April 29, 1969 G. GAUTHERIN ET AL 3,441,732

MASS SPECTROMETER COMPRISING MEANS FOR PRODUCING A HIGH-FREQUENCY TRANSVERSE ELECTRIC FIELD

Filed Jan. 22, 1965 Sheet 1 of 3

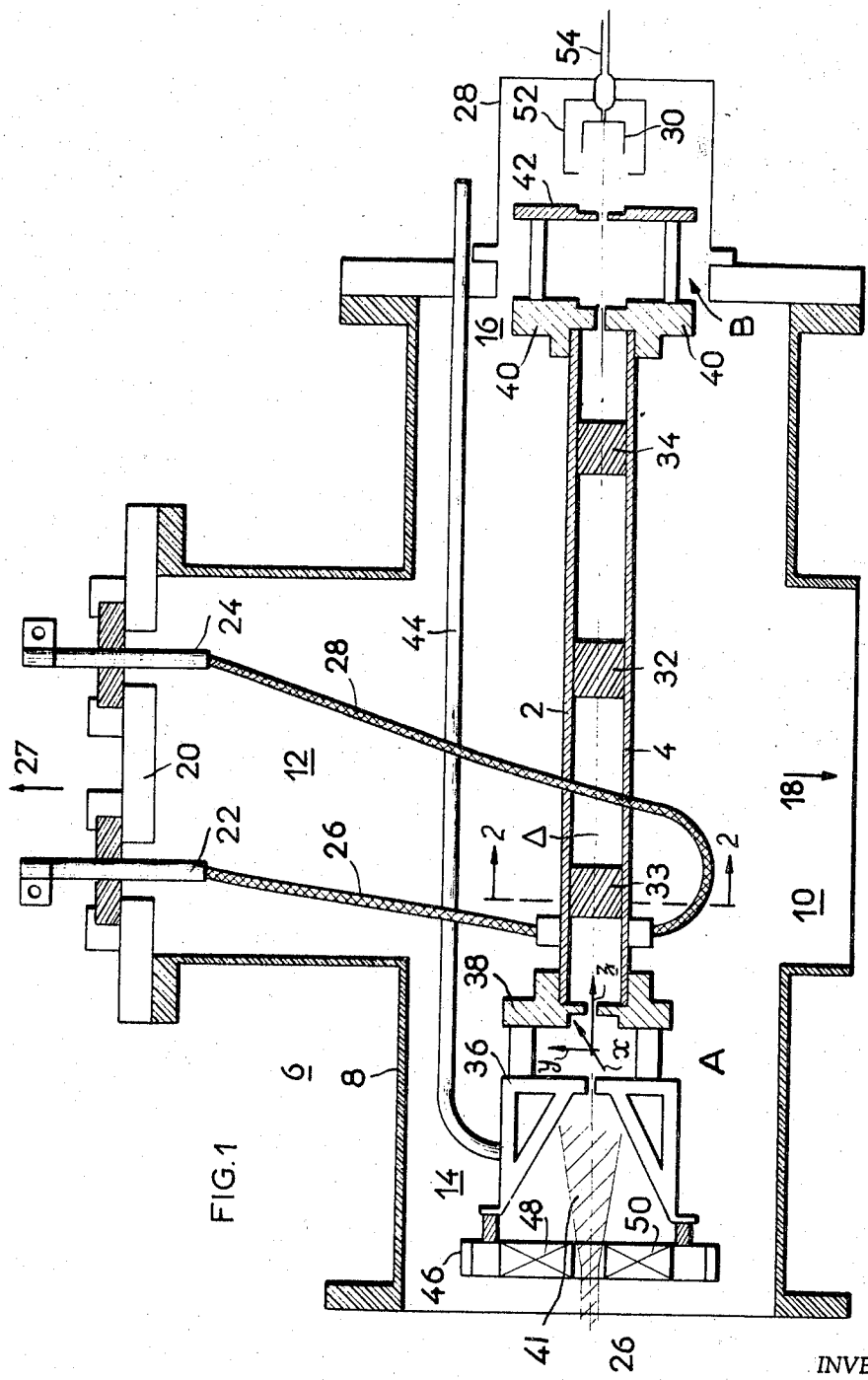

FIG. 1

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FIG. 2

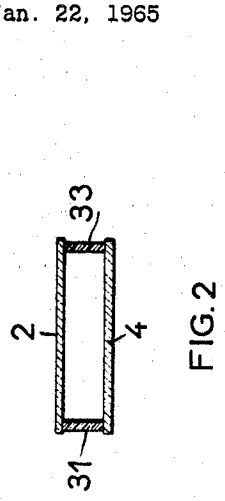

FIG. 3

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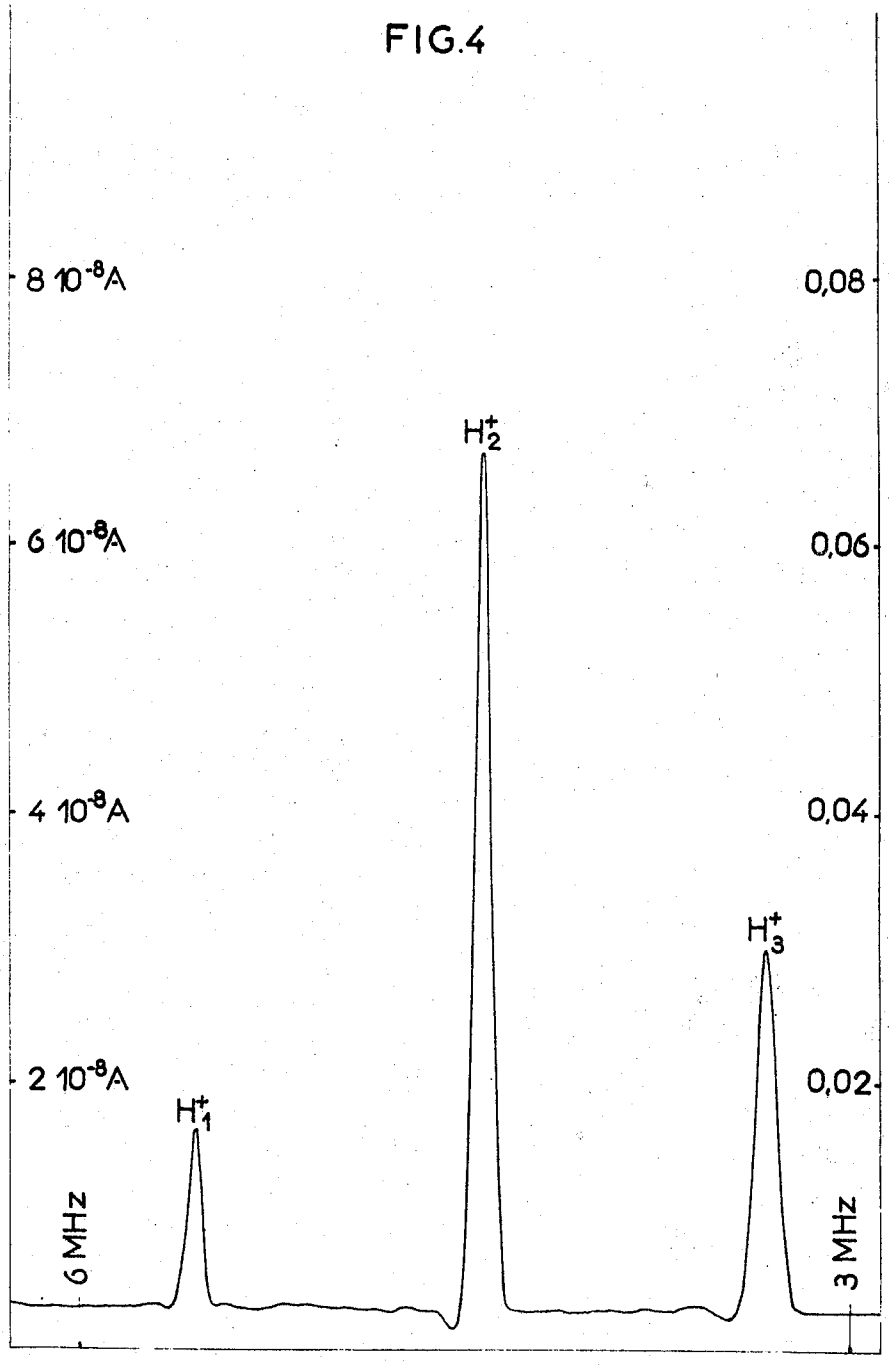
FIG.4



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MASS SPECTROMETER COMPRISING MEANS FOR PRODUCING A HIGH-FREQUENCY TRANSVERSE ELECTRIC FIELD

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Int. Cl. B01d 59/44; H01j 39/34
U.S. Cl. 250—41.9 5 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a method and apparatus for isolating ions of a predetermined mass from a beam of ionized particles as in mass spectrometry. The method of the present invention includes selecting those ionized particles of the beam which have a zero transverse velocity, passing those particles into a high frequency electric field oriented perpendicular to the axis of the ionized beam, and selecting from the resulting beam the ionized particles which still have a zero transverse velocity.

A mass spectrometer for carrying out the process of the present invention includes a polarizing ring through which the sample beam is admitted to the spectrometer. A pair of parallel diaphragms are located in spaced relationship adjacent to the polarizing ring and each diaphragm includes a slit aligned with the beam axis to pass those particles having zero transverse velocity. Ionized particles emitted from the slits pass between a single pair of electrode plates which are energized by a high frequency alternating voltage to cause an electric field perpendicular to the beam axis. A second pair of spaced parallel diaphragms are located behind the electrode plates, each diaphragm again having a slit oriented parallel to the electrode plates in alignment with the beam axis in order to pass those particles still having a zero transverse velocity. The particles passing through the slits of the second pair of diaphragms define the beam of particles of predetermined mass which may be collected by a suitable electrode.

The present invention relates to a novel method of mass spectrometry which takes advantage of the influence of the mass of ions on their time of flight when they are subjected to the action of a high-frequency transverse electric field; the invention is also concerned with a device for the practical application of the above-mentioned method.

Mass spectrometers of the magnetic field type are cumbersome as a result of the curvature of the path followed by the ions which form the beam to be analyzed.

In order to overcome this disadvantage, it is possible to apply a different method of mass spectrometry which makes use of a high-frequency transverse electric field. Two types of apparatus which make use of a transverse high frequency field are presently known. An article by Heym, Joseph, and Loude, published in "Helvetica Physica Acta," pages 444–446, 1961, describes an apparatus which employs a homogeneous field having a field frequency and only operates in short pulses. This apparatus effects the analysis with respect to time of the ion clusters which are injected by making use of the differences in time if flight which exist between ions having different mass. The observation of this amplified current is made by means of an oscilloscope operating at high frequency and the scanning of which is triggered by the oscillator which produces the transverse field. It is difficult to graph the results thus

obtained and, as in the case of all time-of-flight devices, all of the masses arrive at the same receiver.

An article by Von Zahn published in the "Review of Scientific Instruments," vol. 34, page 1, 1963, describes an apparatus, derived from the Paul quadrupole lens filter, which makes use of an inhomogeneous HF field with constant gradient and which operates continuously but only with very low velocity ions which are accelerated to energies of 10 to 100 ev.

This apparatus would not be suitable for the analysis of ion beams of a few kev. to a few tens of kev. which are the most commonly met with in nuclear physics (except by providing slowing-down systems which are always very difficult to design).

The method of mass spectrometry according to this invention, in which the ion beam to be analyzed is subjected in an original manner to a homogeneous high-frequency field which is perpendicular to the axis of said beam and the device for the practical application of said method are not attended by the disadvantages hereinabove referred-to.

Said method is characterized in that ions which form a layer containing the axis of the beam and which have a zero transverse velocity are continuously admitted in the high-frequency field, and in that ions which form a non-continuous layer parallel to the axis of the beam and which also have zero transverse velocity are collected near the exit of the high-frequency field whilst the high frequency of said field varies within a band width which is a function of the atomic mass of the ions which form the beam.

The device for the practical application of the method outlined above is further characterized in that it comprises an ion source which continuously directs between the parallel plates of a capacitor to which is applied a variable high-frequency voltage, a beam having an axis which is parallel to said plates through the slits of two spaced parallel diaphragms which are perpendicular to said plates thus defining a plane which is also parallel to said plates and which contains said beam axis, as well as a coaxial collecting electrode which collects the ions derived from the high-frequency field which have passed through a third diaphragm then a fourth diaphragm having slits which are parallel to those of the two first diaphragms and located in a plane parallel to the capacitor plates, said third and fourth diaphragms being so arranged as to contain said beam axis in the case of a high-frequency field which is sinusoidal in time and to be displaced from said axis in the case of excitation by square-wave voltage or saw-tooth voltage.

According to one preferred form of embodiment, one of the capacitor plates is located within very close proximity to the axis of the beam.

Aside from these main arrangements, there will be described hereinafter secondary arrangements in connection with the structural design of the mass spectrometer for the application of the method which forms the first object of this invention.

The simple structural arrangement envisaged permits of easy mechanical construction, is of small overall size and light in weight. In the form of embodiment herein described, the device according to the invention makes it possible to analyze beams of ions having an atomic mass which is either lower than or equal to 32.

In order that the technical characteristics of the invention may thus be more readily understood, one example of embodiment will now be described hereinafter, it being understood that said example is not given in any limiting sense either in regard to the modes of operation or in regard to the uses to which it may be applied.

In the accompanying drawings:

FIG. 1 represents a mass spectrometer for the practi-

cal application of the method in accordance with the invention.

FIG. 2 is a sectional view along line 2—2 of FIG. 1 and shows a detail of the spectrometer of this figure.

FIG. 3 shows a preferred form of embodiment of the invention.

FIG. 4 represents a spectrum obtained by means of an apparatus in accordance with the invention.

According to the method contemplated by this invention, the ions forming the beam to be analyzed are subjected to a high-frequency transverse electric field E which is in this case chosen so as to have the form $E=E \cos \omega t$.

In this case, the ion beam is directed continuously into the high-frequency field ($\omega/2\pi$) which is generated between capacitor plates (designated by the reference numerals 2, 4 in FIG. 1) which have a length L and to which is applied a pulsating voltage ω. The axis Δ of the beam is parallel to the plates and consequently perpendicular to the electric field. In accordance with the essential characteristics of the method according to the invention, the paths of the ions which pass into the capacitor all have the same ordinates and a zero transverse velocity. Finally, the ions which are collected at the exit of the high-frequency field must have the same ordinate as at the input and a transverse velocity which is also zero.

A study of the movement of ions between the plates 2–4 will be effected by making use of the trihedron having the reference Ox, y, z which is shown in FIG. 1. It should be noted that Oz is parallel to these plates and contained in the plane of the figure, Oy is perpendicular to said plates and, finally, Ox is normal to the figure. The calculations which now follow are made on the basis of the assumption that the plates are of infinite width in the direction Ox.

When the ions pass into the high-frequency field at A, the use of two successive diaphragms makes it possible to establish:

$$Y_0=0 \text{ and } Y'_0=0$$

The ion paths are defined by the coordinates which are provided parametrically by the expressions:

$$y=\frac{eE_o}{m\omega}\sin\tau(\tau-t)+\frac{eE_o}{m\omega^2}(\cos\omega\tau-\cos\omega t) \quad (1)$$

$$z=v(t-\tau) \quad (2)$$

wherein m is the mass of the ion considered; v is its velocity as defined by

$$v=\sqrt{\frac{2e\Phi}{m}}$$

in which $e\Phi$ is the energy of the ion beam; τ is the time of entry into the field E.

The ions which pass out of the high-frequency field are selected by two diaphragms, the first being located at a distance L from the point of entry into the high-frequency field, and we have:

$$y_L=(y'_L)=0$$

and only those ions which satisfy the conditions hereunder pass through the diaphragm:

(a)
$$tg\omega\tau=\frac{-\cos\left(\frac{\omega L}{v}\right)}{\frac{\omega L}{v}-\sin\left(\frac{\omega L}{v}\right)} \quad (3)$$

(b)
$$\sin\left(\omega\tau+\frac{L}{v}\right)=\sin\omega\tau \quad (4)$$

There are found two pulse series which satisfy the above conditions:

$$\omega_1=2kM\frac{v}{L} \quad (5)$$

$$\omega_2\simeq(2k+1)M\frac{v}{L} \quad (6)$$

in respect of a high value of k.

A study of these sinusoidal paths shows that only the first paths are located on one side only of the plane $y=0$. There will be described later a method of elimination of the second paths.

It is therefore possible to analyze the masses of the different ions by varying the high frequency of the voltage applied to the plates 2–4. Inasmuch as the velocity of the ions is a function of their mass in the case of a monoenergetic beam, it is also possible to effect according to the same principle an analysis of the velocities of the ions of a beam when said ions have the same mass.

If the oscillating circuit which controls the frequency of the high-frequency voltage comprises a variable-capacitance capacitor C, the mass of ions which corresponds to the current collected is also a function of the frequency, since we have:

$$v=\sqrt{\frac{2e\phi}{m}} \quad (7)$$

$$\omega=k_1\frac{v}{l} \quad (8)$$

$$LC\omega_{res}^2=1 \quad (9)$$

in which ϕ is the acceleration potential while k can be chosen equal to 1, so we get:

$$\frac{m}{e}=\left(\frac{8\pi^2\phi L}{l^2}\right)C \quad (10)$$

The resolving power P of this spectrometer is given by the expression:

$$R=\frac{1}{4}\frac{E_oL}{\varphi v} \quad (11)$$

in which φ represents the angle of inclination of an ion path which is incident with respect to the plane $y=0$, this angle being determined as will be explained hereinafter. The resolving power does not depend on the mass of ions under analysis but on the width of the input slits.

The spectrometer 6 of FIG. 1 is contained within a casing 8 in the shape of a cross having four arms or branches 10, 12, 14, 16. The lower branch 10 is connected to a pump 18 which has not been shown in the drawings. The upper branch 12 is closed by a cover 20 fitted with two terminals 22, 24 for the transmission of a high-frequency voltage. The branch 14 is connected to an ion source 26 which is not shown, and finally, a tubular portion 28 forms an extension of the branch 16 of the casing and contains the collecting element 30. The central portion of the casing which has a horizontal axis Δ and is extended by the branches 14, 16 contains the horizontal plates 2, 4 which are symmetrical with respect to said axis Δ.

It has been explained earlier that, in a spectrometer of this type, the ions could have two types of paths corresponding to the pulses ω_1 and ω_2 (Equations 3, 4, 5, 6). A simple arrangement makes it possible to eliminate the pulse paths ω_2. Accordingly, in accordance with a preferred embodiment of this invention as shown in FIG. 3, it is merely necessary to intercept the ions by placing one of the plates (4') at a very short distance ϵ from the axis Δ.

The partial view of FIG. 2 shows a cross-section along line 2—2 of FIG. 1 of the arrangement of the plates 2–4, the spacing of which is maintained by means of distance pieces 33, 32, 34 . . . which can be formed of polytetrafluoroethylene. The plates 2–4 are respectively connected to the terminals 22–24 by means of braided metal conductors 26–28. Said terminals are in turn connected to a high-frequency voltage source 27 which has not been illustrated in the drawings.

The entry of ions into the high-frequency field as well as the exit of said ions from said field are respectively defined by two sets of diaphragms 36–38 on the one hand and 40–42 on the other hand which are perpendicular to

the axis and provided with slits which are parallel to the plates, said slits being traversed by said axis (since in this case the HF field is sinusoidally variable with respect to time).

It should be noted that the use of pairs of diaphragms at the entrance (A) as well as at the exist (B) of the high-frequency field makes it possible to satisfy the conditions previously defined.

$$y_0=y'_0=0 \text{ at A}$$
$$y_L=y'_L=0 \text{ at B} \qquad (12)$$

The widths of the slits of the two diaphragms which are placed at the input of the capacitor **2–4** which serves to impose the conditions of injection hereinabove defined (12) on the mean path determine the maximum angle of inclination of an entry path, this value being given in expression (11) of the resolving power.

The beam **41** which issues from the source **26** is directed towards the first diaphragm **36** which is cooled together with its support by a flow of water (circulated through the pipe **44**). The polarizing ring **46** which is coaxial with Δ and magnets **48–50** prevent any errors resulting from secondary electrons produced by the impact of incident ions.

The collector **30** is surrounded by an electrode **52** which forms a screen. The current which is collected by the electrode **30** is transmitted by a coaxial cable **54** which is connected to a display device. A suitable electric polarization of the collector **30** which receives the analyzed ions prevents any disturbances arising from secondary electrons.

A spectrometer of the type which has just been described has been constructed by the present applicants. The capacitor plates have an adjustable length of 0.25 mm. A simple device permits the possibility of making the plates parallel to the axis of the beam. The high frequency of the voltage applied between the plates **2–4** varies over two ranges between 0.6 and 2.7 mc./s. and between 2.7 and 6 mc./s. These ranges which are determined with a view to analyzing a beam of hydrogen of 30 kv. permit the possibility of studying ions having a mass which is lower than or equal to 32. The amplitude of the high frequency field is 500 v./cm., so that the maximum amplitude of ionic oscillations is slightly smaller than the spacing of the plates.

The maximum peak intensity is of the order of 50×10^{-9} amps in respect of a current intensity of injected beam of 10^{-4} amps; the signal/noise ratio is of the order of 50 (the noise is due to stray ions having a high mass (a high value of K)).

The current intensity of the different peaks can be increased to a substantial extent if a low resolving power is considered sufficient (which in certain experiments is not a disadvantage). It is merely necessary for this purpose to enlarge the entry diaphragms.

A spectrum supplied by the apparatus is represented in FIG. 4, wherein the frequencies (in megacycles) are plotted as abscissae and the current intensities (10^{-9} A.) are plotted as ordinates.

The mass resolving power is 60 under given operating conditions. It is possible to increase the resolving power by reducing the width of the selecting slits.

The resolving power of the apparatus can also be increased by applying a high-frequency square-wave voltage or saw-tooth voltage to the capacitor plates instead of a sinusoidal voltage.

What we claim is:

1. A mass spectrometer for separating ions of a predetermined mass from a beam of ionized particles including:

a magnetic polarizing means through which said beam is admitted along the axis of said mass spectrometer,

a first pair of parallel diaphragms spaced apart adjacent to said polarizing ring and perpendicular to the axis of said spectrometer, each of said diaphragms including a slit aligned with said axis to define a path for particles having zero transverse velocity,

a single pair of electrode plates, adapted to be energized by a high frequency alternating voltage, spaced apart parallel to said slits whereby said particle path passes between said plates,

a second pair of parallel diaphragms spaced apart adjacent to said electrode plates, each said diaphragms including a slit parallel to said electrode plates in alignment with said axis to define a further path for particles having zero transverse velocity, and

means for collecting ionized particles which pass through the slits in said second pair of diaphragms.

2. A mass spectrometer as described in claim **1** further including a source of high frequency sinusoidal voltage connected to said electrode plates.

3. A mass spectrometer as described in claim **1** wherein said electrode plates are spaced equidistant from said axis.

4. A mass spectrometer as described in claim **1** wherein one of said electrode plates is located closely adjacent said axis.

5. A mass spectrometer for separating ions of a predetermined mass from a beam of ionized particles including:

a magnetic polarizing means through which said beam is admitted along the axis of said mass spectrometer,

a first pair of parallel diaphragms spaced apart adjacent to said polarizing ring and perpendicular to the axis of said spectrometer, each of said diaphragms including a slit aligned with said axis to define a path for particles having zero transverse velocity,

a single pair of electrode plates, adapted to be energized by a high frequency alternating voltage, spaced apart parallel to said slits whereby said particle path passes between said plates,

a second pair of parallel diaphragms spaced apart adjacent to said electrode plates, each said diaphragm including a slit parallel to said electrode plates and transversely displaced from said axis to define a further path for particles having zero transverse velocity, and

means for collecting ionized particles which pass through the slits in said second pair of diaphragms.

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RALPH G. NILSON, *Primary Examiner.*