

March 8, 1949.

R. V. LANGMUIR
MASS SPECTROMETRY

2,463,545

Original Filed April 30, 1943

2 Sheets-Sheet 1

FIG. 1.

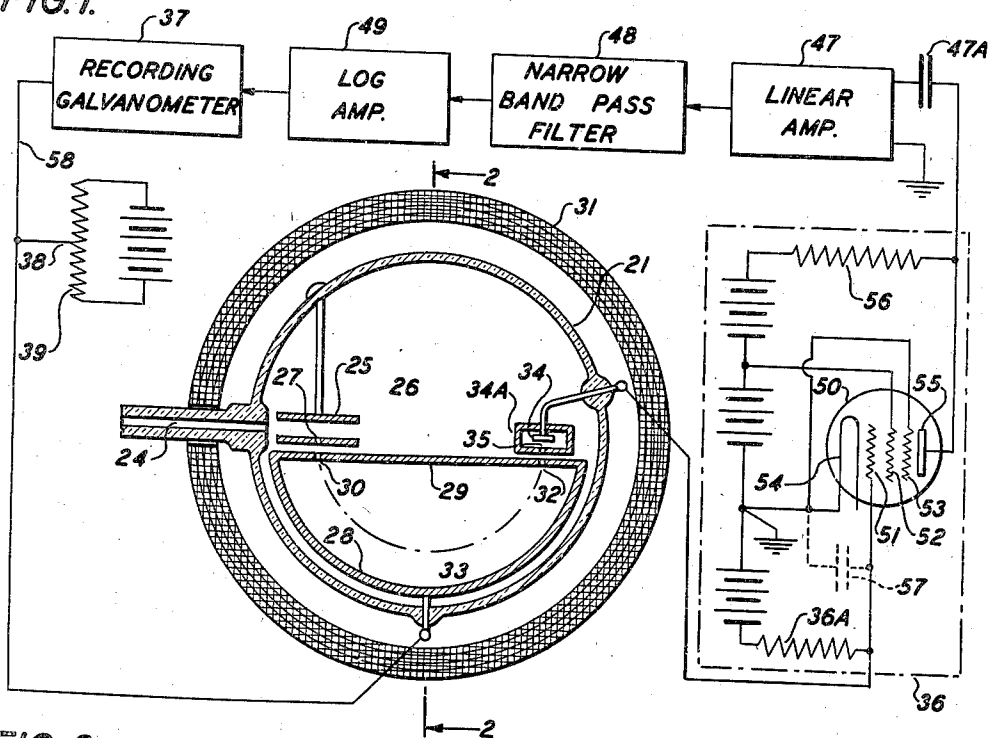
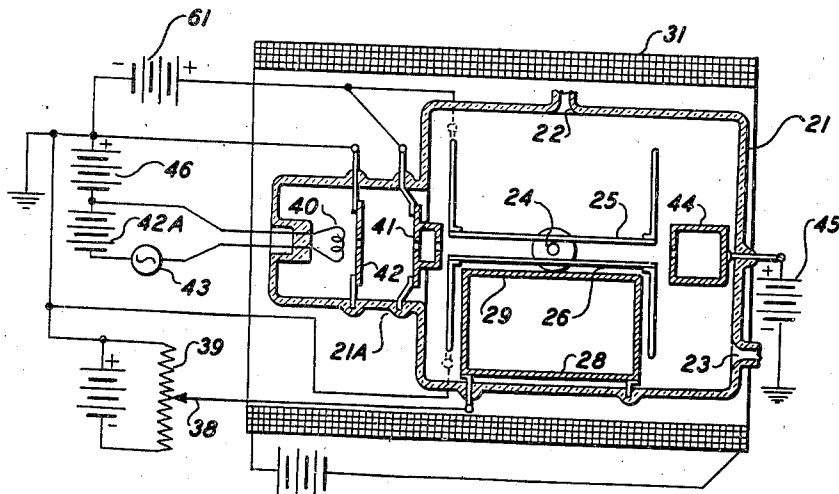


FIG. 2.



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FIG. 3.

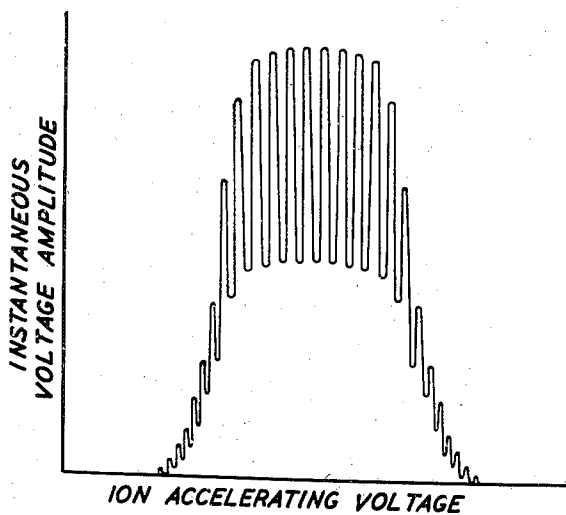
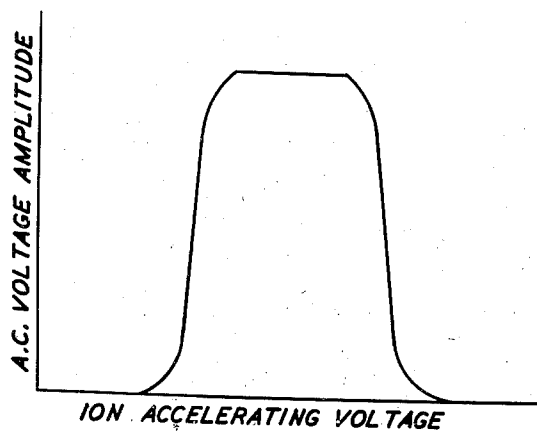


FIG. 4.



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MASS SPECTROMETRY

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Original application April 30, 1943, Serial No.
483,745. Divided and this application October
7, 1946, Serial No. 701,739

5 Claims. (Cl. 250—41.9)

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This invention is concerned with mass spectrometry and contemplates improvements in mass spectrometry involving the production of a pulsating ion current which can be amplified with A. C. instruments. The present invention is a division of my co-pending application Ser. 483,745, filed April 30, 1943 (now United States Patent No. 2,457,162).

In mass spectrometry, a gas sample is bombarded by moving electrons to produce ions of various substances present in the sample, and the ions thus formed are separated into various components having different mass-to-charge ratios by subjecting the ions to the influence of electric or magnetic fields or both. The individual components are then directed upon an ion collector and discharged, and the intensity of the resulting ion current is measured. Thus, the several components may be caused to fall successively upon the collector by varying the electric or magnetic field, or by moving the collector successively into the respective paths of the several components.

In a method of mass spectrometry heretofore proposed, the several components having different mass-to-charge ratios are formed of positive ions. When such components are directed to the ion collector and there discharged, a unidirectional current is set up in a circuit connected to the ion collector and the intensity of this current is measured following amplification by a direct current amplifier. However, this method (especially when the samples of gas to be treated in the mass spectrometer are small) is subject to certain inherent disadvantages arising principally out of the nature of direct current amplifiers. The speed with which a mass spectrum may be measured with a given degree of accuracy depends upon the time constant of the input circuit of the D. C. amplifier. This is necessarily long because of the large input resistance required to detect the small currents available at the collector. The time constant is the product of the input resistance times the input capacitance and may be several seconds or even of the order of minutes. Thus, employing a direct current amplifier, the rate at which a small sample of gas can be analyzed in a mass spectrometer is relatively slow and the capacity of the instrument in terms of useful work is limited.

As disclosed in my co-pending application Serial No. 294,346 filed September 11, 1939, (now United States Patent No. 2,370,673) I have discovered that the speed of analysis can be increased markedly by producing a pulsating ion beam, discharging this beam at the ion collector and amplifying the resulting pulsating ion current with an alternating current amplifier. In accordance

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with my invention, an ion beam is formed in a mass spectrometer by bombardment of a gas with the electrons and the intensity of this ion beam is varied in a predetermined manner. Thus, the ion beam may be caused to pulsate and the pulsating ion beam, upon discharge at an ion collector, produces an oscillating potential which is amplified with an A. C. type amplifier and recorded or measured. For example, a plurality of separate ion beams of different mass-to-charge ratios may be generated or controlled in such fashion that the intensity of each beam varies in a sinusoidal manner. The pulsating ion beams thus formed are caused to fall successively at the collector to produce a mass spectrum. Preferably, the frequency of the ion beams should be smaller than the number of ions falling on the collector per second. Otherwise, statistical variations in the rate at which the ions fall on the collector may mask the pulsations in that rate, and it is these pulsations which should be detected.

The required pulsating ion beam may be formed in several ways, but in all cases the ions of a given mass-to-charge ratio strike the collector and there discharge at a rate which oscillates, pulsates or varies in a regular manner to produce a corresponding pulsating or oscillating electric current which may be amplified with an alternating current amplifier. The required oscillation may be brought about (1) by varying the intensity of the beam of ionizing particles (such as electrons) with which the gas in the mass spectrometer is bombarded; (2) by varying the velocity (or energy) of these ionizing particles (electrons); and (3) by varying the forces acting upon the ions during the separation of ion components having different mass-to-charge ratios, i.e. by varying the field forces which control the deflection of the ions during separation into the components.

Thus, in a mass spectrometer having means for bombarding a gas sample with ionizing particles to produce ions of substances present in the sample, means for separating the ions thus produced according to their mass-to-charge ratios into a plurality of ion beams, means for pulsating the ion beams, and means for collecting ions of a beam to produce an alternating or pulsating current, my invention contemplates the combination which comprises an electrode disposed adjacent the path of the electron stream, means for supplying a potential to the electrode, and means for varying the potential at said electrode in a pulsating manner, whereby the ion beams are caused to pulsate. The electrode supplied with the pulsating potential may be an anode adapted to draw electrons from a filament or other electron source, or it may be an electrode disposed between

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such an anode and such an electron source. Likewise the electrode may be disposed in the region where the electron stream bombards the gas sample, for example it may be one of a pair of plates (one of which has an aperture through which the electrons pass into the analyzing portion of the apparatus). Another manner for causing the ion beam to pulsate is to supply a pulsating potential to a solenoid surrounding the analyzing portion of the apparatus, whereby the radius of curvature of the ion beam is caused to vary in a pulsating manner. The ion beam may also be caused to pulsate (a) by causing the electron beam to pulsate at its source, for example a filament, by varying the temperature at that point and hence the rate of electron emission or (b) by means of a shutter which periodically is interposed in the path of the ionizing particles.

These and other features of my invention will be more thoroughly understood in the light of the following detailed description taken in conjunction with the accompanying figures, in which:

Fig. 1 is a cross-section of one form of mass spectrometer constructed in accordance with my invention (provided with an amplifier, a recorder and a potential source, all shown schematically) and adapted to bring about pulsation of the ion beam through modulating the beam of electrons employed to bombard the gas from which the ions are formed;

Fig. 2 is a longitudinal view, partly in section, taken through the mass spectrometer of Fig. 1 along the line 2-2;

Fig. 3 is a graph showing the relationship of ion accelerating voltage to the voltage in the resistance 20 of the collector circuit for the type of mass spectrometer illustrated in Fig. 2; i. e. in Fig. 3 an A. C. voltage component is superimposed on the D. C. voltage that would be present across resistor 36A if the beam intensity did not pulsate, the A. C. component being proportional to the D. C. voltage at each point;

Fig. 4 illustrates the relationship of the ion accelerating voltage to the amplitude of the A. C. voltage in the output of the amplifier circuit in the spectrometer illustrated in Fig. 2.

Referring to the drawings and particularly to Figs. 1 and 2, it will be observed that the mass spectrometer has an envelope 21 which may be evacuated through vacuum lines 22, 23 connected to the envelope and maintained at low pressure by one or more vacuum pumps (not shown) connected to the vacuum lines.

A capillary tube 24 is connected to the envelope and through it a sample of gas to be analyzed is admitted. Within the envelope adjacent the entrance of the capillary there is disposed a pusher plate 25 and a plate 26 having a slit 27. The plates are disposed respectively on either side of the entrance of the capillary tube so that a gas sample entering the envelope flows into the space between the plates and is there bombarded by a unidirectional electron stream, the strength of which is varied or modulated in a pulsating manner. The bombardment of the gas molecules results in the formation of gaseous ions in the space between the plates, the amount of ions formed in unit time being correspondingly varied in a pulsating manner.

A small negative voltage (relative to the voltage on the pusher plate 25) is established on the plate 26. In consequence, positive gaseous ions formed in the space are drawn toward the plate 26. Some of these ions pass through the slit 27 in this plate. A semi-cylindrical case 28 is dis-

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posed within the envelope adjacent the plate 26. A flat plate 29 forming one side of the case is disposed substantially parallel to the plate 26 and is provided with a second slit 30 which matches the slit in plate 26. A high accelerating potential is maintained between the plate 26 and the case 28. This potential provides an electric accelerating field which causes the positive ions that pass through the first slit 27 to be highly accelerated towards the case. Some of these accelerated ions enter the case 28 through the second slit 30.

A solenoid 31 is disposed around the envelope and produces a magnetic field therein, so that the ions entering the case through the second slit at high velocity follow curved paths within the case.

Due to the combined action of the aforementioned accelerating field maintained between the plate 26 and the case and the magnetic field produced by the solenoid, the ions entering the case are separated into ionic beams of different mass-to-charge ratios. Each beam follows a semi-circular path, the radius of which is determined by the strength of the electric accelerating field, the strength of the magnetic field and the mass-to-charge ratio of the ions in the particular beam. Thus, each beam in effect, originates at the slit 30 and follows its own curved path to focus on the flat plate 29 opposite the slit 30.

A third slit 32 is provided in the flat plate of the case in the region where the beams tend to focus. Ions having a predetermined mass-to-charge ratio follow a substantially semicircular path 33 from the second slit 30 to the third slit 32, pass through the third slit and fall upon an ion collector 34 which is protected by a shield 34A having therein an aperture 35 matching the third slit.

The ions discharge on the ion collector and produce through a resistor 36A of a linear amplifier 36 connected to the ion collector a pulsating electric current that corresponds in frequency and intensity to the collected ion current.

The voltage which results in the resistor 36 is amplified with an A. C. amplifier combination discussed in detail hereinafter and the amplified current is recorded by a galvanometer 37, so that the intensity of the ion beam being discharged at any instant is indicated.

The several ion beams of different mass-to-charge ratio are caused to pass successively through the slits 30, 32, 35 onto the collector 34 by varying the intensity of the accelerating electric field between the plate 26 and the case, this being accomplished by moving a slider 38 on a potentiometer 39. In short, the separate beams existing within the case are successively brought to a focus at the slit 32, so that the intensities of the respective beams are measured successively.

An apparatus is shown in Fig. 2 for varying the ion current in a pulsating manner according to the invention. As shown in this figure, the electrons employed to bombard the gas sample in the space between the plates 25 and 26 originate at an ionizing source represented by the filament 40, an anode structure 41 and a control electrode 42 with the associated batteries 42A, 46 and 61. The filament, the anode structure and the control electrode are disposed within an extension 21A of the envelope at one end thereof. A D. C. potential difference between the anode and the control electrode is maintained by a battery 61, which also supplies current to the plate 25.

The control electrode is disposed between the

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filament and the anode structure and has an aperture therein in line with two other apertures in the anode structure so that the electron beam is directed into the space between the plate 25 and the plate 26 approximately at right angles to the capillary tube through which the gas sample is admitted.

The electrode and the anode structure preferably are maintained at positive potentials with respect to the filament.

In Fig. 2 the method of modulating the electron beam according to the present invention is shown. There is provided an alternating current source 43 connected in the filament circuit in series with a direct current battery 42A. The alternating current supplied to the filament causes the temperature of the filament to alternate in a corresponding manner with resultant variation in thermionic emission (of electrons) from the filament. This alternating potential at the filament controls the emission of the electron beam originating thereat and streaming through the apertures in the control electrode and the anode structure to enter the ionization region between the plates 25 and 26 where the electrons bombard and ionize gas introduced from the capillary tube.

Some of the electrons of the beam or stream may pass all the way between the plates to be picked up by an electron collector or cage 44, disposed in line with the apertures in the control electrode and the anode structure. The vagrant electrons thus picked up flow to ground through a battery 45 connected to the cage.

It will be apparent that the concentration of ions in the space between plates 25, 26 will be substantially proportional to the intensity of the electron beam if the velocity of the electrons is constant.

The frequency of the electron beam modulation, which is controlled by the frequency of the A. C. potential supplied by the A. C. generator 43, preferably is less than the average number of ions falling on the ion collector per second, so that statistical variations in the rate at which the ions reach the collector will not obscure the pulsations that are to be measured. In this manner, the intensity of the ion current varies in an easily controllable manner. However, some of the advantages of my invention may be retained if the ion beam is modulated at a frequency higher than the average number of ions falling on the collector per second.

To facilitate amplification of the output of the mass spectrometer, it is preferable to produce pulsating ion currents that vary in a sinusoidal manner, this being accomplished by employing an electron beam that pulsates in this fashion.

The alternating portion of the ion current appearing at the collector 34 is amplified in a circuit including the first linear amplification stage 36, a second linear amplification stage 47, a narrow band pass filter 48, a logarithmic amplifier 49 and indicated at the recording galvanometer 37. The two amplification stages are coupled through the coupling and blocking condenser 47A, which filters out the D. C. component of the signal appearing in the output of the first stage.

The amplifier stage 36 has, as indicated above, a linear characteristic and comprises one or more tubes. Thus, the first amplifier stage may comprise an amplifier tube 50 of the pentode type provided, as shown in Fig. 1, with a control grid 51, a screen grid 52 and a suppressor grid 53 together with a cathode 54 and an anode 55. Suitable resistors, including the resistor 36A and a

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second resistor 56 are connected to suitable batteries for maintaining the control grid and the anode respectively at correct operating potentials. The input capacity between the control grid and the cathode is represented by the dotted structure 57.

The alternating portion of the signal voltage appearing between the screen grid 52 and the cathode 54 may be calculated according to the following formula

$$e_s = \frac{R}{1 + j\omega RC} i \quad (1)$$

where i is the alternating portion of the ion current falling on the collector 33 and C is the input capacitance 57 of the tube 50. As indicated above, the corresponding output voltage appearing at the anode 55 of the first amplifier stage 36 is further amplified by the amplifier 47, passed through the narrow band pass filter 48, amplified further by the logarithmic amplifier 49 and impressed on the recording galvanometer 37. The band pass filter preferably is designed to pass a very narrow band of frequencies in the region of

$$f = \frac{W}{2}$$

For this purpose a resonant circuit having a very high Q may be employed. For example, a Q obtained from a resonant circuit utilizing electro-mechanical units such as magnetostriction oscillators or tuning forks is desirable. The use of a narrow band pass filter or a sharp resonant circuit permits an increase in the signal-to-noise ratio of the circuit so that smaller ion currents than would otherwise be possible can be detected. This will be apparent from the following:

Due to thermal agitation within the resistor 36A, noise will be impressed on the control grid 51 and amplified by the system. If only a small range of frequencies is passed by the filter 48 the magnitude of the input noise is given by

$$E_N = \sqrt{\frac{4KTR}{1 + 4\pi^2 R^2 C^2 f^2}} df \text{ approx.} \quad (2)$$

where T is temperature in degrees Kelvin, K is Boltzmann's gas constant, and df is the effective band width of filter 48.

Hence, the signal-to-noise ratio in the output is

$$\frac{E_s}{E_N} = 0.8 \cdot 10^{10} \sqrt{\frac{R}{df}} i \quad (3)$$

Inasmuch as the current i to be measured may be as low as 10^{-17} ampere, I prefer to utilize as large a resistance 36A as possible of the order of 10^{10} or 10^{14} ohms, and the narrow band pass filter 48, and in this manner achieve high ultimate sensitivity and provide high signal-to-noise ratio.

Following the filter 48, I prefer to utilize an amplifier the output of which is proportional to the logarithm of the input, thus making possible the recording of a wide range of ion intensities on a recording medium of limited width. Logarithmic amplifiers suitable for this purpose are well known to those skilled in the art.

In the form of my invention illustrated I utilize a common control connection 58 to coordinate the movement of the recording medium within the recorder 37 with the magnitude of the accelerating or analyzing electric field provided between the plate 26 and the case 28 by the potentiometer 39. In this manner, I am able to produce a continuous record in which one coordinate measures intensity of ion current. Thus,

the control connection is connected not only to the potentiometer and the galvanometer but also to the case 28.

It is to be understood that the recording speed necessary to attain a predetermined resolving power varies as an inverse function of the width (df) of the band passed by the filter 48, the term "resolving power" being employed to define the ability to differentiate and accurately measure the relative intensity of neighboring peaks on the final record obtained.

It is clear that the ultimate sensitivity, resolving power, and recording speed are interrelated with the characteristics of the filter 48. In the preferred form of my invention the recording speed is made as rapid as possible without causing undue loss of sensitivity or resolving power.

In the apparatus illustrated by Fig. 2 the alternating current in the outlet circuit, in resistance 36A, is of the same frequency as that generated in the alternating voltage source 43. In this case, the ion accelerating voltage provided by the potentiometer 39 is varied gradually. As each beam passes by the exit slit, some of the ions impinge upon the plate 29 of the case. The rate at which ions from a given beam pass through the slit 32 pulsates or varies periodically, so that the rate of collection of charges from the ions at the collector 34 is likewise modulated.

The manner in which the rate of collection at the collector 34 varies in the case of the apparatus of Fig. 2 is shown by Fig. 3. The alternating current voltage across the resistance 36A is, of course, proportional to the rate of ion collection so the voltage across the resistance 36A will likewise vary as illustrated by Fig. 3. However, the capacitance effect of the condenser 47A of Fig. 1 blocks any D. C. component of the voltage generated in the plate (cathode) circuit of the tube 52, so that the voltage appearing at the output of the amplifier 36 will be of the alternating current type and will vary in amplitude as the voltage supplied by the potentiometer 39. For ions of a given mass-to-charge ratio, the voltage amplitude in the output of amplifier 36 is a single peak as shown in Fig. 4.

The height of the single peak of Fig. 4 is proportional to the concentration of a gas from which ions of the particular mass-to-charge ratio are being produced, the constant of proportionality depending upon the individual gas, the mass-to-charge ratio of the ions in question, and naturally upon the constants of the apparatus.

As described hereinbefore, sources of square wave voltages may be provided, in which case the intensity of the beam striking the collector 34 is periodically changed between two values for a given setting of potentiometer. This results in a production of square wave voltage across resistance 36A. The square wave voltages contain numerous sinusoidal components and any desired component may be selected therefrom and amplified. It is preferable by means of filter 48 to select the strongest component, as determined from a Fourier analysis of the square wave voltage across the resistance.

If the alternating square wave voltage provided by the source has adequate amplitude, the beam striking the collector may be intermittently cut off completely.

With this apparatus a logarithmic, or other variable sensitivity, amplifier can be provided which amplified weak signals more than strong signals, so that signals of widely varying strength

may be accurately recorded with a conventional recording galvanometer 37.

I claim:

1. In a mass spectrometer having means for bombarding a gas sample with an electron beam to produce ions of the substances present in said sample, means for separating according to their mass-to-charge ratios the ions thus produced into a plurality of ion beams, and means for collecting ions of a beam, the combination comprising means for producing said electron beam, said last-named means comprising an electron emanating cathode, an anode adapted to form the electrons into a beam and means for pulsating the voltage supplied to said electron emanating cathode so as to vary the thermionic emission from said cathode.

2. In a mass spectrometer having means for bombarding a gas sample with an electron beam to produce ions of the substances present in said sample, means for separating according to their mass-to-charge ratios the ions thus produced into a plurality of ion beams, and means for collecting ions of a beam, the combination comprising means for producing said electron beam said last-named means comprising an electron emanating cathode, an anode adapted to form the electrons into a beam, an electrode disposed between the said electron emanating cathode and said anode and adjacent the path of said electron beam, and means for uniformly pulsating the voltage supplied to said cathode so as to vary the thermionic emission from said cathode.

3. In a mass spectrometer having means for bombarding a gas sample with ionizing particles to produce ions of substances present in said sample, means for separating according to their mass-to-charge ratios the ions thus produced into a plurality of ion beams and means for collecting ions of a beam, the combination which comprises a filament at which the ionizing particles originate by thermionic emission, means for supplying a potential to said filament, and means for varying said potential in a pulsating manner.

4. In a mass spectrometer according to claim 1 a combination which comprises a filament at which the ionizing particles originate by thermionic emission, a direct current source directed to said filament and means for supplying an alternating potential to said filament whereby the electron beam is caused to pulsate.

5. The method of mass spectrometry which comprises generating electrons with an electron emanating filament, supplying said filament with an alternating potential so as to vary the quantum of electrons produced thereby, forming said electrons into an electron beam, ionizing the sample to be analyzed by bombardment thereof with said beam of electrons of varying quantum, forming the resultant ions into an ion beam, causing ions of said ion beam having a predetermined mass-to-charge ratio to impinge on an ion collector, and measuring the pulsating charge appearing on said ion collector.

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The following references are of record in the file of this patent:

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Number	Name	Date
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