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(71) Applicant(s):
Thermo Fisher Scientific (Bremen) GmbH
(Incorporated in the Federal Republic of Germany)
Hanna-Kunath-Str. 11, 28199 Bremen,
Federal Republic of Germany

(72) Inventor(s):
Alexander Makarov
Dmitry E Grinfeld
Mikhail A Monastyrskiy

(74) Agent and/or Address for Service:
Boult Wade Tennant
Verulam Gardens, 70 Gray's Inn Road,
LONDON, WC1X 8BT, United Kingdom

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(56) Documents Cited:
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GB 2080021 A
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WO 2006/102430 A3
WO 2005/001878 A3
DE 004408489 A
US 20070176090 A1

(58) Field of Search:
INT CL **H01J**
Other: **ONLINE: EPODOC, WPI**

(54) Abstract Title**: Multi-reflectron time-of-flight mass spectrometer**

(57) The present invention provides a method of reflecting ions in a multi-reflection time of flight mass spectrometer comprising providing an ion mirror having a plurality of electrodes, the ion mirror having a cross section with a first, minor axis (Y) and a second, major axis (X) each perpendicular to a longitudinal axis (Z) of the ion mirror which lies generally in the direction of time of flight separation of the ions in the mirror. Ions are guided towards the ion mirror and a voltage applied to the electrodes so as to create an electric field which: (a) causes the mean trajectory of the ions to intersect a plane of symmetry of the ion mirror which contains the longitudinal (Z) and major axes (X) of the mirror; (b) causes the ions to reflect in the ion mirror; and (c) causes the ions to exit the ion mirror in a direction such that the mean trajectory of ions passing through the ion mirror has a component of movement in a direction (Y) perpendicular to and diverging from the said plane of symmetry thereof. This arrangement is said to improve the resolving power of the mass spectrometer. Further embodiments relate to other positions and orientations of the mirrors in order to further improve resolving power.

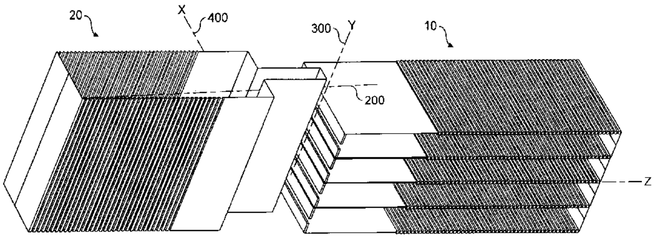

FIG. 1

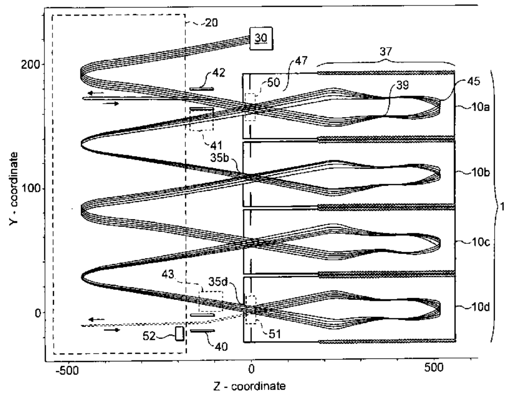

FIG. 3

GB 2 455 977 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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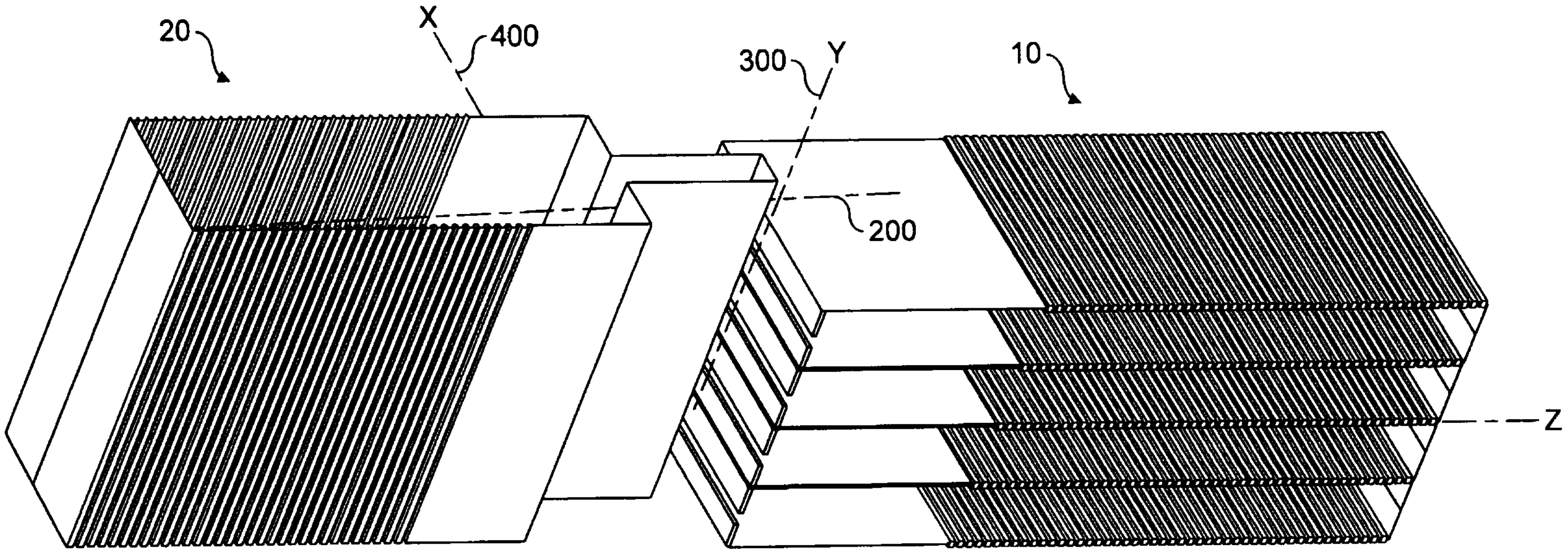


FIG. 1

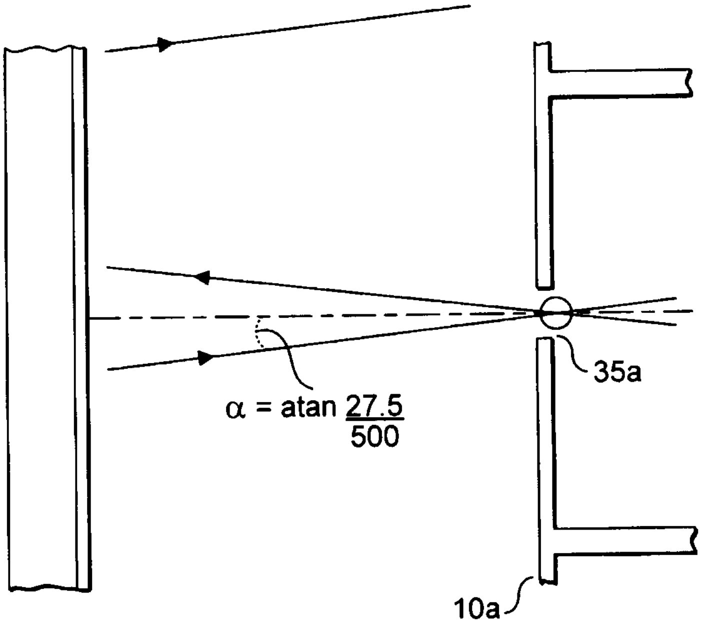


FIG. 2

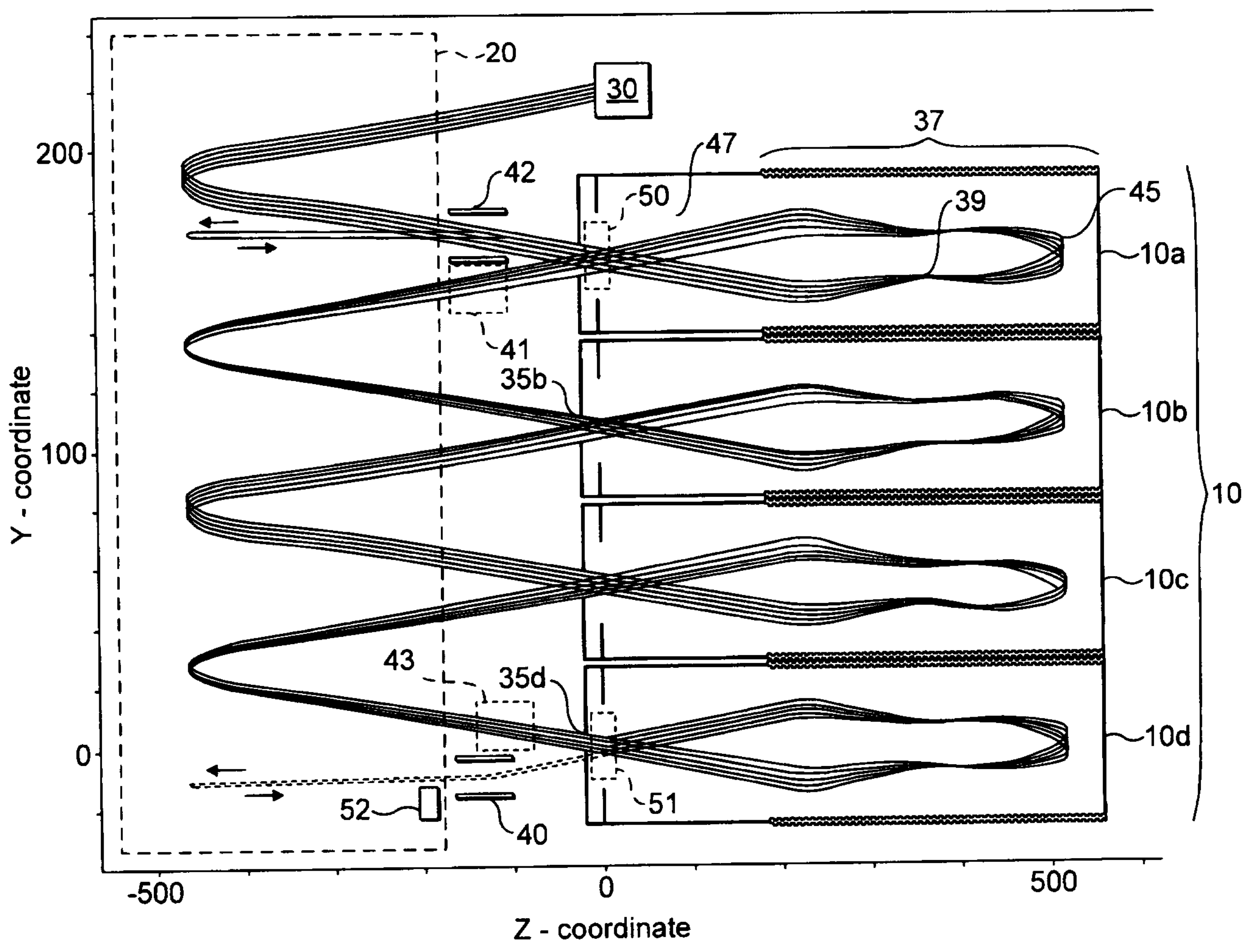
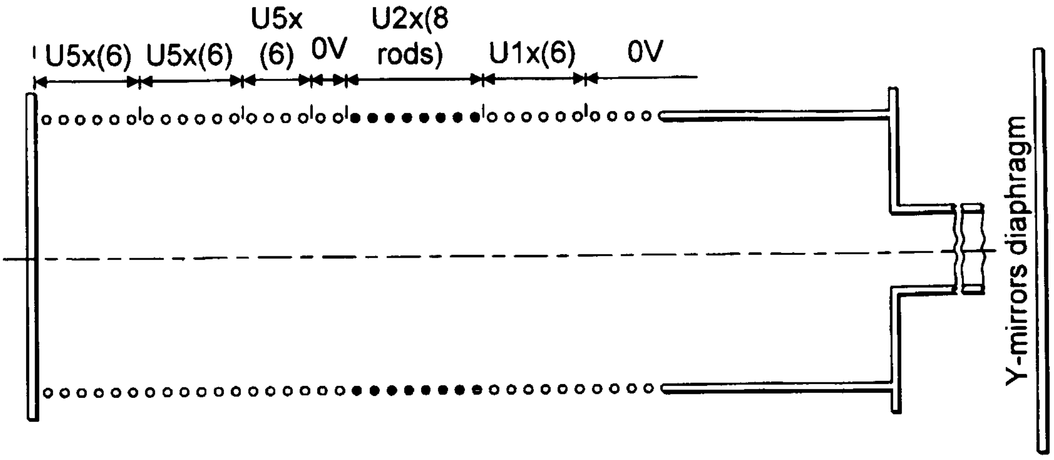
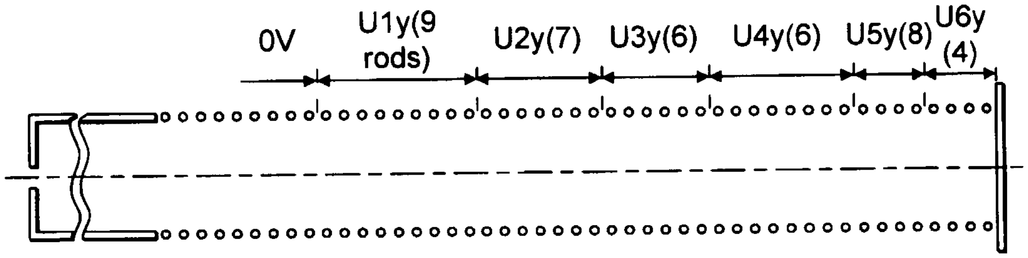

20
30
37
47
42
50
39
45
10a
41
35b
10b
10
10c
43
35d
10d
52
51
40
200
100
0
Y - coordinate
-500
0
500
Z - coordinate

FIG. 3



U1x	-528
U2x	-7802
U3x	7733
U4x	162
U5x	3910

FIG. 4



U1y	-2482.0
U2y	-6130.5
U3y	-1511.5
U4y	716.5
U5y	1987.0
U6y	2605.0

FIG. 5

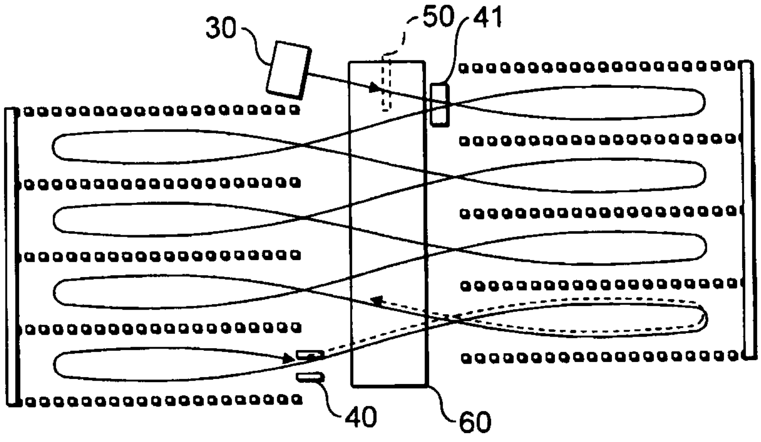


FIG. 6

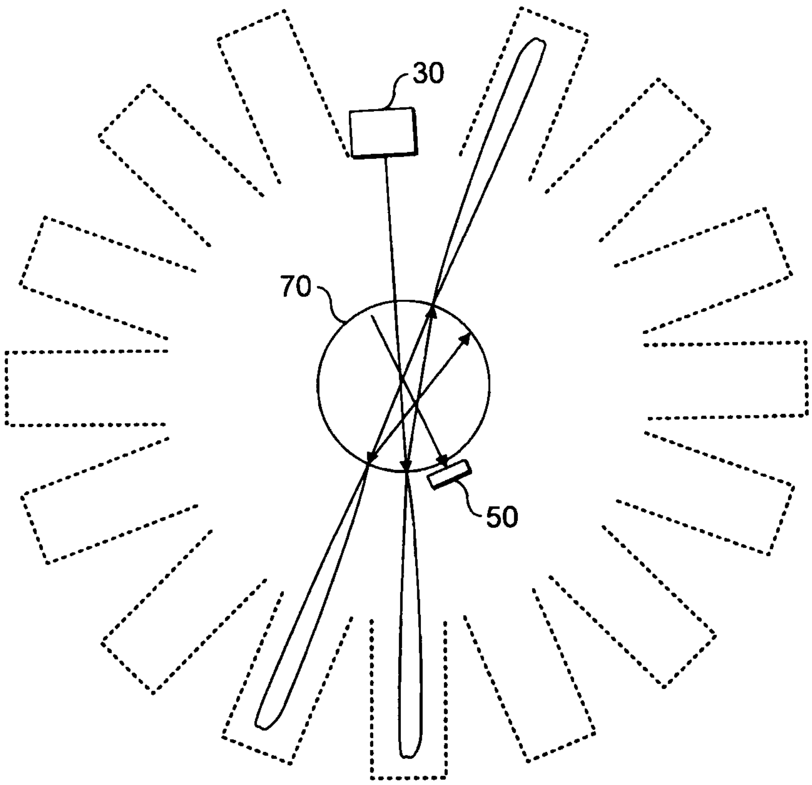


FIG. 7

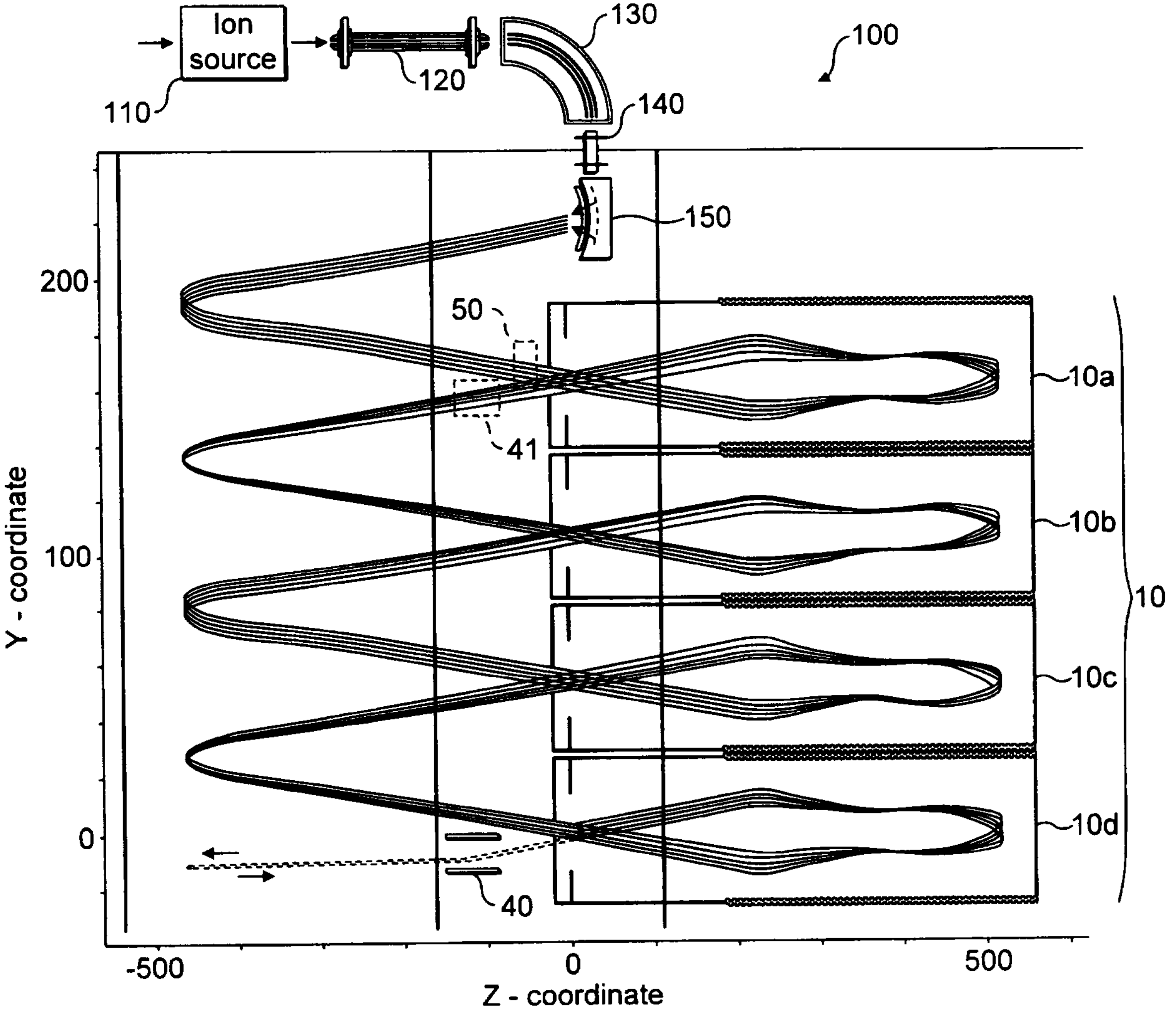

Ion source
110
120
130
140
100
150
50
41
40
10a
10b
10c
10d
10
200
100
0
Y - coordinate
-500
0
500
Z - coordinate

FIG. 8

Multireflection Time-of-flight Mass Spectrometer

Field of the Invention

This invention relates to a multireflection time-of-flight (TOF) mass spectrometer.

Background of the invention

Mass spectrometry is a well known analytical tool for identification and quantitative analysis of elements, compounds and so forth. The key qualities of a mass spectrometer are its resolving power, mass accuracy and sensitivity. One specific form of mass spectrometry, time-of-flight mass spectrometry (TOF-MS) involves accelerating ions in an electric field and then drifting them to a detector at a known distance. Ions of different mass to charge ratios (m/z) but having the same kinetic energy move at different velocities towards the detector and so separate according to their m/z.

The resolving power of TOF-MS is typically related to the flight length: the longer the distance between the location of ion packet formation and the detector, the greater the resolving power. To an extent, therefore, the resolution of a TOF-MS can be improved by maximizing the linear distance between the electric field and the detector. However, beyond a certain linear separation, practical problems arise as the instrument size increases, leading to an increased costs, additional pumping requirements, and so forth.

To address this, so called multireflection time-of-flight mass spectrometry (MR TOF-MS) has been developed In a simplest embodiment of MR TOF-MS, two coaxial mirrors are provided (see, for example, US-A-3,226-543, US-A-6,013,913, US-A-6,107,625 or WO-A-2002/103747). The problem with such an arrangement is that it severely limits the mass range that can be analyzed. This is because, as the ions of different m/z separate, the initial single pulse of ions becomes a train of pulses whose duration depends on the flight length they have travelled and the range of m/z ions within the train. On increasing separation this train of pulses separates to such an extent that ions at the front of the train reach around to the back of the train, and ion mixing begins rendering m/z analysis of those ions impossible. Consequently in such coaxial multireflection analysers, either the flight path length or the range of m/z must be limited for meaningful analysis to be possible. To achieve high resolving power, a long flight path length is required, and consequently the mass range of ions in the analyser mush be restricted.

Multireflection ion mirrors for TOF-MS that addressed this limited mass range are described in GB-A-2,080,021 to Wollnik. Here, each mirror provides a single reflection and is functionally independent of the other mirrors. Although the arrangement of Wollnik addresses the limited mass range of other prior art devices, it does not offer a practical solution which could implement the large number of ion mirrors in the case where a large ion incidence angle provides higher resolution.

SU-A-1,725,289 describes a TOF-MS with two opposed planar ion mirrors that allows for repeated reflections in a direction generally transverse to a drift direction (Y). Unlimited beam divergence in that drift (Y) direction limits the usefulness of this design with modern ion sources (electrospray, MALDI etc).

The problem of defocussing in a drift direction is addressed by Verentchikov et al in WO-A-2005/001878. Here, as in other prior art, the reflectors are extended in the shift direction. Because of the limited focussing in this plane, multiple planar lenses are inserted orthogonally to the drift direction (Y) so as repeatedly to refocus the ion beam as it spreads in that Y direction. Nonetheless, the amount of refocussing in that drift direction remains relatively weak (compared to the focusing in the other directions). Moreover, the presence of the planar lenses in the middle of the mirror assembly complicates the practical realization of the device, since, for example, it is then difficult to locate an ion detector and an ion source in the same plane (which is normally coincident with the plane of time of flight focussing of the mirrors). This in turn necessitates an additional isochronous ion transfer as shown in, for example, US-A-2006/0214100. It is also costly due to the inclusion of multiple additional components.

Summary of invention

Against this background, there is provided a method of reflecting ions in a multireflection time of flight mass spectrometer comprising:

providing an ion mirror having a plurality of electrodes, the ion mirror having a cross section with a first, minor axis (Y) and a second, major axis (X) each perpendicular to a longitudinal axis (z) of the ion mirror which lies generally in the direction of time of flight separation of the ions in the mirror;
guiding ions towards the ion mirror;
applying a voltage to the electrodes so as to create an electric field which:
(a) causes the mean trajectory of the ions to pass through a plane of symmetry of the ion mirror which contains the longitudinal (z) and major axes (X) of the mirror;
(b) causes the ions to reflect in the ion mirror; and
(c) causes the ions to exit the ion mirror in a direction such that the mean trajectory of ions passing through the ion mirror has a component of movement in a direction (Y) perpendicular to the said plane of symmetry thereof.

Thus embodiments of the present invention, in its first aspect, provide for a MR TOF MS wherein ions move across a minor axis (Y) (such as, for example, a short side) of an ion mirror thereof as they undergo reflection within the ion mirror. This is in contrast to prior art arrangements such as, for example, the ion mirror arrangement of the above referenced Verentchikov publication, in which ions have a "shift direction" which is across a major axis of the ion mirror.

By generating a drift direction across the short or minor axis of the ion mirror, multiple ion mirrors can be stacked adjacent to one another with a relatively limited (shallow) angle of reflection within each mirror. Thus a large path length through a MR TOF MS can be created whilst adjacent mirrors can be shielded from one another by the presence of the mirror electrodes themselves. Furthermore, space charge effects are reduced.

Although, throughout the description, cartesian coordinate axes X, Y and Z are employed, it is to be understood that this is merely for ease of explanation and that the absolute orientation of the MR TOF MS is not important. Moreover, in defining the longitudinal axis to be generally in the direction of TOF separation it is recognized that the ions actually have a mean path through the ion mirror that is not parallel with the electrodes thereof at all times. Thus the longitudinal direction is simply intended to identify the cartesian direction which lies orthogonal to the sectional axes.

In a particularly preferred embodiment of this aspect of the present invention a voltage may be applied to the electrodes so as to create an electric field which causes ions to cross the plane of symmetry at least three times. In other words, ions described a "gamma" shape viewed in a plane containing the longitudinal and minor axes of the ion mirror.

The electric field of the ion mirror may be arranged to enhance spatial focussing by causing the ions to undergo spatial compression at least once (and preferably twice) during passage through the ion mirror.

In one particularly preferred embodiment, the ion mirror forms part of a stack of ion mirrors together constituting a first ion mirror arrangement. A second ion mirror arrangement is also provided, opposed to the first ion mirror arrangement. Ions are directed into the first ion mirror of the first mirror arrangement where they reflect back towards the second ion mirror arrangement, and are then reflected into a second ion mirror of the first ion mirror arrangement, back to the second ion mirror arrangement and so forth. Thus ions describe a series of "gamma" shaped loops within the first ion mirror arrangement, being reflected back each time by the second ion mirror arrangement. In this way, a "shift" direction in the direction of the minor axis of each ion mirror of the first ion mirror arrangement is established. Spatial focussing within each ion mirror of the first ion mirror arrangement obviates the need to have spatial focussing means elsewhere which is a significant drawback of the Verentchikov arrangement described above.

In one alternative, the second ion mirror arrangement likewise comprises a plurality of (for example, four) ion mirrors, each opposed to a corresponding ion mirror within the first ion mirror arrangement. In an alternative embodiment, however, the second ion mirror arrangement has a plane of symmetry containing a longitudinal axis generally perpendicular to a plane of reflection of the second ion mirror arrangement, and a minor axis of the cross section of the second ion mirror arrangement, and ions intersect that plane of symmetry of the second ion mirror arrangement as they reflect within it. This plane of symmetry of the second ion mirror arrangement is, preferably, perpendicular to the plane of symmetry defined by the longitudinal and minor axes of each ion mirror in the first ion mirror arrangement.

It has been discovered that, optimally, four ion mirrors are preferable within the first ion mirror arrangement. Four ion mirrors appears to optimise the degree of TOF focussing.

It is possible to arrange for ions having passed through the first and second ion mirror arrangements in zig-zag fashion to be detected upon their exit. Alternatively, ions may be passed to a further ion processing device such as a fragmentation chamber or the like. Furthermore, ions may be reflected back through the MR TOF MS and, most preferably, reflected once again in the forward direction to make a total of three passes through the MR TOF MS. Because of the difference in time of flight of ions of different mass to charge ratios, increasing the number of passes through the device beyond three leads to an undesirably small mass range of analysis, in a similar manner to that described in relation to the coaxial mirror arrangement of the prior art.

In accordance with a second aspect of the present invention, there is provided a method of reflecting ions in a multireflection time of flight mass spectrometer comprising:

providing a first ion mirror having a plurality of electrodes and defining a longitudinal axis generally orthogonal to a plane of reflection of ions within the first ion mirror;

providing a second ion mirror generally opposed to the first ion mirror, the second ion mirror having a plurality of electrodes and defining a longitudinal axis generally orthogonal to a plane of reflection of ions within the second ion mirror;

guiding ions towards the first ion mirror;

supplying a voltage to the electrodes of the first ion mirror so as to create an electric field which causes the ions entering the first ion mirror to be reflected back out of it;

directing ions reflected out of the first ion mirror into the second ion mirror;

supplying a voltage to the electrodes of the second ion mirror so as to create an electric field which causes the ions entering the second ion mirror to be reflected back out of it;

wherein the steps of guiding the ions towards the first ion mirror, creating an electronic field in the first ion mirror, and/or directing ions reflected out of the first ion mirror into the second ion mirror include controlling a mean ion trajectory so that ions pass through a plane of symmetry of the first ion mirror, in which the longitudinal axis thereof lies, at least three times before they are reflected by the second ion mirror.

In accordance with another aspect of the present invention, there is provided a method of reflecting ions in a multireflection time of flight mass spectrometer comprising: providing a first ion mirror arrangement including at least one ion mirror which has a longitudinal axis generally perpendicular with a plane of reflection of ions within that at least one ion mirror; the or each ion mirror further having electrodes define a cross section with a first, minor axis and a second, major axis each orthogonal to the longitudinal axis of the, or the respective, ion mirror;

providing a second ion mirror arrangement including at least one ion mirror which has a longitudinal axis generally perpendicular with a plane of reflection of ions within that at least one ion mirror; the or each ion mirror further having electrodes define a cross section with a first, minor axis and a second, major axis each orthogonal to the longitudinal axis of the, or the respective, ion mirror, wherein the or each ion mirror of the first ion mirror arrangement has a plane of symmetry which contains the longitudinal and major axes thereof, wherein the or each ion mirror of the second ion mirror arrangement likewise has a plane of symmetry which contains the longitudinal and major axes thereof, wherein the first and second ion mirror arrangements are arranged in opposition to each other so that ions may pass between them, and wherein the plane of symmetry of the or each ion mirror of the first ion mirror arrangement intersects the plane of symmetry of the or each ion mirror of the second ion mirror arrangement; the method comprising:

directing ions into a first ion mirror of the first ion mirror arrangement;

reflecting ions out of that first ion mirror of the first ion mirror arrangement;

directing ions into the second ion mirror arrangement; and

reflecting ions out of that second ion mirror arrangement back towards the first ion mirror arrangement.

The invention also extends to a multireflection time of flight mass spectrometer (MR TOF MS) comprising:
a first ion mirror arrangement including at least one ion mirror which has a longitudinal axis generally perpendicular

with a plane of reflection of ions within that at least one ion mirror; the or each ion mirror further having electrodes define a cross section with a first, minor axis and a second, major axis each orthogonal to the longitudinal axis of the, or the respective, ion mirror;
a second ion mirror arrangement including at least one ion mirror which has a longitudinal axis generally perpendicular with a plane of reflection of ions within that at least one ion mirror; the or each ion mirror further having electrodes define a cross section with a first, minor axis and a second, major axis each orthogonal to the longitudinal axis of the, or the respective, ion mirror;
means for supplying a voltage to the electrodes of the first and second ion mirror arrangements so as to establish electric fields therein; and
an ion guiding means for introducing ions from an ion acceleration region into the MR TOF MS so as to cause ions so introduced to reflect between the first and second ion mirror arrangements at least once prior to exiting them for subsequent processing or detection.

Further preferred embodiments and advantages will be apparent from the description which follows, and the claims.

Brief description of the drawings

The present invention may be put into practice in a number of ways and some embodiments will now be described by way of example only and with reference to the accompanying figures in which:

Figure 1 shows a third angle elevation of a preferred embodiment of a multireflection time of flight mass spectrometer, with Type 1 and Type 2 opposed ion mirror arrangements;

Figure 2 shows a part of the arrangement of Figure 1, in the plane YZ thereof;

Figure 3 shows a section through the MR TOF MS of Figure 1 in the plane YZ thereof, along with exemplary ion trajectories in that plane;

Figure 4 shows, in section in the XY plane, one possible arrangement of electrodes within a Type 2 ion mirror of Figure 1, along with some suitable voltages;

Figure 5 shows, again in section in the YZ plane of Figure 1, one possible arrangement of electrodes within a ion mirror of the type 1 ion mirror arrangement in Figure 1, along with some suitable voltages;

Figure 6 shows, again in section in the YZ plane, an alternative arrangement of ion mirrors embodying the present invention; and

Figure 7 shows, again in section in the YZ plane, a third embodiment of the present invention; and

Figure 8 shows a mass spectrometer system comprising an ion source, a linear trap and the MR TOF MS of Figure 3..

Detailed description of preferred embodiments

Figure 1 shows a third angle projection (perspective) view of a multireflection time of flight mass spectrometer (MR TOF MS). The MR TOF MS includes two separate ion mirror arrangements. The first ion mirror arrangement 10 forms one of a pair of systems of planar mirrors which are designated "Type 1" in the following description. The MR TOF MS of Figure 1 also includes a second ion mirror arrangement 20 which is generally orthogonal with the first ion mirror 10 and designated "Type 2" in the following description.

It will be noted that the first ion mirror arrangement 10 comprises, in the preferred embodiment of Figure 1, four ion mirrors stacked on top of each other in a direction parallel with the Y axis 300 as shown in figure 1. Each ion mirror comprises a set of electrodes (a preferred embodiment of which is shown in Figure 5 below) which, when energized, create an electric field within each ion mirror. It will also be noted that the electrodes extend only part way along the longitudinal axis (in the Z direction 200 of Figure 1) of each ion mirror so that there is a field free region between the second ion mirror arrangement 20 and the electrodes of the ion mirrors of the first ion mirror arrangement 10.

Each ion mirror of the first ion mirror arrangement has two planes of symmetry, a first containing the X and Z axes 400, 200, and a second containing the Y and Z axes. It is the first plane of symmetry, in the XZ direction, that is of most relevance for the ion mirrors in the first ion mirror arrangement 10, as will be explained in further detail in connection with Figures 2 and 3 in particular.

Finally with regard to Figure 1 it will be noted that the second ion mirror arrangement 20 comprises a single ion mirror which likewise has two planes of symmetry (in the XZ and YZ planes) but, here, it is the plane of symmetry in the YZ plane that is of most interest.

Referring now to Figures 2 and 3, the mean trajectory of ions through the MR TOF MS will now be described. Ions are generated by an ion source 30 which is outside of the MR TOF MS. Following optional preprocessing in one or more stages of mass spectrometry, and/or ion cooling, for example, and storage in, for example, a linear trap, ions are ejected towards the MR TOF MS. In known manner, ions are accelerated through an electric field of known magnitude and are then allowed to drift without further acceleration towards the MR TOF MS. These ions are then directed towards the ion mirror arrangements 10, 20 and, after a first reflection in the second ion mirror arrangement 20, arrive at a slot 35a of a mirror 10a, seen best in Figure 2, and which is formed in a front face of a first, upper (in the Y direction) ion mirror of the ion mirror arrangement 10. It will be seen that ions arrive at the aperture 35a at an angle α to the plane of symmetry as identified above (that is, the plane of symmetry in the XZ plane). Thus, the ion trajectory passes through that plane of symmetry for a first time at or around the entrance slot of 35a the first ion mirror 10a.

Ions continue generally in the direction that they enter the first ion mirror 10a since the first part of the ion mirror 10a in the longitudinal direction is a field free region without electrodes 47. Approximately one third of the way into the ion mirror (that is, approximately one third of the distance between the entrance slot 35a and the plane at which reflection occurs further along the longitudinal axis), ions enter an electric field established by a plurality of electrodes 37.

The electric field has the effect of spatially focussing the ion for a first time at a saddle point 38. The ions then continue in a direction generally parallel with the longitudinal axis of the ion mirror 10a before being reflected back at a turning point 45 defining a plane of reflection. It is at this point 45, where the ions change direction, that they intersect the plane of symmetry in the XZ plane for a second time.

The ions are then spatially focussed for a second time at a second saddle point 39 and then carry on again in a direction generally parallel with the longitudinal axis of the ion mirror 10a, before exiting the electric field of the ion mirror 10a into the field free region 47. The ions are deflected before leaving the electric field of the ion mirror 10a so that they once more have a component of movement in the Y direction. Thus they intersect the plane of symmetry in the XZ plane of the ion mirror 10a for a third and final time, again generally in the region of the elongate slot 35a as they pass back out of the ion mirror 10a.

Thus the shape described by the ions may be likened, generally, to the Greek "gamma" and ions intersect the plane of symmetry three times.

Having passed back through the elongate aperture 35a, ions continue moving right to left in Figure 3 and enter the orthogonal second ion mirror arrangement (type 2). The ions remain generally in the plane of symmetry (YZ) of the second ion mirror arrangement 20 but intersect the longitudinal (Z) axis thereof at an acute angle which may or may not be the angle α at which ions entering the first ion mirror arrangement 10 intersect the plane of symmetry of that mirror.

Following the second reflection in the second ion mirror arrangement 20, ions travel generally in a straight line back towards the first ion mirror arrangement 10 where they enter an elongate slot 35b of a second ion mirror 10b of the first ion mirror arrangement 10 which is adjacent the first ion mirror 10a of it, but whose longitudinal axis is displaced in the Y direction. The second ion mirror 10b is preferably of a identical construction to the first ion mirror 10a and thus has a set of electrodes extending part way along the longitudinal axis to provide an electric field for reflection of ions entering the second ion mirror 10b.

Ions again describe the "gamma" shape through the second ion mirror 10b so that they intersect the plane of symmetry of the second ion mirror 10b three times and so that ions leaving the second ion mirror 10b do so in a direction that has a component in the Y direction again.

Ions then pass back into the second ion mirror arrangement 20 where they are reflected at an angle to the longitudinal axis and thus continue with a component in the Y direction downwards (when viewed in the orientation of Figures 1, 2 and 3). Ions then enter a third ion mirror 10c of the first ion mirror arrangement 10, execute the loop "gamma" trajectory in it and are directed back again into the second ion mirror arrangement 20 for a further time. Here they are reflected again, still with a component of drift in the Y direction downwards, into a fourth and final ion mirror 10d of the first ion mirror arrangement 10. After completing a final traverse through the fourth ion mirror 10d, ions exit the elongate slot 35d of the fourth ion mirror 10d after which they arrive at detector 52, for detection. Only after the fourth ion mirror 10d of the first ion mirror arrangement 10a do aberrations of 1st, 2nd and 3rd order achieve a minimum and thus provide an optimized quality of time of flight focussing.

Thus the arrangement of Figures 1, 2 and 3 significantly increases the total path length between the acceleration region upstream of the MR TOF MS and the detector. However, the flight path may be increased further (effectively doubled) by reversing the direction of ion travel in the ion mirror arrangements 10, 20 as shown in Figure 3 by the lower dashed line opposite the fourth ion mirror 10d of the first ion mirror arrangement 10. instead of proceeding to detector 52, a second deflector 40 may be used to straighten the trajectories on their entrance into the second ion mirror arrangement 20 as they exit the fourth ion mirror 10d of the first ion mirror arrangement 10, and then return ions exactly on the incoming trajectory. On the way back, ions may be deflected in the X direction by third deflector 41, and captured by a second detector 50 located above the plane of the drawing in the X direction. The third deflector 41 could be energized only after all the ions of interest have passed through the MR TOF MS on the forward pass, and this of course limits the mass range, since heavy ions are just passing the third deflector 41 when relatively lighter ions are already coming back. However, this becomes a problem only for ions with ratios of time of flights of about 8:1, that is, for ratios of M/Z: $(M/Z)_{max}/(M/Z)_{min}>60$. This limitation is of limited practical concern as RF transmission devices normally used in the ion source 30 impose much more stringent limitations on the mass range.

The flight path may be increased still further by employing a fourth deflector 42 instead of the third deflector 41. The fourth deflector straightens up the path of the ions but keeps them generally in the YZ plane (in contrast to third deflector 41 which deflects ions up out of the YZ plane for detection at second detector 50) - see the upper part of Figure 3. Ions whose trajectories have been straightened relative to the longitudinal axis of the second ion mirror arrangement 20 are reflected within in so as to return back along a path generally parallel with the direction in which they enter the field of the second ion mirror arrangement 20, following which they are deflected back into the first ion mirror arrangement 10 at an angle to the longitudinal axis of the first ion mirror 10a so as to traverse a path through the two ion mirror arrangements 10, 20 similar to the path traversed during the first pass there through. Since ions, in this embodiment, pass through the MR TOF MS three times, twice in the forward direction and once the "reverse" direction, they arrive at the elongate slot 35d of the fourth ion mirror 10d of the first ion mirror arrangement 10 and first deflector 43 is then activated to deflect the ions up out of the plane of the paper of Figure 3 (in the X direction) towards the first detector 51. Preferably, the first deflector 43 is switched on once heavy m/z have passed it on their way back from deflection by the second deflector 40. Then ions are taken away from their second forward pass onto the first detector 51, with light m/z first followed by heavier m/z. In this case, the ratios of times of flight are about 2.4:1. This results in a much more modest $(m/z)_{max}/(m/z)_{min} \approx 6$. Any further increase in the flight path (for example, by passing the ions through two ion mirror arrangements 10, 20 a fourth time) further reduces the mass range of analysis though improves resolving power. Steeper deviation from the ion path, for example by locating the deflectors just before the detectors, or indeed integrating the deflectors with the detectors can improve this ratio by around 10-20%.

Instead of the first and/or second detectors 50, 41, as the case may be, ions may instead be removed from the plane of transmission through the MR TOF MS in the X direction to another stage of mass analysis (not shown in the Figures). For example, a fragmentation device may be situated out of the plane of Figure 3 (in the X direction) so that, following fragmentation, ions can be reinjected into the same MR TOF MS or into another mass analyser.

Although the ion mirrors 10a-10d of the first ion mirror arrangement 10 as shown in Figures 1, 2 and 3 are planar, there is no requirement that they should be so formed. In particular, elliptic or circular cross section ion mirrors could equally be employed. Though not essential, it is preferable that the cross section of each ion mirror has a major and minor axis (that is, the sections are, for example, rectangular or elliptical), with the "gamma" shaped ion trajectories in each ion mirror causing a drift direction of the ions to be established in the Y direction, which is the direction of the minor rather than the major axis.

For non planar ion mirrors, electrodes may be formed by stamping or electrochemical etching. A preferred implementation employs flat plates on its edges to minimise fringing fields, so as to constitute a planar mirror. The flat plates are located, in preference, at least one mirror height away from the ion trajectories, and preferably more than 1.5 to 2 mirror heights.

The second ion mirror arrangement 20 may likewise be a single planar mirror (as shown in Figure 1) or it may be a single elliptical mirror. To increase the flight length even further, additional layers of type 2 mirrors may be employed above or below the single second ion mirror arrangement 20 of Figure 1 (that is, in the +Y and/or -Y directions). Ions may be transferred from layer to layer using a pair of opposing deflector plates that allow ions to enter each type 2 mirror arrangement always along the plane of symmetry. Furthermore, instead of a single ion mirror in each type 2 mirror arrangement, multiple mirrors could instead be employed, which may be planar or non planar (e.g. elliptic or circular in cross section). Such an arrangement is shown in Figure 6, where all mirrors in the first and second ion mirror arrangements are Type 1, with a single planar lens 60 formed between them. The planar lens 60 acts to focus ions in the "X" direction, that is, into the plane of paper of Figure 6, since without the crossed planes of symmetry of earlier embodiments (Figure 1, for example), there is no other source of ion focussing in that direction.

Though focussing of this planar lens 60 is unlikely to be as strong as the arrangement of Figures 1 to 3, the construction of Figure 6 does have an advantage of higher tolerance to space charge, because ion packets will be shielded from ions of other m/z moving in neighbouring mirrors, at their turning points where the influence of space charge is expected to be most significant. This shielding occurs whilst the ions are within the Type 1 mirrors and so in the embodiment of figure 6, the ions are shielded at all of their turning points. The arrangement of Figure 6 may also be more straightforward to manufacture since the single "Type 2" electrode of Figure 1 can become difficult to maintain within suitable tolerances for longer path lengths.

As with the arrangement of Figure 3, the forward pass through the MR TOF MS of Figure 6 could be reversed by using deflectors 40 and 41 to double the flight length as shown by the dashed lines - detector 50 is once again located above or below the plane of the drawing of Figure 6. Still a further increase in the flight length may be achieved by passing ions back through the arrangement of Figure 6 for a third time (in the "forward" direction once more) as has been described previously in connection with Figure 3. Furthermore, multiple layers of the lens 60 could be employed.

Figure 7 shows still a further embodiment which extends the principles of Figure 6 further. Instead of arranging the first and second ion mirror arrangements so that they are linearly opposed, as shown in Figures 3 and 6, the ions mirrors may instead be oriented towards a common centre with a circular lens 70 in the middle, so that ions move around a generally circular arrangement of ion mirrors.

Although the arrangements of Figures 6 and 7 show planar mirrors, as previously, the mirrors may instead be elliptical in cross section, or of other geometric shape. This may be advantageous since an elliptical cross section mirror, for example, may provide spatial focussing also perpendicular to the plane of trajectory. Of course, it is necessary to organise that orthogonal focussing so that aberrations are not significantly increased. By employing elliptical cross section mirrors, it may be that the lens 60/70 of Figures 6 and 7 may not be necessary.

Figure 8 shows a mass spectrometer system 100, which includes an MR TOF MS as described above. The specific embodiment of MR TOF MS shown in figure 8 is that of figure 3 though the figure 6 or figure 7 embodiments could of course equally be employed.

Only those parts of the system 100 that are relevant to an understanding of the invention are shown in figure 8. The system includes an ion source 110 such as an electrospray or MALDI source. This generates a quasicontinuous stream of ions that are guided via lens 120 into a collision cell 130. Here, ions are (optionally) fragmented and then guided via second lens 140 into a linear trap 150. The linear trap 150 may take various forms such as a linear quadrupole, hexapole or octapole trap with straight elongate rods, or it may be curved (that is, has curved elongate rods with a constant section and a constant rod separation along the direction of elongation). Most preferably, the linear trap 150 is curved but with a non-linear sectional area along the axis of elongation, such as is described in our co-pending application no. GB 0626025.1, the contents of which are incorporated herein entirely.

In use, ions generated in the ion source 110 pass through the lens 120, and into the fragmentation cell 130. Here they may be fragmented or not depending upon the ions being analysed and the user's choice. They then pass via second lens 140 into the linear trap 150 where they are captured and cooled. Some crude mass selection may also take place within the linear trap 150. Ion packets are then ejected generally in a direction the curved axis of elongation of the linear trap, as is described in the above referenced GB 0626025.1, and are focussed downstream of the trap 150. They then pass into the second ion mirror arrangement 20 and continue onwards as described above in connection with figure 3.

After one, two or three passages through the MR TOF MS, ions may be deflected out of the plane of the drawing such as for example by deflector 41 deflecting ions to detector 50 out of the plane of the paper.

One specific embodiment of the Type 2 mirror is shown in XZ section in Figure 4, and a specific embodiment of the Type 1 mirror also is shown in section in the YZ plane in Figure 5. Figures 4 and 5 show the geometric and electric parameters of the ion mirrors in detail. A series of voltages are supplied from a power supply (not shown) to the electrodes of each, and potentials are applied to a set of precision-ground metallic rods. For example, the rods may be formed of stainless steel, invar or metal-coated glass, for example. Alternatively, a set of thin or thick metal plates, or printed circuit boards could be used to provide the same effect. The specific voltages employed in the preferred embodiment for the second and first ion mirror arrangements 20, 10 are shown in tables in Figures 4 and 5 respectively, for ions accelerated by 2kV..

It is preferable to sustain a pressure lower than around 10^{-9} … 10^{-8} mbar within this system, preferably using split flow turbomolecular pumps. The preferable overall flight length of an MR TOF MS in accordance with preferred embodiments lies in the range of 10 to 200 metres, with an overall length of the system being between about 0.5 to 1 metre. The average ion acceleration is preferably in the range of 1 to 20kv, 2kv being used in the arrangements of Figures 4 and 5.

The arrangements thus described provide a large increase in the path length relative to a single reflection time of flight mass spectrometer, but at the same time enhance spatial focussing, improved shielding of ion packets from each other to minimize space charge effects, and provide a simplified ion injection scheme due to the removal of spatial conflict between the ion source and the fringing fields of an ion mirror.

Claims

1. A method of reflecting ions in a multireflection time of flight mass spectrometer comprising:
providing an ion mirror having a plurality of electrodes, the ion mirror having a cross section with a first, minor axis (Y) and a second, major axis (X) each perpendicular to a longitudinal axis (z) of the ion mirror which lies generally in the direction of time of flight separation of the ions in the mirror;
guiding ions towards the ion mirror;
applying a voltage to the electrodes so as to create an electric field which:
(a) causes the mean trajectory of the ions to pass through a plane of symmetry of the ion mirror which contains the longitudinal (Z) and major axes (X) of the mirror;
(b) causes the ions to reflect in the ion mirror; and
(c) causes the ions to exit the ion mirror in a direction such that the mean trajectory of ions passing through the ion mirror has a component of movement in a direction (Y) perpendicular to the said plane of symmetry thereof.

2. The method of claim 1, wherein the step of applying a voltage comprises:

applying a voltage so as to create an electric field which causes ions to cross the said plane of symmetry at least three times per reflection in the ion mirror.

3. The method of claim 2, wherein the step of guiding the ions into the ion mirror comprises:
guiding the ions into the ion mirror at a non zero angle to the plane of symmetry so that the ions intersect that plane of symmetry for a first time upstream of a plane of reflection of the mean trajectory of the ions;
and wherein the applied voltage is arranged to cause the ions to pass through the plane of symmetry for a second time at or adjacent the plane of reflection within the ion mirror, and to eject the ions from the ion mirror again so that they intersect the plane of symmetry for a third time downstream of the plane of reflection.

4. The method of any preceding claim, wherein the electric field causes ions within the ion mirror to undergo spatial focussing at least once during passage through the ion mirror.

5. The method of claim 4, wherein the step of focussing ions comprises focussing ions in a direction (Y) perpendicular to the plane of symmetry of the ion mirror.

6. The method of claim 4 or claim 5, wherein the step of focussing ions comprises focussing ions within the ion mirror.

7. The method of any of the preceding claims, wherein the ion mirror forms one of a plurality of (n+1) ion mirrors in a first ion mirror arrangement, the further

n ion mirrors in the first ion mirror arrangement each having a plurality of electrodes, wherein each further ion mirror has a cross section with a first, minor axis (Y) and a second, major axis (X), each of which is perpendicular to a longitudinal axis (Z) of the ion mirror which lies generally in the direction of time of flight separation of the ions in each further n ion mirror, wherein the said longitudinal axes of each of the further n ion mirrors in the first ion mirror arrangement lie generally parallel with the others and with the longitudinal axis (Z) of the first ion mirror; the method further comprising the step of:

(d) causing ions that have exited a first ion mirror of the first ion mirror arrangement to be directed back into a second ion mirror of the first ion mirror arrangement generally in the same direction as the ions had entered the first ion mirror; and

(e) repeating steps (a) to (c) of the method, for that second ion mirror.

8. The method of claim 7, further comprising:

(f) causing ions that have exited the second ion mirror of the first ion mirror arrangement to be directed back into the further (n-1) ion mirrors of the first ion mirror arrangement in turn, the ions entering each further (n-1) ion mirror generally in the same direction as the ions had entered the first ion mirror; and

(g) repeating steps (a) to (c) of the method, for each said further (n-1) ion mirrors.

9. The method of claim 8 wherein the first ion mirror arrangement comprises four ion mirrors, or an integer multiple of four ion mirrors.

10. The method of any of claims 5 to 9 further comprising reflecting ions that have passed through the first ion mirror arrangement back through the first ion mirror arrangement in a reverse direction.

11. The method of claim 10, further comprising reflecting ions back through the ion mirror in a forward direction for a second time once they have passed through it in the reverse direction.

12. The method of any of claims 5 to 11, wherein the step (d) and/or (f) of causing ions to be directed back towards the first ion mirror arrangement comprises reflecting ions in a second ion mirror arrangement having a cross section with a first, minor (X) and a second, major (Y) axis each generally orthogonal to a longitudinal axis (Z) of the second ion mirror arrangement which extends generally in a direction of time of flight separation of ions in that second ion mirror arrangement; wherein a plane of symmetry of the second ion mirror arrangement, which contains the longitudinal (Z) and major (Y) axes, intersects the plane of symmetry of the first ion mirror arrangement at a non-zero angle.

11. The method of claim 10, wherein the plane of symmetry of the second ion mirror arrangement intersects the

plane of symmetry of the first ion mirror arrangement substantially at right angles.

12. The method of any of claims 5 to 11, wherein the step (d) and/or (f) of causing the ions to be directed back towards the first ion mirror arrangement comprises: reflecting ions in a second ion mirror arrangement comprising a plurality m of ion mirrors, each of the m ion mirrors of the second ion mirror arrangement having a plurality of electrodes, wherein each further ion mirror has a cross section with a first, minor axis (Y) and a second major axis (X) each of which is perpendicular to a longitudinal axis (Z) of the ion mirror which lies generally in the direction of time of flight separation of the ions in each of the m ion mirrors, wherein the longitudinal axes (Z) of each of the m ion mirrors in the second ion mirror arrangement lie generally parallel with each other and with the longitudinal axes (Z) of the ion mirrors in the first ion mirror arrangement, and wherein the first and second ion mirror arrangements are opposed to one another so that ions reflect back and forth between the first and second ion mirror arrangements.

13. The method of claim 11, wherein each of the ion mirrors of the second ion mirror arrangement comprises a plane of symmetry including the longitudinal (Z) and major (X) axes of each said ion mirror, and wherein the plane of symmetry of each ion mirror in the second ion mirror arrangement is generally parallel with the plane of symmetry of each ion mirror in the said first ion mirror arrangement.

14. The method of claim 13, further comprising:
focussing ions in a direction (X) generally parallel with the said major axis of each ion mirror.

15. The method of claim 14, further comprising focussing ions in the said (X) direction using an ion optical device positioned between the first and second ion mirror arrangement.

16. The method of any preceding claim, further comprising detecting ions following passage through the or each ion mirror.

17. The method of claim 16, wherein the step of detecting ions comprises detecting ions at a detector which is displaced out of the plane of symmetry of the or each ion mirror.

18. The method of any preceding claim, further comprising directing ions that have passed through the or each ion mirror to a further stage of mass spectrometry such as a fragmentation device.

19. A method according to any preceding claim, further comprising:
generating ions at an ion source;
storing generated ions or derivatives/fragments thereof in a linear trap; and
ejecting ions from the linear trap towards the MR TOF MS.

20. The method of claim 19, further comprising ejecting the ions orthogonally from the linear trap towards the MR TOF MS.

21. The method of claim 19 or claim 20, further comprising fragmenting ions prior to storage in the linear trap.

22. A method of reflecting ions in a multireflection time of flight mass spectrometer comprising:
providing a first ion mirror having a plurality of electrodes and having a longitudinal axis (Z) generally parallel with the time of flight spread of ions within the first ion mirror;
providing a second ion mirror generally opposed to the first ion mirror, the second ion mirror having a plurality of electrodes and defining a longitudinal axis (Z) generally parallel with the time of flight spread of ions within the second ion mirror;

guiding ions towards the first ion mirror;

supplying a voltage to the electrodes of the first ion mirror so as to create an electric field which causes the ions entering the first ion mirror to be reflected back out of it;

directing ions reflected out of the first ion mirror into the second ion mirror;

supplying a voltage to the electrodes of the second ion mirror so as to create an electric field which causes the ions entering the second ion mirror to be reflected back out of it;

wherein the steps of guiding the ions towards the first ion mirror, creating an electric field in the first ion mirror, and/or directing ions reflected out of the first ion mirror into the second ion mirror include controlling a mean ion trajectory so that ions pass through a plane of symmetry of the first ion mirror, in which the longitudinal axis (Z) thereof lies, at least three times before they are reflected by the second ion mirror.

23. The method of claim 22, wherein the steps of guiding the ions towards the first ion mirror, creating an electric field in the first ion mirror, and/or directing ions reflected out of the first ion mirror into the second ion mirror include controlling the mean ion trajectory so that ions pass through the plane of symmetry of the first ion mirror three times, once within the field created by the electrodes of the first ion mirror and twice outside that field.

24. The method of claim 22 or 23, further comprising: directing ions out of the second ion mirror back towards a third ion mirror generally opposed to the second ion mirror, the third ion mirror having a longitudinal axis (Z) generally parallel with the longitudinal axis of the first ion mirror but offset therefrom, and a plurality of electrodes which when energized create an electric field that causes ions to be reflected back out of the third ion mirror.

25. The method of claim 24, further comprising controlling the direction of entrance of ions from the second ion mirror into the third ion mirror and/or controlling the electric field of the third ion mirror so that the mean ion trajectory from the second to the third ion mirror

and back again crosses a plane of symmetry of the third ion mirror, in which the longitudinal axis thereof lies, at least three times.

26. The method of claim 25, further comprising directing the ions from the third ion mirror back into the second ion mirror again.

27. The method of claim 25, further comprising directing the ions from the third ion mirror back towards a fourth ion mirror which is arranged adjacent the second ion mirror, which is generally opposed to the first and third ion mirrors, and which has a longitudinal axis (Z) parallel with but offset from the longitudinal axis (Z) of the said second ion mirror.

28. The method of claim 26, further comprising: directing ions from the second ion mirror towards a fourth ion mirror generally opposed to the second ion mirror, the fourth ion mirror having a longitudinal axis (Z) generally parallel with, but displaced from, the longitudinal axes of the first and third ion mirrors, and a plurality of electrodes which when energized create an electric field that causes ions to be reflected back out of the fourth ion mirror towards the second ion mirror again;

reflecting ions in the second ion mirror;

directing ions from the second ion mirror towards a fifth ion mirror generally opposed to the second ion mirror, the fifth ion mirror having a longitudinal axis (Z) generally parallel with, but displaced from, the longitudinal axes of the first, third and fourth ion mirrors, and a plurality of electrodes which when energized create an electric field that causes ions to be reflected back out of the fifth ion mirror towards the second ion mirror.

29. The method of claim 28, further comprising, after the step of reflecting ions out of the fifth ion mirror towards the second ion mirror, the steps of:
reflecting ions back towards the fifth ion mirror so that they enter it travelling generally in an opposite direction to the direction from which they previously left it; and
subsequently directing the ions back through the second, fourth, second, third, second and first ion mirrors in a reverse direction.

30. The method of any of claims 22 to 28, further comprising arranging the longitudinal axes of each of the ion mirrors to be each generally parallel with one other but not coaxial with each other.

31. The method of claim 29, further comprising displacing the longitudinal axis of each ion mirror from the longitudinal axis of each other longitudinal axis in a direction of drift of ions through the MR TOF MS.

32. A method of reflecting ions in a multireflection time of flight mass spectrometer comprising:

providing a first ion mirror arrangement including at least one ion mirror which has electrodes defining a cross section with a first, minor axis (Y) and a second, major axis (X) each orthogonal to a longitudinal axis (Z) of the, or the respective, ion mirror defined generally in the direction of TOF separation of ions in that or those ion mirror(s);

providing a second ion mirror arrangement including at least one ion mirror which has electrodes defining a cross section with a first, minor axis (Y) and a second, major axis (X) each orthogonal to a longitudinal axis of the, or the respective, ion mirror defined generally in the direction of TOF separation of ions in that or those ion mirror(s), wherein the or each ion mirror of the first ion mirror arrangement has a plane of symmetry which contains the longitudinal (Z) and major (X) axes thereof, wherein the or each ion mirror of the second ion mirror arrangement likewise has a plane of symmetry which contains the longitudinal (Z) and major (X) axes thereof, wherein the first and second ion mirror arrangements are positioned in opposition to each other so that ions may pass between them, and wherein the plane of symmetry of the or each ion mirror of the first ion mirror arrangement intersects the plane of symmetry of the or each ion mirror of the second ion mirror arrangement; the method comprising:

directing ions into a first ion mirror of the first ion mirror arrangement;

reflecting ions out of that first ion mirror of the first ion mirror arrangement;

directing ions into the second ion mirror arrangement; and

reflecting ions out of that second ion mirror arrangement back towards the first ion mirror arrangement.

33. The method of claim 32, further comprising reflecting the ions between second, third and fourth ion mirrors of the first ion mirror arrangement, and the second ion mirror arrangement, in a generally 'zig-zag' pattern.

34. A multireflection time of flight mass spectrometer comprising one or more ion mirrors and configured to carry out the method steps of any of the preceding claims.

35. A multireflection time of flight mass spectrometer (MR TOF MS) comprising:
a first ion mirror arrangement including at least one ion mirror which has electrodes that define a cross section with a first, minor axis (Y) and a second, major transverse axis (X) each orthogonal to a longitudinal axis (Z) of the, or the respective, ion mirror, the longitudinal axis being defined generally in the direction of TOF spread of ions in the ion mirror;
a second ion mirror arrangement including at least one ion mirror which has electrodes defining a cross section with a first, minor axis (Y) and a second, major axis (X) each orthogonal to a longitudinal axis (Z) of the, or the respective, ion mirror again defined generally in the direction of TOF separation of ions in the ion mirror;
means for supplying a voltage to the electrodes of the first and second ion mirror arrangements so as to establish electric fields therein; and

an ion guiding means for introducing ions from an ion acceleration region into the MR TOF MS so as to cause ions so introduced to reflect between the first and second ion mirror arrangements at least once prior to exiting them for subsequent processing or detection;
wherein the first ion mirror arrangement has a first plane of symmetry containing the longitudinal (Z) and major axis (X) thereof;
wherein the second ion mirror arrangement has a second plane of symmetry containing the longitudinal (Z) and major (X) axis thereof, and wherein the first and second planes of symmetry intersect one another at a non-zero angle.

36. A multireflection time of flight mass spectrometer (MR TOF MS) comprising:

a first ion mirror arrangement including at least one ion mirror which has electrodes that define a cross section with a first, minor axis (Y) and a second, major transverse axis (X) each orthogonal to a longitudinal axis (Z) of the, or the respective, ion mirror, the longitudinal axis being defined generally in the direction of TOF spread of ions in the ion mirror;

a second ion mirror arrangement generally opposed to the first ion mirror arrangement and including at least one ion mirror which has electrodes defining a cross section with a first, minor axis (Y) and a second, major axis (X) each orthogonal to a longitudinal axis (Z) of the, or the respective, ion mirror again defined generally in the direction of TOF separation of ions in the ion mirror;

means for supplying a voltage to the electrodes of the first and second ion mirror arrangements so as to establish electric fields therein; and

an ion guiding means for introducing ions from an ion acceleration region into the MR TOF MS so as to cause ions so introduced to reflect between the first and second ion mirror arrangements at least once prior to exiting them for subsequent processing or detection; wherein the or each ion mirror of the first ion mirror arrangement has a plane of symmetry containing the longitudinal (Z) and major (X) axes, wherein the or each ion mirror of the second ion mirror arrangement has a plane of symmetry containing the longitudinal (Z) and major (X) axes, each of which plane of symmetry of the second ion mirror(s) is parallel with but offset from a corresponding one or ones of the planes of symmetry of the second ion mirror arrangement in the direction of the minor axis (Y), so that, in use, ions have a net movement along the minor (Y) axis of the ion mirror arrangements as they pass through the MR TOF MS.

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Claims searched: 1 - 31 **Date of search:** 24 June 2008

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1	WO 2005/001878 A3 (LECO CORPORATION) Abstract and Figure 4.
X	1	US 2007/0176090 A1 (VERENTCHIKOV) Abstract and Figure 1
X	1	GB 2403063 A (VERENTCHIKOV) Abstract and Figure 4.
A	-	GB 2080021 A ((HERMANN WOLLNIK) Whole document.
A	-	WO 2006/102430 A3 (LECO CORPORATION) Whole document.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

H01J

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI

International Classification:

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Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	32, 35 & 36	WO 2006/102430 A3 (LECO CORP) Abstract and Figures.
A	32, 35 & 36	WO 2007/044696 A (LECO CORP) Abstract and Figures.
A	32, 35 & 36	GB 2403063 A (LECO CORP) Abstract and Figures.
A	32, 35 & 36	GB 2080021 A (WOLLNIK) Abstract and Figures.
A	32, 35 & 36	DE 4408489 A (STREHLE) Abstract and Figures.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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International Classification:

Subclass	Subgroup	Valid From
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