

Nov. 8, 1966

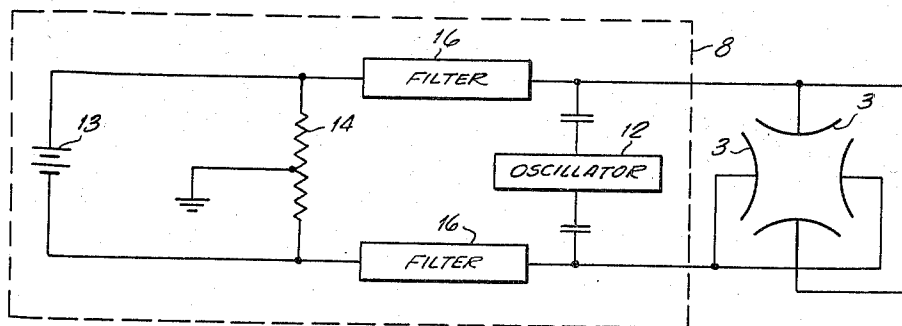
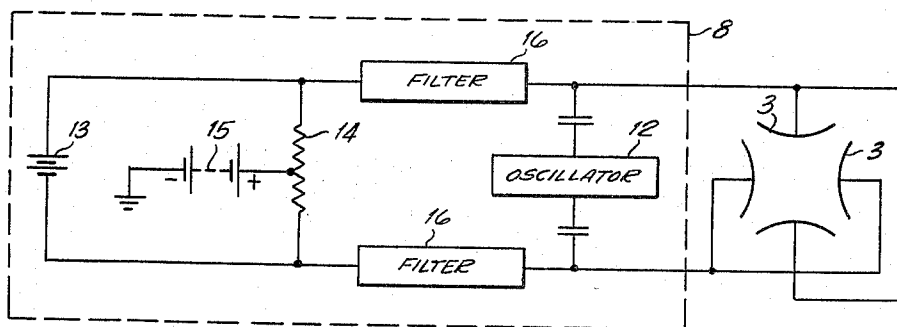
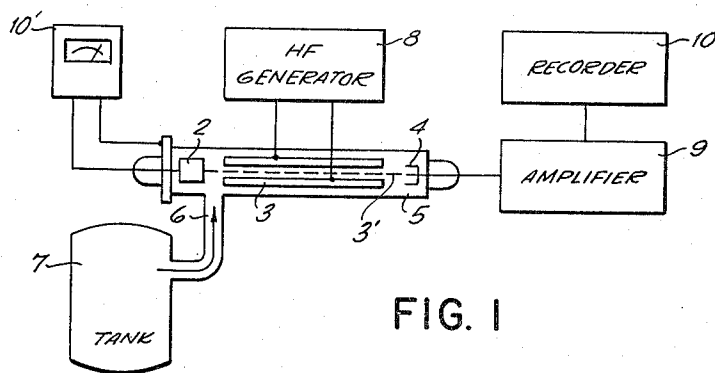
U. VON ZAHN

3,284,629

MASS FILTER HAVING AN ION SOURCE STRUCTURE WITH PRESELECTED
RELATIVE POTENTIALS APPLIED THERETO

Filed Feb. 4, 1963

3 Sheets-Sheet 1



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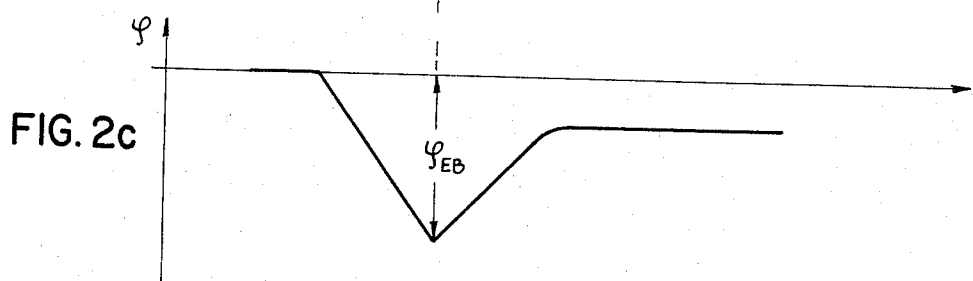
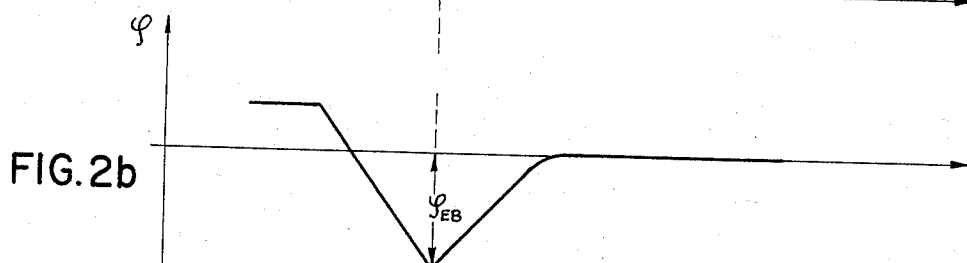
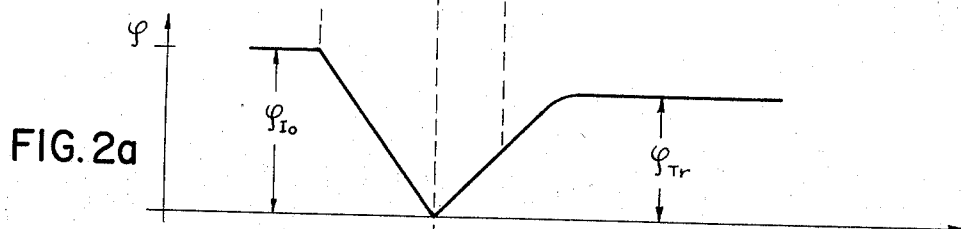
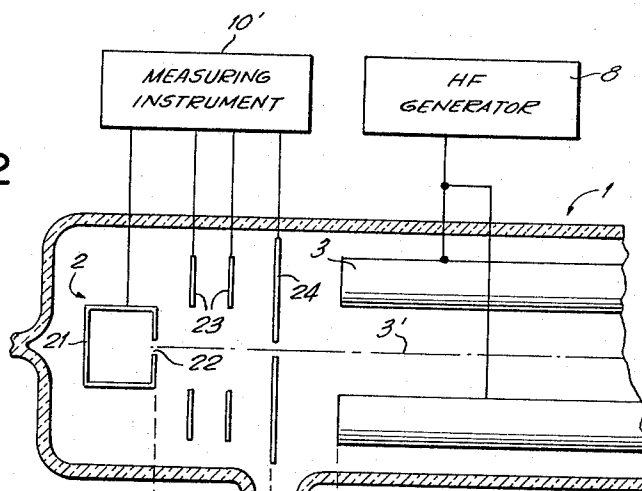
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FIG. 2



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3 Sheets-Sheet 3

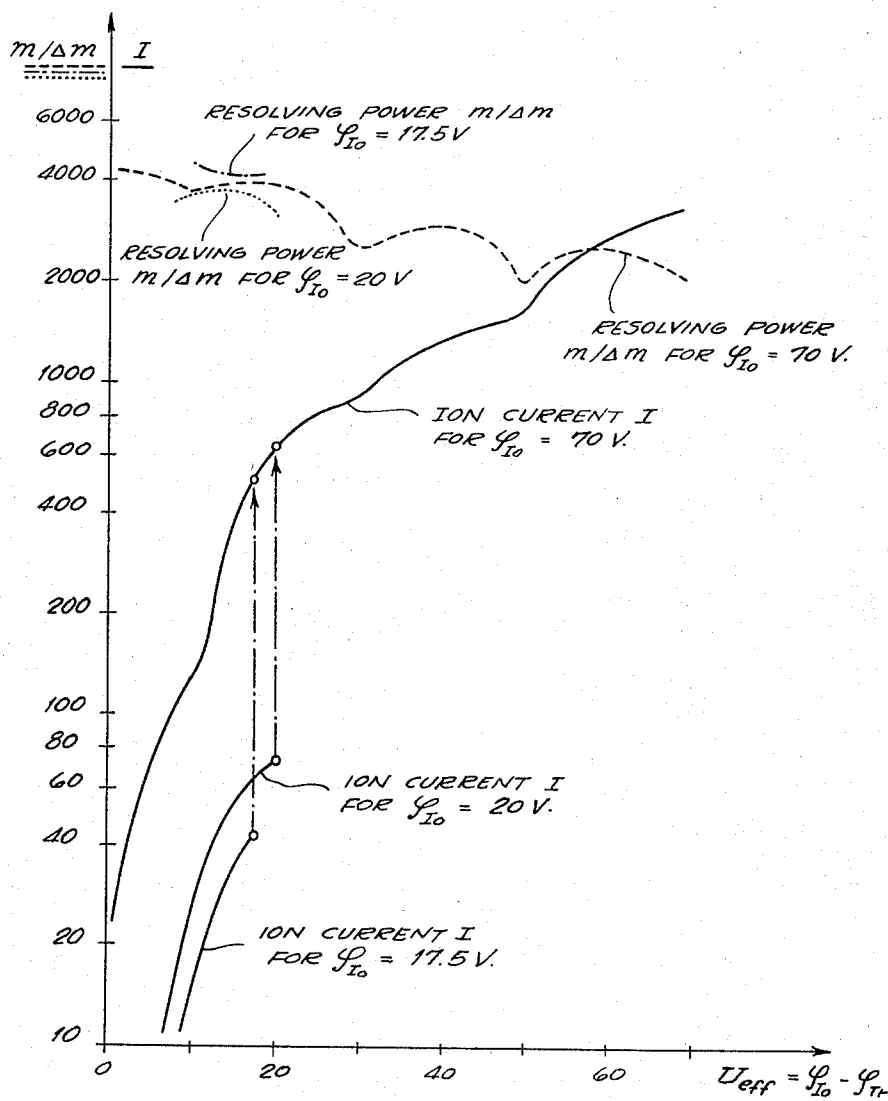


FIG. 4

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MASS FILTER HAVING AN ION SOURCE STRUCTURE WITH PRESELECTED RELATIVE POTENTIALS APPLIED THERETO

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3 Claims. (Cl. 250-41.9)

My invention relates to the separation of ions of respectively different charge-to-mass ratios in periodically varying electric fields whose potential is a square function of the space coordinates. Such mass separation, disclosed in Patent 2,939,952, requires shooting the ions into an electric periodic field the potential $\varphi(x, y, z)$ of which is a square function of the space coordinates x, y, z defined by the general equation $\varphi = f(t)(\alpha x^2 + \beta y^2 - \gamma z^2)$ wherein $f(t)$ is an arbitrary periodic function of time t .

In a field of this type the travelling ions may perform two kinds of motion. In one kind they follow stable paths, that is, the ions oscillate about the center of symmetry of the field with amplitudes not exceeding a maximum value which is different for each ion. In the other kind of motion, the amplitudes increase with time so that, after a sufficient dwell of travel time in the field, the corpuscles impinge upon the field-producing electrodes or upon other neighboring components of the device and are thus separated. They then follow instable paths.

With a given field, it depends only upon the specific electric charge or charge-to-mass ratio e/m , of an ion whether the ion will thus travel along a stable or instable path. For a predetermined field there are stable or instable ranges for ions having the specific electric charge e/m . The location and width of these ranges may be varied within very broad limits solely by variation of the amplitude, the frequency or the wave shape of the field-producing voltages.

It follows that the separation of instable ions requires a certain minimum time during which the ions must remain in the analyzer field. It has been found, however, that it is not the absolute dwell time which is decisive for the quality of separation, the so-called resolving power of such fields, but rather the number n of cycle periods of the function $f(t)$ during which the ions remain travelling in the analyzer field. More particularly, experimental tests with a cylindrically symmetrical field ($\alpha=0, \beta=\gamma=1$) have proved that the obtainable resolving power increases at a ratio proportional to n^2 . In practically all the applications of such fields it is, therefore, desirable to make the value n as large as possible.

Increasing the number n of cycles of ion travel may be accomplished by operating with a very high frequency at which $f(t)$ oscillates; by providing long and extensive fields; or by using slow ions. Each of these possibilities entails severe disadvantages.

In the first place, the high frequency power for operating a mass filter of this type increases rapidly with frequency. For example, in the case of a cylindrically symmetrical field, the increase in energy demand is proportional to the fifth power of the frequency. In practice, therefore, an increased frequency is advantageous only within very narrow limits.

The provision of extremely long fields requires a considerable amount of equipment and extra space, and although theoretically possible, is essentially impractical. For instance, fields as long as about 10 m. with a dimensional precision of the apparatus in the tolerance range of about 1 micron would be required for precise atom-mass determination on this principle.

For using slow ions, the acceleration voltage with which the ions are extracted from the ion source must be low. Hence, the extracted ion current is also low. This difficulty can be partly overcome by initially using a high voltage for extracting the ions and then decelerating them before they pass into the analyzer field. However, many ions, thus decelerated, enter the analyzer field at a considerable angle to the shoot-in direction so that most of them are not subjected to mass separation because many of the ions travelling along theoretically stable paths are also separated and impinge upon the field electrodes. The maximum oscillation amplitude of such ions is greater than the distance of the field electrodes from the field axis. The efficiency and resolving power of such mass filters, therefore, is rather poor.

For obtaining a desired resolving power, mass filters have also been built on a compromise of the two last-mentioned methods.

It is an object of my invention to provide an improved ion separating method and means while avoiding the above disadvantages.

Another object of my invention is to provide an ion separating method and means of higher resolving power than has hitherto been available with similar equipment, particularly at corresponding ion currents.

Yet another object of my invention is to provide an ion separating method and means having a higher ion current than that obtainable with conventional methods and apparatus of similar size and power, particularly with corresponding resolving power. More specifically, the invention aims at increasing the separated ion current, obtainable with conventional methods and apparatus, by more than one order of magnitude.

Another object of the invention is to improve ion separating methods and means and achieve an increase in the resolving power, of the ion current or both, with conventional apparatus only slightly modified.

Another object of the invention is to provide an ion separating method and means which is advantageous despite considerable energy inhomogeneity in the ions utilized and which does not restrict the applicability of the general separating processes and means.

According to a feature of my invention, I separate ions having respectively different specific electric charges by first accelerating them, and then subjecting them to an electric field which is periodically varying as a function of time and the potential of which is a square function of the coordinates x, y, z having the general formula

$$\varphi = f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2) + f_2(t)$$

wherein $f_1(t)$ and $f_2(t)$ may be any desired periodic functions of time. After they have entered the electric analyzer field, I decelerate the ions.

According to another feature of the invention, I connect the entrance diaphragm or tube through which the ions pass into the analyzer field to ground so as to have a potential $\varphi_{EB}=0$ and I apply to the analyzer rods a voltage so that the potential of the analyzer field is described by the equation $\varphi = f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2) + \varphi_{Tr}$, wherein φ_{Tr} stands for a constant deceleration potential for the shot-in ions.

According to another feature, I apply to the entrance diaphragm or tube through which the ions pass into the analyzer field a potential $\varphi_{EB} \neq 0$, and define the potential of the analyzer field by the equation

$$\varphi = f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2)$$

preferably while maintaining the ion forming space at a positive potential. According to yet another feature of the invention, I apply, particularly when electron impact ion sources are utilized, a ground potential to the ionization space in which the atoms to be separated are ionized

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preferably while applying to the rods a negative potential and to the entrance diaphragm an even more negative potential. According to another feature of the invention, I vary the location width of the stable or instable ranges by varying the amplitude, the frequency and/or the oscillatory form of the field-producing voltages. According to still another feature, for embedding narrow instable ranges into a stable range, I superimpose further alternating voltages having small amplitudes.

As another feature of the invention, I maintain the average or mean potential of the analyzer field φ_{Tr} lower by a minute degree than the potential at which the ions are formed (φ_{Io}). Other objects and advantages of the invention will become obvious from the following description of an embodiment of the present invention with reference to the accompanying drawings in which:

FIG. 1 is a schematic and block diagram of a mass filter system according to the invention;

FIG. 2 is a schematic illustration of part of a mass or spectroscopic filter. FIGS. 2a, 2b, 2c are graphs of the potentials appearing within the filter of FIG. 2;

FIGS. 3 and 3a are schematic representations of two circuits suitable for energizing the field electrodes of the mass filter in FIG. 2; and

FIG. 4 is a graph showing measurements of the ion collector current and of the resolving power ($m/\Delta m$) relative to the effective energizing voltage of the apparatus in FIG. 1.

According to FIG. 1, the mass-filter cell 1 is provided with an envelope 5 which contains an ion source 2, and a group of rod-shaped deflector electrodes 3 having individually a circular cross section. Located at the end of the ion-beam path is a cup-shaped collector electrode 4. The ion source 2 and the collector electrode 4 are coaxially spaced from each other and thus define a center axis for the ion beam issuing from the source 2 toward the electrode 4. The electrode rods 3 are uniformly distributed about the ion-beam axis and extend parallel thereto. A total number of four such electrodes are used.

The above-mentioned envelope 5 of the cell 1 is vacuum-tightly sealed and has a nipple or neck 6 connected with a tank 7 containing the gaseous mixture to be investigated. The rod electrodes 3 are electrically connected in pairs to a high-frequency generator 8 which supplies electric energy of suitable voltage and frequency. The current due to the ions impinging upon the collector 4 is amplified by an amplifier 9 and supplied to a recorder 10 or other indicating or measuring device. Another measuring instrument 10' is provided for supervising the electron emission of the cathode in the ion source 2.

During operation, a beam of ions is continuously extracted from the source 2 and is directed toward the collector 4. However, only the ions of a given specific electric charge, or within a given range of charges, can reach the collector 4. Those ions which have different specific charges travel on instable, pendulous paths and thus impinge upon the deflector electrodes 3, thus being filtered out of the mixture. This is more fully explained in the copending applications Serial No. 859,030, filed December 11, 1959 now U.S. Patent No. 3,075,076 (F-1974); No. 97,244, filed March 21, 1961 now U.S. Patent No. 3,105,899 (F-2145); No. 94,071, filed March 7, 1961 now U.S. Patent No. 3,143,647 (F-2158); and in the before-mentioned Paul patent.

FIG. 2 is a detailed view of part of the filter cell or vessel 1 together with energizing components. Comprising the ion source 2 is an ionization space 21 with an exit diaphragm 22, two intermediate diaphragms 23 and a shoot-in or entrance diaphragm 24. The space 21 and diaphragms 23, 24 connect to respective potentials in the instrument 10' which also constitutes a grounded voltage source. The high-frequency generator 8 applies to the rods 3 a voltage to produce a potential

$$\varphi(t) = f(t)(\alpha x^2 + \beta y^2 - \gamma z^2)$$

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plus the D.-C. potential as shown and discussed relative to FIGS. 2a, 2b, 2c, 3 and 3a.

According to one embodiment of the invention the instrument 10' applies to exit diaphragm 22, 250 volts D.-C. and to the entrance diaphragm 24, 0 volts, or ground potential. Simultaneously the high-frequency generator 8 in addition to the alternating field applies to the rods 3 a D.-C. potential of 150 to 200 volts. A diagram illustrating the potentials within the vessel 1 for these conditions is shown in FIG. 2a.

FIGS. 2b and 2c illustrate D.-C. voltage conditions according to two other embodiments of the present invention. In all cases the abscissas represent distance along the vessel axis, the potential graphs being aligned vertically with the components corresponding to the potentials indicated. FIG. 2a illustrates the embodiment where the entrance diaphragm is connected to ground. The formation of ions occurs at a high positive potential; the entire ion deceleration analyzer field being almost as high in potential.

In the embodiment illustrated by the graph in FIG. 2b the generation of ions is effected at a low positive potential φ_{Io} and the analyzer field, just like in conventional methods, is symmetrical with respect to ground. In this case, however, a strong negative potential φ_{EB} is applied to the entrance diaphragm.

In the embodiment explained by FIG. 2c, the ions are generated at zero potential. They are then accelerated towards the entrance diaphragm 24 which has a high negative bias voltage, and then again decelerated to the low negative potential of the analyzer field.

FIGS. 3 and 3a illustrate respectively two embodiments of the high frequency generator 8 connected to the rods 3 as exemplified in FIGS. 2 and 2a. The analyzer rods 3 are supplied with voltage by a high-frequency oscillator 12 and by a constant voltage source 13. Parallel-resonant filter circuits 16 prevent the high frequency from reaching the direct-voltage source. In FIG. 3, a potentiometer 14 is centrally tapped and connected to ground via a constant voltage source 15. The latter achieves the potential φ_{Tr} of FIG. 2a. In FIG. 3a the constant voltage source is omitted and the potential φ_{Tr} of FIG. 2a is achieved by shifting the tap of the voltage divider out of its central position. For achieving the corresponding negative potential of FIG. 2c for the rods 3, the source 15 in FIG. 3 is reversed, and the position of the tap in FIG. 3a of divider 14 is shifted to the other side of the center. The value of the voltage is according to the values of FIG. 2c.

Thus the potential distribution in accordance with FIGS. 2a and 2c is effected by supplying the constant voltage portion U of the function $f(t)$ to the mass filter in an asymmetrical relationship with respect to ground, rather than in the usual symmetrical relationship with respect thereto. This is achieved by the bias voltage 15 (FIG. 3) or by the asymmetrical ground connection (FIG. 3a).

Measured results using the latter in embodiment of a generator 8 for energizing a device such as illustrated in FIG. 1 with the D.-C. values of FIG. 2a, are shown in FIG. 4. Use was made of a cylindrically symmetrical device ($\varphi = (U + V \cos \omega t)(x^2 - y^2)/r_0^2$). The ions were generated in a normal electron impact source at a potential φ_{Io} and were accelerated towards a ground-connected entrance diaphragm 24. They entered the analyzer field through said diaphragm with respective energies of 70, 20 or 17.5 eV. The deceleration potential φ_{Tr} was superimposed upon the analyzer field so that the ions travelled through the analyzer field with an energy

$$eU_{eff} = e(\varphi_{Io} - \varphi_{Tr})$$

wherein e is the unit charge. The ion current of $132_{Xe}+$ was measured at the collector, and the resulting resolving power was a function of U_{eff} . FIG. 4 is a graph of re-

solving power $m/\Delta m$ and ion current relative to effective voltage U_{eff} for three values of potential φ_{Io} namely 17.5, 20, and 70 volts.

According to FIG. 4 the energy $eU_{\text{eff}} = e(\varphi_{\text{Io}} - \varphi_{\text{Tr}})$ of the ions in the analyzer field may at most be 20eV for all values of φ_{Io} , if a resolving power of approximately 4000 is to be achieved. If the energy eU_{eff} of the ions is increased to 70 along the abscissa, the resolving power ($m/\Delta m$) decreases to 2000. However, when $U_{\text{eff}} = 20$ volts and the ion source 2 is operated at 20 volts the resulting ion current is lower by a factor of 8.6 than the ion current which is obtained when the ions are decelerated in accordance with the present invention from 70eV to 20eV. If these values are compared at $\varphi_{\text{Io}} = 17.5$ volts, the intensity is greater by a factor of 12. Experimentally within measurement accuracy limits the present invention achieves the same resolving power as the conventional method, provided that the energy of the ions in the analyzer field is the same. The fact that the curves do not exhibit a completely continuous or monotonous path is due to the specific construction of the apparatus as used. Measurements indicate that the energy homogeneity of the ions was not substantially altered by the decelerating action of the present invention. Consequently, the method of the present invention is adapted to improve considerably the performance of mass filters, particularly for a small apparatus wherein it is difficult to reach the required number n .

The values α , β and γ are constants satisfying the equation $\alpha + \beta = \gamma$.

While various embodiments of the invention have been described in detail it will be obvious to those skilled in the art that the invention may be practiced otherwise.

I claim:

1. A mass spectroscopy system, comprising an ion source including an ion forming device and a field entrance diaphragm, an evacuated vessel surrounding the ion source and including therein analyzer field means, power means for energizing said ion source and for applying to said ion forming device and said entrance diaphragm the respective direct potentials φ_{Io} and φ_{EB} , where $\varphi_{\text{Io}} > \varphi_{\text{EB}}$, voltage means for applying to said field means a potential $\varphi = +f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2) + \varphi_{\text{Tr}}$, where $f_1(t)$ is any desired periodic function of time, x , y and z are

space coordinates and α , β and γ are constants satisfying the equation $\alpha + \beta = \gamma$, and wherein $\varphi_{\text{Tr}} > \varphi_{\text{EB}}$.

2. A mass spectroscopy system, comprising an ion source including an ion forming device and a field entrance diaphragm, an evacuated vessel surrounding the ion source and including therein analyzer field means, power means for energizing said ion source and for applying to said ion forming device and said entrance diaphragm the respective direct potentials φ_{Io} and φ_{EB} , where $\varphi_{\text{Io}} > \varphi_{\text{EB}}$, voltage means for applying to said field means a potential

$$\varphi = +f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2) + \varphi_{\text{Tr}}$$

where $f_1(t)$ is any desired periodic function of time, x , y and z are space coordinates and α , β and γ are constants satisfying the equation of $\alpha + \beta = \gamma$, and wherein $\varphi_{\text{Tr}} > \varphi_{\text{EB}}$, said voltage means including a high-frequency source having D.-C. source means connecting said high-frequency source to zero ground potential for producing a field potential φ_{Tr} .

3. A mass spectroscopy system, comprising an ion source including an ion forming device and a field entrance diaphragm, an evacuated vessel surrounding the ion source and including therein analyzer field means, power means for energizing said ion source and for applying to said ion forming device and said entrance diaphragm the respective direct potentials φ_{Io} and φ_{EB} , where $\varphi_{\text{Io}} > \varphi_{\text{EB}}$, voltage means for applying to said field means a potential $\varphi = +f_1(t)(\alpha x^2 + \beta y^2 - \gamma z^2) + \varphi_{\text{Tr}}$, where $f_1(t)$ is any desired periodic function of time, x , y and z are space coordinates and α , β and γ are constants satisfying the equation $\alpha + \beta = \gamma$, and wherein $\varphi_{\text{Tr}} > \varphi_{\text{EB}}$, said voltage means including a high-frequency source, a direct voltage across the outputs of said source, said direct voltage being grounded at a potential intermediate the extremes of said source for producing at said field a potential $+\varphi_{\text{Tr}}$.

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