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(54) METHOD OF ANALYZING IONS IN AN APPARATUS INCLUDING A TIME OF FLIGHT MASS SPECTROMETER AND A LINEAR ION TRAP

VERFAHREN ZUR UNTERSUCHUNG VON IONEN IN EINEM APPARAT MIT EINEM FLUGZEIT-SPEKTROMETER UND EINER LINEAREN QUADRUPOL-IONENFALLE

PROCEDE D'ANALYSE D'IONS DANS UN APPAREIL COMPRENANT UN SPECTROMETRE DE MASSE A TEMPS DE VOL ET UN PIEGE A IONS LINEAIRE

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- **CHIEN B M ET AL: "ANALYSIS OF THE FRAGMENTS FROM COLLISION-INDUCED DISSOCIATION OF ELECTROSPRAY-PRODUCED PEPTIDE IONS USING A QUADRUPOLE ION TRAP STORAGE/REFLECTRON TIME-OF-FLIGHT MASS SPECTROMETER" ANALYTICAL CHEMISTRY, vol. 66, no. 10, 15 May 1994, pages 1630-1636, XP000449869**
- **SHEVCHENKO A. ET AL: "Rapid 'de Novo' Peptide Sequencing by a Combination of Nanoelectrospray, Isotopic Labeling and a Quadrupole/Time-of-Flight Mass Spectrometer" RAPID COMMUNICATIONS IN MASS SPECTROMETRY, vol. 11, 1997, pages 1015-1024, XP002101143 cited in the application**

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Description

FIELD OF THE INVENTION

[0001] This invention relates to mass spectrometry, and more particularly is concerned with a method of analyzing ions in an apparatus including a time of flight mass spectrometer.

BACKGROUND OF THE INVENTION

[0002] In the field of mass spectrometry, a wide variety of different spectrometers have been developed, and combinations of different spectrometer elements. One well-known type of spectrometer is a quadrupole mass spectrometer, and it is known to provide devices with two or more mass analyzing quadrupole stages to provide MS/MS capabilities. It is also known to combine a quadrupole stage with a time of flight mass spectrometer (TOF MS), as detailed below. A TOF MS has the advantages of high scan speed, unlimited mass range and, if a reflectron is used, a resolution of 10,000 or more. However, TOF MS does not normally provide MS/MS capabilities. 3D ion trap mass spectrometers can perform MS/MS analysis in a comparatively simple device, but generally are operated at a lower resolution than a reflectron TOF MS. Higher resolution can be achieved with an ion trap mass spectrometer, but only with very low scan speeds. As well, it is difficult to inject ions from an external source into a 3D ion trap and the mass range is limited.

[0003] One proposal by one of the inventors of the present invention is disclosed in U.S. Patent 5,179,278. This patent describes the use of an RF multipole ion guide as an interface between an ion source and an ion trap. The intention is to improve the duty cycle of the ion trap mass spectrometer. However, there is no specific teaching of using the multipole device itself in a full trapping mode to provide MS/MS capabilities. Rather, the teaching is that the trapping is obtained by applying selected electric potentials at the ends of the space in the multipole device, to cause ions to be reflected from a second, outlet end to a first, inlet end and then back again towards the second, outlet end. This retains the ions in the space for a longer period of time, this being long enough for analysis to be carried out on a previous ion sample fed to the ion trap spectrometer.

[0004] U.S. Patent 5,652,427 describes the use of an RF multipole that includes a number of separate stages with different degrees of vacuum. However, the arrangement is intended simply to transfer ions from a high pressure source to a mass spectrometer. There is no teaching of trapping of ions in any multipole stage nor any teaching of MS/MS capabilities through resonant excitation and ejection and the like.

[0005] U.S. Patent 5,420,425 (Bier et al. and assigned to Finnigan Corporation) is concerned with an ion trap mass spectrometer, for analyzing ions. It has electrodes shaped to promote an enlarged ion occupied volume. A quadrupole field is provided to trap ions within a predetermined range of mass-to-charge ratios, and the field is then changed, so that trapped ions with specific masses become unstable and leave the trapping chamber in a direction orthogonal to the central axis of the chamber. The ions leaving the spectrometer are detected, to provide a signal indicative of their mass-to-charge ratios. The patent does teach a method of first introducing ions within a pre-determined range of mass-to-charge ratios into the chamber and subsequently changing the field to select just some of the ions for further manipulation. The quadrupole field is then adjusted so as to be capable of trapping product ions of the remaining ions. The remaining ions are then dissociated or reacted with a neutral gas to form those product ions. The quadrupole field is then changed again, to remove, for detection, ions whose mass-to-charge ratios lie within the desired range. It is noteworthy that the ions are not detected by a Time of Flight (TOF) instrument. The Finnigan device, since it uses radial ejection, will produce a stream of ions having broad space and velocity distributions. It would be difficult to manage such a beam and introduce it into a TOF MS analyzer.

[0006] Other workers have demonstrated interfacing a TOF MS to an electrospray source, using a linear RF quadrupole operated at moderately high pressure (for example Chernushevich et al., presented at the 44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, Oregon, May 12-16, 1996). Also, other workers have used hexapole and octopole ion guides instead of a quadrupole. In hexapole and octopole fields, ions of different m/z do not normally have well defined frequencies of motion and so resonant excitation or ejection of selected ions is not possible, and this is a significant advantage of using a quadrupole.

[0007] It has also been known to use a 3D ion trap as an interface between an ion source and a TOF MS (S. M. Michael et al, *Rev. Sci. Instr.* 63, 4277-4284, 1992; Purves and Li, *J. Microcolumn Separations* 7 (6) 603, 1995). The 3D ion trap can be provided with MS/MS capability (Qian and Lubman, *Rap. Commun. Mass. Spec.* 10, 1079, 1996). Use of a three dimensional ion trap has a number of disadvantages. Firstly, ion injection efficiency is at least ten times less than the efficiency with a two dimensional quadrupole. Secondly, the ion storage volume is less in the three dimensional trap, so that only a relatively small number of ions can be stored, without space charge problems, and for this reason, the concentration dynamic range is limited in a three dimensional trap.

[0008] A related approach has been proposed using two separate multipoles and then a TOF mass spectrometer (H. R. Morris et al., *Rap. Commun. Mass. Spec.* 10, 889,1996). Here, selection of ions in a given m/z is carried out conventionally in a first quadrupole mass filter. These are then passed to an RF only hexapole and dissociated by collision with a neutral gas. Resulting ions then pass through to a TOF MS, to obtain a spectrum of the product ions. In addition, a system with a first mass analyzing quadrupole and a second RF only quadrupole has been described (Chevchenko Rapid Communications in Mass Spectrometry, Vol 11, Page 1015-1024, 1997). Both of these systems are relatively complex and expensive and have a number of stages, which will likely lead to loss of sensitivity.

[0009] Finally, a more recent proposal is found in an article entitled "A New Technique for Decomposition of Selected Ions in Molecule Ion Reactor Coupled with Ortho-Time-of-Flight Mass Spectrometry" (A. Dodonov et al. *Rapid Communications in Mass Spectrometry,* 11, 1649-1656, 1997). This paper shows restricted experimental results carried out on, in effect, pre-selected ions, i.e. the tests were carried out with a single chemical compound. There is no specific teaching of using the apparatus to carry out the selection stage. Two modes of ion dissociation are disclosed. In a first mode, the motion of parent and fragment ions is chosen to be stable, and the RF electric field forces the ions to oscillate around the quadrupole axis. Simultaneously, a DC potential is applied along the axis of the device to accelerate the ions, and the strength of this field controls the collision induced fragmentation of the ions. The quadrupole is filled with gas at around 1 mbar of pressure for this purpose. There is no ion mass to charge ratio selection and all ions present will be accelerated by this field. Fragment ions with mass-to-charge ratios both above and below the m/z of a parent ion can be transmitted to a TOF mass analyzer for analysis. It can be noted that the applied field will also cause acceleration and possible further fragmentation of the fragment ions, although control over the strength of the field can limit this to some extent. Nonetheless, the applied axial field will not discriminate between the different types of ions.

[0010] In a second mode, ions are fragmented by confining them in the quadrupole with the RF electric field chosen to have an amplitude and frequency such that desired ions are close to the limit for stable ion motion with Mathieu's parameter q=0.9. This causes an increase of the parent ion velocity and thus leads to collisional "heating" and fragmentation of the parent ions. Then, only those ions with m/z ratios above that of the precursor or parent ion are stable in the quadrupole and only these ions are transmitted to the detector, i.e. the TOF MS. Ions with an m/z ratio smaller than that of the parent ion are rejected due to the unstable character of their motion. For multiply charged ions this may not be a severe limitation because some fragment ions may have lower charges and hence higher mass to charge ratios, but for singly charged ions no fragments will be detected.

[0011] A disadvantage of both modes is that all ions in the quadrupole are excited at the same time and dissociate- If there are two compounds present, they would both fragment and in general it would not be possible to tell which fragments came from which precursor.

[0012] U.S. patent 5,576,540 (Jolliffe) discloses a unique mass spectrometer with radial ejection. One of the rods of a convention quadrupole rod set is provided with a slot, and aligned with the slot is an "ion pipe" which directs ejected ions to a detector. The ion pipe essentially consists of a number of sets of rods configured somewhat as adjacent quadrupole rod sets, for guiding ions to a detector. The suggestion is that a final mass analysis step is carried out by scanning ions sequentially out from from the quadrupole rod set through the slot in one of the rods, to the detector. In other words, there is no suggestion that this quadrupole rod configuration be combined with another complete mass analyzer section, such as a time-of-flight mass anlyzer.

[0013] U.S. patent 5,689,111 is also of interest It discloses a time-of-flight mass spectrometer, with a linear two-dimensional ion guide coupling an ion source to the inlet of the time-of-flight instrument. The two-dimensional ion guide can be used as an ion storage device, to improve the duty cycle of the time-of-flight instrument.

SUMMARY OF THE INVENTION

[0014] The present inventors have realised that one can obtain the capabilities of a tandem mass spectrometer in a relatively simple device, by combining a linear quadrupole, or other multipole, with a TOF MS. The quadrupole, or other multipole, is operated as an ion trap, and an ion is selected by resonant ejection of ions of other masses or otherwise. The isolated ions are then excited and caused to undergo collision induced dissociation or fragmentation, in the quadrupole or other multipole.

[0015] In accordance with the present invention, there is provided a method of analyzing ions in a mass spectrometer apparatus comprising an ion source, a linear RF quadrupole and a time of flight mass spectrometer, the method comprising the steps of:

(1) generating ions from the ion source and passing the ions into the linear RF quadrupole;
(2) applying potentials at either end of the linear RF quadrupole and operating the linear RF quadrupole as an ion trap;
(3) selecting ions of interest in the linear RF quadrupole and ejecting unwanted ions;

characterized in that the method includes:

(4) exciting the ions and causing the ions to collide with a neutral gas, to cause collision induced dissociation thereof, thereby forming fragment ions for analysis in the time of flight mass spectrometer;
(5) adjusting the potential of one end of the linear RF quadrupole, to pass the selected and the fragment ions through to the time of flight mass spectrometer; and
(6) obtaining a spectrum of the selected and the fragment ions in the time of flight mass spectrometer.

[0016] It is preferred to use a quadrupole device, as these inherently have well-defined stability parameters and frequencies of excitation for a particular ion. The x and y motions are separate and either can be excited with good selectivity. However, for some applications, it might be desirable or possible to use other 2D multipole designs, such as a hexapole or octopole. If such an instrument is operated with low RF voltages, the ion motion is approximately harmonic motion with well defined frequencies (as described by Gerlich in Advances in Chemical Physics vol 82 1992, pages 1-176). It should also be noted that the linear RF quadrupole or multipole can comprise a single quadrupole or multipole or alternatively two sets of quadrupole or multipole rods can be provided in tandem.

[0017] A further aspect of the present invention is that the linear RF quadrupole can be used to carry out multiple mass spectrometry steps, so as to perform MS^n. Thus the method can include, after step (4), an additional step of isolating and exciting one or more fragment ions, in the linear RF quadrupole, to cause collision induced dissociation of one or more of the fragment ions to form further fragment ions. Further, the method can include multiple cycles of isolating and exciting one or more of the fragment ions in the linear RF quadrupole, wherein each cycle comprises isolating and exciting at least one or more of the fragment ions formed in the previous cycle to form further fragment ions. In each cycle all the fragment and the selected ions can be excited to cause collision induced dissociation.

[0018] The selected ions and/or the fragment ions can be excited by one of (i) exciting the selected ions by resonance excitation at a particular secular frequency and (ii) applying a broadband excitation waveform, to cause collision induced dissociation of the selected ions.

[0019] Yet another aspect of the invention provides an apparatus incorporating one or more linear RF quadrupoles, or other multipoles, and a time of flight mass spectrometer, and adapted to carry out the method of the present invention.

BRIEF DESCRIPTION OF THE DRAWING

[0020] For a better understanding of the present invention and to show more clearly how it may be carried into effect, reference will now be made, by way of example, to the accompanying drawing, which shows schematically a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0021] With reference to the drawing, an electrospray source is indicated at 2. It will be appreciated that any suitable ion source could be used such as EI (electron ionization), CI (chemical ionization), laser desorption, etc. Ions from the source 2 pass through an orifice 4. A supply of nitrogen gas, which maybe heated, is provided as indicated, to promote vaporization of solvent. The ions then pass into a chamber 5 provided with a connection to a rotary pump, to maintain a desired low pressure. A skimmer 6 then provides an orifice through which desired ions pass into a first RF quadrupole 8. In known manner, this includes a quadrupole rod set provided with usual connection for supply of RF and DC voltages. The quadrupole 8 is operated in the RF only mode , to transmit ions of a broad range of mass to charge ratios. For simplicity, details of electrical connections, and electrical supplies are omitted.

[0022] An entrance lens 10 separates the first quadrupole 8 from a second RF quadrupole 12, but note that the lens 10 does not separate two chambers as the two quadrupoles 8, 12 are essentially in a single chamber, although two chambers at different pressures could be used. The second quadrupole 12 is also operated in the RF only mode. As indicated at 11, a connection is provided to a turbo pump, for maintaining a pressure of, for example, around 1-10 millitorr. As indicated, the first quadrupole 8 is shorter than the second quadrupole 12. For example, the first quadrupole 8 can have a length of 5 cm and the second quadrupole 12 can have a length of 20 cm, i.e. the quadrupoles need not be of the same length.

[0023] At the exit from the second quadrupole 12, there is an exit aperture 14 and then a series of additional lens or electrodes 16, for controlling the ion beam and ensuring that it passes into a source region 18 of a time of flight mass spectrometer (TOF MS) 20.

[0024] Here, the time of flight mass spectrometer 20 is shown orthogonal to the axis of the quadrupoles 8, 12. It will be appreciated that the TOF MS 20 could equally be axially arranged relative to the quadrupoles 8,12. In known manner, a connection 22 is provided, to enable the TOF MS to be pumped down to the desired level of vacuum.

[0025] In use, if potentials of the entrances and exits of the quadrupoles 8, 12 are set to continuously transmit ions, then conventional operation of the TOF MS 20 gives a mass spectrum of ions from the source 2. In known manner, the electrodes at the source region 18 of the TOF MS 20 are activated to collect and provide pulses of ions travelling through the TOF MS, whose time of flight is measured, to give a spectrum for those ions.

[0026] Now, in accordance with the present invention, stopping potentials can be applied at the entrance and exit of either one or both of the first and second quadrupoles 8, 12. This serves to trap ions in the respective quadrupole. Then, unwanted trapped ions can be ejected by resonant excitation at the secular frequencies of the ions. Also, ions of a single m/z value can be trapped and isolated by ejection of all other ions with a filtered noise field or SWIFT waveform as is known, this essentially being a noise waveform with a notch or gap at the frequency corresponding to the secular frequency of the ion of interest. The isolated ions can then be excited and dissociated by collision with a neutral gas. There are a number of ways of causing excitation, collision and fragmentation. Then, the resultant ion fragments can be driven or transferred into the TOF MS 20 by lowering the trapping voltage on the electrode 14 between the second quadrupole 12 and the TOF MS 20. The ions enter the source region of the TOF MS 20 and the mass spectrum of fragment ions can be obtained.

[0027] Ions can be permitted to enter the source region 18 of the TOF MS with near thermal energies that they may have from the second quadrupole 12. Alternatively, they can be accelerated towards the source region 18 by setting up a suitable axial field in the second RF quadrupole 12 (as described by B.Thomson et al., at the 44th ASMS conference on mass spectrometry and allied topics, May 12-16th, Portland, Oregon, 1996). Thermal ions typically take of the order of tens of milliseconds to transfer to the source region of the TOF MS and accelerating the ions into the TOF MS 20 has the advantage of reducing the transfer time down to ca. 1 ms.

[0028] Thus, for example, in ICP-MS, intense Ar^+ ions can cause difficulties and can effectively paralyze the detector. To overcome this, a sample of ions from the source 2 can be passed into the first quadrupole 8. There, potentials can be applied to the skimmer 6 and lens 10, and a field applied at the resonance frequency of the Ar^+ ions to effectively eject them from the ion sample. Then, the voltage on the lens 10 can be adjusted to cause the ion sample to pass into the second quadrupole 12. There, a filtered noise field or SWIFT waveform could be provided to further isolate an ion of interest. The voltage at the aperture 14 and lens 16 would then be adjusted to cause the desired ion to pass into the TOF MS 20.

Claims

1. A method of analyzing ions in amass spectrometer apparatus comprising an ion source (2), a linear RF multipole (12) and a time of flight mass spectrometer (20), the method comprising the steps of :

(1) generating ions from the ion source (2) and passing the ions into the linear RF multipole (12);
(2) applying potentials at either end of the linear RF multipole (12) and operating the linear RF multipole (12) as an ion trap;
(3) selecting ions of interest in the linear RF multipole (12) and ejecting unwanted ions;

characterized in that the method includes:

(4) exciting the selected ions and causing the ions to collide with a neutral gas, to cause collision induced dissociation thereof, thereby forming fragment ions for analysis in the time of flight mass spectrometer (20);
(5) adjusting the potential of one end of the linear RF multipole (10), to pass the selected and the fragment ions through to the time of flight mass spectrometer (20); and
(6) obtaining a spectrum of the selected and the fragment ions in the time of flight mass spectrometer (20).

2. A method as claimed in claim 1, wherein step (3) comprises ejecting ions having a predetermined secular frequency by excitation at said secular frequency.

3. A method as claimed in claim 1, wherein step (3) comprises applying a filtered noise field to eject ions other than a desired ion having a single m/z value or ions having a range of m/z values.

4. A method as claimed in claim 1, 2 or 3, which includes, after step (4), an additional step of exciting one or more of the fragment ions, in the linear RF multipole (12), to cause collision induced dissociation of one or more of the fragment ions to form further fragment ions.

5. A method as claimed in claim 4, which includes multiple cycles of exciting one or more of the fragment ions in the linear RF multipole (12), wherein each cycle comprises exciting one or more of the fragment ions formed in the previous cycle to form further fragment ions.

6. A method as claimed in claim 5, wherein in each cycle all the fragment and the selected ions are excited to cause collision induced dissociation.

7. A method as claimed in any preceding claim, which includes exciting the selected ions by resonance excitation at a particular secular frequency.

8. A method as claimed in any one of claims 1 to 6, which includes applying a broadband excitation waveform, to cause collision induced dissociation of the selected ions.

9. A method as claimed in claim 5, which includes exciting the selected ions and one or more of the fragment ions by exciting the selected and fragment ions by resonance excitation at particular secular frequencies.

10. A method as claimed in claim 5, which includes exciting the selected ions and one or more of the fragment ions by applying a broadband excitation waveform, to cause collision induced dissociation of the selected and fragment ions.

11. A method as claimed in any preceding claim, which comprise carrying out the method using one of a hexapole and an octopole rod set as the linear RF multipole (12).

12. A method as claimed in any one of claims I to 10, which comprises carrying out the method using a quadrupole rod set as the linear RF multipole (12).

Patentansprüche

1. Verfahren zum Analysieren von lonen in einer Massenspektrometervorrichtung, die eine lonenquelle (2), einen linearen RF-Mehrpol (12) und ein Flugzeit-Massenspektrometer (20) umfasst, wobei das Verfahren folgende Schritte umfasst:

(1) das Erzeugen von lonen aus der lonenquelle (2) und Lenken der lonen in den linearen RF-Mehrpol (12);

(2) das Anlegen von Potentialen an jeweiligen Enden des linearen RF-Mehrpols (12) und Betreiben des linearen RF-Mehrpols (12) als lonenfalle;

(3) das Auswählen von lonen von Interesse im linearen RF-Mehrpol (12) und Ausstoßen unerwünschter lonen;
dadurch gekennzeichnet, dass das Verfahren umfasst:

(4) das Anregen der ausgewählten lonen und Kollidieren-Lassen der Ionen mit einem neutralen Gas, um deren durch Kollision herbeigeführte Dissoziation zu bewirken, wodurch Fragment-lonen für die Analyse im Flugzeit-Massenspektrometer (20) gebildet werden;

(5) das Einstellen des Potentials an einem Ende des linearen RF-Mehrpols (10), um die ausgewählten und die Fragment-Ionen durch das Flugzeit-Massenspektrometer (20) hindurchzuschicken; und

(6) das Erhalten eines Spektrums der ausgewählten und der Fragment-lonen im Flugzeit-Massenspektrometer (20).

2. Verfahren nach Anspruch 1, worin Schritt (3) das Ausstoßen von Ionen mit einer vorbestimmten sekulären Frequenz durch Anregen mit der sekulären Frequenz umfasst.

3. Verfahren nach Anspruch 1, worin Schritt (3) das Anlegen eines Felds mit gefiltertem Rauschen umfasst, um andere lonen als ein erwünschtes lon mit einem einzigen m/z-Wert oder lonen mit einem Bereich an m/z-Werten auszustoßen.

4. Verfahren nach Anspruch 1, 2 oder 3, das nach Schritt (4) einen zusätzlichen Schritt des Anregens eines oder mehrerer Fragment-Ionen im linearen RF-Mehrpol (12) umfasst, um durch Kollision herbeigeführte Dissoziation eines oder mehrerer der Fragment-Ionen zu bewirken, um weitere Fragment-Ionen zu bilden.

5. Verfahren nach Anspruch 4, das mehrere Zyklen des Anregens eines oder mehrerer der Fragment-Ionen im linearen RF-Mehrpol (12) umfasst, worin jeder Zyklus das Anregen eines oder mehrerer der Fragment-Ionen umfasst, die im vorherigen Zyklus gebildet wurden, um weitere Fragment-Ionen zu bilden.

6. Verfahren nach Anspruch 5, worin in jedem Zyklus alle Fragment- und die ausgewählten lonen angeregt werden, um durch Kollision herbeigeführte Dissoziation zu bewirken.

7. Verfahren nach einem der vorangegangenen Ansprüche, das das Anregen der ausgewählten Ionen durch Resonanzanregung bei einer bestimmten sekulären Frequenz umfasst.

8. Verfahren nach einem der Ansprüche 1 bis 6, das das Anlegen einer Breitband-Anregungswellenform umfasst, um durch Kollision herbeigeführte Dissoziation der ausgewählten lonen zu bewirken.

9. Verfahren nach Anspruch 5, das das Anregen der ausgewählten lonen und eines oder mehrerer der Fragment-lonen durch Anregen der ausgewählten und Fragment-lonen durch Resonanzanregung mit bestimmten sekulären Frequenzen umfasst.

10. Verfahren nach Anspruch 5, das das Anregen der ausgewählten lonen und eines oder mehrerer der Fragment-lonen durch Anlegen einer Breitband-Anregungswellenform umfasst, um durch Kollision herbeigeführte Dissoziation der ausgewählten und der Fragment-Ionen zu bewirken.

11. Verfahren nach einem der vorangegangenen Ansprüche, welches die Durchführung des Verfahrens unter Verwendung eines aus einem Hexapol- und einem Octopol-Stabsatz als linearer RF-Mehrpol (12) umfasst.

12. Verfahren nach einem der Ansprüche 1 bis 10, das die Durchführung des Verfahrens unter Verwendung eines Quadrupol-Stabsatzes als linearer RF-Mehrpol (12) umfasst.

Revendications

1. Un procédé d'analyse d'ions dans un appareil à spectromètre de masse comprenant une source d'ions (2), un multipôle HF linéaire (12) et un spectromètre de masse à temps de vol (20), le procédé comprenant les étapes consistant à :

    (1) produire des ions à partir de la source d'ions (2) et faire passer les ions dans le multipôle HF linéaire (12) ;
    (2) appliquer des potentiels à chaque extrémité du multipôle HF linéaire (12) et faire fonctionner le multipôle HF linéaire (12) en tant que piège à ions ;
    (3) sélectionner des ions intéressants dans le multipôle HF linéaire (12) et éjecter les ions non désirés ;
    caractérisé en ce que le procédé comprend :
    (4) l'excitation des ions sélectionnés et l'amenée des ions à entrer en collision avec un gaz neutre pour provoquer une dissociation de celui-ci induite par la collision, en formant ainsi des ions fragmentés pour une analyse dans le spectromètre de masse à temps de vol (20) ;
    (5) le réglage du potentiel d'une extrémité du multipôle HF linéaire (10), pour faire passer les sons sélectionnés et les ions fragmentés à travers le spectromètre de masse à temps de vol (20) ; et
    (6) l'obtention d'un spectre des ions sélectionnés et des ions fragmentés dans le spectromètre de masse à temps de vol (20).

2. Un procédé tel que revendiqué à la revendication 1, dans lequel l'étape (3) comprend le fait d'éjecter des ions présentant une fréquence séculaire prédéterminée par excitation à ladite fréquence séculaire.

3. Un procédé tel que revendiqué à la revendication 1, dans lequel l'étape (3) comprend le fait d'appliquer un champ parasite filtré pour éjecter des ions autres qu'un ion désiré présentant une valeur m/z unique ou des ions présentant une gamme de valeurs m/z.

4. Un procédé tel que revendiqué à la revendication 1, 2 ou 3, qui comprend, après l'étape (4), une étape supplémentaire consistant à exciter un ou plusieurs des ions fragmentés, dans le multipôle HF linéaire (12), pour amener une dissociation induite par collision d'un ou de plusieurs des ions fragmentés afin de constituer d'autres ions fragmentés.

5. Un procédé tel que revendiqué à la revendication 4, qui comprend des cycles multiples d'excitation d'un ou de plusieurs des ions fragmentés dans le multipôle HF linéaire (12), dans lequel chaque cycle comprend le fait d'exciter un ou plusieurs des ions fragmentés formés dans le cycle précédent afin de constituer d'autres ions fragmentés.

6. Un procédé tel que revendiqué à la revendication 5, dans lequel, dans chaque cycle, tous les ions fragmentés et les ions sélectionnés sont excités pour amener une dissociation induite par collision.

7. Un procédé tel que revendiqué dans une quelconque revendication précédente, qui comprend le fait d'exciter les ions sélectionnés par une excitation de résonance à une fréquence séculaire particulière.

8. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 6, qui comprend le fait d'appliquer une forme d'onde d'excitation de bande large, pour provoquer une dissociation induite par collision des ions sélectionnés.

9. Un procédé tel que revendiqué à la revendication 5, qui comprend le fait d'exciter les ions sélectionnés et un ou plusieurs des ions fragmentés par excitation des ions sélectionnés et des ions fragmentés à l'aide d'une excitation de résonance à des fréquences séculaires particulières.

10. Un procédé tel que revendiqué à la revendication 5, qui comprend le fait d'exciter les ions sélectionnés et un ou plusieurs des ions fragmentés en appliquant une forme d'onde d'excitation de bande large, pour provoquer une dissociation induite par collision des ions sélectionnés et des ions fragmentés.

11. Un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, qui comprend le fait de mettre en oeuvre le procédé en utilisant un jeu de barres hexapôles et de barres octopôles pour le multipôle HF linéaire (12).

12. Un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 10, qui comprend le fait de mettre en oeuvre le procédé en utilisant un jeu de barres quadripôles pour le multipôle HF linéaire (12).

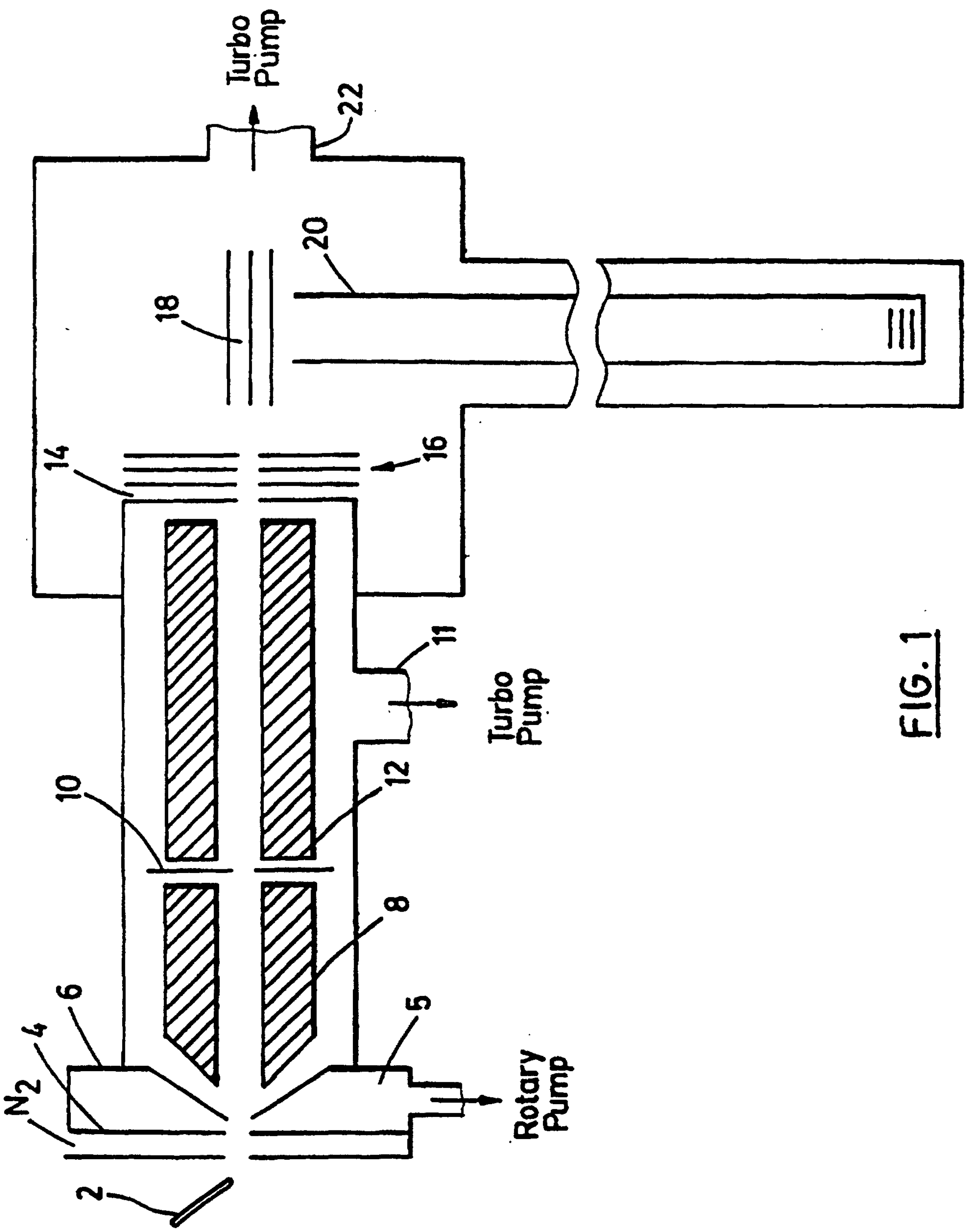
Turbo Pump
22
20
18
14
16
11
Turbo Pump
10
12
8
6
4
5
N_2
Rotary Pump
2

FIG. 1