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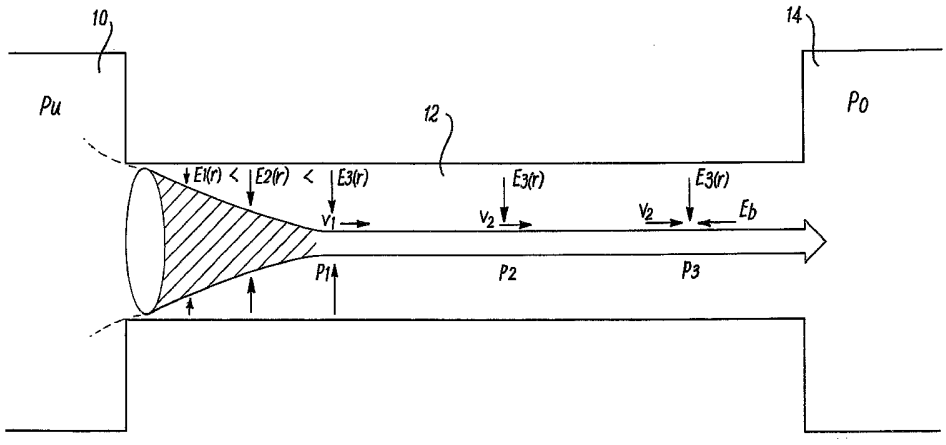

(57) Abstract: There is disclosed a method of extracting ions comprising the steps of: providing a source of ions; entraining said ions in a laminar flow of a carrier gas; providing a barrier region in which an electrical field is applied across the laminar flow of carrier gas, the magnitude and direction of the electrical field being selected so as to prevent at least some of the ions entrained in the laminar flow from passing through the electrical field; and varying the electrical field so as to allow ions of chosen characteristics to pass through the electrical field.

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ION EXTRACTION

This invention relates to ion extraction devices, analytical devices incorporating same, methods of extracting ions and methods of analysing ions or physical phenomena associated with ions, with particular, but by no means exclusive, reference to mass spectrometry.

The use of radio frequency (RF) ion guides at elevated pressures to efficiently transmit ions from one portion of a spectrometer to another is now widespread. These devices work on the principle of so called "effective potential wells" (Gerlich et al, (1992) Inhomogeneous Electrical Radio Frequency Fields: A versatile tool for the study of processes with slow ions. Adv. In Chem Phys LXXXII, 1.ISBN 0-471-53258-4, John Wiley and Sons). Ions may be trapped in these wells for extended periods of time either by the use of cylindrical geometry devices such as conventional Paul traps , or using linear geometry devices such as multipole guides or ring sets with end plates providing trapping D.C. potential. These RF devices are able to trap in three dimensions in a way which is impossible to achieve using purely electrostatic ion optical elements. This is because Laplace's equation, which describes the behaviour of electrostatic fields, contains no true potential minima but only saddle points which on their own are insufficient to give true three dimensional trapping. An oscillatory A.C. field applied to quadrupoles, hexapoles, and octopoles (collectively known as multipoles) or to ring sets gives rise to the so called ponderomotive force which acts in the direction of weaker field i.e. towards the central optic axis of the multiple or ring set. In the absence of gas, ions will oscillate in the potential well with an amplitude dependent upon their radial energy. In the relatively simple case of quadrupoles the restoring force towards the optic axis is proportional to the distance from it and so an ion with finite energy may be seen to exhibit simple harmonic motion on a macroscopic level within the well. The addition of gas molecules to such a device acts to dampen this radial motion so that ions are in effect cooled and concentrated to the centre of the device. As ions

are cooled in these linear multipoles or ring sets they loose any forward impetus they had to traverse the length of the device. The ions are rapidly thermalised and will remain in the guide until the space charge effect from other ions behind pushes them along. This sluggish motion of ions in the guides has led to problems when interfacing with fast scanning devices such as analytical quadrupoles. US 4,283,626 describes the use of a "leaky dielectric" inserted inside the multiple to allow for the provision of a drift field to speed the ions through a collision cell. This leaky dielectric is transparent to the RF field (thus maintaining a potential well) but has enough resistivity to allow a potential gradient to be applied axially along its length. US 4,283,626 recognises that such a drift field in the presence of gas may be used to separate ions for analytical purposes. US 5,847,386 describes a number of different methods to induce a smooth axial field along the length of the linear guides to speed the transmission of ions through them. Such methods include segmenting of the rods themselves, or using external ring electrodes, or tapering the rods themselves or using different pitch circle diameters for oppositely phased rod sets at either end of the guide. US patent publication 2002/0070338 describes the use of segmented rods to provide an axial D.C. field and to give separation of the ion species according to their Ion mobility. Again, RF confinement is combined with a drift field in the presence of gas. This combination is versatile since ions may be manipulated in a wide variety of ways using D.C travelling waves in the axial direction to create moving potential wells while maintaining radial confinement with the ponderomotive force from the RF supply. Related techniques are described in US 5,206,506 and US 6483109. The contents of US 4,283,626; US 5,847,386; US 2002/0070338; US 5,206,506 and US 6,483,109 are hereby incorporated by reference.

All of above described techniques which use RF ponderomotive confinement, axial field & gas cooling to separate ions for analytical purposes rely on the concept of dragging ions through a viscous medium (a gas) using an axial D.C field. The resulting separation is based upon the differing velocities with which the ions are able to pass through the gas according to their mobility. The achievement of an axial field with a RF confinement requires the construction of complex electrode geometries such as segmentation, tapering,

changes in pitch circle diameter as previously described. It would be desirable to simplify the geometry of a mobility spectrometer.

The present invention addresses this desire and, furthermore, provides numerous non-limiting advantages which are set forth below.

According to a first aspect of the invention there is provided a method of extracting ions comprising the steps of:

providing a source of ions;

entraining said ions in a laminar flow of a carrier gas;

providing a barrier region in which an electrical field is applied across the laminar flow of carrier gas, the magnitude and direction of the electrical field being selected so as to prevent at least some of the ions entrained in the laminar flow from passing through the electrical field; and

varying the electrical field so as to allow ions of chosen characteristics to pass through the electrical field.

Preferably, the electrical field is applied axially across the laminar flow.

The method may further comprise the step of confining the entrained ions radially with respect to the axis of flow of the laminar flow of carrier gas. The step of confining the entrained ions may comprise radially confining the ions by a ponderomotive force. It is preferred to radially confine the ions, since this prevents diffusion losses of ions. The ponderomotive force may be supplied by suitable means such as an RF multipole or ring set. The step of varying the electrical field may comprise reducing the magnitude of the electrical

field to a level that permits ions of a first range of ion mobilities to pass through the electrical field by preventing ions of a second range of ion mobilities from passing through the electrical field. The electrical field may be reduced in a stepwise manner or a continuous manner.

Prior to the step of varying the electrical field, an isolating electrical field may be applied so as to prevent ions upstream of the isolating electrical field from being carried to the barrier region. After the step of varying the electrical field, the isolating electrical field may be reduced so as to permit ions upstream of the isolating electrical field to be carried to the barrier region.

The step of varying the electrical field may be performed so as to extract ions from the barrier region in a pulsed manner. The electrical field may be varied between at least a first state and a second state, with the peak magnitude of the electrical field in the second state being less than the peak magnitude of the electrical field in the first state, so that ions of a defined range of mobilities can be extracted from the barrier region when the electrical field is in the second state and prevented from passing out of the barrier region when the electrical field is in the first state. The location of the peak magnitude of the electrical field in the second state may be upstream of the location of the peak magnitude of the electrical field in the first state so that only ions of a desired range of mobilities which are situated in a predetermined range of locations are extracted.

When the magnitude of the electrical field is reduced to a level that permits ions of a first range of ion mobilities to pass through the electrical field but prevents ions of a second range of ion mobilities passing through the electrical field, a scheme may be employed in which the magnitude of the electrical field is first reduced, and then pulsed extraction of ions is performed.

The electrical field in the barrier region may be selected so as to produce a spatial

separation of ions of different ion mobilities in the barrier region.

The method may further comprise the step of applying a drift field to at least a portion of the laminar flow of carrier gas. An arrangement comprising a leaky dielectric shield may be used to provide the drift field. The arrangement may be a multipole arrangement.

The velocity distribution of the carrier gas as a function of radial position of the laminar flow in the barrier region may be substantially parabolic.

According to a second aspect of the invention there is provided a method of analysing ions or phenomena associated with ions comprising the steps of:

providing analysis means for analysing ions or phenomena associated with ions;

extracting ions into the analysis means using a method according to the first aspect of the invention; and

analysing the extracted ions or phenomena associated with the extracted ions.

The analysis means may comprise mass spectrometry means such as a time of flight (TOF) mass spectrometer, or a multipole, Fourier transform or ion trap mass spectrometer. Other forms of analysis means, such as a spectroscopic technique, may be employed instead. Phenomena associated with ions, such as ion-molecule, ion-radical or ion-ion reactions, might be analysed using techniques to analyse reaction products, measure reaction rates and study reaction dynamics.

The analysis means may comprise a collision cell. Ions may be extracted from the collision cell using a method according to the first aspect of the invention.

According to a third aspect of the invention there is provided an ion extraction device comprising:

gas flow means including a gas flow conduit suitable for generating a laminar flow of carrier gas therethrough;

ion entrance means through which ions can be introduced into the gas flow conduit so that said ions become entrained in said laminar flow; and

electrical field producing means for applying an electrical field to a barrier region of the gas flow conduit, the electrical field producing means being operable to apply the electrical field across the direction of laminar flow in said gas flow conduit so as to prevent at least some ions entrained in a laminar flow in the gas flow conduit from passing through the electrical field;

in which the electrical field producing means is variable so as to allow ions of chosen characteristics to pass through the electrical field.

The ion extraction device may further comprise ion radial confinement means for confining entrained ions radially with respect to the axis of flow of the laminar flow of carrier gas through the gas flow means. The ion radial confinement means may comprise means for generating a ponderomotive force in the gas flow means. The ion radial confinement means may comprise an RF electrode set.

The ion extraction device may further comprise drift field applying means for applying a drift field along at least a portion of the gas flow conduit.

The gas flow conduit may comprise a duct.

The electrical field producing means may be variable so as to reduce the magnitude of the electrical field to a level that permits ions of a first range of ion mobilities to pass through the electrical field but prevents ions of a second range of ion mobilities from passing through the electrical field.

The ion extraction device may further comprise ion isolation means operable to apply an isolating electrical field upstream of the barrier region so as to prevent ions upstream of the isolating electrical field from being carried to the barrier region.

The electrical field producing means may be operable to extract ions from the field in a pulsed manner.

The ion extraction device may further comprise an ion source.

According to a fourth aspect of the invention there is provided an analytical device comprising:

an ion extraction device according to the third aspect of the invention; and

analysis means for analysing ions or phenomena associated with ions;

in which the analysis means is coupled to the ion extraction device so that ions extracted from the ion extraction device are introduced to the analysis means.

The analysis means may comprise mass spectrometry means, such as a time of flight (TOF) mass spectrometer, or a multipole, Fourier transformation or ion trap mass spectrometer.

The analytical device may further comprise a collision cell. The collision cell may

comprise:

a collision cell gas flow conduit through which the laminar flow of the carrier gas generated in the ion extraction device can be introduced and sustained;

collision gas inlet means for introducing a gas to the gas flow conduit; and

collision cell electrical field producing means for applying an electrical field to a barrier region of the collision cell gas flow conduit, the collision cell electrical field producing means being operable to apply the electrical field across the direction of laminar flow in said collision cell gas flow conduit so as to prevent at least some ions entrained in the laminar flow in the collision cell gas flow conduit from passing through the electrical field;

in which the collision cell electrical field producing means is variable so as to allow ions of chosen characteristics to pass through the electrical field.

The collision cell may further comprise collision cell drift field applying means for applying a drift field along at least a portion of the collision cell gas flow conduit of sufficient magnitude to overcome the force provided by a gas entering the collision cell through the collision gas inlet means.

The collision cell drift field applying means may comprise a leaky dielectric shield. The collision cell drift field applying means may comprise a multipole electrode set. The number of electrodes in the multipole electrode set may be greater than four, eg, an octapole or hexapole arrangement might be used. Alternatively, a quadrupole might be used. This multipole electrode set can also provide radial confinement of the ions.

It is well known that the passage of a gas through a long tube with smooth walls may

lead to fully developed laminar flow conditions. The nature of this gas flow is described by Hagen- Poiseuille equations which determine the "mass flow" through such a tube. It is known that the radial velocity profile of gas flow in a round tube under laminar flow conditions follows a parabaloid profile with zero velocity at the walls and maximum velocity in the centre. The current invention exploits these properties, and utilises laminar flow as an aid to analytical separation in a fashion somewhat analogous to a D.C. axial field. The present invention can utilise this gas flow in combination with D.C. axial fields to increase the analytical utility of mobility spectrometers. It will be seen from the ensuing description that utilisation of the gas flow as an additional analytical tool significantly enhances the versatility of RF confinement devices.

Ions that are present in, for example, a tube will be swept along with the same velocity as the carrier gas flowing through it. Thus the kinetic energy of any ion in the tube depends only on its mass and its position in the duct. The ponderomotive force from the effective potential well squeezes the ions radially to the centre of the device where the gas velocity is at its maximum. The gas velocity around the centre varies only slightly from this value as one moves radially outwards over short distances due to the nature of the parabaloid profile of the gas flow. If the tube is long enough to give rise to laminar flow conditions then over a short axial distance the velocity can be considered independent of axial position . Therefore, for the purposes of a simple one dimensional analysis the ions can be considered to be of a single defined velocity. A potential barrier field may impede the motion of the ions according to their ion mobility. For a certain field strength the impeding force due to the barrier field equals the driving force from the carrier gas and then the ion comes to a standstill in the tube, diffusion losses being prevented by the ponderomotive radial confinement. If the barrier field is then reduced the ion continues on it way into subsequent stages of the spectrometer. By sweeping the barrier potential sequentially from high to low values ions of lower to higher mobilities are able to escape the device. This device therefore creates a new type of axial well somewhat analogous to the electrostatic axial potential wells used in trapping linear multipoles. This new well is a hybrid type which is gas driven on

one side and electrostatically driven on the other side. The trapping characteristic of this well depends upon an ion's mobility as well as the applied potential.

This new "Barrier Spectrometer" provided by the present invention is advantageous over prior art in that it allows a flexible time scale of ejection of ions of chosen mobility that is not limited to the millisecond timescale of separation common to drift tube based devices. Furthermore, knowledge of gas pressures and velocities along the duct and the application of an axial field of desired profile can lead to ions of differing mobilities occupying different static positions along the length of the device. This spatial dispersion offers advantages in terms of a reduction in space charge effects, the space charge capacity of a line being greater than that of a point. A further advantage of the spatial dispersion is the possibility of selectively fragmenting or reacting ions at specific locations in the device either by optical, resonance or other means. It is a still further advantage of the spatial separation provided by the present invention that ions at the end of the device may be pulsed out by well defined short duration extraction pulses for purposes of efficient interfacing to subsequent spectrometer stages e.g. quadrupole, TOF, FTMS, or other MS devices. In particular, it is possible to optimise the collision energy of a fragmentation stage downstream from the device. Ion of a certain mobility may have a well characterised optimum collision energy for efficient fragmentation, and therefore the output of the barrier spectrometer can be controlled to provide the optimum collision energy for an ion so all ions of preselected type exiting the device undergo optimum fragmentation. The spatial separation between ions can be varied for a given set of ions by varying the length of the barrier region and, in particular, by varying the profile of the electrical field within the barrier region. Non-limiting examples of separations between ions are in the range 10 to 300 mm. It should be noted that this spatial separation between ions is a static separation, since the spacial positioning of the ions and their spatial separations are maintained as long as the electrical field is maintained constant. Furthermore, the spatial separation can be varied as desired by appropriate variations of the electrical field. This static spatial separation can be contrasted with the temporal separation between ions which is provided by the prior art techniques discussed

above which rely on differing times of flight of differing ions. Although the differing times of flight associated with different ions is manifest in a spatial separation of ions, the spatial separation is not a constant one (but rather increases as a function the flight time). Furthermore, the ions are of course in motion, in contrast to the present invention in which the electrical field in the barrier region (in combination with the force provided by the laminar flow) can hold ions in a spatially distinct, static position.

Embodiments of devices and methods in accordance with the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 shows the effective ponderomotive potential acting on a gas flow containing ions;

Figure 2 shows the velocity of an ion and electric fields acting on the ion in the barrier region of the device shown in Figure 1;

Figure 3 shows a number of ions of differing mobilities in the barrier region of an ion extraction device and the associated electric potential;

Figure 4 shows the variation of isolation and barrier potentials in order to perform fill, isolate and scan steps;

Figure 5 shows a scheme for extracting ions through use of a pulsed extraction field;

Figure 6 shows (a) an embodiment of an analytical device

of the invention and (b) a tandem mobility instrument of the invention;

Figure 7 is a potential energy diagram for the passage of an ion through the instrument of Figure 6 (b);

Figure 8 shows an embodiment of an intermediate stage for use in the tandem mobility instrument of Figure 6 (b); and

Figure 9 shows a further embodiment of an ion extraction device of the invention.

Ions in devices of the present invention can be subject to three different types of force which are reviewed in some detail below. The first force is the ponderomotive force in the radial direction caused by an inhomogeneous oscillatory field which has its direction towards the weaker field. The ponderomotive force provides radial confinement and prevents diffusion losses of the ions. The second force is of the flowing carrier gas which sweeps the ions along at the same velocity as the gas. The third force is created by the field supplied by a potential barrier which may impede or extract ions as desired according to their size and polarity. Preferably, this "barrier" field is oriented axially with respect to the direction of flow of the carrier gas.

The ponderomotive force can be generated by an effective potential well created by an oscillating (RF) electric field. The ponderomotive force allows trapping in three dimension as in the case of the Paul trap, which trapping is impossible to achieve by purely electrostatic means because Laplace's equation dictates that stationary points are always saddle points i.e. there are no real potential minima. The RF field is typically applied to a multiple rod set or ring set. The size and nature of the effective potential of a multiple has

been derived using the adiabatic approximation of Gerlich *et al*, ibid, and is shown to be:

$$V^* = \frac{n^2 q^2 V_o^2 r^{2n-2}}{4m\Omega^2 r_o^2} \qquad (1)$$

where 2n is the number of electrodes, q is the charge of an ion, Vo is the magnitude of the applied RF field, is the angular frequency, m is the mass of an ion, r_o is the radius of the multipole, and r the normalised radial position. The equation shows a 2n-2 power dependence of radial position, meaning octopoles have steeper sided flatter bottomed potential wells than do hexapoles or quadrupoles. The action of such a potential well on an ion in the presence of a background gas is to confine the ion radially to the central axis of the multipole or ring set. Such radial confinement prevents diffusion losses which would otherwise reduce the sensitivity of the instrument.

The impetus to the ions that is provided by the flowing gas depends on the nature of the duct through which it is flowing. In non-limiting embodiments the ion extraction device is placed between two vacuum chamber of differing pressures, and the natural gas flow between these chambers provides the driving force necessary for the operation of the device. Steady laminar flow is desirable for operation of the device. The special case of such flow in a circular pipe is described by the Hagen-Poiseuille law, see for example "Mechanisms of fluids" by Bernard Massey and John Ward Smith - Nelson Thornes Press (reprinted 2001), ISBN 0-7487-4043-0. This law shows that the velocity of the gas v_g as it flows in the x direction is given by:

$$v_g = \frac{-1}{4\mu}\frac{dP}{dx}(R^2 - r^2) \qquad (2)$$

Where R is the radius of the duct, μ is the coefficient of absolute viscosity, P is the pressure in the duct at the point of consideration and r is the radial position in the duct. This parabolic function shows that the velocity is at an maximum at the duct centre slowing down to zero at the duct wall i.e. the velocity varies slowly at the duct centre slowing down more and more rapidly as one approaches the walls. Laminar flow is best established when the length of the duct is large compared to its radius. It is common for the flow between two chambers of a spectrometer to become choked, that is to say limited by the conductance of the aperture pipe between the chambers rather than by the pumping speed of the pump in the down stream chamber. It is envisaged that the present invention may operate in a choked flow manner. In any case the Hagen-Poiseuille equation allows us to determine the velocity of the gas and therefore the velocity of the swept ion at any point in the duct given knowledge of upstream and downstream pressure and duct geometry. Laminar flow is ensured by consideration of pressure differential and duct geometry. A useful parameter is the Reynolds number which for a circular duct is given by:

$$\mathrm{Re} = \frac{\rho \bar{u} d}{\mu} \qquad (3)$$

and for laminar flow should be less than 2000.

The third force experienced by ions flowing through the duct is from the potential barrier. This electric field can accelerate or retard ions depending on is size and direction. The motion of an ion at these elevated pressures depends on an ion's mobility rather than its mass to charge ratio as would be the case of a collision less medium. A comprehensive review by E A Mason and E W McDaniel "The mobility and diffusion of ions in gases" Wiley series in plasma physics, John Wiley & Sons 1973 ISBN 0-471-58387-1 sets out the framework of the concept of ion mobility. The drift velocity, v_d of an ion under the influence of an electric field is given by:

$$v_d = KE_b \qquad (4)$$

where K is a constant of proportionality and is known as the scalar of mobility, and E_b is the barrier potential field. The relationship is valid if ions acquire velocities that are below or of the order of thermal velocities otherwise K becomes a tensor. For the purposes of our analysis we assume a scalar value for the ion mobility: the ion mobility does however decrease with increasing pressure. In the present invention the pressure in the duct or other conduit changes along its length as the pressure in the duct changes. Knowledge of this pressure variation and the application of the desired axial field profile can lead to the spatial separation of the ions as previously described.

The interaction of the three forces in the present invention can be described with reference to Figure 1, which shows a first chamber 10 at a relatively high pressure Pu, a guide duct 12 in which laminar gas flow is developed, and a second chamber 14 at a relatively low pressure Po. The effective (ponderomotive) potential confines ions radially as they progress down the guide in the presence of a gas (for presentational purposes, electrodes which are used to generate the potential are not shown in Figure 1). Note that, if the upstream pressure Pu is high, then the effective potential field may be reduced at the upstream end of the guide. As the pressure decreases along the length of the guide the value of the effective potential field increases to a constant value where by the reduction due to high pressure collisions is minimal (the effective potential field is reduced when the number of collisions an ion undergoes during an RF period is high - for a comprehensive explanation see A V Tolmachev, Nuclear instruments and method in physics research B, 124 (1997) 112-119). Further down the ion guide, the effective potential field is of a constant form E3(r), the effective potential field being some function of radius dependant on multipole geometry and laminar flow, laminar flow having been established and having a characteristic maximum velocity v_3 at guide pressure P3. Ions are also subjected to a barrier potential field E_b. Figure 2 shows the case where the guide duct is long compared to the extent of the

potential barrier so the velocity of the gas flow v_g can be considered constant over the length of the barrier. Ions are prevented from passing the barrier if $|KE_b| > |v_g|$, where KE_b is as defined with reference to equation (4) and the two forces (from the gas and the barrier field) are opposing each other. By reducing the value of E_b temporally (either stepwise or continuously) ions of progressively higher and higher mobilities are allowed through to subsequent stages of the instrument. Figure 3 shows a potential barrier where the field reduces linearly, that is to say the voltage reduces parabolically from its maximum value. Ions of higher mobility are shown in Figure 3 as small spheres compared to the large spheres representing ion of lower mobility. This illustrates the spatial spread of ions of differing mobilities. Lowering the barrier voltage by a certain extent will allow ion 1 to escape while the remaining ions will move closer to the barrier edge. The extent to which the barrier voltage can be lowered in order to allow ion 1 to escape whilst retaining the other ions is calculable using the principles and equations described above and, furthermore, can readily be established empirically. The spectrometer is preferably operated in a fill-isolate-scan operation cycle. In such a scheme there is a fill cycle in which ions are allowed to accumulate behind the potential barrier, and an isolate cycle in which no more ions are admitted to the device. This prevents ions of low mobility entering the device after the barrier is lowered to eject the initial population, that is to say aliasing in the resultant spectrum is avoided. The device is then scanned to eject ions of higher and higher mobilities. The isolation stage is preferably fitted upstream of the barrier stage, and advantageously this isolation stage may itself accumulate ions for subsequent release to the barrier thus retaining a 100% duty cycle (complete utilisation of ions from the source). Figure 4 shows the electric field generated in the spectrometer during these different stages. Note that for simplicity the isolation stage is always shown having steep sides to the potential gradient - it should be understood that the size of the electric field of the isolation stage should be simply high enough to prevent any ions being transmitted to the barrier stage. Figure 4d-4f shows how the barrier stage is scanned from high to low field allowing ions of progressively higher mobility to traverse the barrier to subsequent stages of the spectrometer. The barrier field

may be decreased stepwise down to the minimum value or it may be scanned continuously.

It is an advantage of the present invention that the ions of differing mobilities may be ejected when desired. This is in contrast to the drift tube experiments whereby ions exit at ever decreasing mobilities on the timescale of the drift tube separation itself, this timescale is commonly milliseconds. This flexibility of temporal ejection means that the barrier spectrometer may be optimally interface to the subsequent stages of the spectrometer; be they detector, quadrupole, TOF, FTMS, ion trap, or a combination of any of these components.

In a further embodiment of the invention the spatial separation of ions shown in Figure 3 may be exploited by using a pulsed extraction field at the end of the barrier. This pulsed extraction field may be adjusted to penetrate only the very end of the ion extraction device so that ions of a desired mobility or range of mobilities may be extracted in pulses of any desired duration. This makes the present invention even more flexible in terms of interfacing to other pulsed spectrometers e.g. orthogonal acceleration time of flight (OA-TOF) whereby increase in duty cycle to almost 100% may be achieved (see EP 1,271,138 and US 5,689,111, the contents of both of which are hereby incorporated by reference). Figure 5 shows how such a scheme may be employed. There are two states, 1 & 2, for the pulsed extraction fields. The scheme depicted in Figure 5 can be an adjunct to the scheme shown in Figure 4, in which the alternation between states 1and 2 is taking place on a faster time scale than the variation in barrier height. In such embodiments, the pulsed extracting field can be considered to be an auxiliary field which is imposed upon the variation in barrier field in the scan mode shown in Figure 4. Again the barrier may be scanned continuously or in a stepwise fashion. One method of operation would be to set up a particular maximum barrier field E_{max}, and then alternate between state 1 and 2 until no more ions are extracted, then to reduce the barrier height to a new lower value of E_{max} and repeat the stepping between states 1 and 2. Other schemes would suggest themselves to the skilled reader.

In its simplest form, analytical devices of the present invention comprise an ion

source, a barrier stage and a detector. When using electrospray ionisation the spectrometer may be constructed using only a single rotary pump. Typically pressure would be in the millibar region but pressures as high as 20 mbar and as low as 10^{-3} millibar may be employed. Figure 6a is a schematic diagram of this embodiment, which may be portable and so suitable for field use, comprising an ion source 60, an ion extraction device 62 and a detector 64. In the ion extraction device 62 ions from the ion source 60 are entrained in a laminar flow of a carrier gas and the barrier potential is developed using the principles set forth herein. The detector 64 can be any detector suitable for analysing the ions extracted from the ion extraction device 62 or for analysing physical phenomena associated in some way with ions extracted from the ion extraction device 62. The detector 64 might comprise a spectroscopic technique or a mass spectrometric technique. Non-limiting examples of mass spectrometric techniques comprise quadruple, TOF, and FTMS techniques. It is possible to utilise a plurality of detection techniques in the detector 64 stage. The invention is not limited to the use of electrospray ionisation as the source of ions. Other ions sources might be used, such as, for example, MALDI (Matrix Assisted Laser Desorption Ionisation), electron impact, chemical ionisation, fast atom bombardment, field ionisation, field desorption, and soft ionisation techniques employing vacuum ultraviolet or soft X-ray radiation produced by a convenient light source such as a laser. MALDI (and other laser based ionisation techniques) is pulsed in nature, and thus it is not necessary in such instances to employ an ionisation stage to prevent build-up of ions.

Figure 6b shows a tandem mobility instrument which can be - but is not limited to - a tandem mobility TOF instrument. The instrument comprises in common with the embodiment shown in Figure 6 (a) an ion source 60, and an ion extraction device 62. Additionally, the instrument comprises a MS detector 66 and a further stage 68 at intermediate pressure situated between the ion extraction device 62 and the MS detector 66. The stage 68 may itself take the form of a further ion extraction device having a barrier potential which can be selectively varied to allow chosen ions entrained in a common flow of a carrier gas to exit the stage 68. Alternatively, the stage 68 may act as a collision cell to

fragment ions of a known mobility emerging from ion extraction device 62.

It is common to fragment ions in multiple collision cells to obtain fragmentation information. Such collision cells are often placed between two mass spectrometers such as in the case of triple quadrupoles and Q-TOF instruments. The collision energy of such instruments may be optimised according to the mass to charge selected by the first mass spectrometer. In a similar way, knowledge of the ion mobility of an ion selected using the present invention can lead to optimum setting of the collision energy for the chosen species. In such a scheme, ions are extracted from the ion extraction device 62 using potentials devised to impart the optimum collision energy to the extracted ion. A further advantageous facet of this configuration makes use of the fact that the ion extraction device can be configured as a storage device. This means that all ions of all mobilities may be optimally fragmented thus yielding very high information content from complex mixtures. Further improvement in duty cycle for fragment ions may be realised by the use of the second ion extraction device blocking ions after fragmentation. Figure 7 shows the potential energy diagram an ion sees in such a spectrometer, i.e. a spectrometer in which the stage 68 is also an ion extraction device of the present invention. Ion extraction device 62 may be of the scanning type as shown in Figure 4 or of the pulsed extraction type as shown in Figure 5. Stage 68 is preferably of the pulsed extraction type in the instance in which the detector 66 is an orthogonal TOF as this configuration allows a 100% duty cycle for the fragment ions generated upstream of a stage 68.

Figure 8 shows a possible construction method for stage 68 shown in Figure 7. This spectrometer may double as a collision cell with gas being introduced part way down the cell through gas inlet 70. The stage 68 comprises a central duct 72 which may be formed of a leaky dielectric material of internal diameter D of constant resistivity, with a multiple rod set 74 providing the ponderomotive radial confinement force. The spectrometer further comprises electrodes 76, 78, 80. The gas is introduced a distance L1 from the input end of the duct 72 and laminar flow conditions can be established in opposing directions towards

each of the ends of the tube. This is because the outside chamber pressure is lower than in the duct 72. Ions input the cell and overcome the force due to gas flow by the application of potentials 1 and 2 to metalised electrodes 76, 78. The potential field of the type shown previously in Figure 3 can be created by application of potentials 2 and 3 to the electrodes 78, 80. The diameter of the duct 72 varies in the region of between electrodes 78 and 80 . The constant resistivity of the leaky dielectric means that most of the potential drop and therefore higher electric field takes place at the exit end of the duct 72. An auxiliary pulsed output field may now be derived from a pulsed voltage 4 applied to an end plate 82 at the output end of the device.

Figure 9 shows another method of construction of an ion extraction device whereby a duct 90 is positioned between an upstream chamber 92 and a downstream chamber 94. The duct 90 comprises a ring set 96 spaced by insulators 98 which are pushed or bonded together to create a gas tight construction. The duct need not be long enough to establish a full parabolic laminar flow profile at the region in which the barrier potential is established as the gas proceeds down the duct it changes velocity profile from flat to parabolic as shown with profiles A,B &C. The important point is that at the centre of the duct the velocity does not vary rapidly in the radial direction and that the ions are confined to the centre of the device by the time they reach the potential barrier which in the diagram is applied to electrode number 6. In the diagram an aperture plate 100 is shown, potential applied to this plate may also provide a barrier field in accordance with the invention.

CLAIMS

1. A method of extracting ions comprising the steps of:

providing a source of ions;

entraining said ions in a laminar flow of a carrier gas;

providing a barrier region in which an electrical field is applied across the laminar flow of carrier gas, the magnitude and direction of the electrical field being selected so as to prevent at least some of the ions entrained in the laminar flow from passing through the electrical field; and

varying the electrical field so as to allow ions of chosen characteristics to pass through the electrical field.

2. A method according to claim 1 further comprising the step of confining the entrained ions radially with respect to the axis of flow of the laminar flow of carrier gas.

3. A method according to claim 2 in which the step of confining the entrained ions comprises radially confining the ions by a ponderomotive force.

4. A method according to any of claims 1 to 3 in which the step of varying the electrical field comprises reducing the magnitude of the electrical field to a level that permits ions of a first range of ion mobilities to pass through the electrical field but prevents ions of a second range of ion mobilities from passing through the electrical field.

5. A method according to claim 4 in which the electrical field is reduced in a stepwise manner.

6. A method according to claim 4 in which the electrical field is reduced in a continuous manner.

7. A method according to any previous claim in which, prior to the step of varying the electrical field, an isolating electrical field is applied so as to prevent ions upstream of the isolating electrical field from being carried to the barrier region.

8. A method according to claim 7 in which, after the step of varying the electrical field, the isolating electrical field is reduced so as to permit ions upstream of the isolating electrical field to be carried to the barrier region.

9. A method according to any previous claim in which the step of varying the electrical field is performed so as to extract ions from the barrier region in a pulsed manner.

10. A method according to claim 9 in which the electrical field is varied between at least a first state and a second state, in which the peak magnitude of the electrical field in the second state is less than the peak magnitude of the electrical field in the first state, so that ions of a defined range of mobilities can be extracted from the barrier region when the electrical field is in the second state and prevented from passing out of the barrier region when the electrical field is in the first state.

11. A method according to claim 10 in which the location of the peak magnitude of the electrical field in the second state is upstream of the location of the peak magnitude of the electrical field in the first state so that only ions of a desired range of mobilities which are situated in a predetermined range of locations are extracted.

12. A method according to any of claims 9 to 11 when dependent on claim 4 in which the magnitude of the electrical field is reduced, and then pulsed extraction of ions is performed.

13. A method according to any previous claim in which the electrical field in the barrier region is selected so as to produce a spatial separation of ions of different ion mobilities in the barrier region.

14. A method according to any previous claim further comprising the step of applying a drift field to at least a portion of the laminar flow of carrier gas.

15. A method according to claim 14 in which an arrangement comprising a leaky dielectric shield is used to provide the drift field.

16. A method according to claim 15 in which the arrangement is a multipole arrangement.

17. A method according to any previous claim in which the velocity distribution of the carrier gas as a function of radial position of the laminar flow in the barrier region is substantially parabolic.

18. A method of analysing ions or phenomena associated with ions comprising the steps of:

providing analysis means for analysing ions or phenomena associated with ions;

extracting ions into the analysis means using a method according to any of claims 1 to 17; and

analysing the extracted ions or phenomena associated with the extracted ions.

19. A method according to claim 18 in which the analysis means comprises mass spectrometry means.

20. A method according to claim 19 in which the mass spectrometry means comprises a time of flight (TOF) mass spectrometer.

21. A method according to claim 19 in which the mass spectrometry means comprises a multipole, Fourier transform or ion trap mass spectrometer.

22. A method according to any of claims 19 to 21 in which the analysis means comprises a collision cell.

23. A method according to claim 22 in which ions are extracted from the collision cell using a method according to any of claims 1 to 17.

24. An ion extraction device comprising:

gas flow means including a gas flow conduit suitable for generating a laminar flow of carrier gas therethrough;

ion entrance means through which ions can be introduced into the gas flow conduit so that said ions become entrained in said laminar flow; and

electrical field producing means for applying an electrical field to a barrier region of the gas flow conduit, the electrical field producing means being operable to apply the electrical field across the direction of laminar flow in said gas flow conduit so as to prevent at least some ions entrained in a laminar flow in the gas flow conduit from passing through the electrical field;

in which the electrical field producing means is variable so as to allow ions of chosen characteristics to pass through the electrical field.

25. An ion extraction device according to claim 24 further comprising ion radial confinement means for confining entrained ions radially with respect to the axis of flow of the laminar flow of carrier gas through the gas flow means.

26. An ion extraction device according to claim 25 in which the ion radial confinement means comprises means for generating a ponderomotive force in the gas flow means.

27. An ion extraction device according to claim 26 in which the ion radial confinement means comprises an RF electrode set.

28. An ion extraction device according to any of claims 24 to 27 further comprising drift field applying means for applying a drift field along at least a portion of the gas flow conduit.

29. An ion extraction device according to any of claims 24 to 28 in which the gas flow conduit comprises a duct.

30. An ion extraction device according to any of claims 24 to 29 in which the electrical field producing means is variable so as to reduce the magnitude of the electrical field to a level that permits ions of a first range of ion mobilities to pass through the electrical field but prevents ions of a second range of ion mobilities from passing through the electrical field.

31. An ion extraction device according to any of claims 24 to 30 further comprising ion isolation means operable to apply an isolating electrical field upstream of the barrier region so as to prevent ions upstream of the isolating electrical field from being carried to the barrier region.

32. An ion extraction device according to any of claims 24 to 31 in which the electrical field producing means is operable to extract ions from the field in a pulsed manner.

33. An ion extraction device according to any of claims 24 to 32 further comprising an ion source.

34. An analytical device comprising:

an ion extraction device according to any of claims 24 to 28; and

analysis means for analysing ions or phenomena associated with ions;

in which the analysis means is coupled to the ion extraction device so that ions extracted from the ion extraction device are introduced to the analysis means.

35. An analytical device according to claim 34 in which the analysis means comprises mass spectrometry means.

36. An analytical device according to claim 35 in which the mass spectrometry means comprises a time of flight (TOF) mass spectrometer.

37. An analytical device according to claim 35 in which the mass spectrometry means comprises a multipole, Fourier transformer or ion trap mass spectrometer.

38. An analytical device according to any of claims 34 to 37 further comprising a collision cell.

39. An analytical device according to claim 38 in which the collision cell comprise:

a collision cell gas flow conduit through which the laminar flow of the carrier gas generated in the ion extraction device can be introduced and sustained;

collision gas inlet means for introducing a gas to the gas flow conduit; and

collision cell electrical field producing means for applying an electrical field to a barrier region of the collision cell gas flow conduit, the collision cell electrical field producing means being operable to apply the electrical field across the direction of laminar flow in said collision cell gas flow conduit so as to prevent at least some ions entrained in the laminar flow in the collision cell gas flow conduit from passing through the electrical field;

in which the collision cell electrical field producing means is variable so as to allow ions of chosen characteristics to pass through the electrical field.

40. An analytical device according to claim 39 in which the collision cell further comprises collision cell drift field applying means for applying a drift field along at least a portion of the collision cell gas flow conduit of sufficient magnitude to overcome the force provided by a gas entering the collision cell through the collision gas inlet means.

41. An analytical device according to claim 40 in which the collision cell drift field applying means comprises a leaky dielectric shield.

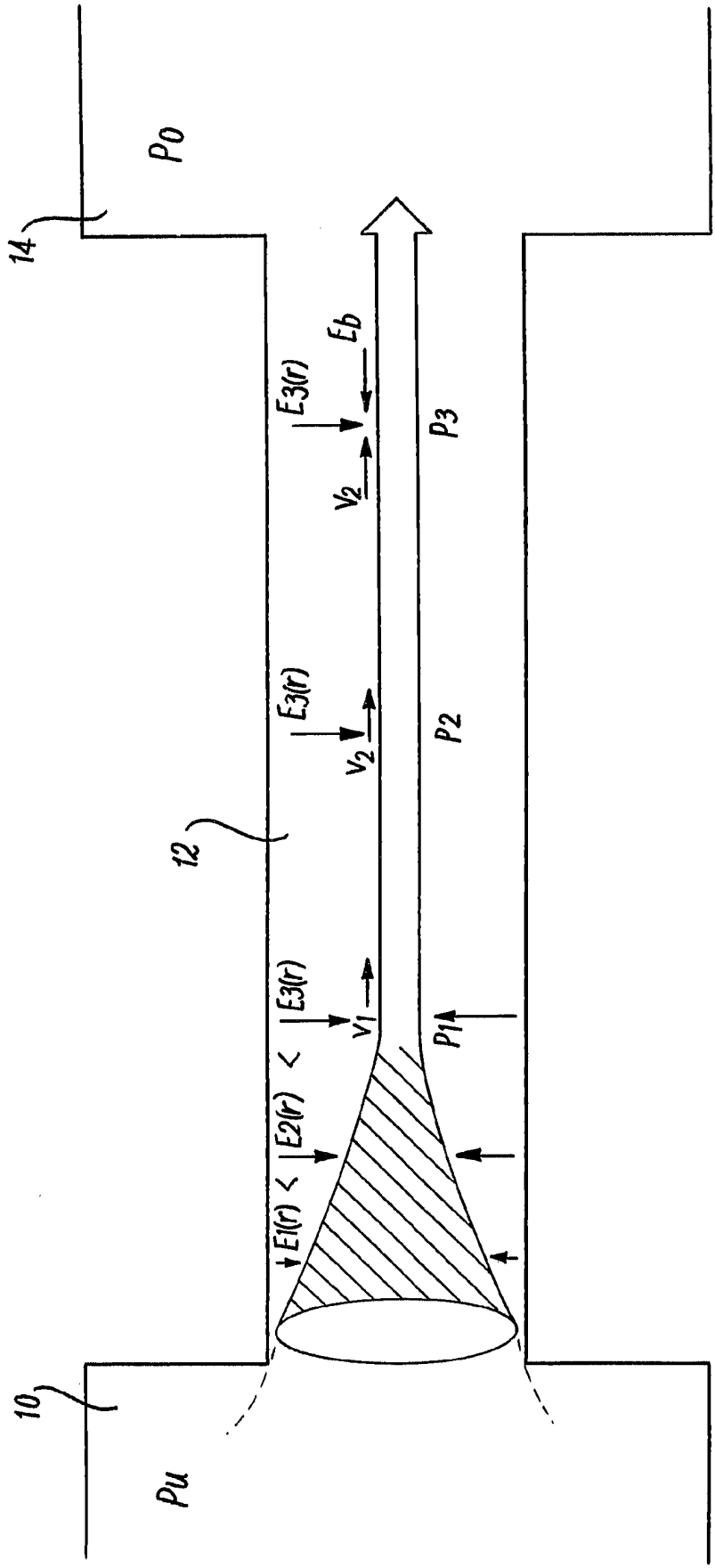

FIG.1

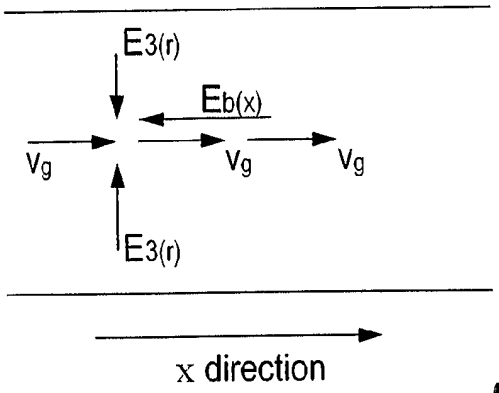
E3(r)
Eb(x)
Vg
Vg
Vg
E3(r)
x direction

FIG. 2

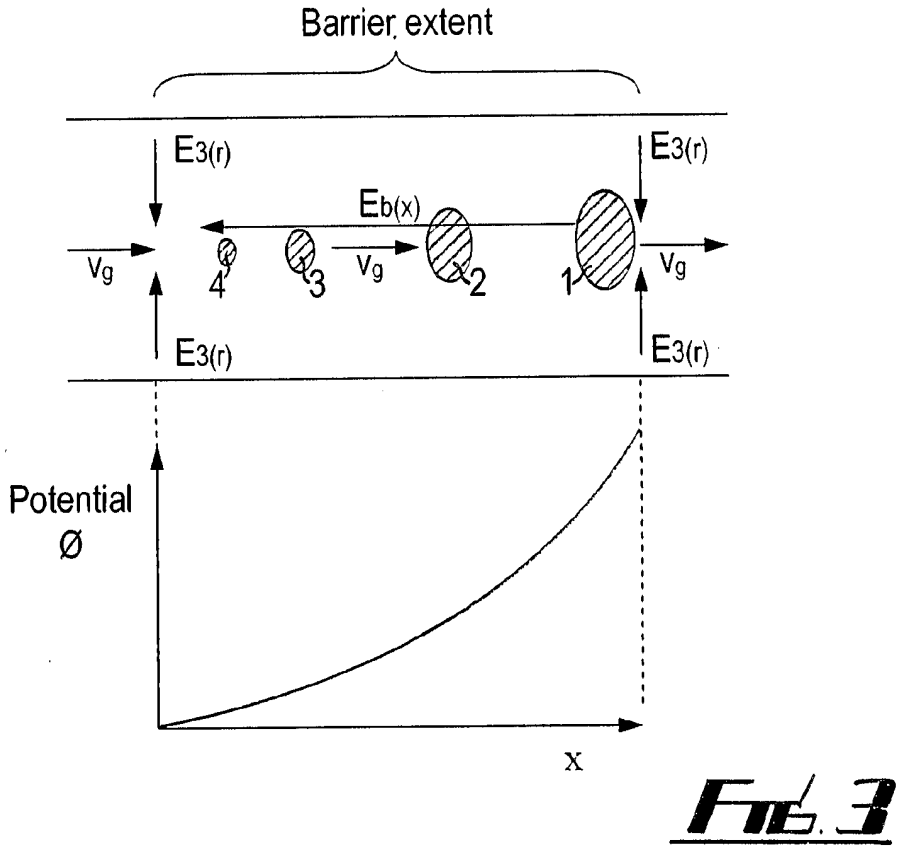
Barrier extent
E3(r)
E3(r)
Eb(x)
Vg
4
3
Vg
2
1
Vg
E3(r)
E3(r)
Potential
Ø
x

FIG. 3

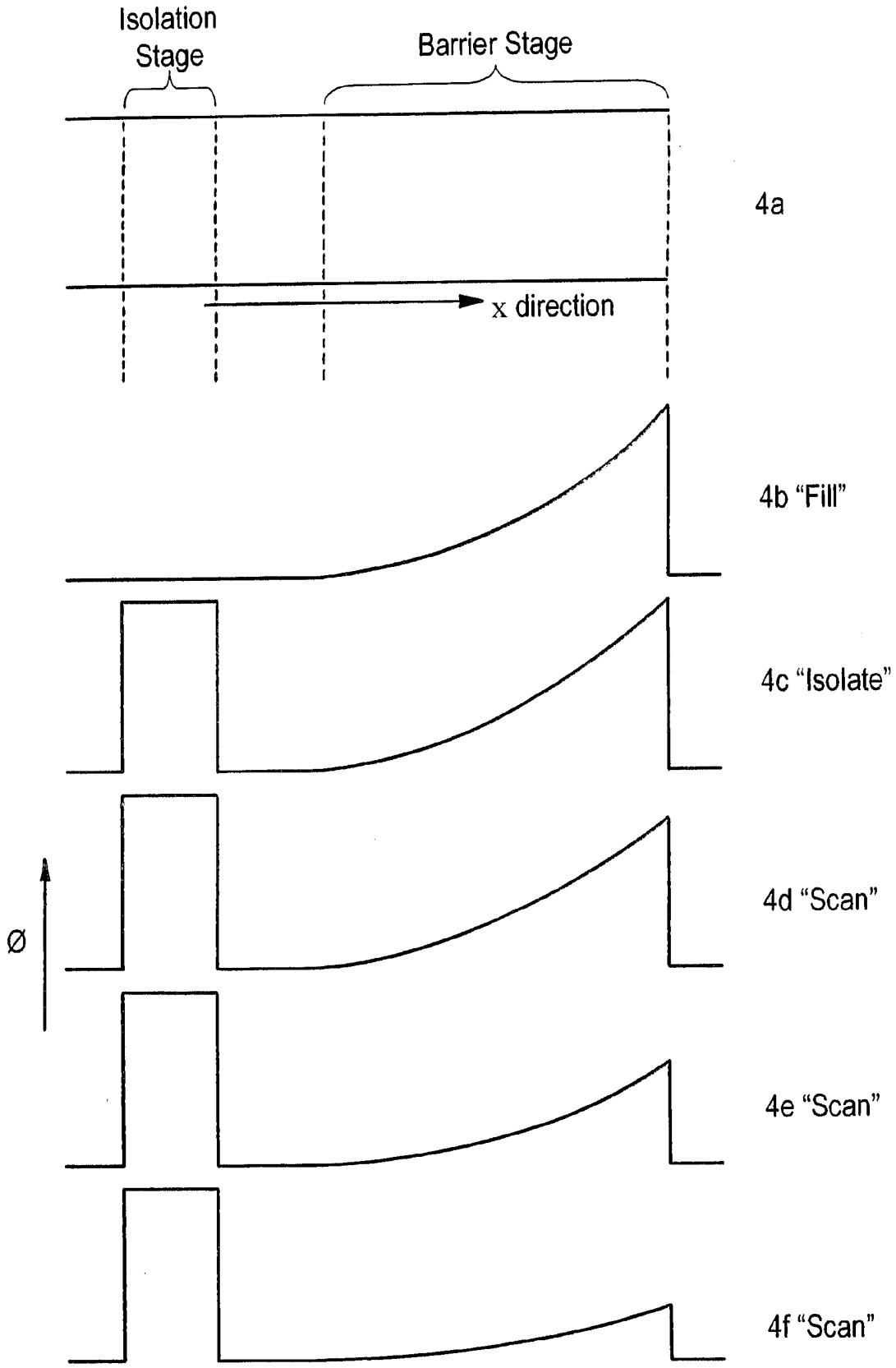
Isolation Stage
Barrier Stage
4a
x direction
4b "Fill"
4c "Isolate"
Ø
4d "Scan"
4e "Scan"
4f "Scan"

FIG. 4

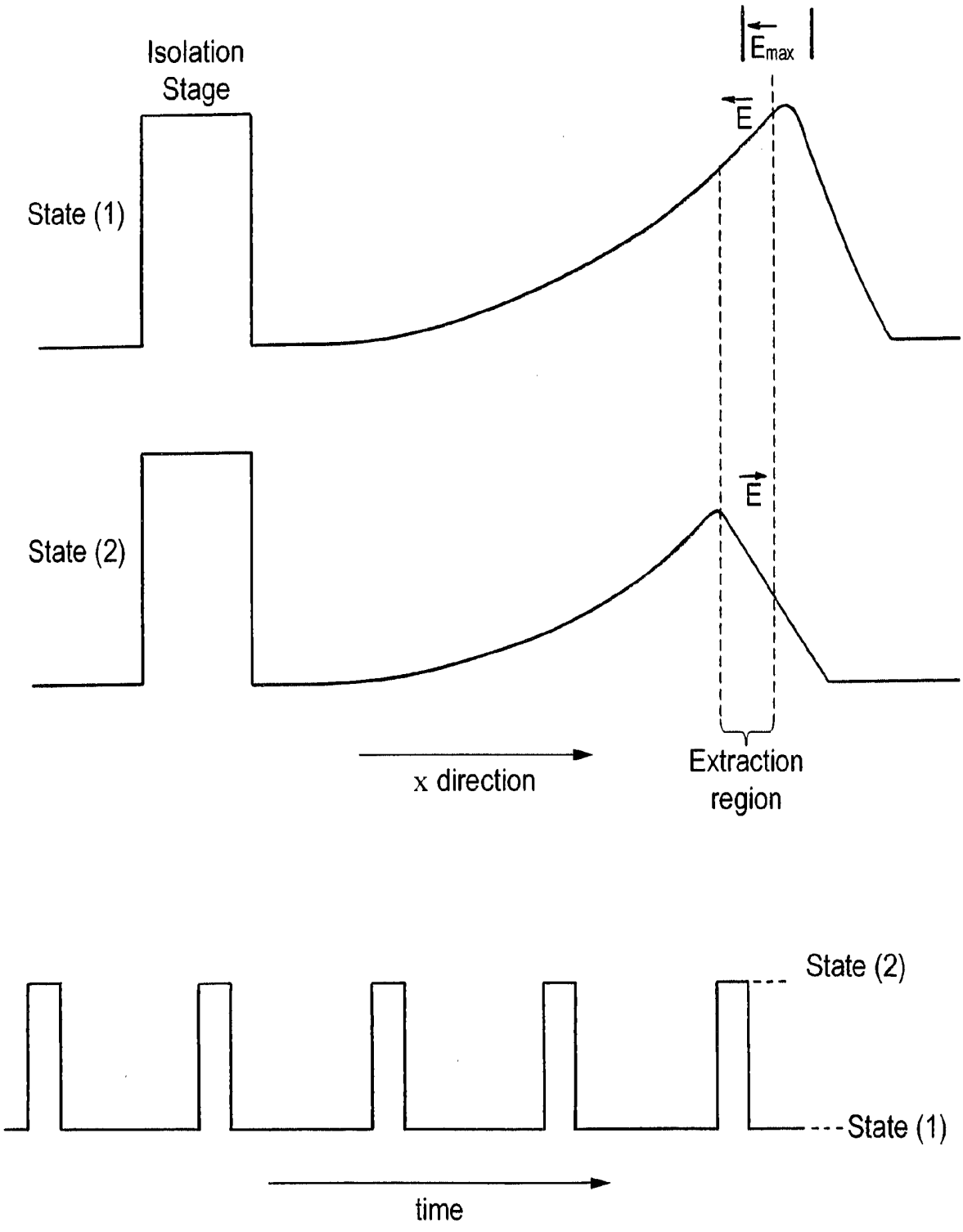
Isolation Stage
State (1)
State (2)
E_{max}
E
E
x direction
Extraction region
State (2)
State (1)
time

FIG. 5

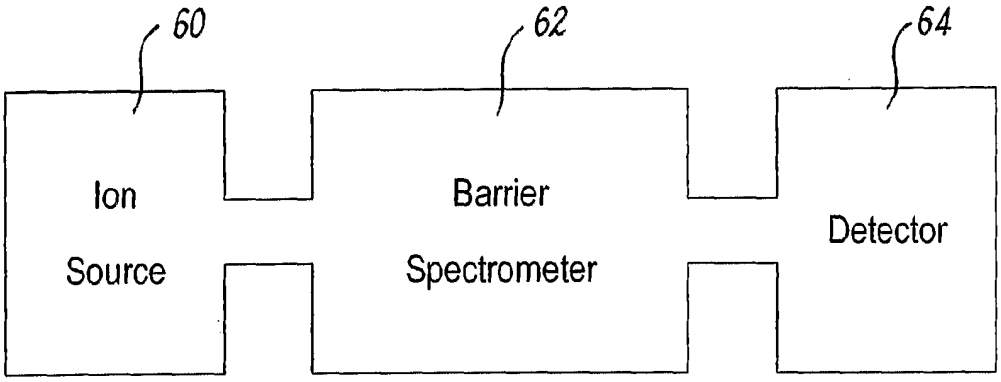
60
62
64
Ion Source
Barrier Spectrometer
Detector

Fig 6a

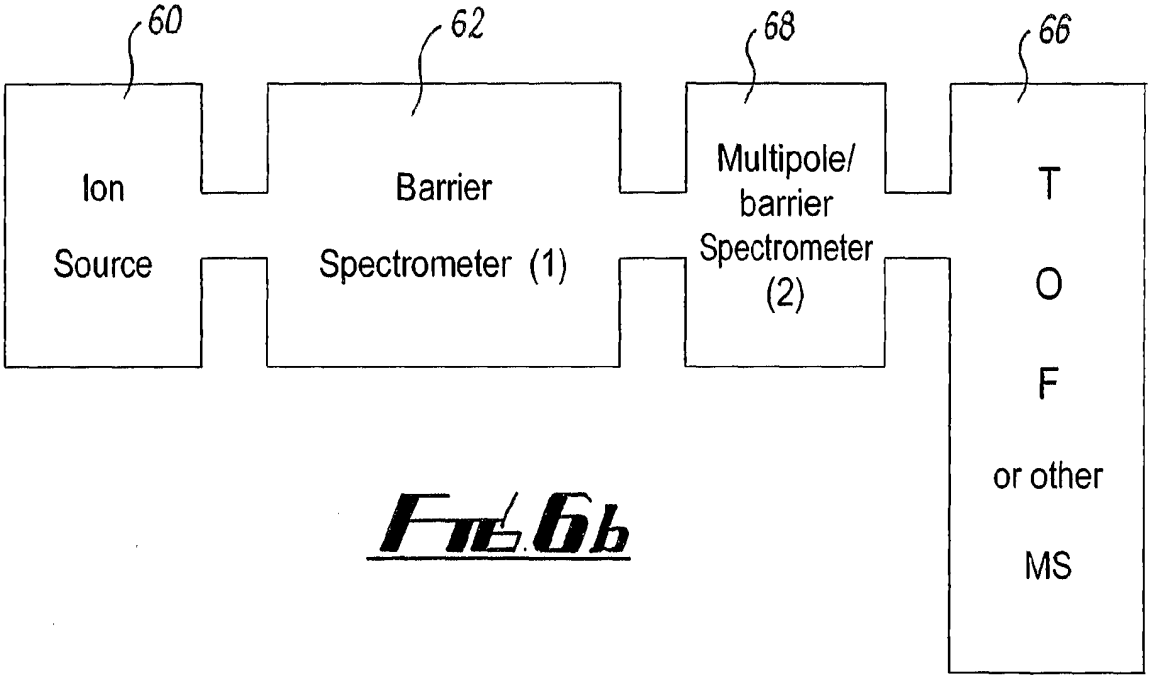
60
62
68
66
Ion Source
Barrier Spectrometer (1)
Multipole/ barrier Spectrometer (2)
T O F or other MS

Fig 6b

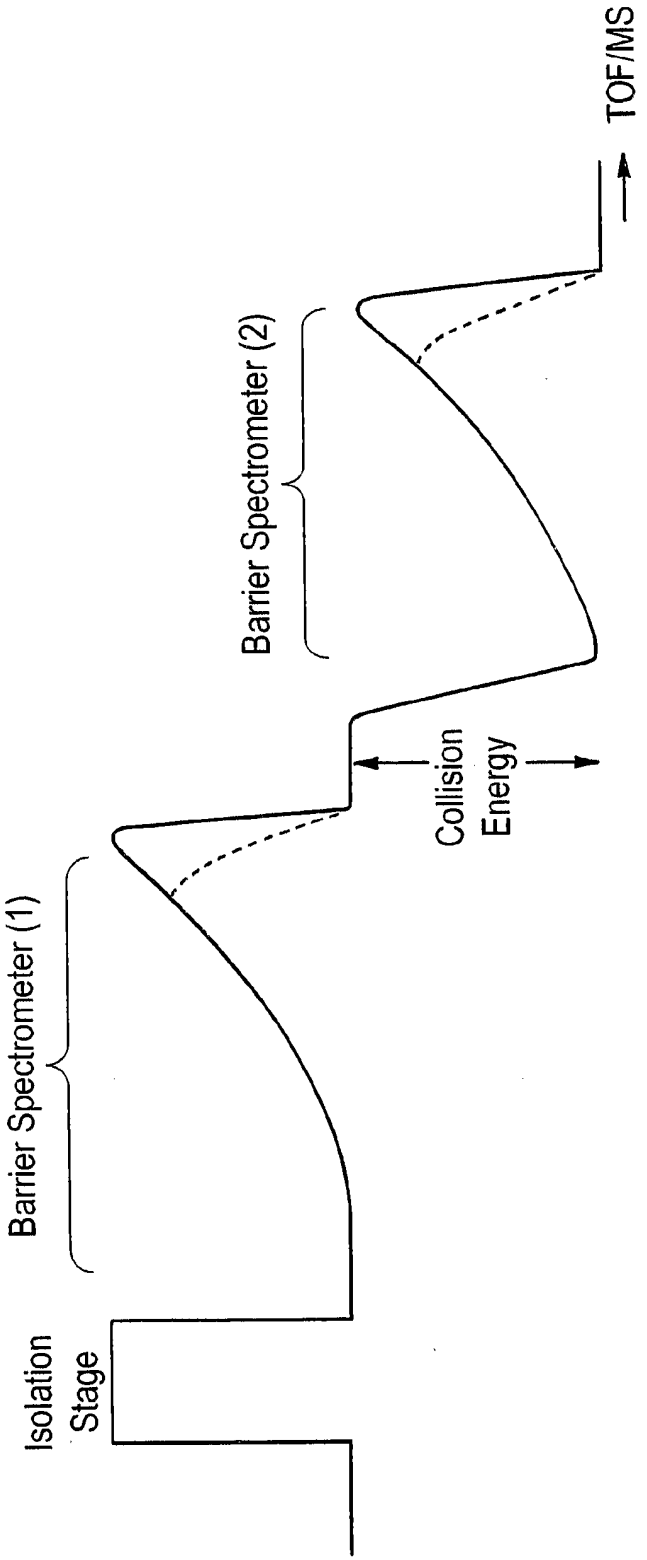
Isolation Stage
Barrier Spectrometer (1)
Collision Energy
Barrier Spectrometer (2)
TOF/MS

FIG. 7

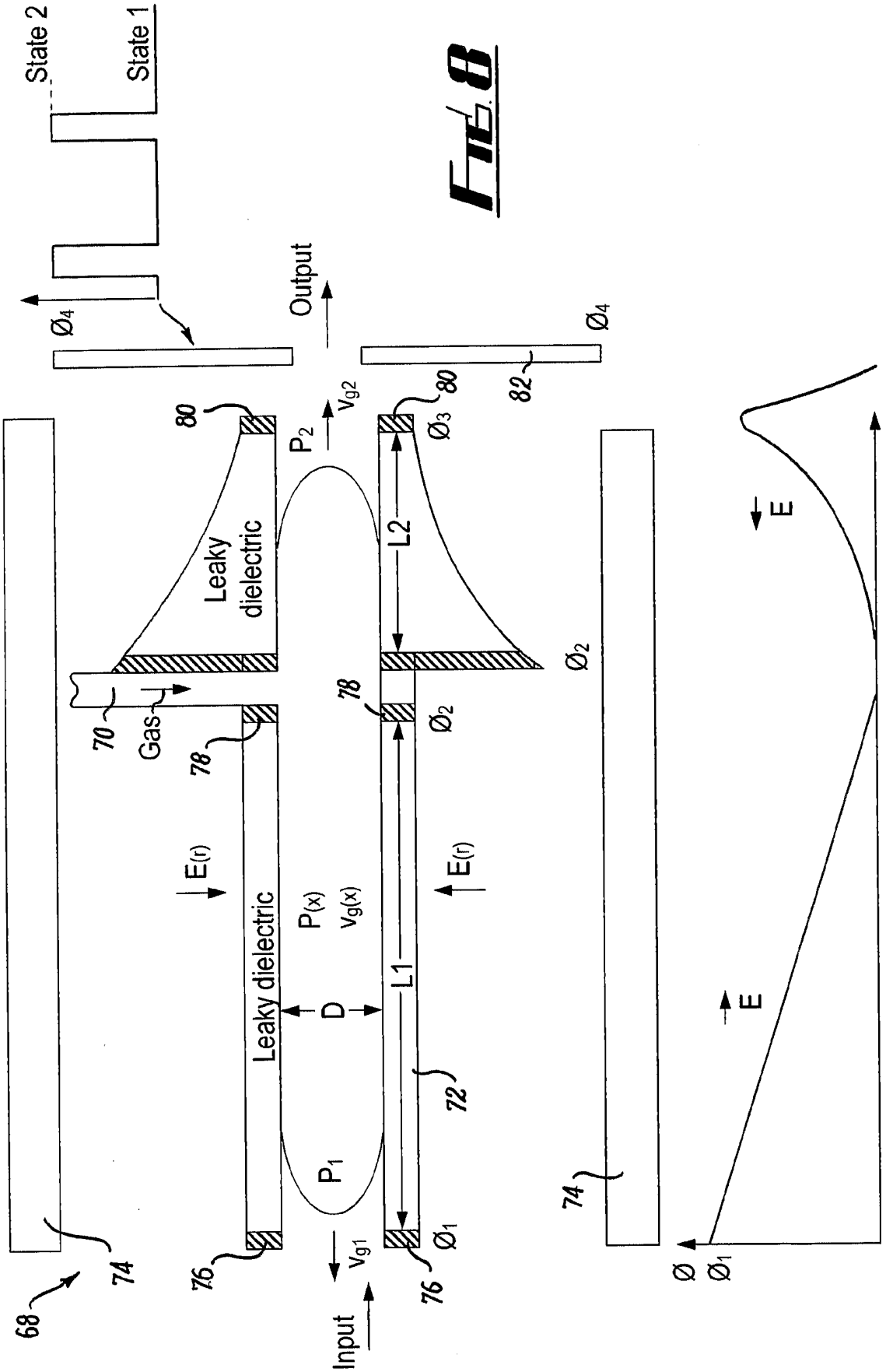
State 2
State 1
Ø4
Output
Ø4
80
82
80
P2
Vg2
Ø3
Leaky dielectric
L2
Ø2
78
70
Gas
78
Ø2
E(r)
E(r)
P(x)
Vg(x)
Leaky dielectric
D
L1
72
P1
Vg1
Ø1
76
76
74
68
Input
74
E
E
Ø
Ø1

FIG. 8

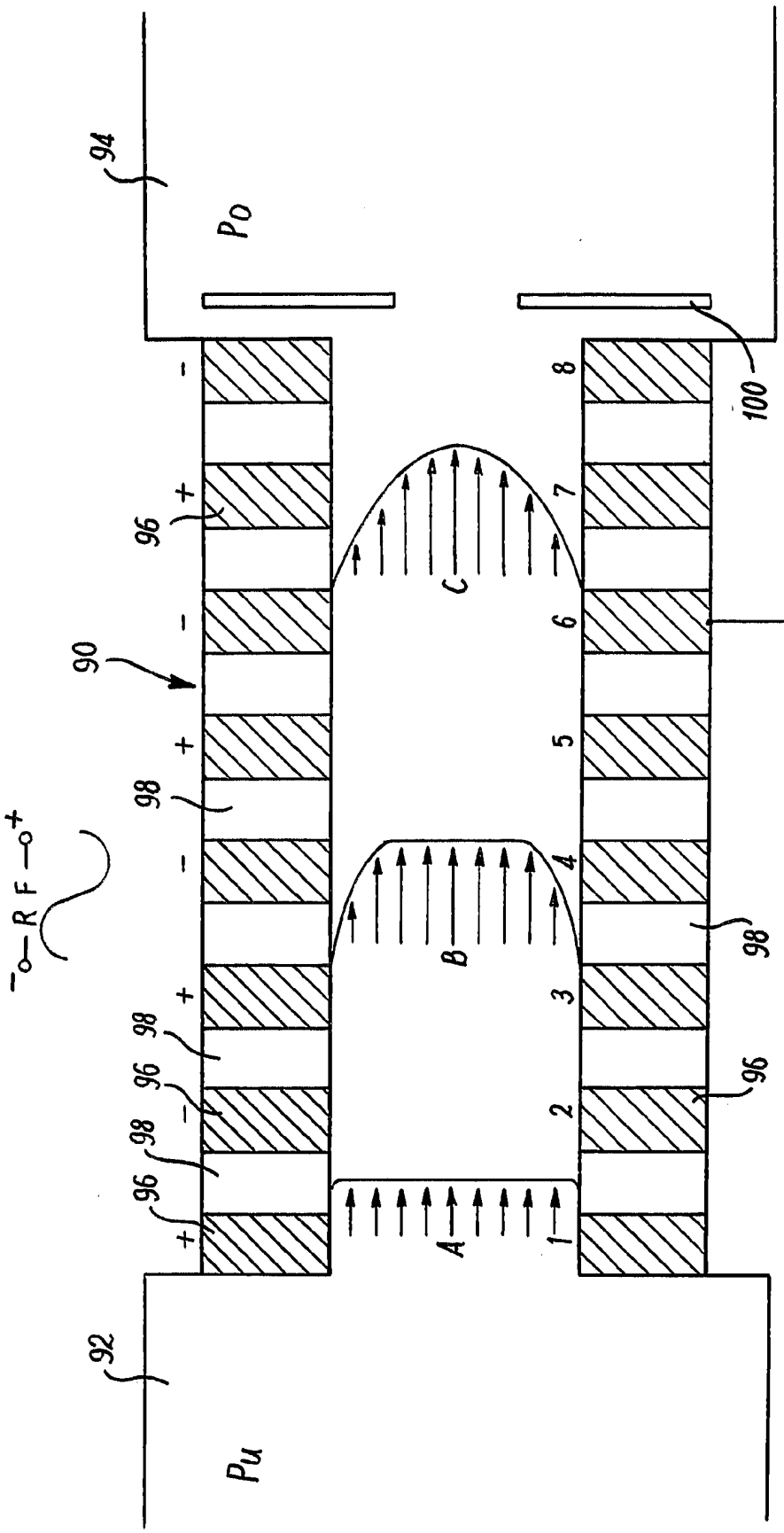

Fig 9