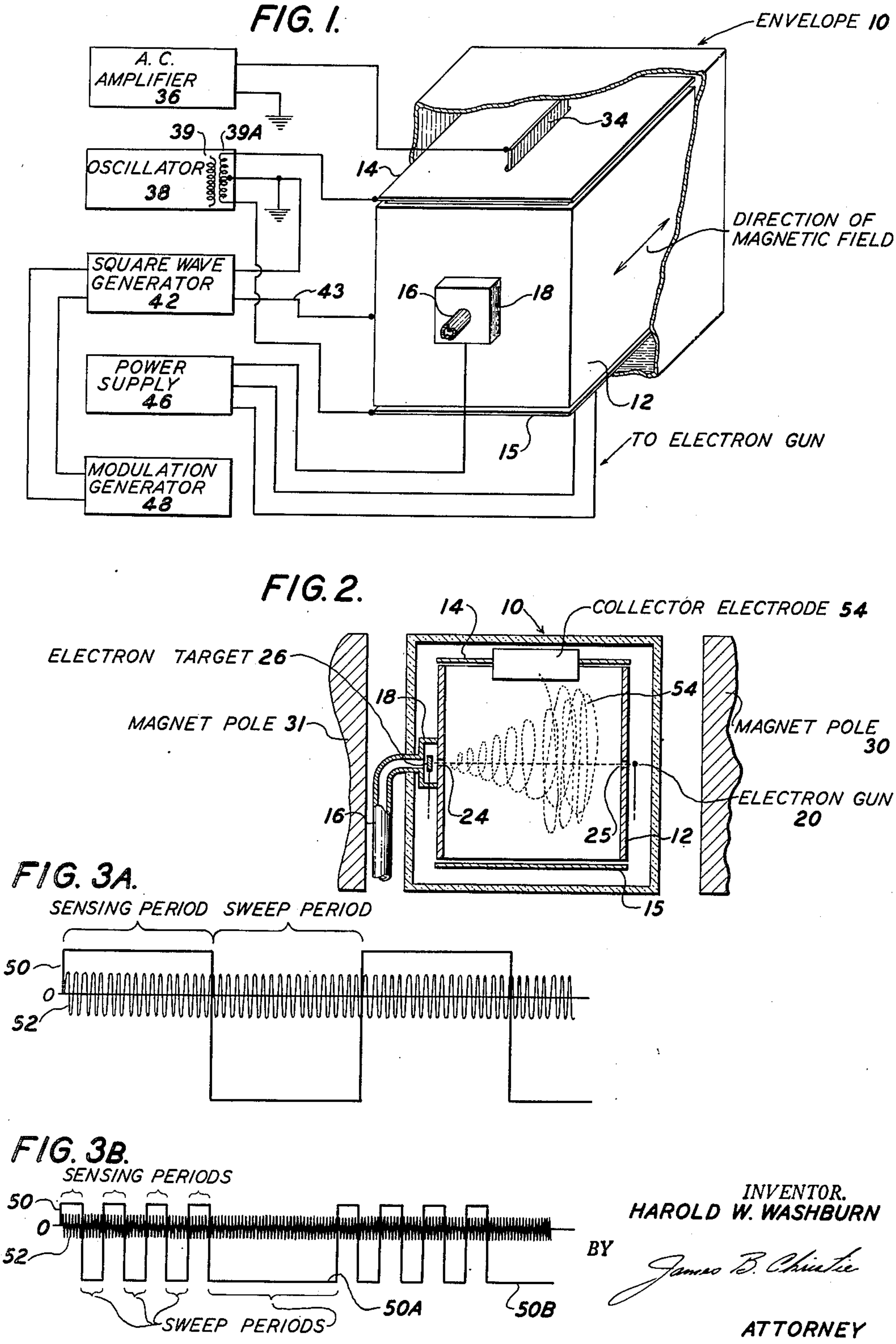

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MASS SPECTROMETRY

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This invention is directed to improvements in mass spectrometry and is more particularly related to the field of mass spectrometry wherein ions are caused to pursue expanding spiral paths between a point or points of formation and the point of collection.

In mass spectrometry in general, a gas sample to be analyzed is ionized, as for example by bombardment with an electron beam, and the various ions formed from the gas are separated as a function of their mass-to-charge ratio. In one common method of operation this separation is brought about by propelling the ions from the point of formation toward a target or collector electrode and through an intervening magnetic field. In passing through the magnetic field, ions of different mass-to-charge ratios assume different radii of curvature in their course toward the collector electrode. By controlling the speed of ion travel, as by fixing the potential applied to accelerating electrodes located adjacent the point of ion formation, or by controlling the strength of the magnetic field through which the ions pass, ions of a given mass-to-charge ratio can be selectively caused to impinge on and discharge at the target electrode. Varying either or both of these functions will cause ions of a different mass-to-charge ratio to impinge on the collector. The magnitude of the discharge current developed at the target electrode by ions of a given mass-to-charge ratio may be used to determine the partial pressure of the parent particles in the gas sample under investigation.

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. The resonant frequency, like the radius of curvature in a magnetic field, is related to the mass-to-charge ratio. This type of selection is accomplished by subjecting the ions to an alternating electrical field and a magnetic field normal to the electrical field whereby the ions are excited to motion, with those ions of a resonant frequency corresponding to the frequency of the alternating field traveling in a uniformly expanding spiral path from the point of origin or the point of introduction into the alternating field. A collector or target electrode disposed in this path will collect these ions while the non-resonant ions travel in different paths which theoretically will not carry them to the target electrode. One form of mass spectrometer operating in the foregoing principles is described and illustrated in my co-pending application Serial No. 736,758, filed March 24, 1947.

A mass spectrometer of the type selective to differences in resonant frequency exhibited by ions of various masses has certain advantages over the more well known instrument which is selective on the basis of differences in the radius of curvature in a magnetic field of ions of differing mass-to-charge ratio. A mass spectrometer

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selective to differences in resonant frequency can be made small and compact and exhibits an extremely high resolving power. Moreover, it is less sensitive to irregularities in collimation or variation in the ionizing electron beam.

There are, however, problems encountered which are not present in the more conventional type of mass spectrometry. Prominent among these is the tendency towards an undesirable accumulation of ions in the field. Non-resonant ions, i. e. those ions having a resonant frequency differing from the established frequency of the alternating field, assume paths which tend to hold them within the field. In general, the non-resonant ions travel in spirals which expand non-uniformly to a limit and then collapse back to the point of origin, and so on, or in other paths conforming in general to a Lissajous figure and defined by the boundaries of the fields. Accumulation of non-resonant ions in the field results in a progressive increase of space charge until the potentials are such that some of the ions are driven toward the walls of the chamber. As a result, ions of a given mass in resonance with the alternating field will not be collected at the same efficiency when the number of non-resonant ions varies with a change in gas sample composition. To achieve the necessary degree of linear superposition therefore, it is necessary to avoid excessive accumulation of non-resonant ions.

I have now discovered an effective method of avoiding this undesirable accumulation of space charge in the practice of mass spectrometry based on segregation between ions of differing resonant frequency. The invention contemplates in mass spectrometry involving the formation of ions, the separation thereof on the basis of their resonant frequency by means of an alternating electrical field established across a space in which the ions are confined and a magnetic field established across the space and normal to the alternating field, and selectively collecting ions of a resonant frequency corresponding to the frequency of the alternating field, the improvement comprising developing a potential at the boundaries of the space paralleling the alternating field and periodically varying this potential so that it is alternately positive and negative with respect to the alternating field.

When the potential at the boundaries is at one polarity a potential field is maintained within the space which prevents most ions from escaping to the boundaries and keeps the spiralling resonant ions within the confines of the space until they reach the ion collector. Under this condition the non-resonant ions accumulate and build up a space charge. When the polarity of the boundary potential is reversed, a potential field is established in the space which drives the accumulated ions toward the boundaries where they are conveniently discharged. Most of the ions can be forced to leave the space by migration to the boundaries by developing a potential field of the reversed polarity. When the polarity of the boundary potential reverts back to this accumulation condition new ions are formed and are caused to assume their characteristic pattern of movement which brings the resonant ions to the collector electrode.

The frequency of polarity reversal of the boundary potential must, of course, be low enough to allow an appreciable portion of the resonant ions to reach the collector electrode. At the same time this frequency must be high enough to avoid excessive build up of space charge. By the proper adjustment of this frequency of polarity reversal of the boundary potential, the space charge effect can be reduced to the point where ions of one mass will be collected at substantially the same efficiency regardless of the number of ions of other masses which are present.

I have also developed an improved mass spectrometer adapted to carry out the foregoing described method comprising the combination of an analyzer chamber, means for ionizing a gas sample admitted to the chamber, electrodes disposed at opposite ends of the chamber and insulated therefrom, means for impressing a high frequency alternating potential between the electrodes to develop across the space defined by the chamber an alternating field having a frequency of alternation corresponding to the resonant frequency of ions of a given mass, means for impressing between said electrodes and the walls of the chamber a potential of such character that the walls of the chamber are alternately negative and positive with respect to the electrodes, means for producing a magnetic field across the analyzer chamber normal to the alternating field whereby certain of the ions disposed in said chamber will be caused to pursue an expanding spiral path in the chamber and a target electrode disposed in this expanding spiral path.

The above described boundary potential by means of which the space charge is held under control is developed in the apparatus by the means for impressing a potential between the chamber walls and the A. C. field producing electrodes. Conveniently the potential applied between the chamber walls and the electrodes is in the nature of a square wave conveniently varying between a positive value of suitable magnitude, and a negative value of similar or greater amplitude than the positive value.

The current developed at the collector electrode responsive to ion discharge must, of course, be amplified for recording purposes. The present method and apparatus are adapted to A. C. or D. C. amplification as desired. The character of the discharge current is determined by the nature of the voltage employed to develop the boundary potential. If this voltage is in the form of a square wave of non-variant frequency the discharge current will be in the nature of pulses of a like frequency. An amplifier having a frequency response lower than this frequency will respond to the discharge current as a D. C. current. On the other hand, an amplifier having a frequency response corresponding to the pulse frequency will function as an A. C. amplifier. A. C. amplification of the individual discharge pulses is complicated by extraneous signals resulting from capacitive coupling between the collector electrode and the chamber walls since the frequency at which the voltage applied to the walls reverses in polarity determines the frequency of the discharge pulses. However, I have found that by modulating the voltage employed to develop the described boundary potential, the discharge current may be pulsed at a different frequency to which an A. C. amplifier is sensitive. Thus this potential is controlled to render the chamber walls alternately positive and negative at a frequency greater than the frequency response to the amplifier network so that the net effect is to develop at the collector electrode a discharge current which appears as a steady current. By periodically rendering the chamber walls negative with respect to the alternating field for an extended period of considerably greater duration than the periods during which the chamber walls are positive with respect to the alternating field, no ions will impinge on the collector electrode for a period to which the amplification system is sensitive. The effect of the foregoing operation is to develop at the collector electrode a pulse type discharge current with each pulse comprising the discharge current developed over a number of cycles of the square wave potential as applied between the chamber walls and the alternating field electrodes.

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

Fig. 1 is a perspective diagrammatic view of apparatus in accordance with the invention;

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

Figs. 3A and 3B are graphs showing the nature of the square wave voltage applied between the A. C. electrodes and the walls of the confining chamber and the relationship of the square wave voltage to the A. C. potential applied to the A. C. electrodes.

Referring to Figs. 1 and 2 of the drawing, the instrument there shown comprises an envelope **10**. Certain standard auxiliary equipment such as evacuating means etc. are omitted as being conventional and unnecessary to an understanding of the invention. A four-sided rectangular conductive box or shell **12** is disposed within the envelope, and a pair of electrodes **14, 15** are mounted adjacent the open ends of the shell **12** and are insulated therefrom as by a small air gap as illustrated. A tube **16** is carried through a wall of the envelope and opens into an inlet chamber **18** conveniently carried on a side of the shell **12**. An electron target **26** is mounted in the inlet chamber **18**. An aperture **24** in the wall of the box **12** enclosing chamber **18** permits the gas sample to migrate into the interior of the box. An electron gun **20** is mounted exteriorly of the box opposite inlet chamber **18** to develop an electron beam which is directed across the box through an aperture **25** aligned with and in the opposite wall from aperture **24**.

The arrangement is such that an electron beam generated at the gun **20** is directed though aperture **25** and through the box **12** on a central axis thereof midway between electrodes **14, 15** to the target electrode **26**. Gas molecules introduced through the inlet tube **16** are ionized as they intersect the electron beam. Hence all ions are formed on 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 an alternating field developed between the A. C. electrodes 14, 15. A collector electrode projects into the space defined by the box 12 through the electrode 14 with its collecting face lying parallel to the electron beam.

An A. C. amplifier 36 is connected to the collector electrode 34 and ground so that the collector electrode is essentially at ground potential. The collector can be operated at some other potential if desired. A high frequency oscillator 38 is connected across the A. C. electrodes 14, 15 through a transformer 39 with the electrodes 14, 15 being connected to opposite ends of the secondary winding 39A of the transformer. The oscillator supplies a high frequency alternating voltage to the A. C. electrodes 14, 15 so that a high frequency A. C. field is developed between the electrodes across the space defined by the shell 12. A square wave generator 42 is connected between the midpoint of the transformer secondary winding 39A and the box 12. The square wave generator thus develops a potential between the box 12 and the electrodes 14, 15 which is independent of the A. C. potential developed across the electrodes by the oscillator 38. The character and function of the potential applied between the box 12 and the A. C. electrode will be described in greater detail with reference to Figs. 3A and 3B.

A power supply 46 is connected by appropriate leads to the electron gun 20, and electron target 26 to supply the necessary voltages to these elements. A modulation generator 48 is connected to the square wave generator 42 to modulate the output of the square wave generator in the pattern shown in Figs. 3A, 3B.

Referring to Figs. 3A and 3B, Fig. 3A shows a portion of the square wave voltage and the high frequency A. C. voltage applied to the accelerating electrode. The square wave voltage is shown by the curve 50, this being the voltage that is applied between the box 12 and A. C. electrodes 14, 15, and the high frequency A. C. voltage is shown by the curve 52, this being the voltage applied by the oscillator 38 across the A. C. electrodes 14, 15. It is noted that the frequency of alternation of the A. C. voltage is greater than the frequency of the voltages developed by the square wave generator. The curves 50, 52 are not intended to represent any given frequency ratio. In Fig. 3B the amplitude and time cycles of the voltage curves are reduced considerably to show the entire pattern of the square wave voltage.

From either Figs. 3A or 3B it is seen that the square wave voltage 50 goes through a number of cycles in which it is alternately positive and negative with respect to the A. C. field, the duration of the positive and negative half cycles being approximately the same. After a number of cycles of substantially uniform frequency, a negative pulse of disproportionate duration as illustrated by the portion 50A of the curve 50 is developed by the modulation generator. The extended negative pulse 50A separates a group of uniform cycles from another group of uniform cycles, which other group is, in turn, followed by an extended negative pulse represented by the portion 50B of the curve. Hence the pattern of the square wave voltage developed by the square wave generator and responsive to the modulation generator is repetitive comprising a number of cycles with all of the positive and all of the negative pulses being of uniform amplitude. A number of cycles of pulses of uniform frequency are set off from a like number of cycles by a negative pulse of similar amplitude but of considerably greater duration than the uniform negative pulses. In the drawing the negative pulses are shown to be of greater amplitude than the positive pulses for purposes of illustration. This need not be the case and in fact there is no known reason why succeeding pulses need be of uniform amplitude.

The operation of the instrument is apparent with reference to the voltage patterns shown in Figs. 3A and 3B and 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 in the box 12 by means of the electron beam travelling between the electron gun 20 and target electrode 26. A high frequency alternating field is developed across the box transverse to the electron beam between electrodes 14 and 15 responsive to the high frequency A. C. voltage applied across these electrodes and represented by the curves 52 in Figs. 3A and 3B. A magnetic field is developed across the space defined by the box by magnetic poles 30, 31 with the magnetic field being normal to the alternating field and parallel to the electron beam. The effect of the perpendicular electrical and magnetic fields is to set the ions in motion with the ions of varying mass-to-charge ratio following different paths of travel within the confines of the box.

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 back and forth between the opposite side walls of the box and until the radius of the spiral path is such as to reach the collector electrode 34 at which the ions travelling in this path are discharged. The non-resonant ions confined within the box travel in various paths depending upon their resonant frequency and generally in the nature of Lissajous' figures. For example, certain of the non-resonant ions may travel in an expanding spiral path of progressively diminishing radial increments to a maximum and collapse in a spiral path of decreasing radius to the point of origin and so on. The magnitude of the A. C. and magnetic fields are controlled so that the maximum radius of travel of the non-resonant ions is short of the collector electrode which, therefore, selectively collects only the resonant ions.

The square wave voltage applied between the shell 12 and electrodes 14 and 15 alternately repels the ions from the shell when the shell is positive with respect to the electrodes, and attracts the ions to the shell when the latter is negative with respect to the electrodes. During the intervals in which the shell is positive, the ions will tend to migrate first towards one wall and then towards an opposite wall and will in each instance be repelled back towards the center. During this oscillation between opposite walls of the shell the resonant ions will be travelling in a spiral of uniformly increasing radius until they strike the collector. When the square wave voltage renders the shell negative with respect to the electrodes, the reverse situation will result and all of the ions in the space defined by the shell will be attracted to and discharged at the walls so as to sweep the space clear of ions. This way an undesirable accumulation of non-resonant ions is avoided. The duration of the positive half cycle of the square wave voltage must be such as to allow some of the resonant ions originating at the electron beam to reach the collector electrode.

The frequency of the alternation of the A. C. field is higher than the frequency of the square wave. However, the square wave frequency is sufficiently high that an A. C. amplifier of normal frequency response is insensitive to the pulses developed at the collector electrode responsive to ions impinging thereon during the intervals when the square wave voltage is positive. In short, therefore, the current developed at the collector electrode responsive to ion collection during the positive intervals of square wave voltage is in effect a single pulse and if uninterrupted would require D. C. amplification. By modulating the square wave voltage so that periodically the voltage is held negative for an extended interval corresponding to several cycles of alternation, the current developed at the collector electrode is pulsed by interruption during the extended interval for a period sufficient to render the A. C. amplifier sensitive to the interruption. In this fashion the collector output appears to the A. C. amplification system as a series of pulses with each pulse actually constituting a series of individual pulses of such high frequency as to be undetectable by the amplification system.

It is clear that I have provided a method of mass spectrometry and apparatus adapted to carry out the method whereby the tendency of non-resonant ions to accumulate and produce an undesirable space charge has been overcome and where the means for overcoming this tendency may be utilized to control the output current from the collector electrode in such a fashion as to adapt it to A. C. amplification. It is obvious that other forms of apparatus may be used to periodically sweep accumulated ions from the space in which the A. C. and magnetic fields are developed, and likewise other means may be employed to develop a pulsating output current on the collector electrode. In this latter respect, for example, it is quite possible to periodically interrupt the ion generating electron beam so that there will be intervals during which no ions are formed in the space and hence no current is developed at the collector electrode. However, I have found it convenient to combine the means for periodically sweeping accumulated ions from the space and for developing a pulsating ion current as described.

I claim:

1. In a mass spectrometer, the combination comprising an analyzer chamber, means for admitting a gas to said chamber, means for ionizing the gas admitted to the chamber, electrodes disposed at opposite ends of the chamber and insulated therefrom, means for impressing a high frequency alternating potential on said electrodes to develop across a space in said chamber an alternating field having a frequency of alternation corresponding to the resonant frequency of ions of a given mass, means for impressing between said electrodes and the walls of said chamber a potential of such character that the chamber walls are alternately negative and positive with respect to the electrodes at a frequency less than the alternation frequency of said alternating field, means for producing a magnetic field across the analyzer chamber normal to the alternating field whereby certain of the ions disposed in said chamber will be caused to pursue an expanding spiral path in the chamber, and a collector electrode disposed in this expanding spiral path.

2. In a mass spectrometer, the combination comprising an analyzer chamber, means for admitting a gas to said chamber, means for ionizing the gas admitted to the chamber, electrodes disposed at opposite ends of the chamber and insulated therefrom, means for impressing a high frequency alternating potential on said electrodes to develop across a space in said chamber an alternating field having a frequency of alternation corresponding to the resonant frequency of ions of a given mass, means for varying the frequency of the alternating potential, means for impressing between said electrodes and the walls of said analyzer chamber a potential of such character that the chamber walls are alternately negative and positive with respect to the electrodes at a frequency less than the alternation frequency of said alternating field, means for producing a magnetic field across the analyzer chamber normal to the alternating field whereby certain of the ions disposed in said chamber will be caused to pursue an expanding spiral path in the chamber, and a collector electrode.

3. In a mass spectrometer, the combination comprising an analyzer chamber, means for admitting a gas to said chamber, an electron gun for directing a beam of electrons across the chamber to ionize gases in the chamber, electrodes disposed at opposite ends of the chamber and insulated therefrom, means for impressing a high frequency alternating potential on said electrodes to develop across a space in said chamber and transverse to said electron beam an alternating field having a frequency of alternation corresponding to the resonant frequency of ions of a given mass, means for impressing between said electrodes and the walls of said analyzer chamber a potential of such character that the chamber walls are alternately negative and positive with respect to the electrodes at a freuency less than the alternation frequency of said alternating field, means for producing a magnetic field across the analyzer chamber normal to the alternating field and parallel to the electron beam, whereby certain of the ions disposed in said chamber will be caused to pursue an expanding spiral path in the chamber, and a collector electrode.

4. Apparatus according to claim 3 wherein the collector electrode is disposed in the chamber adjacent one of said electrodes with its collecting face parallel to the magnetic field.

5. In a mass spectrometer, the combination comprising an analyzer chamber, means for admitting a gas to said chamber, means for ionizing the gas admitted to the chamber, electrodes disposed at opposite ends of the chamber and insulated therefrom, means for impressing a high frequency alternating potential on said electrodes to develop across a space in said chamber an alternating field having a frequency of alternation corresponding to the resonant frequency of ions of a given mass, means for impressing between said electrodes and the walls of said chamber a potential of square wave form, means for modulating the square wave potential, means for producing a magnetic field across the analyzer chamber normal to the alternating field whereby certain of the ions disposed in said chamber will be caused to pursue an expanding spiral path in the chamber, and a target electrode.

6. Apparatus according to claim 5 wherein the means for impressing a potential between said

electrodes and the chamber walls comprising a square wave generator adapted to develop a square wave voltage which is alternately negative and positive for like periods, and the means for modulating the square wave potential comprises a modulation generator which periodically alters the square wave developed by the square wave generator to the extent of producing a negative pulse of extended duration.

7. In a mass spectrometer, the combination comprising an envelope providing a closed chamber to which gases may be admitted, means for ionizing the gases admitted to said chamber, means in the form of a four-sided conductive member defining a space in said chamber, a separate electrode disposed across each open end of said member and insulated from the member to substantially enclose said space, means including said electrodes for developing an alternating field in the said space, means for impressing a potential between said electrodes and said member to alternately and periodically drive the member negative and positive with respect to said electrodes, means for producing a magnetic field across said space and normal to said alternating field, means for admitting said gas from the chamber into the space whereby certain of the ions produced from said gas will be caused to pursue a uniformly expanding spiral path under the influence of the magnetic and alternating fields during the periods in which said member is at a positive potential with respect to said electrodes, and a target electrode disposed in said space to collect ions travelling in said uniformly expanding spiral path.

8. In a mass spectrometer, the combination comprising an envelope providing a closed chamber to which gases may be admitted, means for ionizing the gases admitted to said chamber, means in the form of a four-sided conductive member defining a space in said chamber, a separate electrode disposed across each open end of said member and insulated from the member to substantially enclose said space, means including said electrodes for developing an alternating field in said space, means for impressing a potential between said electrodes and said member to alternately and periodically drive the member negative and positive with respect to said electrodes, means for producing a magnetic field across said space and normal to said alternating field, means for admitting said gas from the chamber into the space whereby certain of the ions produced from said gas will be caused to pursue a uniformly expanding spiral path under the influence of the magnetc and alternating fields during the periods in which said member is at a positive potential with respect to said electrodes, and a collector electrode disposed in said space adjacent one of said electrodes and with its collecting face parallel to the magnetic field to collect ions travelling in said uniformly expanding spiral path.

9. In a mass spectrometer, the combination comprising an envelope providing a closed chamber to which gases may be admitted, means in the form of a four-sided conductive member defining a space in said chamber, a separate electrode disposed across each open end of said member and insulated from the member to substantially enclose said space, an electron gun adapted to direct an ionizing electron beam centrally across said member and midway between said electrodes, means including said electrodes for developing an alternating field in said space,

means for impressing a potential between said electrodes and said member to alternately and periodically drive the member negative and positive with respect to said electrodes, means for producing a magnetic field across said space normal to said alternating field, and parallel to said electron beam, means for admitting said gas from the chamber into the space in the region of said electron beam whereby certain of the ions produced from said gas will be caused to pursue a uniformly expanding spiral path under the influence of the magnetic and alternating fields during the periods in which said member is at a positive potential with respect to said electrodes, and a target electrode disposed in said space to collect ions travelling in said uniformly expanding spiral path.

10. In a mass spectrometer, the combination comprising an envelope providing a closed chamber to which gases may be admitted, means in the form of a four-sided conductive member defining a space in said chamber, a separate electrode disposed across each open end of said member and insulated from the member to substantially enclose said space, an electron gun adapted to direct an ionizing electron beam centrally across said member and midway between said electrodes, means including said electrodes for developing an alternating field in said space, means for impressing a voltage between said electrodes and said member to alternately and periodically drive the member negative and positive with respect to electrodes, means for defining the wave form of said voltages so that the member will be periodically negative for a period of time exceeding the duration of the periods of positive polarity, means for producing a magnetic field across said space normal to said alternating field and parallel to said electron beam, means for admitting said gas from the chamber into the space in the region of said electron beam whereby certain of the ions produced from said gas will be caused to pursue a uniformly expanding spiral path under the influence of the magnetic and alternating fields during the periods in which said member is at a positive potential with respect to said electrodes, and a target electrode disposed in said space to collect ions travelling in said uniformly expanding spiral path.

11. In a mass spectrometer, the combination comprising an analyzer chamber, means for developing an alternating electrical field across the chamber, means for developing a magnetic field across the chamber normal to the electrical field, means for selectively collecting ions of a resonant frequency corresponding to the frequency of the alternating field, means for developing a potential at opposite boundary walls of the analyzer chamber, and means for periodically reversing the polarity of the boundary wall potential.

12. In a mass spectrometer, the combination comprising an analyzer chamber, means for developing an alternating electrical field across the chamber, means for developing a magnetic field across the chamber normal to the electrical field, means for selectively collecting ions of a resonant frequency corresponding to the frequency of the alternating field, means developing a potential at opposing boundary walls of the analyzer chamber lying on the axis of the alternating field, and means for periodically reversing the polarity of the boundary wall potential.

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No references cited.