United States Patent [19]

Sakai et al.

[11] **3,784,814**

[45] **Jan. 8, 1974**

[54] **QUADRUPOLE MASS SPECTROMETER HAVING RESOLUTION VARIATION CAPABILITY**

[75] Inventors: **Tadashi Sakai; Masahiko Sakimura; Yoichi Ino,** all of Tokyo, Japan

[73] Assignee: **Nippon Electric Varian, Ltd.,** Tokyo, Japan

[22] Filed: **Mar. 12, 1971**

[21] Appl. No.: **123,687**

[30] **Foreign Application Priority Data**

Mar. 14, 1970 Japan 45/21704
July 18, 1970 Japan 45/63410

[52] **U.S. Cl.** ..... **250/41.9 DS**
[51] **Int. Cl.** **H01j 39/34**
[58] **Field of Search** ..... 250/41.9 DS

[56] **References Cited**

UNITED STATES PATENTS

2,950,389	8/1960	Paul et al.	250/41.9
3,280,325	10/1966	Brunnee et al.	250/41.9
3,321,623	5/1967	Brubaker et al.	250/41.9
3,413,463	11/1968	Brubaker	250/41.9

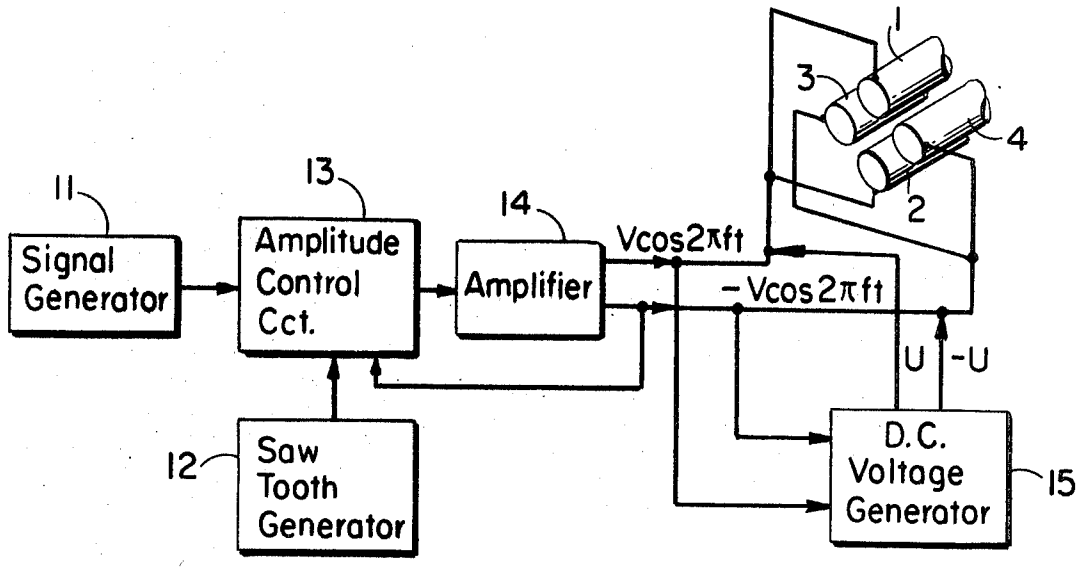
Primary Examiner—William F. Lindquist
Attorney—Sandoe, Hopgood and Calimafde

[57] **ABSTRACT**

A quadrupole mass spectrometer includes an ionization chamber, an ion detector, and a quadrupole structure having four electrodes extending therebetween. A d.c. voltage U and a high frequency voltage of amplitude V are linearly superimposed and are applied to the electrodes while maintaining the relationship $U=\alpha_M V - K$, where α M denotes a critical U/V ratio. This constrains the mass peaks of a spectrum to be of substantially uniform shape. Variation of the parameter K permits the spectrometer resolution to be varied.

In accordance with one aspect of the present invention, the d.c. voltage is maintained constant at values lower than the peak value of the stability curve for atomic hydrogen in a range of smaller values of the voltage amplitude V. The spectrum for atomic hydrogen can thereby be isolated.

5 Claims, 18 Drawing Figures



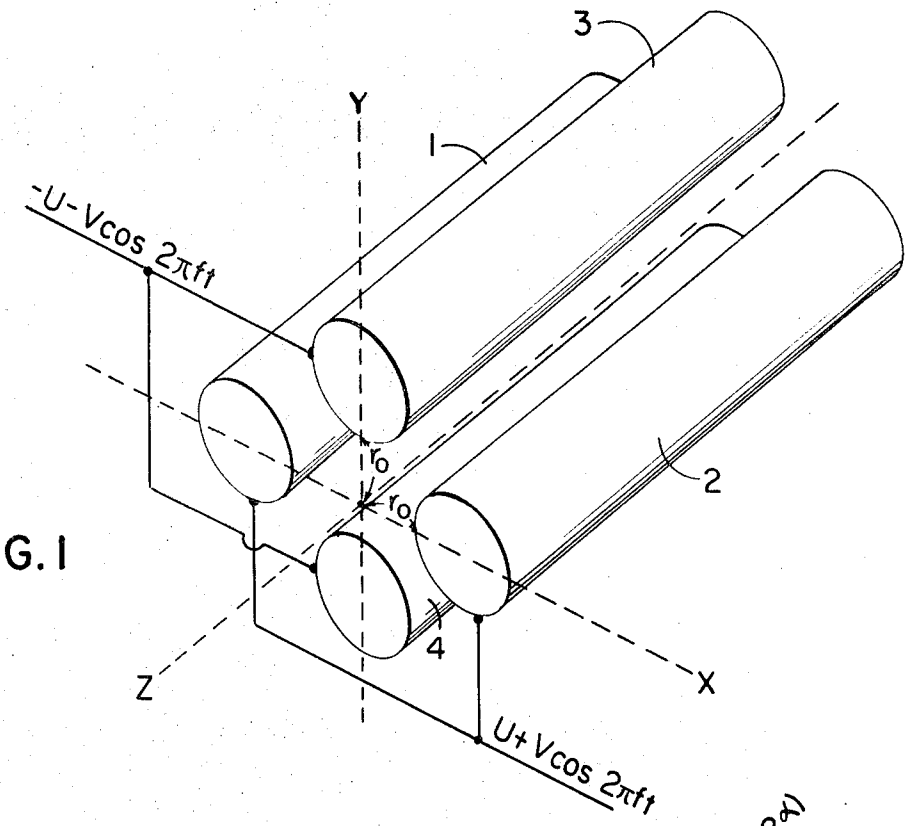


FIG. 1

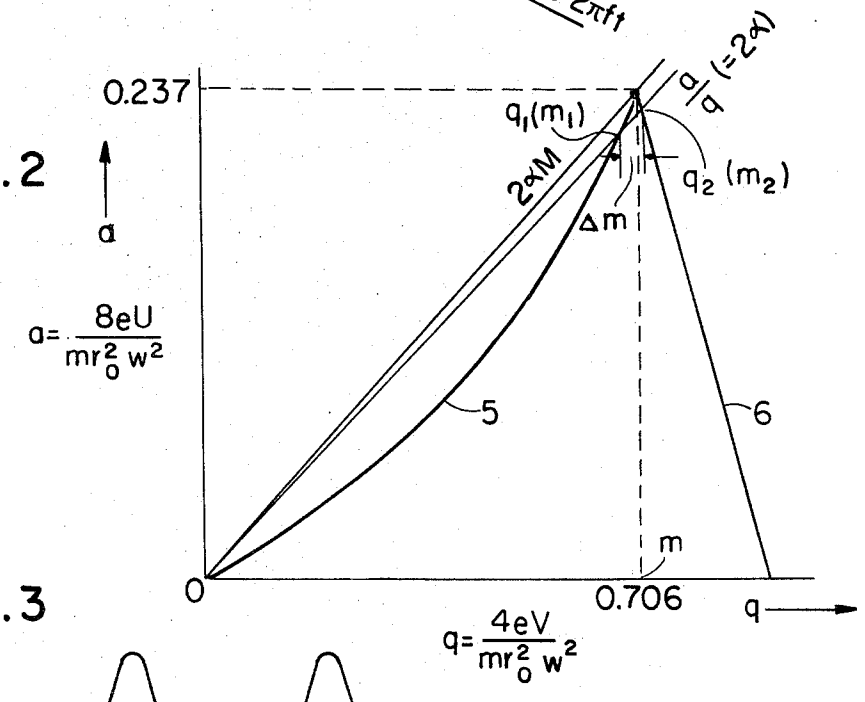


FIG. 2

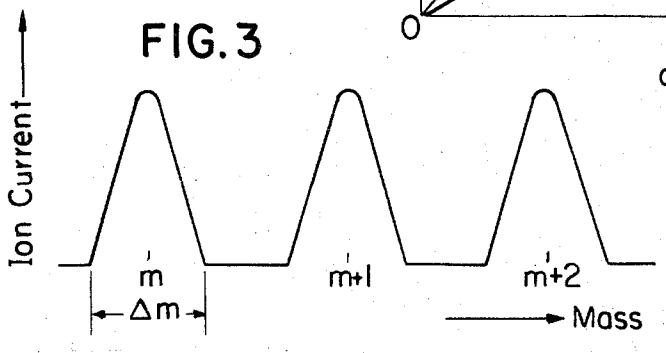
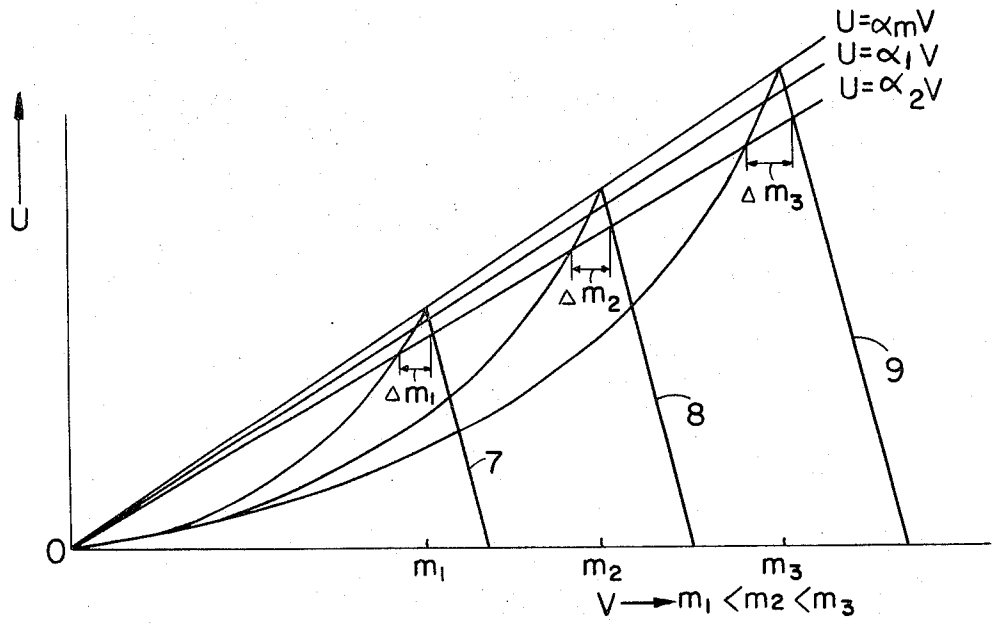


FIG. 3

INVENTORS
TADASHI SAKAI
MASAHIKO SAKIMURA
YOICHI INO
by
Sandoe, Hopgood & Calimafde
ATTORNEYS



(Prior Art)

FIG. 4

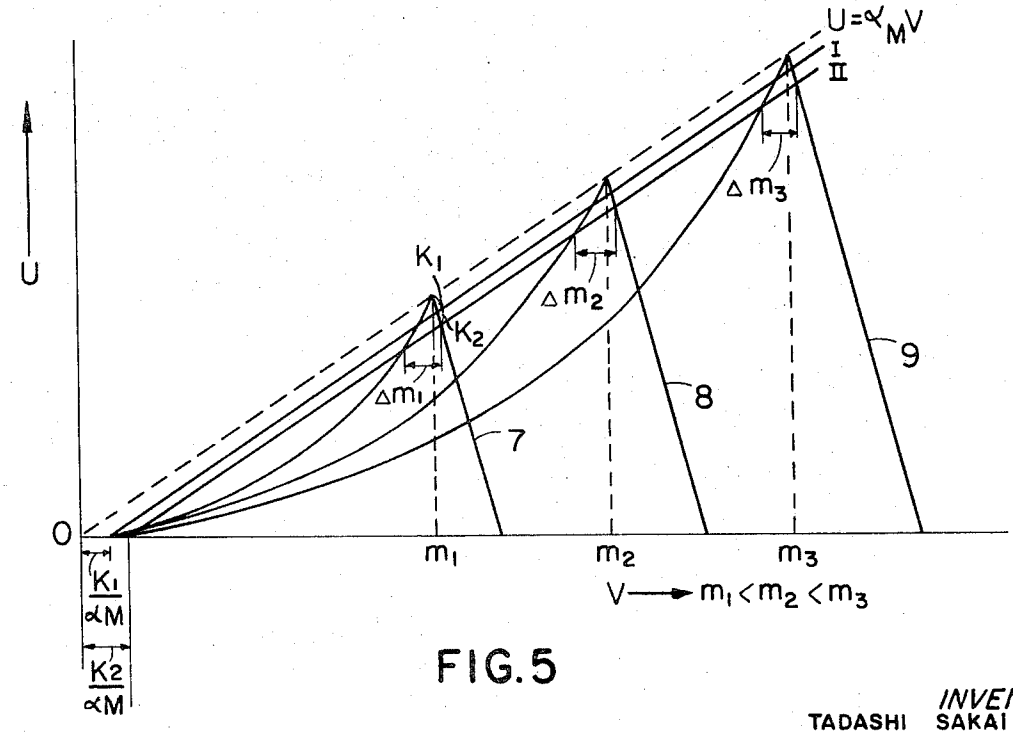


FIG. 5

INVENTORS
TADASHI SAKAI
MASAHIKO SAKIMURA
YOICHI INO
by
Sandoe, Hopgood & Calimafde
ATTORNEYS

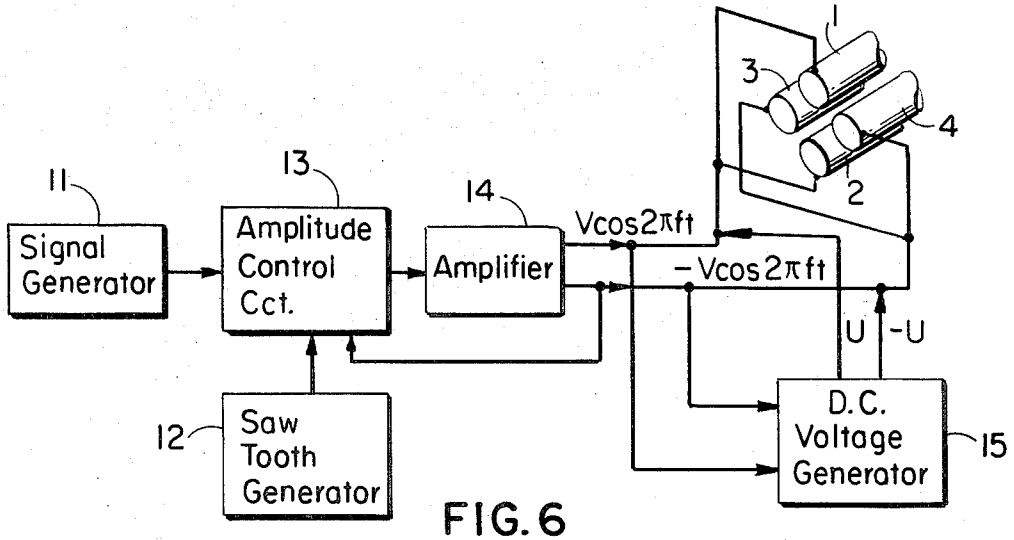


FIG. 6

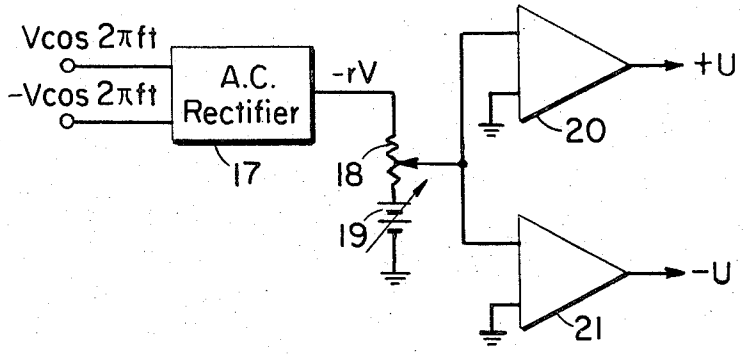


FIG. 7

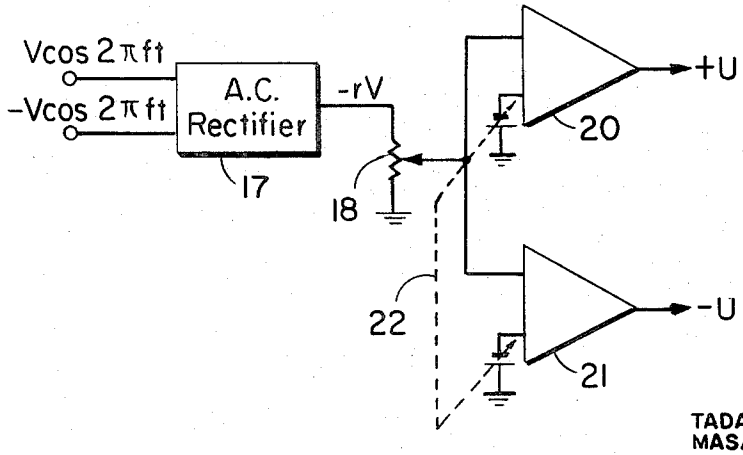


FIG. 8

INVENTORS
TADASHI SAKAI
MASAHIKO SAKIMURA
YOICHI INO
by
Sandoe, Hopgood & Calimafde
ATTORNEYS

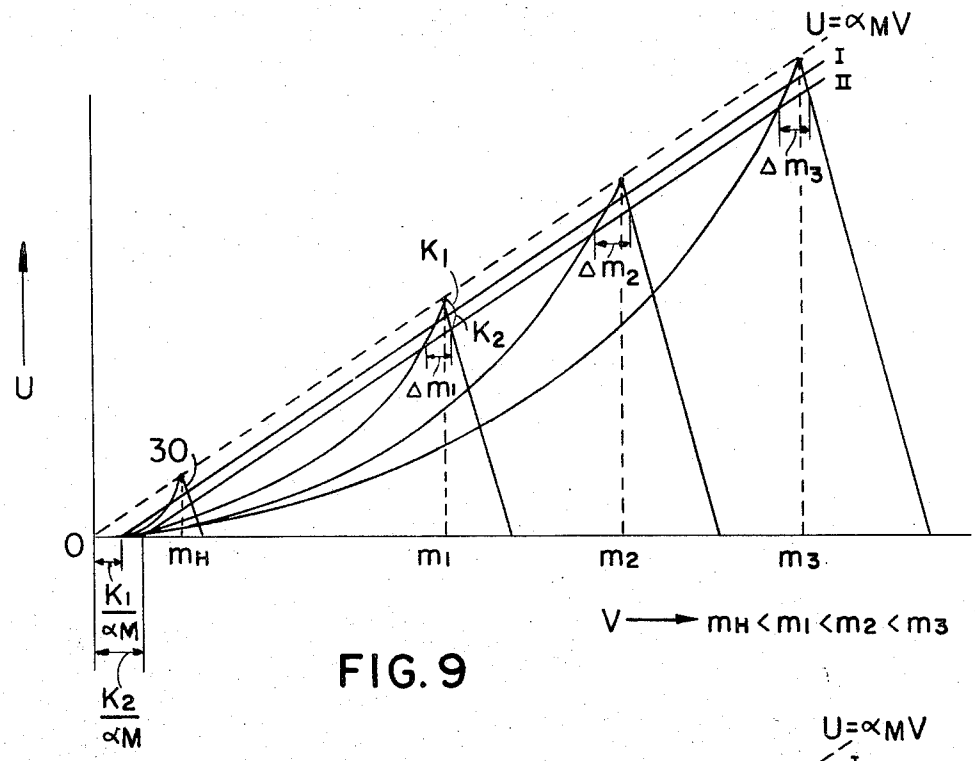


FIG. 9

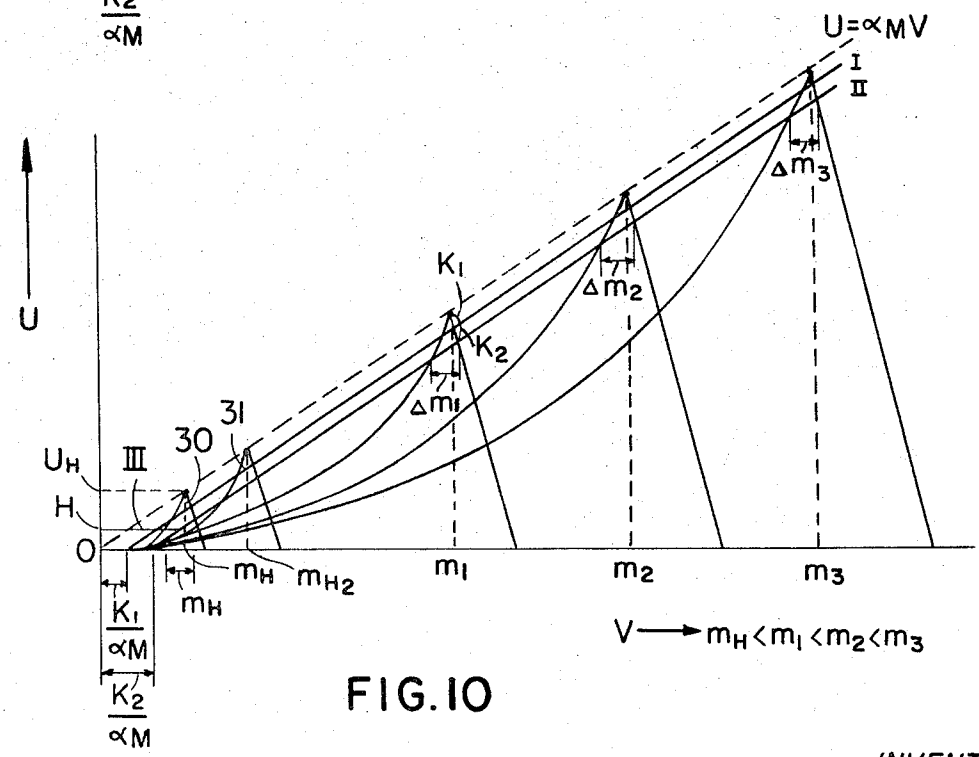


FIG. 10

INVENTORS
TADASHI SAKAI
MASAHIKO SAKIMURA
YOICHI INO
by
Sandoe, Hopgood & Calimafde
ATTORNEYS

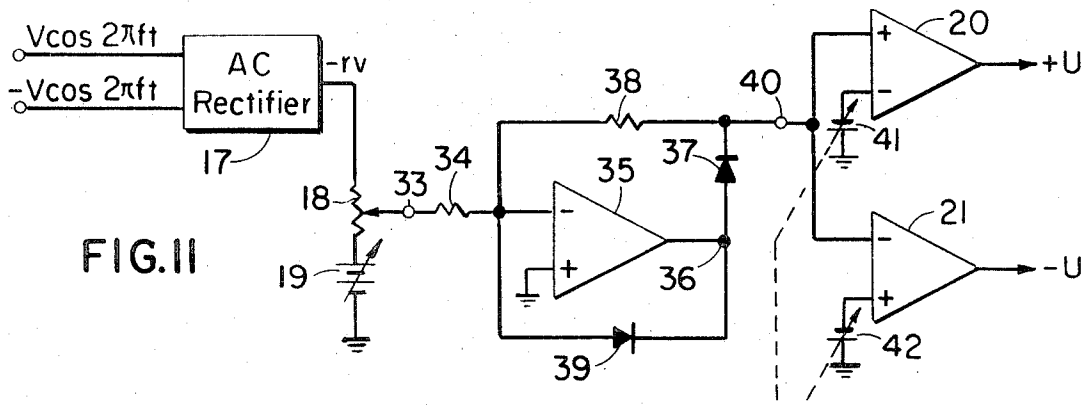


FIG.11

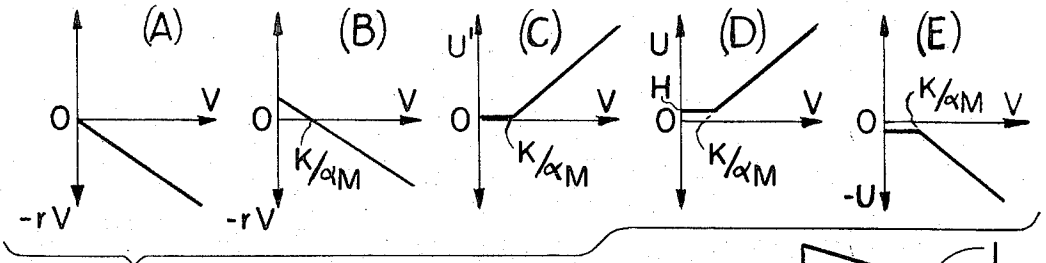


FIG.12

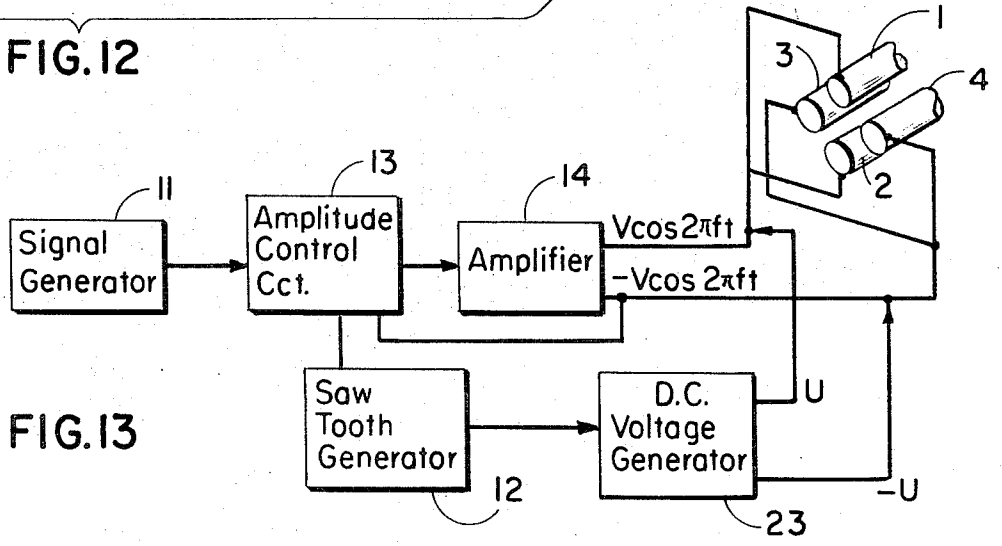


FIG.13

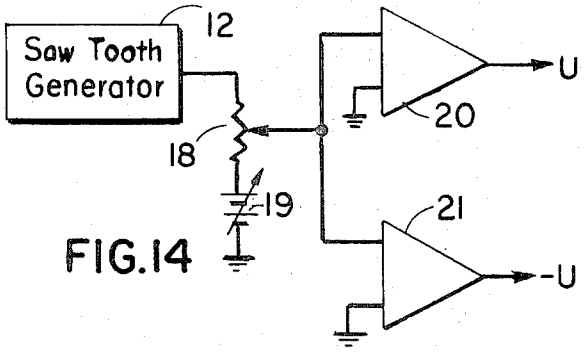


FIG.14

INVENTORS
TADASHI SAKAI
MASAHIKO SAKIMURA
YOICHI INO
by
Sandoe, Hopgood & Calimafde
ATTORNEYS

QUADRUPOLE MASS SPECTROMETER HAVING RESOLUTION VARIATION CAPABILITY

DISCLOSURE OF THE INVENTION

This invention relates to a system for rendering the resolution of a quadrupole mass spectrometer variable and, more specifically, to a spectrometer system wherein the sensitivity ratio for differing masses in the mass spectrum always remains unchanged, even when the resolution is varied.

A quadrupole mass spectrometer, used for determination of the composition of chemical substances, comprises an ionization embodiments a quadrupole electrode structure, and an ion detector. A chemical substance to be analyzed is introduced into the ionization chamber in its gaseous state, and is subjected to an electron bombardment for ionization. The resultant ions are directed to the quadrupole structure. In the quadrupole structure, only those of the ions which have a specific range of charge vs. mass ratio are permitted to pass therethrough. Those ions are collected by the ion detector for conversion into an electric current of a magnitude corresponding to the number of ions which have passed through the quadrupole structure.

The charge to mass ratio of the ions collected by the ion detector is determined by the amplitude and frequency of a high frequency voltage applied to the electrodes of the quadrupole structure. Hence, by changing the magnitude or frequency of the applied voltage, a display can be obtained on an oscillograph or recorder of the number of the ions detected as a function of mass.

In order to determine the composition of the substance from the mass spectrum thus displayed, it is necessary to compare such a spectrum against a reference spectrum obtained for a substance of known mass. During the comparison, it is desirable to have mass spectral peaks of an identical shape on the spectrum.

It has been the practice in providing a mass spectrum display to vary the voltage or frequency thereof over the whole mass range while maintaining constant the ratio of a d.c. voltage U to the amplitude V of the high frequency voltage applied to the quadrupole electrodes. This ratio is generally identified by the symbol α (alpha). This results in a spectrum having spectral peaks which have an increasing peak width (Δm) with an increase of mass (m), with the result that peaks of an identical shape cannot be obtained. Also, variation of the resolution results in a substantial change in the ion sensitivity ratio.

An improvement has been proposed which comprises structure for adjusting the voltage ratio α for matter of differing mass, as will be described later. This proposal involves practical difficulties in adjusting the voltage ratio α to a proper value. A change in the α-value gives rise to a change in the peak width Δm, for the same mass, making the composite system quantitatively unreliable.

It is therefore an object of the invention to provide a variable resolution system for a quadrupole mass spectrometer which allows a mass spectrum to be readily obtained with the peak width Δm being completely independent of the mass m.

It is another object of the invention to provide a variable resolution system for a quadrupole mass spectrometer wherein resolution may be varied while maintaining the ion sensitivity ratio unchanged for ions having different masses.

It is a further object of the invention to provide a variable resolution system for a quadrupole mass spectrometer which effects a clear distinction of the mass spectrum for hydrogen atoms vis-a-vis mass spectra for other substances.

In accordance with the above and other objects of the present invention, a quadrupole mass spectrometer comprises an ionization chamber, an ion detector and a quadrupole structure having four electrodes extending therebetween, wherein a d.c. voltage of magnitude U and the amplitude V of a high frequency voltage, both applied to the electrodes, are varied in a manner to satisfy the relationship $U = \alpha M V - K$. The spectrometer resolution is varied by changing the value of the parameter K. In this manner, the respective mass peaks on the spectrum are given a substantially identical shape.

For small values of V, or under the conditions $O < V \leqq K/\alpha_M - H$, the above-mentioned relationship is modified to $U = H$, and thus made independent of V. The value of the parameter H is fixed at a value smaller than the peak value of the stability curve for a hydrogen atom. This avoids the intersection of the stability curve for hydrogen molecules with the line represented by the relationship $U = H$ at small values of V. As a consequence, in the stability region of hydrogen atoms and for lesser values of V before reaching such a region, the stability region for hydrogen molecules lies below the boundary defined by the relationships $U = H$ and $U = \alpha_M V - K$, so that the spectrum for hydrogen atoms can be obtained in an isolated form.

The above-mentioned and other objects, features and advantages of the invention will become apparent from the following detailed description of the present system taken in conjunction with the accompanying drawings, in which:

FIG. 1 schematically shows a perspective view of a quadrupole structure of a quadrupole mass spectrometer to which the invention is applicable;

FIG. 2 shows a group of curves illustrating the conditions required to permit certain ions to pass through the quadrupole structure shown in FIG. 1;

FIG. 3 shows an example of a mass spectrum;

FIG. 4 shows a group of curves for describing a typical prior art system for varying spectrometer resolution;

FIG. 5 shows a group of similar curves illustrating the operation of the variable resolution system according to the invention;

FIG. 6 shows in block form a typical power supply unit which is applicable to the spectrometer shown in FIG. 1;

FIGS. 7 and 8 are circuit diagrams, partially in block diagram form, of first and second embodimetns incorporating the variable resolution system of the invention illustrated in FIG. 5 and applied to the power supply unit shown in FIG. 6;

FIG. 9 shows a group of similar curves for describing the operation of the improved variable resolution system in its lower mass number portion;

FIG. 10 shows another group of curves illustrating the variable resolution system of the invention;

FIG. 11 is a circuit diagram of a third embodiment incorporating the power supply to which the invention is applied;

FIGS. 12A through 12E are schematic diagrams illustrating the operation of the circuit shown in FIG. 11;

FIG. 13 is a block diagram of another typical power supply unit applicable to the spectrometer shown in FIG. 1; and

FIG. 14 is a schematic circuit diagram of a fourth embodiment incorporating the variable resolution system illustrated in FIG. 5 as applied to the power supply unit shown in FIG. 13.

Referring now to the drawings and, in particular to FIG. 1, the quadrupole structure for a quadrupole mass spectrometer comprises four solid cylindrical electrodes 1, 2, 3 and 4 disposed in parallel relationship with equi-angular intervals about, and spaced by a distance r_o from a center axis Z. Electrodes 1 and 2 are disposed on opposite sides with respect to the axis Z. Similarly, the other pair of electrodes 3 and 4 are disposed opposite to each other with the axis Z lying therebetween. Electrodes 1 and 2, and 3 and 4 are respectively connected in common and supplied with voltages $U + V \cos \omega t$ and $-U - V \cos \omega t$, respectively, where the character U denotes a d.c. voltage, and the character V, the amplitude of a high frequency sinusoidal voltage of angular frequency ω, when $\omega = 2\pi f$. The character t denotes time.

When an ion having a mass m and an electric charge e is generated incident along the center axis Z of the structure, it comes under the influence of the electric field formed in the quadrupole structure, and the components of force exerted on the ion can be represented as follows:

$$Fx = m\, d^2x/dt^2 = -e\,(U + V\cos\omega t)\,(2x/\gamma o^2 \quad (1)$$

$$Fy = m\, d^2y/dt^2 = -e\,(U + V\cos\omega t)\,(2y/\gamma o^2 \quad (2)$$

$$Fz = m\, d^2z/dt^2 = 0 \quad (3)$$

By using the following denotations:

$$\xi = \omega t/2, \quad a = 8eU/mro^2\,\omega^2,$$

$$q = 4eV/mro^2\,\omega^2$$

the above equations (1) and (2) can be converted as follows:

$$d^2x/d\xi^2 + (a + 2q\cos 2\xi)\,x = 0 \quad (4)$$

$$d^2y/d\xi^2 - (a - 2q\cos 2\xi)\,y = 0 \quad (5)$$

These equations (4) and (5) are known as Mathieu's equations, whose description is found in a number of literature references; see, for example, "Theory and Application of Mathieu Function" by N. McLachlam, published from Oxford University Press in 1947.

The solutions of the Mathieu equations (4) and (5) are divided into a periodic stable solution region and an astable solution region. Referring to FIG. 2, the stable solution region is represented by the interior of an approximate triangular curve having the abscissa as its base and formed thereon by two sides 5 and 6 with the apex located at the coordinates ($a = 0.237$, $q = 0.706$). This region represents the ranges of values of the parameters a and q for which an ion having a specific charge vs. mass ratio e/m can repeat its stable oscillation. The exterior of the approximate triangle represents the astable solution region, i.e., the ranges of values of the parameters a and q for which the motion of an ion is unstable with its amplitude rapidly increasing to result in a collision with one of the electrodes. In other words, ions that remain within the stable solution region can repeat stable oscillations and pass through the quadrupole structure, while all other ions are captured by the electrodes failing to pass therethrough.

For the purpose of further description, the ratio of the d.c. voltage to the amplitude V of the high frequency voltage will be hereafter denoted by α. Thus, $\alpha = U/V = a/2q$. This corresponds to a straight line in the $a - q$ plane, passing through the origin and having an inclination of 2α. Denoting the inclination of the line which passes through the apex of the approximate triangle shown in FIG. 2 by $2\alpha_M$, we have $2\alpha_M = 0.3356$, such α_M being referred to as critical ratio. When the inclination of 2α is less than $2\alpha M$, the straight line will intersect with the approximate triangle (stability curve) at points, the q-coordinates of which are designated by q_1 and q_2 respectively. It will be seen from FIG. 2 that as the value of α is varied, the difference between q_1 and q_2, and hence the difference Δm between m_1 and m_2, varies and becomes infinitesimal as α approaches αM. When α is made close to αM, the equivalent molecular weight M/n of an ion which can pass through the quadrupole structure is expressed in terms of practical units as follows:

$$M/n = V/7.219\, f^2 r_o^2 \quad (6)$$

where M denotes the molecular weight; n, charge number of the ion; V, the amplitude of the high frequency voltage in volts, f, the frequency in MHz and r_o the distance mentioned above in centimeters.

Usually, the frequency f is maintained constant while the amplitude V thereof is varied to allow passage through the quadrupole structure of ions having successively changing masses, thereby producing on a display unit a depiction of an ion current as a function of mass. An example of a mass spectrum thus obtained is shown in FIG. 3. The abscissa in the spectrum diagram indicates mass (or the amplitude V), and the ordinate indicates ion current.

In general, the resolution of a mass spectrometer is represented by $m/\Delta m$, where m denotes the mass number at the center of a mass peak and Δm, the width of the peak as shown in FIG. 3. The resolution $m/\Delta m$ of a quadrupole mass spectrometer for the voltage ratio α close to the critical ratio αM is expressed as follows:

$$m/\Delta m = 0.75/1 - (\alpha/\alpha M) \quad (7)$$

as discussed by W. Paul et al. in the articles published in *Zeitschrift für Physik*, Vol. 140, pp. 262–273 (1955) and Vol. 152, pp. 143–182 (1958).

The conventional method varies the high frequency voltage V while maintaining the voltage ratio α unchanged in order to obtain a mass spectrum. As will be evident from the equation (7), this results in a constant resolution $m/\Delta m$ and an increasing peak width Δm with an increase in the mass m of ions. In other words, the

peaks obtained do not have an identical shape. Under this condition, a change in resolution results in a considerable change in the ion sensitivity ratio.

Another conventional method adjusts the value of the voltage ratio α for each of the masses. Referring to FIG. 4, there is shown the stability diagram depicted in the a–q plane in FIG. 2 as transformed on the U–V plane. As shown, the stable regions for ions having masses $m1$, $m2$ and $m3$, permitting these ions to pass through the quadrupole structure are represented by the approximate triangles 7, 8 and 9, respectively, which are similar with respect to each other, and which have the V-axis or abscissa as their base. By drawing straight lines $U = \alpha/V$ and $U = \alpha_2 V$ in FIG. 4, it will be seen that the segments Δm intercepted by intersection of these straight lines with the approximate triangles will increase with an increase in the mass m and also vary with the variation of the value of α even for the same mass.

It has heretofore been proposed in the prior art to vary the voltage ratio α to produce an equal range of Δm for all mass. However, this technique is impracticable because of the practical difficulties involved in the adjustment of the voltage ratio α to a proper value. It is extremely difficult, if not impossible, when the spectrum of a substance having an unknown mass is to be compared with the spectrum of a substance having a known mass, to establish an equal value of α for both of these spectra. If the values of α differ from each other, the values of Δm will be different even for the same mass number with resulting difference in the detected ion currents. This fact is primarily responsible for the general belief that a quadrupole mass spectrometer is not effective for quantitative determinations.

The variable resolution system according to the present invention will now be described with reference to FIG. 5 in which the same stability curves 7, 8 and 9 for masses $m1$, $m2$ and $m3$ are shown as for the case of FIG. 4, with their apices being joined by a straight line having an inclination $\alpha_M = U/V$. Another straight line is drawn in parallel with the α_M line and intersects the U-axis at K_1 below the origin (this being designated as straight line I). A further straight line (straight line II) is drawn parallel to the α_M line and downwardly shifted by K2 therefrom. It will be seen from the drawing that the length along the V-axis of those segments of the straight line I or II which are intercepted by the stability curves 7, 8 and 9, viz., the values of $\Delta m1$, $\Delta m2$ and $\Delta m3$ as obtained from the straight line II, for example, become equal to one another as long as the straight line I or II intersects the stability curves adjacent to their peak points. In other words, the value of Δm becomes constant, independent of ion mass, when U and V are varied in a manner satisfying the relationship represented by the straight line I or II, and its width is determined by the K-value alone; that is, the value of a d.c. voltage opposite in polarity to, and added to the d.c. voltage U.

A mathematical analysis of the foregoing will be given below. Denoting resolution in terms of U and V by substituting for α in the form $\alpha = U/V$ in the equation (7),

$$m/\Delta m = 0.75/(1 - 1/\alpha M, U/V) \tag{8}$$

The straight line I or II shown in FIG. 5 can be expressed as follows:

$$U/V = \alpha M - K/V \tag{9}$$

Substitution of the equation (9) into the equation (8) and solving the result for Δm leads to the following expression:

$$\Delta m = K/0.75\ \alpha M \cdot m/V \tag{10}$$

Representing Δm in terms of practical units by using the equation (6).

$$\Delta M = K\ (\text{volts})/0.9085\ f^2\ (\text{MHz})\ ro^2\ (\text{cm}) \tag{11}$$

where ΔM denotes Δm when expressed in terms of practical units. As will be apparent from equation (11), when the frequency f and the inter electrode spacing ro are both fixed, ΔM depends on K-value alone, making itself completely independent of the equivalent molecular weight M/n.

The variable resolution system of the invention is based on the foregoing theory, and specifically, it operates to vary the d.c. voltage U and the high frequency voltage V in a manner to comply with the relation presented in the equation (9). The practical circuit to accomplish the relation of the equation (9) is one in which the d.c. voltage U varies with the high frequency voltage V in the following manner:

$$U = \beta V - K \tag{12}$$

where β is a parameter, and in which both the parameters β and K are independently variable. The relation presented in the equation (9) is obtained by establishing the β-value substantially at the critical ratio αM.

Before proceeding with the description of such circuit, a typical control power supply circuit for driving a quadrupole mass spectrometer will be described with reference to FIG. 6. One typical example of such control circuit comprises a signal generator 11 for generating a high frequency voltage of frequency f; a generator 12 for producing a saw-tooth wave voltage; an amplitude conrol circuit 13 operable to control the amplitude of the high frequency voltage in accordance with the saw-tooth voltage; a high frequency amplifier 14 for amplifying the output of the amplitude control 13 and producing voltages given by V cos 2 π ft and − V cos 2 ft ; a d.c. voltage generator 15 for deriving d.c. voltages U and -U responsive to the output from the amplifier 14; and circuit connection apparatus for linearly superimposing (adding) the d.c. voltages on the high frequency voltages and applying the superimposed voltages to the electrodes 1, 2 and 3, 4 of the quadrupole structure, respectively.

A first embodiment of the circuit for constructing the variable resolution system of the invention comprises an improvement of the d.c. voltage generator 15 of the circuit shown in FIG. 6. Thus, as illustrated in FIG. 7 by way of example, the first embodiment therefor comprises: an a.c. voltage rectifier 17 for providing rectification of V cos 2π ft and $-V$ cos 2π ft to produce a d.c. voltage -rV proportional to the amplitude V, where r denotes a constant; a variable resistor (potentiometer)

18 for providing voltage division of the d.c. voltage; a power source 19 for producing a variable d.c. voltage which has a polarity opposite to the aforesaid d.c. voltage and which biases the variable resistor 18; and a pair of differential d.c. amplifiers 20 and 21 for producing d.c. voltages U and −U having the same magnitude controlled by the divided d.c. voltage and having opposite polarities. Variation of the movable point on the resistor 18 in this circuit results in a change in the value of β in the equation (12) and variation of the variable d.c. power source 19 results in a change in the value of K.

The variable d.c. voltage source 19 effecting a change of K-value may be connected in a different position. Thus, as shown in FIG. 8, one terminal of the variable resistor 18 may be grounded directly, with one of the inputs of the respective differential d.c. amplifiers 20 and 21 being connected with a variable d.c. voltage source 22 rather than being connected to the ground. The voltage sources 22 for the both amplifiers 20 and 21 are linked together for interlocked variation. It will be evident that the circuit of FIG. 8 effects a similar function as the dircuit of FIG. 7.

It should be understood that the relation of the equation (12) remains effective when the output from the rectifier 17 is taken out with positive polarity by supplying the output from the variable d.c. voltage source 19 or 22 having a negative polarity.

In this manner, the invention maintains the relationship $U = \alpha_M V - K$ as the voltage V is varied to allow successive passage through the quadrupole structure of ions having different masses for the purpose of mass spectroscopy. However, it will be noted that for smaller values of the voltage V, $U = O$, so that in such an area, all of the ion mass will pass through the quadrupole structure, thereby rendering it impossible to obtain isolated spectra of lower mass numbers. Thus, the stable region for atomic hydrogen having the lowest mass number, or m_H=1, exists at a very small value of the voltage V, as indicated by an approximate triangle 30 in FIG. 9. The straight line II starts from inside the stable region 30 for atomic hydrogen and passes thereacross with an increase of the voltage V without thereafter again crossing the stability curve 30. Thus, for V which satisfies $O<V \leqq K_2/\alpha M$, $U = O$, all of the ions having the masses m_H, $m1$, $m2$ and $m3$ will pass through the quadrupole structure. Thereafter, an increase in the voltage V produces astable regions for larger masses to successively inhibit passage of corresponding ions, subsequently followed by passage of atomic hydrogen ions. However, since a further increase of the voltage V does not produce another intersection with the stability curve for atomic hydrogen to thereby delineate the region of its passage, it is impossible to take out only atomic hydrogen ions in the form of its mass spectrum.

Considering now the straight line I, all of the ions in the range defined by the inequality: $O<V \leqq K_1/\alpha M$ pass through the electrodes 1–4. With an increase in the voltage V beyond this range, all of the ions once experience an astable region, and then there appears stable region 30 for atomic hydrogen. At this time, the straight line I provides the stable region for only atomic hydrogen, and therefore atomic hydrogen ions can be taken out in the form of a mass spectrum.

While the detection sensitivity for the ion current increases with the magnitude of Δm, a choice of a value for Δm which is equal to or greater than unity results in a partial overlapping of the mass spectra for the masses m and $m+1$. Thus for the practical use of a mass spectrometer, the value of Δm must not be greater than unity. It has been confirmed by experiments that when K is varied to produce a value of Δm in excess of 0.5, there resulted a tendency toward the situation exhibited by the straight line II, described above in connection with FIG. 9, i.e., the mass spectrum for atomic hydrogen ions overlaps on its lower mass side with the mass spectra of other ions.

In order to obtain an isolated spectrum for atomic hydrogen with a relatively large value of Δm and without upsetting the desirable identity of Δm for differing mass, a technique depicted in FIG. 10 may be used to establish a relation between U and V. Thus, for a small value of V within the range defined by the inequality $O<V \leqq K_2/\alpha M-H$, a straight line III defined by $U = H$ is used, while the straight line II or $U = \alpha_M V - K_2$ is used for a value of V greater than $K_2/\alpha M-H$. The value of the parameter H is fixed at a value lower than the peak value U_H of the stability curve 30 for atomic hydrogen and so as to avoid the intersection in the range $O<V \leqq K_2/\alpha M-H$ between the line U = H and the stability curve 31 for hydrogen molecules H_2 having a mass number that exceeds that of atomic hydrogen by one. It will be noted that $K_2/\alpha M-H$ represents the value of V at the intersection of the straight lines II and III.

With this arrangement, for small values of V before the intersection of the straight line III with the stability curve 30 for atomic hydrogen, all of the ions m_H, m_{H2}, $m1$, $m2$ and $m3$ are in their astable region and hence cannot pass through the quadrupole structure. With an increase of the V-value into the stability region 30 for atomic hydrogen, only atomic hydrogen ions are allowed to pass through the quadrupole structure. The straight line III is continued by the straight line II before entering the stable region 31 for the next higher mass or $m_H + 1$, i.e., molecular hydrogen. After going through the stable region 30 for atomic hydrogen, there once appears an astable region for all of the ions before entering the stable region 31 for hydrogen molecules, so that the mass spectrum for atomic hydrogen can be detected in an isolated form. The adjustment of H-value allows the peak width Δm_H of atomic hydrogen to assume the same value as the peak width of other ions, $\Delta m1$, $\Delta m2$ or $\Delta m3$. Variation of K-value with H-value fixed results in a variation of Δm_H in the similar manner to the peak widths of the masses $m1$, $m2$ and $m3$, thus making it possible to vary the width Δm of the mass spectra while maintaining Δm_H at the same value as the peak width Δm of other ions.

The variation of the voltages U and V in the manner depicted by the straight lines II and III in FIG. 10 may be achieved by a circuit shown in FIG. 11, which comprises a modification of the circuit shown in FIG. 7 wherein the voltage divider terminal 33 of the variable resistor 18 is connected to one of the inputs of a high gain differential d.c. amplifier 35 through a resistor 34, rather than connecting the terminal 33 directly to the aforesaid differential amplifiers 20 and 21. The d.c. amplifier 35 has its other input connected to the ground, and the output 36 thereof is connected to the inverting input through a rectifier 37 and a resistor 38. The resistors 34 and 38 may have an equal resistance. The inverting input and output 36 of the amplifier 35 are interconnected by a rectifier 39 which has approximately the same characteristics as the rectifier 37.

The output terminal **36** of amplifier **35** is connected with the anode of the rectifier **37** and the cathode of the rectifier **39**. The junction **40** between the rectifier **37** and the resistor **38** is connected to one of the inputs of the respective differential amplifiers **20** and **21**. These differential amplifiers **20** and **21** have their other inputs connected with variable d.c. voltage sources **41** and **42**, respectively, for supply of the above-mentioned parameter H therefrom. Variation of the outputs from these d.c. sources **41** and **42** can be effected by interlocked (ganged) operation.

FIG. **12A** shows the relation of the output, $-rV$, from the rectifier **17** with respect to the voltage V, the output being a straight line passing through the origin O. This output, $-rV$, is superimposed on the positive voltage supplied from the d.c. source **19** to yield at the divider terminal **33** a voltage, which is shown by a straight line crossing the V-axis at ($V = K/\alpha M$, $U = O$), as shown in FIG. **12B**.

For a value of V less than $K/\alpha M$, or for the positive range of U, the differential d.c. amplifier **35** produces a negative output at the terminal **36**, thereby bringing the rectifier **37** into a non-conductive state while the rectifier **39** is rendered conductive, thereby maintaining the terminal **40** substantially at ground potential. When V exceeds $K/\alpha M$ and U becomes negative, the amplifier **35** provides a positive output to render the rectifier **37** conductive while the rectifier **39** becomes non-conductive. Accordingly, there is produced at the output terminal **40** an output voltage which corresponds in magnitude (but of opposite polarity) to the voltage at the divider terminal **33**. Thus, the input voltage U′ to the amplifiers **20** and **21**, appearing at the terminal **40**, will have a relationship with respect to the voltage V as represented by a straight line, shown in FIG. **12C**, which begins to rise from the point given by $V = K/\alpha_M$.

The voltage U′ at the terminal **40** forms one of the inputs to the differential amplifiers **20** and **21**, the other input of which is supplied with an output $-H$ from d.c. sources **41** and **42**, respectively. Hence, for smaller values of V, outputs H and $-H$ are obtained, and for a value of V in excess of $K/\alpha_M - H$, positive and negative outputs corresponding to the input U′ are obtained, the resultant outputs being shown in FIGS. **12D** and **12E**. These are the requisite d.c. outputs U and $-U$.

In operation, K is set to zero by reducing the output voltages from the d.c. sources **19**, **41** and **42** to zero. Under this condition, the high frequency voltage V is swept at high speed while watching the mass spectra, with the movable point on the variable resistor **18** varied from sweep to sweep to thereby change the relationship $U = \beta V$. In this manner, a point is determined for the position of the movable point on the variable resistor **18** at which all of the mass spectra just disappear or appear, whereupon the adjustment of the variable resistor **18** is fixed, yielding $\beta = \alpha_M$ (= 0.1678). Then the d.c. source **19** is adjusted to vary the K-value to establish the peak width Δm. Subsequently, the d.c. sources **41** and **42** are adjusted to vary the H-value and fix it at a level such that the mass spectrum for atomic hydrogen can be obtained ian isolated form, desirably with its peak width Δm_H being chosen equal to the peak width $\Delta m1$, $\Delta m2$ and so on of the other mass spectra.

In the foregoing description, the d.c. voltage U has been derived by rectifying the high frequency voltage. It may be likewise obtained from the saw-tooth voltage generator **12** shown in FIG. **6**. One such example is shown in FIG. **13**, in which there is provided a d.c. voltage generator **23** which is driven by the output from the sawtooth voltage generator **12** to produce d.c. voltages U and $-U$ for combining with the high frequency voltages. As explained above regarding the application of the variable resolution system described in connection with FIG. **5**, the output of the saw-tooth voltage generator **12** may be directly supplied to the variable resistor **18**, eliminating the rectifier **17** from the circuit shown in FIG. **7**. Similarly, the output from the saw-tooth voltage generator **12** may be directly coupled to the variable resistor **18** shown in the circuit of FIG. **8** or FIG. **11**.

Although in the above description the inclination α has been established first, followed by adjustment of the voltage K and the voltage H successively to obtain the U–V voltage relationship illustrated in FIGS. **12D** and **12E**, the circuits which establish these three parameters may be varied in any desired order.

Thus it will be understood that according to the variable resolution system of the invention, a desired value of peak width Δm can be established for the masses by selection of a suitable magnitude for the d.c. voltage K, and this value of Δm remains constant for all of the differing subject masses. Stated differently, all the mass peaks have the same shape and the ion sensitivity ratio for the respective masses is therefore kept unchanged, even when the resolution is varied. In particular, the peak width Δm for all mass can be made relatively large while providing for the mass spectrum for the lowest mass, that is, atomic hydrogen, to be obtained in an isolated form by establishing a proper value for the d.c. voltage H. Further, there is the capability of maintaining the peak width Δm_H for atomic hydrogen the same as the peak width for matter of other mass. Also for atomic hydrogen, variation of the d.c. voltage K results in a change for the width of the mass spectrum for atomic hydrogen in the same way as the width of other mass spectra, whereby it is possible to achieve the same constant sensitivity ratio for atomic hydrogen having a mass number of unity as for other mass numbers when apparatus resolution is varied. Therefore, the variable resolution system according to the invention greatly enhances the quantitative determination capability of a quardupole mass spectrometer, compared with prior art apparatus.

While several embodiments of the invention have been described above, various modifications thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the present invention.

What is claimed is:

1. A variable resolution system for a quadrupole mass spectrometer comprising an ionization chamber, an ion detector and a quadrupole structure having four electrodes extending between said detector and chamber; said electrodes being symmetrically disposed with respect to the axis thereof; means for electrically connecting alternate ones of said electrodes together to form two electrode pairs; said electrode pairs having direct current potentials of an opposite polarity applied thereto; wherein the improvement comprises: a variable d.c. source for supplying a d.c. voltage of a magnitude U to said electrodes of said quadrupole structure, a high frequency sinusoidal voltage source for supplying a high frequency voltage of variable amplitude V to

said electrodes, and means for varying the d.c. voltage U and the amplitude V of the high frequency voltage in a manner satisfying the relationship $U = \alpha_M V - K$, where α_M denotes a critical U/V ratio at the limit of stable spectrometer response, and K denotes a constant determining the peak width Δm of a mass spectrum determined by said spectrometer; whereby all the mass peaks of the spectrum are characterized by a substantially identical shape.

2. A variable resolution system for a quadrupole mass spectrometer comprising an ionization chamber, an ion detector and a quadrupole structure having four electrodes extending between said detector and chamber; said electrodes being symmetrically disposed with respect to the axis thereof; means for electrically connecting alternate ones of said electrodes together to form two electrode pairs; said electrode pairs having direct current potentials of an opposite polarity applied thereto; wherein the improvement comprises: a source of high frequency sinusoidal voltage of variable amplitude V; means for producing a d.c. voltage proportional to the amplitude V of the high frequency voltage; variable resistor means forming a voltage divider for said d.c. voltage and for providing a second d.c. voltage of a value $\alpha_M V$, where α_M denotes a critical U/V ratio at the limit of stable spectrometer response; means for biasing said second d.c. voltage of magnitude $\alpha_M V$ with a third d.c. voltage of magnitude $-K$, where K denotes a constant which determines the peak width Δm of a mass spectrum; and means for applying the high frequency voltage and the resultant d.c. voltage of magnitude $\alpha_M V - K$ to said electrodes of said quadrupole structure.

3. A variable resolution system for a quadrupole mass spectrometer comprising an ionization chamber, an ion detector and a quadrupole structure having four electrodes extending between said detector and chamber; said electrodes being symmetrically disposed with respect to the axis thereof; means for electrically connecting alternate ones of said electrodes together to form two electrode pairs; said electrode pairs having direct current potentials of an opposite polarity applied thereto; wherein the improvement comprises: a source of high frequency sinusoidal voltage of variable amplitude V for application to said electrodes of said quadrupole structure; means for generating a d.c. voltage U for connection to said electrodes which remains at a constant value of H for values of V, wherein $0 < V \leq K/\alpha_M - H$ and which varies in accordance with the equation $U = \alpha_M V - K$ for a value of V in excess of $K/\alpha_M - H$, where α_M denotes a critical U/V ratio at the limit of stable spectrometer response and K denotes a constant determining the peak width Δm of a mass spectrum determined by said spectrometer; means for varying the parameter K to vary peak width; and means for varying the parameter H to establish said parameter H at a value smaller than the peak value of the stable spectral response for atomic hydrogen.

4. A variable resolution system for a quadrupole mass spectrometer comprising an ionization chamber, an ion detector and a quadrupole structure having four electrodes extending between said detector and chamber; said electrodes being symmetrically disposed with respect to the axis thereof; means for electrically connecting alternate ones of said electrodes together to form two electrode pairs; said electrode pairs having direct current potentials of an opposite polarity applied thereto; wherein the improvement comprises: a source of high frequency sinusoidal voltage of the variable amplitude V; means for generating a d.c. voltage proportional to the amplitude V of said high frequency voltage; voltage divider means for deriving, by voltage division of said d.c. voltage, a second d.c. voltage of a value $\alpha_M V$, where α_M denotes a critical U/V ratio at the limit of stable spectrometer response, means for biasing said second d.c. voltage with a third d.c. voltage of a value K, where K denotes a parameter that determines the peak width Δm of a spectrum; means for rendering said biased d.c. voltage $\alpha_M V - K$ equal to a null output for a value of V between zero and K/α_M; means for comparing the output from said rendering means with a constant voltage H and choosing the greater of the two as its output U, the value of H being chosen less than the peak value of the stable spectral response for atomic hydrogen and means for applying said output U and said high frequency voltage to the electrodes of the quadrupole structure.

5. A variable resolution system according to claim 4, further including means for varying the magnitude of the voltage H.

* * * * *