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(54) Mass spectrometer with ion fragmentation by reaction with electrons

(57) The invention relates to a mass spectrometer, in particular a time-of-flight mass spectrometer, with fragmentation of pre-selected molecule ions for the acquisition of daughter ion spectra.

The invention consists in an instrument with devices for generating multiply charged ions of the molecule of interest, for selecting a multiply charged ion species by a mass filter, for fragmenting the selected ions by allowing them to react with low energy electrons in an RF ion guide system, and for analyzing the fragment ions in a mass analyzer.

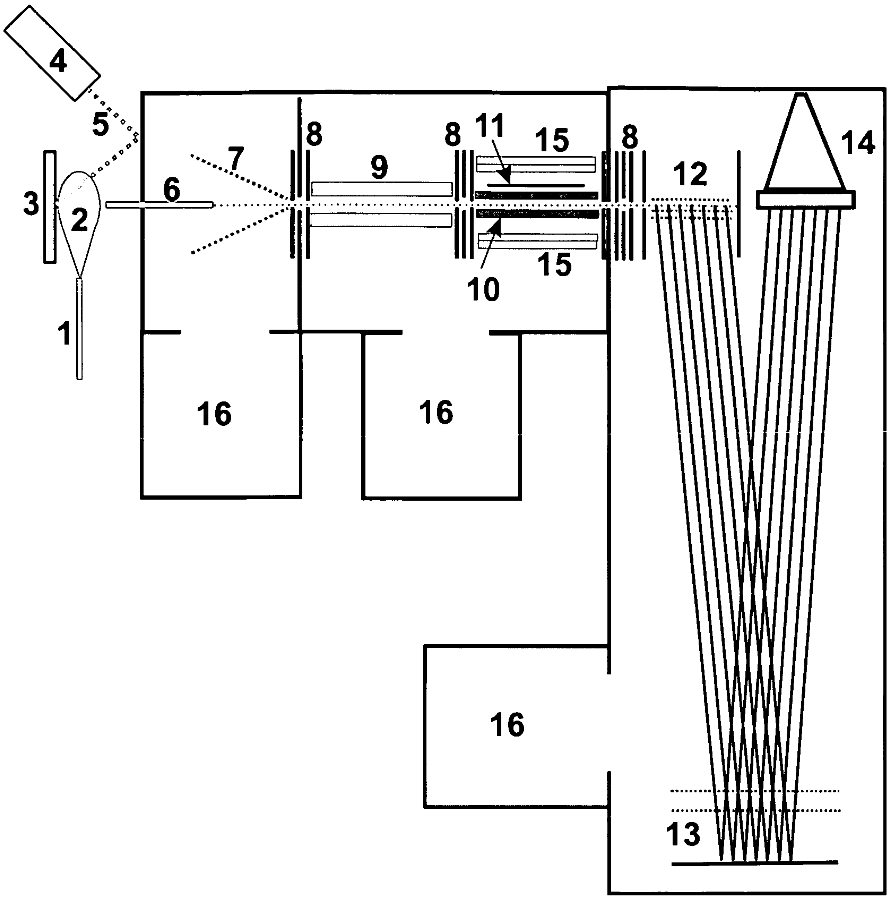

Figure 1

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Description

[0001] The invention relates to a mass spectrometer with a device for the fragmentation of pre-selected molecule ions for the acquisition of daughter ion spectra.

[0002] The invention comprises an instrument with devices for generating multiply charged ions of the molecule of interest, for selecting a multiply charged ion species by a mass filter, for fragmenting the selected ions by allowing them to react with electrons in an RF ion guide system, and for analyzing the fragment ions in a mass analyzer.

Prior Art

[0003] Time-of-flight mass spectrometers with orthogonal ion injection (OTOF for short) are characterized by a high precision of ion mass determination and by a high dynamic ion measuring range. They operate with a continuous ion beam and normally acquire between 10,000 and 20,000 spectra per second, which are added to form sum spectra in real time. If one adds the spectra only over a twentieth of a second, then the mass spectrometer can also follow extremely rapid separation processes with twenty mass spectra per second: adding over a longer time increases the dynamic measuring range of measurement. This type of mass spectrometer can be manufactured at moderate cost and is extraordinarily flexible in its application, something which no other mass spectrometer has so far achieved.

[0004] If these time-of-flight mass spectrometers are set up as tandem mass spectrometers to acquire daughter ion spectra, they have, until now, carried out the fragmentation of selected parent ions to daughter ions using collisions in gas-filled collision cells, named collision induced decomposition or CID for short. The parent ions are usually selected first using quadrupole mass filters; quadrupole, hexapole or octopole rod systems can be used as collision cells for the fragmentation, said systems being operated at high frequency and able to keep ions stably in their interior. The fragment ions obtained as a result of collisions are then injected into the time-of-flight mass analyzer and measured as a daughter ion spectrum.

[0005] New methods for fragmenting biopolymer molecules, mainly from peptides and proteins, have recently been developed in ion cyclotron resonance or Fourier transform mass spectrometry (ICR-MS or FTMS). They consist in allowing multiply charged ions to react with electrons, resulting in the cleavage of the chain-shaped molecules. If one begins with multiply positively-charged ions created as a result of multiple protonation, then the proton attachment energy released by electron capture leads to the cleavage of the chain molecules. The method is called electron capture dissociation, ECD for short. If the molecules were doubly charged, one of the two fragments created remains as an ion. The fragmentation obeys very simple rules in this process (for specialists: there are essentially only c cleavages and few z cleavages between the amino acids of a peptide), so that it is very easy to elucidate the structure of the molecule from the fragmentation pattern. In particular, it is easy to read the amino acid sequence of peptides or proteins from the fragmentation spectrum. Interpreting these ECD fragment spectra is significantly easier than interpreting collision-generated CID fragment spectra.

[0006] It is also possible to fragment triply or multiply positively-charged ions in this way, but the method is particularly impressive when used with doubly charged ions. If electrospray ionization is applied to peptides, the doubly charged ions are generally also the most commonly occurring ions. Electrospray ionization is a method of ionization which is particularly frequently used for biomolecules for the purpose of mass spectrometric analysis in Fourier transform mass spectrometers (FT-MS).

[0007] For fragmentation by electron capture, the kinetic energy of the electrons must be low, since otherwise they cannot be captured. In practice, one supplies electrons having an energy of only a few electron-volts. This is very easy in the extremely strong magnetic fields of the Fourier transform mass spectrometer because the electrons simply drift from a flat thermionic cathode along the magnetic field lines until they reach the cloud of the ions. A second type of electron capture is carried out with electrons having a kinetic energy of some 10 to 30 electron-volts, this being termed "hot electron capture dissociation", "hot ECD" for short. It results in very similar fragmentation.

[0008] If multiply negatively-charged ions are subjected to a reaction with electrons having an energy of 30 to 100 electron-volts, then electron detachment dissociation occurs, which is also associated with a cleavage of the molecule ion. This type is abbreviated to EDD.

[0009] Very recently, it has proved possible to achieve fragmentation of peptide ions using both ECD and also EDD in RF ion traps according to Wolfgang Paul. Fragmentation resulting from reactions with electrons has so far not proved possible in other systems (with the exception of FTMS). In particular, fragmentation of this type in linear quadrupole ion traps, or more generally in RF-operated multipole rod systems, has not become known.

[0010] Multipole rod systems, including linear quadrupole ion traps, are usually operated with a two-phase RF voltage, the two phases being applied in turn across the pole rods. The RF voltage across the rods of the rod system is usually not very high; in the case of commercial ion guide systems it is only a few hundred volts at a frequency of a few megahertz. In the interior, a multipole field is generated which oscillates with the RF voltage and drives the ions above a threshold mass to the central axis, causing them to execute so-called secular oscillations in this field. The restoring forces in the ion trap are sometimes described using a so-called pseudopotential which is determined via a temporal averaging of the forces of the real potential. In the central axis is a saddle point of the oscillating real potential; this decreases, according to the phase of the RF voltage, from the saddle point to the rod electrodes of the one phase and increases towards the other rod electrodes. The saddle point itself is usually at a DC voltage potential with respect to the ground potential.

[0011] These systems are used as ion guide systems and also as collision cells for the fragmentation of ions. They are normally filled with low pressure collision or deceleration gas in order to damp the motion of the ions and to collect them in the axis of the system under the influence of the pseudopotential. Ion guide systems have been developed which have a weak DC voltage drop along the axis, thus driving the ions to one end of the rod system.

[0012] Other types of ion guide systems are not constructed as a system of straight rods. Ion guide systems can also consist of wire pairs having the form of a double helix or quadruple helix being also charged with RF voltages. Ion guide systems can also consist of a large number of coaxially arranged apertured diaphragms, again operated by RF voltage. The notion "ion guide system" as used here includes these forms as well.

[0013] A popular way of ionizing larger biomolecules is electrospray ionization (ESI), which ionizes the biomolecules out of solutions at atmospheric pressure outside the mass spectrometer. These ions are then introduced into the vacuum of the mass spectrometer via inlet systems of known types.

[0014] This ionization produces practically no fragment ions; the ions are principally those of the molecule. However, multiply charged ions of the molecule occur frequently with electrospray ionization. The lack of almost any fragmentation during the ionization process limits the information from the mass spectrum to the molecular weight; there is no information concerning internal molecular structures which can be used for further identification of the substances present. This information can only be obtained by acquiring fragment ion spectra (also called daughter ion spectra).

Objective of the Invention

[0015] The objective of the invention is to provide a mass spectrometer which allows either to perform the classical collisionally induced decomposition (CID) of ions or the new fragmentation by reactions of biopolymer ions with electrons (ECD).

Brief Summary of the Invention

[0016] The invention presents a mass spectrometer comprising an ion source for the generation of multiply charged ions of molecules of interest, a mass filter for the selection of a certain type of multiply charged ions, and a particular ion guide system with an electron supply system for fragmenting the selected ions by reactions with electrons. The electrons may be supplied as free electrons for electron capture dissociation (ECD), hot electron capture dissociation (HECD), electron detachment dissociation (EDD), or from negative ions with loosely bound electrons for electron transfer dissociation (ETD), or even from neutral particles with loosely bound electrons. Highly excited neutral particles as delivered from fast atom bombardment sources usually offer loosely bound electrons. The particular ion guide system can also be used to fragment the selected ions by collisions with collision gas atoms or molecules in the classical manner (CID), or by infrared multiphoton dissociation (IRMPD). The fragment ions thusly generated are injected into the analyzer part of the mass spectrometer. The analyzer may favorably be a time-of-flight analyzer with orthogonal ion injection but any other mass analyzer may be used here.

[0017] The ion guide system in this case can be a multipole rod system, but also a system of interwound helical wires, or a system of coaxial apertured diaphragms, all operated with an RF voltage. Usually the RF voltage has two distinct phases, but multi-phase RF voltages can be applied, too. This ion guide system is preferably equipped with an external electron supply system. The supply system for free electrons may be a hot cathode in the form of an incandescent filament or incandescent ribbon which is at a potential a little higher than the mid potential of the RF voltage. Free electrons can also be generated by laser bombardment of one of the pole rods or of a separate, external surface from which electrons can emerge. Free electrons can penetrate into the ion guide system in the zero crossovers of the RF voltage and react with the ions. A damping inside the ion guide gas makes the ions gathering near the axis. Different systems may be used to deliver electrons loosely bound to negative ions or neutrals.

[0018] The RF voltage here can preferably consist of positive and negative voltage pulses separated by brief periods without voltage. In these voltage-free periods, free electrons can penetrate into the ion guide system without hindrance. It is favorable if the duration of the voltage-free periods can be adjusted. "Voltage-free" is defined here as equal DC potentials at all electrodes of the ion guide, thus providing an interior of the ion guide system free of any electric field. In a preferred embodiment, this potential is equal to the mid potential of the RF voltage.

[0019] A magnetic field generated by permanent magnets or by an electromagnet, both either with or without yoke, can guide the free electrons along the magnetic force lines specifically to the cloud of the ions. The electromagnet can be switched off if necessary.

[0020] The fragmentation of the ions in the ion guide system can be performed while they are in transit, resulting in a continuous mode fragmentation. The ions can also be stored temporarily by means of DC voltage potentials at end terminating diaphragms and fragmented during their storage. The intensity of the fragmentation can be controlled by the temperature of the hot cathode and hence by the intensity of electron emission, by the duration of the emission, and also by the duration of the voltage-free periods in the RF voltage.

[0021] The ion guide system may be able to propel the ions slowly through the damping gas to the end of the system by means of a small voltage drop along the axis of the system. The voltage drop can be generated by a voltage drop at each of the rods of the rod system or at each of the helical wires, for example. There are different methods known to create voltage drops along the axis of the ion guide system.

[0022] If a time-of-flight analyzer is used, the fragment ions can be injected directly out of the ion guide system in which the reactions with the electrons occur into the pulser of the time-of-flight mass analyzer, or they can be passed to the time-of-flight mass analyzer with the help of an additional ion guide system.

[0023] It is, of course, possible to use other types of mass analyzers, such as a quadrupole, ion trap or FTMS mass analyzer, instead of a time-of-flight mass analyzer to acquire the daughter ion spectra, but at present the time-of-flight mass analyzers appear to be the most favorable.

Brief Description of the Illustrations

[0024] Figure 1 shows a schematic representation of a mass spectrometer according to this invention, where the parent ions selected in the mass filter (9) react in the hexapole ion guide system (10) with electrons from the electron emitter (11), resulting in fragmentation.

[0025] Figure 2 illustrates a favorable form of the RF voltage which exhibits voltage-free periods between positive and negative voltage pulses.

[0026] Figure 3 shows a cross-section through a hexapole ion guide system with pole rods (30) wherein the central ion cloud (31) is penetrated by a beam (33) of free electrons from an electron emitter (32), guided by a magnetic field generated by two permanent magnets (35).

Description of Favorable Embodiments

[0027] A favorable embodiment of the invention is shown in Figure 1 and depicts an electrospray ion source with spray capillary (1) and spray cloud (2), with an inlet capillary (6) which transfers the ions together with ambient gas into the vacuum of the mass spectrometer, with an ion funnel (7) to separate the excess gas, with a quadrupole filter (9) to select the parent ions for the fragmentation, and with the ion guide system (10) including an electron filament (11) as electron supply system. The ion guide system (10) can easily be used in conventional manner to fragment ions by collisional decomposition (CID). The ion source (1, 2), selector (9), and fragmentation station (10, 11) can be combined, for instance, with a time-of-flight mass analyzer with pulser (12), reflector (13) and detector (14).

[0028] The electron spray ion source is common in commercial mass spectrometers and no further explanation is required here. The electrospray ionization source used here additionally contains a means by which solid samples, which are prepared with a matrix on a sample support plate (3), can be transported by means of a laser beam (5) from a pulsed laser (4) in vaporized form into the spray cloud (2), where they can be ionized. The matrix material can be an explosive in which case no large molecules of the matrix remain after desorption. This desorption station makes is possible to generate multiply ionized molecule ions from laser desorbed samples off solid surfaces, as are required for the ECD fragmentation in the mass spectrometer front end according to the invention. As has already been described, matrix-assisted laser desorption (MALDI), which is usually used for solid samples, only provides singly-charged ions which cannot be used here.

[0029] After being admitted into the vacuum system through the inlet capillary (6), the ions are liberated from the entrained ambient gas (usually clean nitrogen) by usual means, here an ion funnel (7), and fed through systems of apertured diaphragms (8) to the quadrupole filter (9). Several systems of apertured diaphragms (8) serve to transmit the ions between the various differential pumping sections of the mass spectrometer. The quadrupole filter (9) can be operated in such a way that it admits all ions (above a mass limit). In this mode, the primary mass spectra are acquired in the mass analyzer (12, 13, 14) without any fragmentation. These spectra show which species of ion have been formed. If ions are discovered for which it is desired to acquire the daughter ions, the mode is changed: the quadrupole filter (9) is switched so that it filters and transmits only pre-selected multiply charged, preferably doubly charged, ions of the desired species (the "parent ions"), and in the subsequent ion guide system (10), fragmentation is produced by either medium-energy collisions, when the ions are accelerated into the ion guide system, or by reactions with free electrons from the electron emitter (11), when this emitter is switched to electron emission.

[0030] The quadrupole filter (9) can also be replaced by other types of mass filter, for example by a Wien filter, which consists of an arrangement of crossed homogeneous electric and magnetic fields. Mass filters are characterized by the fact that they transmit only ions of a single mass (or, more precisely, of a single mass-to-charge ratio) or only a narrow range of masses. It is favorable if the mass filter (9) can be operated at the same damping gas pressure as is found in the downstream ion guide system (10).

[0031] For electron capture dissociation, the parent ions selected in this way are then introduced into the ion guide system (10) in which they are to be fragmented, still guided by their momentum and assisted by the small amounts of accompanying gas. The ribbon-shaped glowing cathode (11) is switched on and set at a potential between of a few tenths of a volt and some tens of volts to bring electrons with the desired kinetic energy to the ion cloud in the ion guide system (10). To this end, the potential of the electron emitter (11) can be adjusted with respect to the mid potential of the RF voltage across the ion guide system (10). The RF voltage is switched over to a form consisting of positive and negative voltage pulses with voltage-free periods in between, as shown in Figure 2. In the voltage-free periods, the electrons can thus penetrate into the cloud of the flying ions, where they react with the multiply charged ions. By selecting the polarity of the multiply charged ions and by selecting the energy of the electrons, it is possible to achieve electron capture dissociation (ECD), or hot ECD from positive parent ions, or electron detachment dissociation (EDD) from negative parent ions.

[0032] The ribbon-shaped hot cathode can also be replaced by other forms of electron emitters. It is thus possible to use one or more small-area emitters. The electrons can also be generated as photoelectrons by bombarding a suitable surface with low work function with a laser. This surface can be located outside the ion guide system, or the surface of one of the pole rods can serve as an electron-emitting surface. If a pulsed laser is used, the electron generation can be accurately tuned to those phases of the radio frequency in which the electrons can penetrate into the ion guide system.

[0033] The electron emitter can be replaced by an ion source for generating negative ions, or by a fast atom bombardment (FAB) source for delivering highly excited atoms. Using a FAB source, no magnetic field is necessary to guide the particles; and no change of the RF wave form is necessary.

[0034] The RF voltage of slim ion guide systems which enclose interiors of only some three millimeters is only a few hundred volts when frequencies of a few megahertz are used. The voltages can easily be generated directly, i.e. without an intermediate transformer, from transistor systems, for example from MOSFET systems. These transistor systems also make it possible to generate the voltage pulses (shown in Figure 2) which are necessary for the introduction of free electrons. The voltage-free periods between the voltage pulses, which allow the penetration of the free electrons, need only be very short since low energy electrons are also very fast: periods of the order of 10 to 50 nanoseconds are sufficient. For control purposes it is favorable if the duration of these periods can be adjusted.

[0035] Figure 3 shows a schematic representation of a cross-section through a hexapole ion guide system. The slim pole rods (30) enclose an interior in which an ion cloud (31) is in motion. During the transit of these ions, the cloud is penetrated by a beam (33) of low energy electrons from the electron emitter (32). The electron beam (33) is guided through a magnetic field which, in this case, is generated by flat permanent magnets (35). Experience shows that the magnetic field hardly interferes with the motion of the ions. The magnetic field can also be formed by an electromagnet with yoke. It can then be switched off if desired.

[0036] The ion guide system is filled with damping gas, which causes the ions to collect near the axis of the system as a result of the action of the pseudopotential; there they can be easily reached by the electrons. A favorable pressure range lies between 10^{-3} and 10^{-2} Pascal; a pressure above 10^{-4} Pascal is also sufficient if there is damping in preceding systems, while for strong damping the range to 10^{-1} Pascal and above can also be possible. For strong collisional decomposition, collision gas pressures in the range of 10^{-2} to 10^{-1} Pascal are preferred.

[0037] The ion guide system (10) can also possess a slight DC voltage potential gradient in which the ions are transported to the end of the system. This is particularly helpful if the system is operated at a higher damping gas pressure, as the ions can then easily come to rest in this gas and are no longer able to reach the exit by virtue of their own momentum. A gradient of this type can be achieved by having a DC voltage difference between the beginning and the end and by using slightly resistive rods for the ion guide system (10). It is also possible to achieve a voltage drop of this type across helical wires. Various other possibilities are presented in the literature. The transport of the ions to the exit of the system makes operation easier.

[0038] The fragmentation of the ions by ECD can take place in the continuous flow of the ions, and also when the ions are in a stored state in the ion guide system. For fragmentation of the ions in the flow, a favorable setting of the ion emission and the duration of the voltage-free periods of the RF voltage must be worked out by means of calibrating experiments. The number of electrons reacting must not be too low, as then only daughter ion spectra which are low in fragment ions are measured. But neither must it be too high, as in that case the singly-charged fragment ions already formed will discharge as a result of further recombinations with electrons and will thus be destroyed. The fragmentation in the flow has the advantage of continuous operation, or at least continuous within the prescribed measuring time for acquiring a daughter ion sum spectrum.

[0039] The ions can be stored in the ion guide system (10) by setting barrier potentials for the passage of the ions at the apertured diaphragm systems (8) at the entrance and exit ends. The confined ions can then be fragmented, it being favorable if the ions still move backwards and forwards between the reflecting diaphragm systems (8). Only subsequently are they released from the ion guide system, preferably again by switching on an axial propelling voltage.

[0040] The ions can then be threaded directly out of this ion guide system into the pulser (12) of the time-of-flight mass analyzer. They also can be stored temporarily in an additional ion guide system, damped again, for example, and be fed to the time-of-flight mass analyzer from here.

[0041] The ions must fly into the pulser (12) in the form of a beam which is as fine and as parallel as possible in order to achieve maximum possible mass resolution of the time-of-flight mass analyzer. The ions fly in relatively slowly with energies of around only 20 electron-volts. If the pulser (12), which is around two centimeters long, is filled with ions which are of most interest so that they just reach the back, then the ions are ejected as a pulse at a right angle to their previous direction of flight. A string-shaped ion cloud is therefore ejected as a pulse which, on its path, forms individual ion fronts, each of which contains ions having the same mass. These are normally reflected in a reflector (13) causing a further energy focusing to occur, and steered to a detector (14). The detector is a multichannel plate with secondary-electron multiplication. The amplified ion current is usually changed into a digital value approximately every 500 picoseconds; the measured values are constantly added to a memory.

[0042] The time-of-flight mass analyzer can also have several reflectors or be constructed as a system of cylindrical capacitors. It is then possible to achieve higher mass resolutions and mass accuracies.

[0043] It is, of course, also possible to use other types of mass analyzers to acquire the daughter ion spectra instead of the time-of-flight mass analyzer. At present, however, the time-of-flight mass analyzer appears to be the most favorable choice, in terms of value-for-money, for achieving a high mass accuracy, a high dynamic measurement range and a short measuring time which can be flexibly adjusted.

[0044] It is favorable to operate a collisionally induced fragmentation in addition to an ECD-type fragmentation, the former producing different types of spectra and permitting specific information to be obtained, particularly compared to ECD daughter ion spectra. The collisionally induced fragmentation can be undertaken in the same ion guide system by injecting the parent ions into the gas-filled ion guide system with energies between 30 and 100 electron-volts. They then fragment by gradual energy absorption in a large number of collisions (CID = collision induced dissociation), a process which essentially excites the atomic oscillation systems in the molecule. Infrared photons can also be injected into the ion guide system for the same purpose, the parent ions here fragmenting as a result of the gradual energy absorption in the form of absorbed photons and producing daughter ion spectra which are very similar to those produced as a result of collisionally induced fragmentation (IRMPD = infrared multi photon dissociation).

[0045] With knowledge of this invention, the specialist will also be able to construct different types of mass spectrometer with a fragmentation of the ions by electron reactions, where the reactions with the electrons do not have to take place in the mass analyzer itself, as was previously the only known method.

Claims

1. Mass spectrometer for acquiring daughter ion spectra of an analyte, comprising

a) an ion source for generating ions of substances including the analyte,
b) a mass filter for selecting, as parent ions, ions within a pre-selected range of mass-to-charge ratios required to be fragmented to daughter ions,
c) an RF ion guide system equipped with an electron supply system, for the fragmentation of the parent ions inside the ion guide system by reaction with electrons, and
d) a mass analyzer for acquiring the daughter ion spectra.

2. Mass spectrometer according to Claim 1, wherein the RF generator for the ion guide system generates an RF voltage consisting of positive and negative voltage pulses separated by voltage-free periods.

3. Mass spectrometer according to Claim 2, wherein the duration of the voltage-free periods in the RF voltage is adjustable.

4. Mass spectrometer according to one of the Claims 1 to 3, wherein free electrons are produced by the electron supply system and a magnetic field guides the electrons to the ion cloud inside the ion guide system.

5. Mass spectrometer according to one of the Claims 1 to 4, wherein the electron supply system is a hot cathode supplying free electrons.

6. Mass spectrometer according to Claim 5, wherein the electron supply system has the form of a filament extending along a part of the ion guide system.

7. Mass spectrometer according to one of the Claims 1 to 4, wherein the electron supply system is a surface out of which electrons are extracted by means of laser bombardment.

8. Mass spectrometer according to one of the Claims 1 to 4, wherein the electron supply system is a generator for producing negatively charged ions with loosely bound electrons.

9. Mass spectrometer according to one of the Claims 1 to 4, wherein the electron supply system is a generator for highly excited neutral particles with loosely bound electrons.

10. Mass spectrometer according to one of the Claims

1 to 9, wherein the ion guide system is a hexapole rod system.

11. Mass spectrometer according to one of the Claims 1 to 10, wherein the ion source is an vacuum-external electrospray ion source.

12. Mass spectrometer according to Claim 11, wherein the electrospray ion source is equipped with means of laser-desorbing molecules from a surface.

13. Mass spectrometer according to one of the Claims 1 to 12, wherein the ion guide system is equipped with means to perform collisionally induced fragmentation of the parent ions.

14. Mass spectrometer according to one of the Claims 1 to 13, wherein the ion guide system is equipped with means to perform infrared multiphoton fragmentation of the parent ions.

15. Mass spectrometer according to one of the Claims 1 to 14, wherein the analyzer is a time-of-flight mass analyzer with orthogonal ion injection.

16. Mass spectrometer according to Claims 15, wherein in front of the time-of-flight mass analyzer there is an additional ion guide system in which the motion of the daughter ions is damped.

17. Method for operating a mass spectrometer according to one of the Claims 1 to 16, wherein the ions in transit through the ion guide system react with the electrons.

18. Method for operating a mass spectrometer according to one of the Claims 1 to 16, wherein the ions in the ion guide system are stored before they react with the electrons.

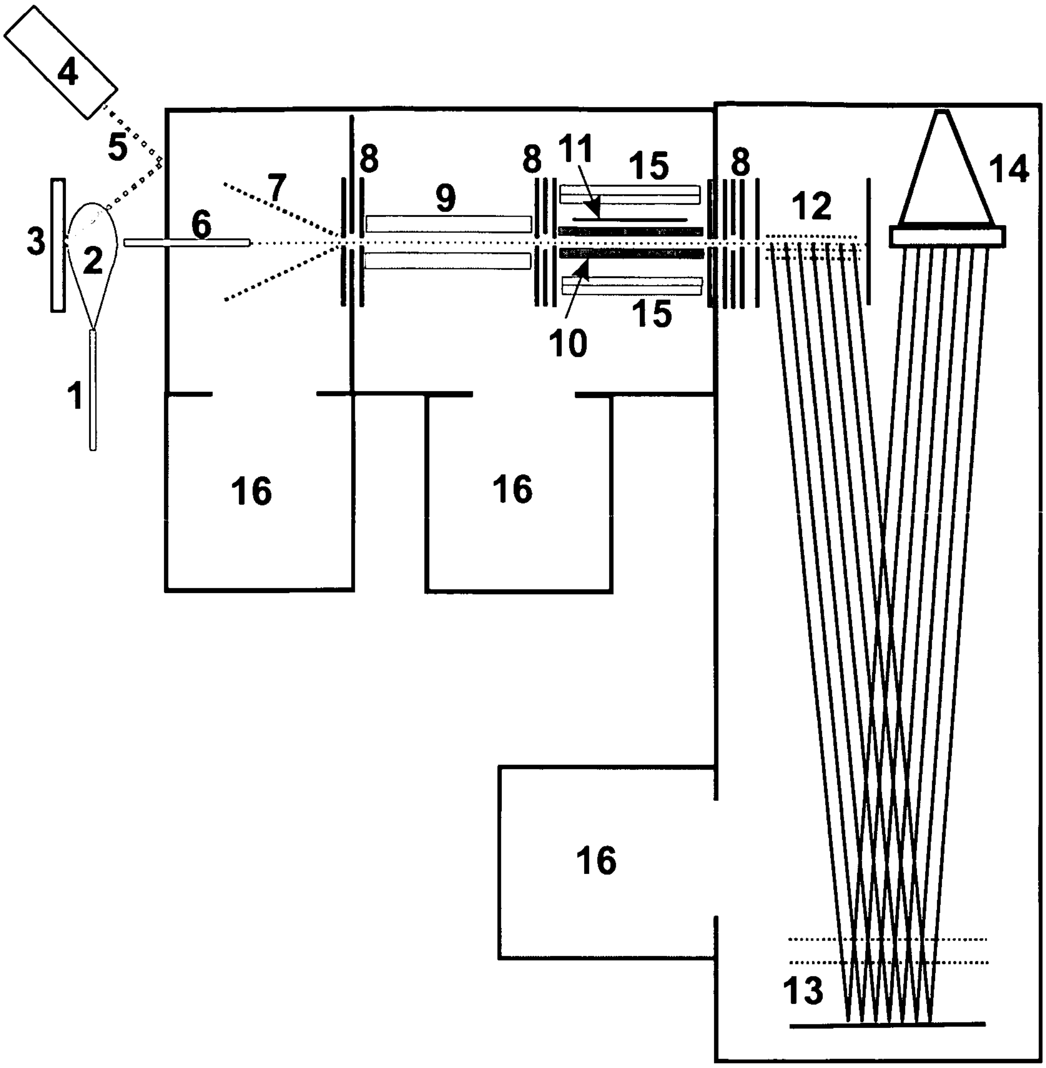

Figure 1

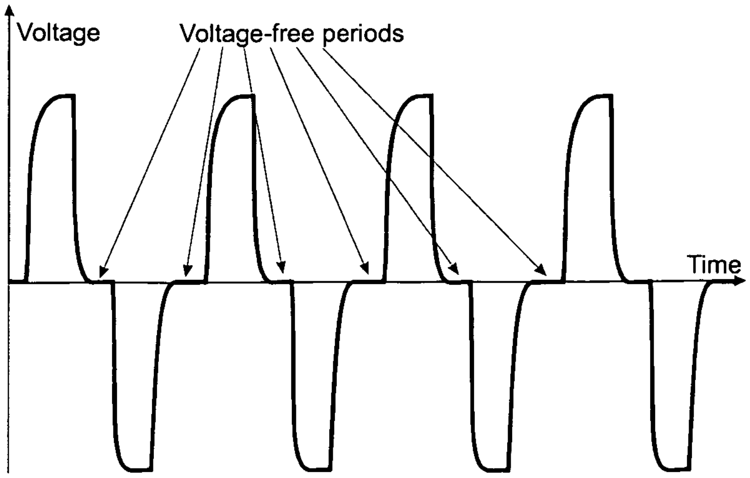

Figure 2

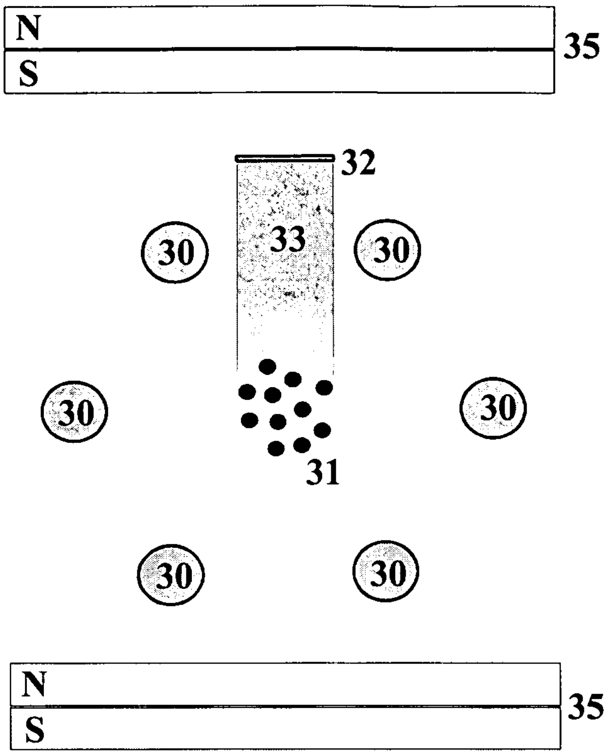

Figure 3