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(54) Mass spectrometer

(57) A mass spectrometer includes a chemical ionization source (22) comprising an ion molecule reaction region (33), a mass analyzer (12) and an interface (23) coupling the chemical ionization (22) source to the mass analyzer (12). The interface (23) comprises a first chamber (50) comprising a radio frequency focusing device (61), to be arranged adjacent to a gas conductance limiting exit aperture (38) of an ion molecule reaction region of the chemical ionization source (22) or adjacent to a gas conductance limiting aperture for feeding ambient air, the chamber (50) defining a collisional declustering region, at least one interface vacuum chamber (45) arranged downstream of the first chamber, the at least one interface vacuum chamber (45) being separated from the first chamber (50) by a further gas conductance limiting aperture (53). The pressure in the first chamber (50) is 0.01 mbar or more. This setup improves ion transmission into the interface stage (45) following the first chamber (50). Further, the radio frequency focusing device (61) more efficiently dissipates ion kinetic energy originating from expansion into the first chamber (50), improving achieved mass resolving power and mass accuracy in particular for applications where a chemical ionization source (22) is a component of an orthogonal time-of-flight mass spectrometer.

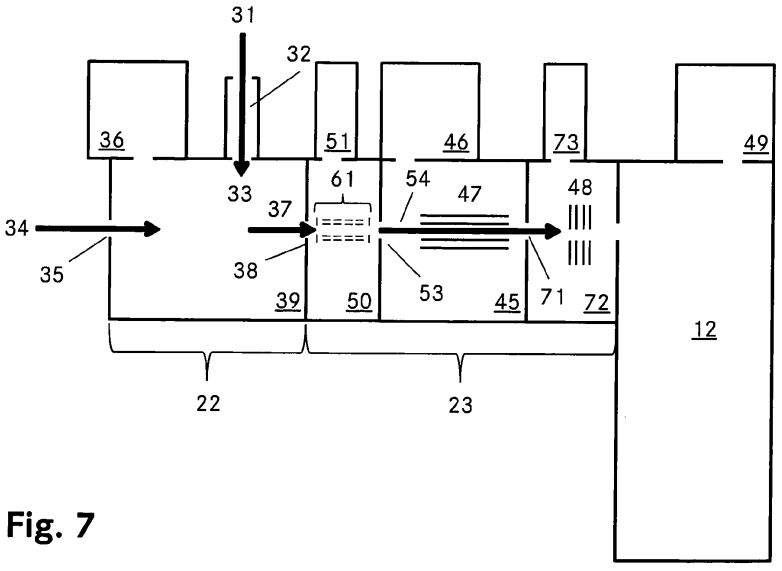

Fig. 7

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Description

Technical Field

[0001] The invention relates to a mass spectrometer including a chemical ionization source comprising an ion molecule reaction region, a mass analyzer and an interface, coupling the chemical ionization source to the mass analyzer. The invention further relates to a method for feeding ions from a chemical ionization source to a mass analyzer and to a method for using the mass spectrometer for the analysis of ions produced by chemical ionization and for the analysis of ambient ions.

Background Art

Mass Spectrometry

[0002] A mass spectrometer (MS) is a device for measuring the mass-to-charge ratio *(m/Q)* of ions. It can be used for chemical analysis. Mass spectrometers are commonly used for chemical analysis of gaseous, liquid, solid and plasma samples in a broad range of disciplines. All types of MS operate by subjecting charged, gas-phase molecules or atoms (ions) to electric and/or magnetic fields within a reduced pressure (vacuum) environment.

[0003] For a given sample, a MS generally records data for several chemical species corresponding to a broad range of *m/Q.* Data are often presented as a histogram of observed signal intensity as a function *of m/Q,* called a mass spectrum.

[0004] The mass of an ion is a function of the specific atom(s) comprising the ion. For instance the most abundant water isotopologue cation, $H_2{}^{16}O^+$, has a mass of 18.01 Dalton (1 Da = $m(^{12}C)/12 = 1.66 \times 10^{-27}$ kg), which is the sum of the masses of 2 hydrogen atoms and 1 oxygen-16 atom minus one electron. With a net charge of 1 elementary charge ($e = 1.602 \times 10^{-19}$ coulomb), this cation *has m/Q* = 18.01 thomson (Th).

[0005] The mass spectrum of a sample can be used to deduce the identity of the molecules in the sample based on the observed *m/Q* value(s). For cases where the response of the MS can be appropriately calibrated, MS data can also quantify the concentration of specific molecules within the sample.

[0006] Mass spectrometer performance is often characterized by mass accuracy and mass resolution. The former quantifies how accurately a MS measures the *m/Q* of an ion, and the latter quantifies the ability of the MS to distinguish two ions of similar *m/Q.*

[0007] One type of a MS is the time-of-flight mass spectrometer (TOFMS). A TOFMS includes a TOF analyzer (TOF) that determines the *m/Q* of an ion by measuring the time required for that ion to travel a known distance after ions are accelerated to a known kinetic energy or by a known impulse. For any ion in a TOF the observed ion time-of-flight will be proportional to the square root of the ion's *m/Q.*

[0008] Orthogonal extraction (0) TOFMS is a well-known implementation of TOFMS. As depicted in Figure 1, ions to be measured enter the TOF 12 along a primary axis 11 that is orthogonal to the TOF drift axis 14 on which ion velocities are to be measured. Within the TOF, ions moving on the primary axis are subjected to an impulse 13 that accelerates them along the drift axis towards a detector 15. The data acquisition system 16, records the time of ion detection relative to the time at which the accelerating impulse occurred.

[0009] An ideal TOF analyzer refocuses all ions in time, independent on their initial conditions. This means an ion's flight time depends only on its *m/Q* and not on the ion's position and/or energy at the instance the extraction impulse is applied.

[0010] In reality, flight times are affected by initial ion velocities and initial positions as well as non-idealities in the applied electric fields, and differences in the fields experienced by ions owing to the spatial distribution of the primary beam (which is the collection of ions traveling along the primary axis).

[0011] For a population of ions all having equal *m/Q,* these non-idealities will lead to the observation of a distribution of flight times, rather than a discrete flight time.

[0012] OTOFMS performance is improved (made more ideal) by minimizing the spatial spread (width) of the primary beam on the axis parallel to drift and by minimizing the velocity of all ions in the primary beam along the drift axis, prior to acceleration. Minimization of each of these values reduces uncertainty in the drift velocity after acceleration, and therefore uncertainty in the determination of *m/Q* (mass accuracy and mass resolution).

[0013] A TOF must operate at a pressure low enough to ensure that ion trajectories are determined by electric fields and not perturbed by collisions with neutral background gas molecules. Such random collisions can slow ions, therefore broadening observed time-of-flight peaks and/or preventing ions from reaching the TOF detector, therefore reducing the sensitivity of the TOF analyzer. The necessary pressure depends on the TOF analyzer geometry, but typical TOF analyzer pressures are below 1×10^{-5} mbar.

[0014] Samples that do not originate in the gas phase must be converted to the gas phase (vaporization or desorption) before analysis.

[0015] Further, the molecules and/or atoms of the sample (analyte) must be given a charge (ionized) prior to analysis.

[0016] Vaporization (if necessary) and ionization of the sample can take place in devices separate from the mass analyzer. We refer to the volume within which ionization takes place and the associated hardware as the ionization source.

[0017] Numerous techniques exist for vaporization and ionization. The two processes may occur in separate steps. For instance, a solid sample may be heated until it is vaporized, and then the resultant gas phase molecules may be ionized by an independent mechanism. Or, the two processes may be coupled and occur in a single step. For instance, a solid sample may be irradiated with an intense laser that causes both vaporization and ionization.

[0018] All embodiments of this disclosed invention relate to a specific, well known class of methods for ionization of gas-phase molecules, called chemical ionization (CI).

Chemical Ionization

[0019] In CI methods, a gas-phase analyte molecule, A, acquires a positive or negative charge through collision with a gas-phase reagent ion, $R^{+/-}$, which can be described by the generic reaction:

$$A + R^{+/-} \rightarrow P^{+/-} + B \qquad \text{(equation 1)}$$

[0020] Where A is the neutral analyte molecule, and $P^{+/-}$ is a charged product (molecule or non-covalent adduct) of the collisional interaction that includes atoms of A, and B is a potential byproduct (e.g., molecule, adduct, or electron) of the interaction.

[0021] CI methods have been described using a large number of different reagent ions, and ionization mechanisms vary between reagent ions. These mechanisms include, but are not limited to, proton transfer reactions, proton abstraction reactions, electron transfer reactions, and covalent and non-covalent adduct formation. Inter alia, CI is broadly applied in atmospheric science for the analysis of trace gases.

[0022] Prior to the chemical ionization step, the reagent ion must be produced by ionization of a neutral reagent molecule.

[0023] Ionization of the reagent molecule is accomplished in a variety of ways, including, but not limited to, electron ionization of the neutral reagent, discharge ionization of the neutral reagent, or bombardment of the reagent gas with radioactive decay products, such as alpha or beta particles. This reagent ionization may take place in the same volume as or in a separate volume from the volume where the analyte is ionized.

[0024] All CI mechanisms require a collision between the analyte molecule and the reagent ion. To ensure that such collisions take place, the ionization volume of the CI source contains reagent ions at a high pressure, typically between 0.001 and 1000 mbar.

[0025] For the embodiments described in this disclosure, we refer to the region of ion source where analyte molecules and reagent ions collide as the ion molecule reaction (IMR) region.

[0026] The efficiency with which analyte ions are formed can be strongly dependent on the IMR region pressure; therefore this pressure should be a variable parameter in the source.

[0027] Under certain conditions, the CI reaction product will form weakly bound (non-covalent) clusters with other species present in the IMR region, for instance water. In some cases, these weakly bound clusters are the desired product for analysis (i.e., $P^{+/-}$).

[0028] In other cases, clustering undesirably spreads the production signal across multiple *m/Q* values, depending on the number of weakly bound complexes. For instance, weak binding of neutral molecules, N, may be represented as:

$$A + R^{+/-} \rightarrow (P^{+/-})N_1 + (P^{+/-})N_2{}^{+} + (P^{+/-})N_x + B \qquad \text{(equation 1)}$$

[0029] In which case, ionization of A by $R^{+/-}$ produces a mass spectrum with x product peaks. To minimize the number of observed product peaks, many CI implementations include a collisional declustering chamber (CDC), which ions pass through immediately after exiting the IMR region. In this region, non-covalent clusters are broken apart (declustered) in low-energy collisions with neutral, background gas molecules (G).

$$(P^{+/-})N + G \rightarrow (P^{+/-}) + N + G$$

[0030] The pressure of the CDC and the voltages of the electrodes are adjusted to maximize ion transmission and optimize break-up of non-covalent complexes without causing fragmentation of covalent bonds within the product ion.

[0031] Certain CDC designs allow voltage and pressure conditions that do not cause the break-up of clusters, therefore enabling analysis based on reagent ion chemistry that forms either non-covalent or covalent product ions.

Ions from ambient air

[0032] Earth's atmosphere includes charged molecules, referred to here as air ions. Air ions play a potentially important role in aerosol formation, and there is therefore great interest in characterizing the composition and reactive progression of ambient ions.

[0033] Air ions can cluster together to form ionic clusters. And, by attachment with trace neutral gases ambient ions or ionic clusters can evolve into aerosols, some of which are charged. We refer to the collection of air ions, ionic clusters, and charged aerosols as ambient ions.

[0034] Ambient ions can potentially be measured directly by mass spectrometry. See for instance: Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039-1053.

[0035] Ionic clusters are similar in nature to the weakly bound clusters sometimes formed in chemical ionization sources. As is the case for CI, it would be desirable to analyze these ionic clusters with a mass spectrometer capable of both measuring intact clusters or alternatively breaking-up clusters and measuring the constituent ions.

Interface

[0036] The conditions (e.g., geometries and pressures) of ionization sources vary greatly, as do the energy distributions of ions produced by the various sources.

[0037] Despite the broad range of sample types and ionization mechanisms, a handful of mass analyzer configurations are used for nearly all MS analysis. Specifically: TOF, quadrupole, ion trap, magnetic sector, ion cyclotron resonance, and orbitrap mass analyzers.

[0038] Each of these analyzer configurations has rigid physical design constraints (geometry and pressure) as well as specific energetic and spatial requirements for the population of ions to be analyzed.

[0039] Sensitive analysis requires that ions are efficiently transferred from the ion source to the mass analyzer. The mechanism for coupling the ion source to the mass analyzer must reconcile any pressure differential between the ion source and the analyzer. And, it must appropriately tailor the beam to match the demands of the mass analyzer. We refer to the hardware used to couple an ion source to a mass analyzer as the interface. And, we refer to the collection of the ion source, the interface, and the mass analyzer as the mass spectrometer.

[0040] This disclosure describes an improved interface for the coupling of a CI ionization source to a mass analyzer.

[0041] Figure 2 outlines the major components of a CI-MS device, which includes in succession an optional vaporization region 21, the chemical ionization source 22, the interface region 23, and the mass analyzer 24. Correspondingly, Figure 3 shows a CL-TOFMS device, including the (optional) vaporization region 21, the chemical ionization source 22, the interface region 23 and the TOF mass analyzer 12 shown in Figure 1, whereas the TOF drift axis 14 is essentially orthogonal to the primary axis 11 of the ions.

[0042] A well-known CI-MS design is depicted in more detail in Figure 4. A neutral gas flows (flow 31) through a region 32 containing an alpha-particle emitting substance, such as Polonium-210 (^{210}Po) or Americium-241 (^{241}Am) to generate reagent ions, which proceed into an ion molecule reaction region (IMR) 33 of a chamber 39. Neutral analyte molecules 34 enter the IMR through a separate, flow-rate-determining aperture 35 and are ionized in collisions with reagent ions. The IMR region is held at a pressure between 10 and 1000 mbar, as determined by the reagent flow rate, analyte flow rate, and the effective speed of the vacuum pump 36 operating on the IMR region. A combination of fluid dynamics and electric fields direct the generated ion population 37, which includes reagent ions, CI product ions, and charged, non-covalent complexes, from the IMR region through an aperture 38 into a collisional declustering chamber (CDC) 40.

[0043] In some designs, the IMR is a hollow chamber, having a body held at a constant DC voltage (see for example J. P. Kercher et al: Chlorine activation by N205: simultaneous, in situ detection of CIN02 and N205 by chemical ionization mass spectrometry, Atmos. Meas. Tech., 2, 193, 2009; P. Veres et al.: Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, Int. J. Mass Spec., 274, 2008, 48). In other designs, the IMR chamber has axial fields, which direct reagent and product ions towards the exit of the IMR. See for example J. Zheng et al: Atmospheric Pressure-Ion Drift Chemical Ionization Mass Spectrometry for Detection of Trace Gas Species, Anal. Chem. 2010, 82 (17), 7302; US 7'375'317 B2; D. Hanson et al: Proton transfer reaction mass spectrometry at high drift tube pressure, Int. J. Mass Spectrometry, 223-224, 2003, 507; W. Lindinger et al.: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research,

Int. J. Mass Spectrometry and Ion Processes, 173, 1998, 191.

[0044] A vacuum pump 41 attached to the CDC 40 holds this region at pressure lower than or equal to that of the IMR region, typically 1 to 5 mbar. The CDC device is a series of ring electrodes 42 having tunable DC voltages. Ion transmission and dissociation of clusters are optimized by tuning the CDC electrode voltages, the entrance and exit aperture voltages, and the CDC pressure.

[0045] The de-clustered population of ions 44 passes from the CDC 40 through an exit aperture 43 into a differential vacuum stage 45, with pressure between the CDC and that of the mass analyzer. This stage is typically pumped by a turbo molecular pump 46 and contains an RF-only multipole device 47 (e. g. quadrupole, octopole, or hexapole) or a RF ion funnel for ion focusing. Such RF focusing devices are commonly used in MS interfaces to move ions across the transitional stages between regions of high and low pressure. If the pressure of the stage is high enough, low energy collisions between ions and neutral background gas in the multipole or trap can dampen the energy distribution of the ions (ion cooling), such that ion trajectories are concentrated in space, and total transmission through the stage is increased. A collection of DC-voltage ion focusing lenses 48 may follow the RF focusing device, within the same vacuum stage.

[0046] Ions pass from the transitional vacuum stages of the interface into the mass analyzer 24 through a conductance-limiting, electrode aperture. The mass analyzer is often a quadrupole, but may also be a TOF or any other type of mass analyzer. The mass analyzer stage is typically pumped by a turbo molecular pump 49.

[0047] We differentiate this IMR-CDC-type design from the type described by, for instance, Hanson, 2003, in which reagent and analyte ions react in a high pressure drift tube, having strong axial electric fields that both direct ion motion and induce declustering of weakly bound clusters, such that no CDC region is necessary.

[0048] The ions passing into the CDC from the IMR region have varied energy and trajectory, determined primarily by the fluid dynamics of the expansion into the lower pressure region.

[0049] In addition to driving the dissociation of weakly bound clusters, the electrodes of the CDC are intended to direct ion trajectories through the CDC exit aperture and into the next stage of the interface. Those ions that cannot be appropriately focused go undetected.

[0050] For a given ion, the motion induced by the fields of the DC ring electrodes 41 is a function of both the initial trajectory and energy of the ion. As a result, only a subset of the ions in the expansive population can be focused through the exit aperture.

[0051] One could potentially improve the net transmission by increasing the size of the CDC exit aperture. But, because the next vacuum stage typically requires a pressure much lower than that of the CDC, the exit aperture of the CDC must limit gas conductance. Design is ultimately a balance of aperture size, desired pressure, and available pumping speeds. Typical diameters of this exit aperture are between values between 0.1 and 1 mm.

[0052] As explained earlier, for analysis with OTOFMS, mass resolving power and mass accuracy are improved by reducing ion energy spreads (temperature). Thus, in addition to affecting sensitivity, the energy distribution of the expansive beam exiting the IMR has consequences for achievable mass resolving power and mass accuracy in a CI-OTOFMS.

Summary of the invention

[0053] It is the object of the invention to create a mass spectrometer pertaining to the technical field initially mentioned, that allows for improved mass resolution, sensitivity and accuracy in a mass analyzer.

[0054] The solution of the invention is specified by the features of claim 1. According to the invention the interface comprises

a) a first chamber comprising a radio frequency focusing device, to be arranged adjacent to a gas conductance limiting exit aperture of an ion molecule reaction region of the chemical ionization source or adjacent to an inlet for feeding ambient air, the chamber defining a collisional declustering region;

b) at least one interface vacuum chamber arranged downstream of the first chamber, the at least one interface vacuum chamber being separated from the first chamber by a further gas conductance limiting aperture;

whereas

c) a pressure in the first chamber is 0.01 mbar or more; and whereas

d) the first chamber of the interface is arranged adjacent to a gas conductance limiting exit aperture of the ion molecule reaction region.

[0055] Correspondingly, a method for feeding ions from a chemical ionization source to a mass analyzer according to the invention comprises the steps of:

a) feeding ions from the ionization source through a gas conductance limiting exit aperture into a first chamber comprising a radio frequency focusing device, whereas a pressure in the first chamber is 0.01 mbar or more;

b) transmitting ions from the first chamber through a further gas conductance limiting aperture into an interface vacuum chamber, whereas a pressure in the interface vacuum chamber is substantially lower than a pressure in the first chamber;

c) transmitting ions from the interface vacuum chamber into the mass analyzer.

[0056] It is to be noted that the ions do not have to be transmitted from the interface vacuum chamber directly into the mass analyzer but there may be further chambers arranged in between the interface vacuum chamber and the mass analyzer, i. e. the device according to the invention comprises the first chamber, the interface vacuum chamber and optionally one or more chambers arranged between the interface vacuum chamber and the mass analyzer.

[0057] The disclosed interface comprises a RF ion focusing device in the form of a radio frequency (RF) focusing device (RFFD), rather than the more common set of DC ring electrodes, in the CDC region. Typical frequencies to be applied to electrodes of the RFFD are in the range of about 0.1 - 10 MHz. Accordingly, the disclosed interface differs significantly from hardware described in US 6,987,264 (Analytica of Branford, Inc.) and RE 40,632 (Thermo Finnigan LLC) in both purpose and design. First of all, the interface according to the invention is suitable for use with a broader range of IMRs, most notably, IMRs operated at pressures much below atmospheric pressure. The interface according to the invention does not include a capillary for transfer of ions out of the IMR, and in the interface according to the invention, the pressure stage immediately following the IMR contains a RFFD. Whereas, in the mentioned other designs, the first stage does not contain an RFFD.

[0058] Ions enter the first chamber with a broad range of energies, originating from expansion into the chamber. The RF-fields constrain ion motion near the central axis of the RFFD, and collisions with neutral, background gas molecules effectively dissipate kinetic energy originating from the expansion.

[0059] The RFFD improves ion transmission into the interface stage following the first chamber relative to the more commonly DC ring electrode assembly. Further, the RFFD more efficiently dissipates ion kinetic energy originating from expansion into the first chamber, improving achieved mass resolving power and mass accuracy in particular for applications where a CI source is a component of an OTOFMS.

[0060] Due to the higher transmission the sensitivity of a mass spectrometer comprising the inventive interface may be increased independent of the type of mass analyzer used. Furthermore, where the mass analyzer is a TOFMS, the inventive combination of the first chamber and the interface vacuum chamber allows for a more efficient "cooling" of the ion beam and therefore enables higher mass resolving power in the mass analyzer.

[0061] It is to be noted that collisional declustering happens in the first chamber or the region near the transition between the first and second chamber if a clustered sample is present and if the pressure as well as voltages are chosen in an appropriate range. Depending on the analysis objectives declustering may be desired or not. Any way, the construction of the inventive interface allows for declustering by choosing suitable parameters.

[0062] The RFFD is differentiated from RF-only multipole devices commonly used in CI-MS (See, for example, octopole ion guides in Kercher 2009, Veres 2008 and J. D. Crounse et al.: Measurement of gas-phase hydroperoxides by chemical ionization mass spectrometry, Anal Chem 78 (19): 6726 (2006)), by the combination of facts that (i) it operates in the region immediately following the IMR of the CI source (ii) it operates at pressure greater than 0.01 mbar, and (iii) at least one interface vacuum chamber exists between the first chamber, which contains the RFFD, and the mass analyzer.

[0063] Possible applications of the interface according to the invention encompass the use for analyses where the sample to be analyzed originates in the gas, liquid, or solid phase. In particular, the interface may be used in atmospheric science, e. g. for the following applications:

1. Qualitative and quantitative measure of trace gases in the atmosphere (ambient air) and in reaction chambers simulating the atmosphere;

2. Qualitative and quantitative measurement of molecules comprising aerosol particles or droplets in the atmosphere (ambient air) and in reaction chambers simulating the atmosphere, where the aerosol particles or droplets are converted to gas phase molecules in a step occurring before or simultaneous to the chemical ionization step;

   a. Such conversion can involve, for instance, thermal desorption, laser desorption, or exposure to hot gas.

3. Qualitative and quantitative measurement of gas phase species and aerosol particle and droplet molecular composition of both man-made and natural emission sources, including: exhaust flows from vehicular, industrial, commercial and residential combustion powered motors, engines, turbines, electrical generators, furnaces, heaters, stoves, evaporators and other combustion powered devices; emissions arising from agricultural activities including fertilizer and pesticide applications, manure management, feedlot and dairy operations, crop harvesting, processing and storage and tillage activity; emissions from open burning including: trash burning, accidental and planned building fires, crop residue burns, prescribed fires, and wildfires; and, natural biogeochemical emissions including volcanic eruptions and emissions, windblown soil and dust plumes, windblown lake, river and sea spray; wetland and forest biogenic trace gas and particle emissions.

4. Qualitative and quantitative measurement of gas and aerosol particles and droplet chemical species in human breath.

a. Where the instrument includes some method for transmitting breath to the sampling inlet of the CI source

b. Where aerosol particle and droplet species are detected following a step similar to 2a.

[0064] In a preferred embodiment, the radio frequency focusing device comprises an ion funnel constituted by a series of ring electrodes to which RF voltages are applied. The ring electrodes may all have the same diameter or the diameter may decrease in the focusing direction. Alternatively or in addition, the inner diameter of the funnel may be constant or varied across the ion drift axis. Similarly, the spacing between adjacent ring electrodes may be constant or varied.

[0065] In another preferred embodiment, the radio frequency focusing device comprises a tube having a resistive structure to which RF voltages are applied. Corresponding tubes are described in European patent application No. 07 405 077.4 of 08 March 2007 of the same applicant. The tube may be made from a resistive material or from an insulating material (e. g. glass) having a resistive coating. The cross-section of the tube may be circular but also e. g. triangular, rectangular or of another shape.

[0066] Preferably, an interior of the tube is separated into at least two chambers by the gas conductance limiting aperture or a plurality of gas conductance limiting apertures. This allows for a simple and compact design of the interface. Electrodes for both the first chamber as well as the interface vacuum chamber (and possibly for further chambers) may be realised as resistive structures. More than two chambers may be present within the tube, whereas further chambers are divided in particular by further gas conductance limiting apertures.

[0067] In a further preferred embodiment, the radio frequency focusing device is a multipole defined by a number of electrodes, in particular a quadrupole, defined by 4 electrodes. However, multipoles of other orders such as hexapoles or octopoles are also possible.

[0068] Generally, the electrodes of the multipole can have any cross section. In a preferred implementation, the electrodes of the multipole are solid rods with circular cross section. The electrodes of the multipole can be continuous, or discontinuous along the primary ion axis. In the first case, the potential at all points along an electrode will be equal. In the second case, i.e. when the electrodes of the multipole are segmented along the primary ion axis, the potential of the individual segments can be separately adjusted. One such embodiment may use a device similar to the molecule ion reactor described by A. Dodonov et al.: New Technique for Decomposition of Selected Ions in Molecule Ion Reactor Coupled with Ortho-Time-of-flight Mass Spectrometry, Rapid. Commun. Mass Spectrom. 11, 1649, 1997.

[0069] The orientation of the electrodes of the multipole may be parallel to a primary ion axis. Alternatively, the orientation of the electrodes of the multipole is angled such that an inscribed diameter at an entrance of the multipole is different from an inscribed diameter at an exit of the multipole. In some embodiments, the inscribed diameter at the entrance of the multipole is greater than the inscribed diameter at the exit. In other embodiments, the inscribed diameter at the entrance is smaller than that at the exit. By choosing the appropriate geometry the focusing properties of the RFFD may be optimized depending on the ions to be analyzed, the operation parameters and the geometry of the first chamber.

[0070] In some embodiments of the invention, the radio frequency focusing device creates in addition to the RF field (s) at least one DC field oriented along a primary ion axis. In some implementations the entrance aperture of the first chamber has an independently adjustable DC voltage. In some implementations the exit aperture of the first chamber has an independently adjustable DC voltage. In some implementations, there are electrodes with adjustable DC voltages between the entrance and the exit aperture of the first chamber.

[0071] In embodiments having continuous multipole electrodes, an adjustable DC bias voltage may be applied to those electrodes. In other embodiments with segmented multipole electrodes, separate adjustable DC bias voltages can be applied to each of the electrodes.

[0072] In combination with the gas pressure inside the first chamber, the combination of RF and DC voltages can be used to induce dissociation of non-covalent complexes originating from the IMR region or they may be chosen in a

combination that does not induce dissociation of non-covalent complexes originating from the IMR region.

[0073] Alternatively, no DC field is created within the first chamber and the cooling and transport of the ions is accomplished exclusively by the RF field(s).

[0074] Preferably, at least one of said at least one interface vacuum chamber (following the first chamber comprising the radio frequency focusing device) includes an RF-only multipole. The main task of this multipole is ion focusing. If the pressure of the stage is high enough, low energy collisions between ions and neutral background gas in the multipole or trap can dampen the energy distribution of the beam, such that ion trajectories are primarily determined by the forces of the ion optics, and total transmission through the stage is increased.

[0075] However, it is feasible to have interface vacuum chambers not including RF electrodes but solely DC electrodes (e. g. usual ion lenses) or even no electrodes at all in cases where the ions enter the chamber in a focused state and with sufficient momentum and where the chamber is rather short and has a relatively large exit aperture.

[0076] In preferred embodiments of the invention, at least one of said at least one interface vacuum chamber includes a mass filtering device that selectively transmits ions having specific values of m/Q. Suitable filters comprise e. g. multi poles such as quadrupole mass filters.

[0077] In some such embodiments, a device follows the mass filtering device that is capable of fragmenting the transmitted ions, in order to enable MS/MS analysis.

[0078] In further preferred embodiments, the interface comprises a further device capable of fragmenting incoming ions. This further device is arranged downstream of the chamber including the mass filtering device. Fragmentation may be induced by choosing the RF and DC voltages applied to respective electrodes in such a way that covalent bonds originating from the IMR region are broken up. This enables MS analysis based on fragments.

[0079] The inventive interface may be used as an interface or first interface region following the ionization volume in any CI implementation, especially when the pressure in the ion molecule reaction region (IMR) is 1 mbar or more.

[0080] In some implementations, the IMR volume is at atmospheric pressure or higher and the CDC is the first reduced pressure stage of the vacuum system. In other implementations, the IMR is pumped by a vacuum pump to achieve a pressure below atmospheric pressure. In all implementations, the IMR is a constrained three-dimensional volume having defined physical boundaries.

[0081] In some implementations at atmospheric or reduced pressure, the IMR volume includes DC electric fields to direct ions into the first chamber of the interface. In some implementations at atmospheric or reduced pressure, the IMR volume includes RF electric fields to direct ions into the first chamber. Other implementations feature DC as well as RF electric fields.

[0082] In further implementations at atmospheric or reduced pressure the IMR is a flow tube, with no controlled electric fields along the primary beam axis. The IMR body may be constructed from a tube with a resistive structure similar to the radio frequency focusing device mentioned above. In some such implementations, the entire body is held an equal voltage, in other implementations, RF voltages are applied to the resistive structure. Furthermore, DC voltages may be applied in order to generate an axial drift field.

[0083] The inventive interface is especially suited for mass spectrometers having a time-of-flight mass analyzer. The inventive interface allows for reducing the pressure to such values that ion trajectories within the TOFMS are determined by electric fields and not perturbed by collisions with neutral background gas molecules. Such random collisions can slow ions, therefore broadening observed time-of-flight peaks and/or preventing ions from reaching the TOF detector, therefore reducing the sensitivity of the TOF analyzer. The necessary pressure depends on the TOF analyzer geometry, but typical TOF analyzer pressures are below $1 \cdot 10^{-5}$ mbar.

[0084] Preferably, the time-of-flight mass spectrometer is installed in an orthogonal extraction configuration. By using the inventive interface, the spatial spread (width) of the primary beam on the axis parallel to drift as well as the velocity of all ions in the primary beam along the drift axis, prior to acceleration, are minimized. Minimization of each of these values reduces uncertainty in the drift velocity after acceleration, and therefore uncertainty in the determination of *m*/*Q* (mass accuracy and mass resolution).

[0085] Instead of a time-of-flight mass spectrometers, other mass analyzers known as such may be used such as e. g. a quadrupole mass filter.

[0086] A single interface and mass analyzer arranged downstream of the interface may be used for the analysis of ions produced by chemical ionization and for the analysis of ambient ions. For that purpose, the chemical ionization source is replaced by an inlet for feeding ambient air, i. e. the interface is used as an interface or first interface region following the inlet for feeding ambient air. In particular, the inlet that replaces the chemical ionization source is a conductance limiting "pin hole" aperture, which serves as the boundary between ambient air and the vacuum chamber containing the RFFD. Alternatively, the inlet that replaces the chemical ionization source is a conductance limiting tube, which extends from ambient air into the vacuum chamber containing the RFFD.

[0087] The inlet that replaces the chemical ionization source may include a vacuum chamber held at a pressure less than or equal to ambient pressure and greater than or equal to the pressure of the first chamber. Sampled air traverses this chamber before entering the first chamber containing the RFFD. The entrance aperture of this vacuum chamber

can be a pin hole or a tube.

[0088] After replacement of the CI source by the inlet, the interface and the mass analyzer arranged downstream of the interface may be used for the analysis of ambient ions. This allows for alternately using the mass spectrometer to analyze the two kinds of ions, whereas any duration can be spent in each analysis configuration.

[0089] Preferably, such a method comprises the following steps:

a) Installing a chemical ionization source in front of the interface and activating the chemical ionization source to produce ions by chemical ionization within a ion molecule reaction region;

b) transmitting said ions through the interface into the mass analyzer and analyzing said transmitted ions by the mass analyzer;

c) removing or rendering inactive the chemical ionization source and installing or configuring an inlet for sampling ambient air, such that ambient air is sampled through said inlet into the interface;

d) transmitting ions of said ambient air into the mass analyzer and analyzing said transmitted ions by the mass analyzer;

e) repeating the sequence of steps a) - d).

[0090] The IMR of the chemical ionization source may remain installed, whereas when analyzing ambient ions the volume of the IMR is not used for chemical ionization. Rather, ambient air is sampled directly into the IMR through an aperture and the chemical constitutions of the air traverse the volume of the IMR without being exposed to a reagent ion. Constituents of the air then pass into the RFFD. In some such embodiments, the IMR volume is held at atmospheric pressure. In other embodiments, the IMR is held at a pressure less than atmospheric pressure and greater than or equal to the pressure of the chamber containing the RFFD.

[0091] In some such embodiments, the IMR has no electric fields, such that motion of ambient ions is determined primarily by gas flow. In other embodiments, the IMR has electric fields that guide ambient ions toward the RFFD.

[0092] Alternatively, the chemical ionization source is removed when analyzing ambient ions, or the inlet for ambient ions is coupled to an aperture of the first chamber separate from the aperture accepting ions from the chemical ionization source.

[0093] In some uses of embodiments for the analysis of ambient ions, the conditions of the RFFD are adjusted to maximize transmission of intact clusters.

[0094] In some uses of embodiments for the analysis of ambient ions, the conditions of the RFFD are adjusted to induce break-up of clusters, so that the mass spectrometer analyzes constituents of the clusters.

[0095] Other advantageous embodiments and combinations of features come out from the detailed description below and the totality of the claims.

Brief description of the drawings

[0096] The drawings used to explain the embodiments show:

Fig. 1 The essential regions of an orthogonal extraction time-of-flight mass spectrometer (OTOFMS) as known from the prior art;

Fig. 2 the essential regions of a chemical ionization mass spectrometer (CI-MS);

Fig. 3 the essential regions of a chemical ionization orthogonal extraction time-of-flight mass spectrometer;

Fig. 4 a well known CL-MS design;

Fig.5 a schematic representation of an embodiment of the inventive mass spectrometer comprising an RFFD;

Fig. 6a, b a side view and a cross sectional view of the preferred embodiment of the RFFD, which is an RF-only quadrupole having parallel, segmented electrodes;

Fig. 7 a second embodiment of the inventive mass spectrometer, including a CI source, RFFD, an interface chamber containing an RF-only quadrupole, an interface chamber containing DC focusing optics, and TOF

mass analyzer in an orthogonal configuration;

Fig. 8 the essential regions of a mass spectrometer configured for analysis of ambient ions;

Fig. 9 a schematic representation of an embodiment of a mass spectrometer configured for analysis of ambient ions, where the IMR of the CI source remains installed but chemical ionization is not active;

Fig. 10 a schematic representation of a further embodiment of a mass spectrometer configured for analysis of ambient ions having an inlet including a pumping stage between ambient air and the first interface chamber; and

Fig. 11 a schematic representation of a further embodiment of a mass spectrometer configured for analysis of ambient ions having an inlet consisting of a conductance limiting tube extending from ambient air into the first interface chamber.

[0097] In the figures, the same components are given the same reference symbols.

Preferred embodiments

[0098] Figure 5 is a schematic representation of an embodiment of the inventive mass spectrometer comprising an RFFD. A neutral gas flows (flow 31) through a region 32 containing an alpha-particle emitting substance, such as Polonium-210 (^{210}Po) or Americium-241 (^{241}Am) to generate reagent ions, which proceed into an ion molecule reaction region (IMR) 33 of a chamber 39. Neutral analyte molecules 34 enter the IMR through a separate, flow-rate-determining aperture 35 and are ionized in collisions with reagent ions. The IMR region is held at a pressure between 10 and 100 mbar, as determined by the reagent flow rate, analyte flow rate, and the effective speed of the vacuum pump 36 operating on the IMR region. A combination of fluid dynamics and electric fields direct the generated ion population 37, which includes reagent ions, CI product ions, and charged, non-covalent complexes, from the IMR region through an aperture 38 into a further chamber 50.

[0099] In some designs, the IMR is a hollow chamber, having a body held at a constant DC voltage (see for example Kercher 2009; Veres 2008). In other designs, the IMR chamber has axial fields, which direct reagent and product ions towards the exit of the IMR. See for example Zheng, 2010; US 7'375'317 B2.

[0100] A vacuum pump 51 attached to the further chamber 50 holds this region at pressure lower than or equal to that of the IMR region, typically 1 to 5 mbar. Within the chamber 50 an RFFD 52 is arranged which is described in more detail below, in connection with Figure 6. Ion transmission and dissociation of clusters are optimized by tuning the electrode voltages, the entrance and exit aperture voltages, and the pressure within chamber 50.

[0101] The cooled and/or de-clustered population of ions 54 passes from the chamber 50 through an exit aperture 53 into a differential vacuum stage 45, held at a pressure in between the pressure in chamber 50 and that within the mass analyzer 24. This stage is pumped by a turbo molecular pump 46 and contains an RF-only multipole device 47 (quadrupole, octopole, or hexapole) or a RF ion funnel for ion focusing. Such RF focusing devices are commonly used in MS interfaces to move ions across the transitional stages between regions of high and low pressure. If the pressure of the stage is high enough, low energy collisions between ions and neutral background gas in the multipole or trap can dampen the energy distribution of the beam, such that ion trajectories are primarily determined by the forces of the ion optics, and total transmission through the stage is increased. A collection of DC-voltage ion focusing lenses 48 may follow the RF focusing device, within the same vacuum stage.

[0102] Ions pass from the transitional vacuum stages of the interface into the mass analyzer 24 through a conductance-limiting, electrode aperture. The mass analyzer is often a quadrupole, but may also be a TOF or ion trap. The mass analyzer stage is pumped by another turbo molecular pump 49.

[0103] Figure 6a shows a side view and Figure 6b shows a cross sectional view of the preferred embodiment of an RFFD, which is an RF-only quadrupole having parallel, segmented electrodes. The RFFD 61 comprises four parallel multipole electrodes (rods) which are aligned in symmetric manner, such when viewed along the primary ion axis (Fig 6b), the rods lie on the corner of a square. Oscillating RF voltages are applied to the electrodes, in a manner that is known as such for quadrupole devices, with rods on opposite corners of the square being electrically connected, and with the two pairs of connected rods receiving RF signals that are exactly out of phase. We refer to the two sets of rods as the positive electrodes 63 and the negative electrodes 67, and the applied voltages as the positive phase RF voltages 68 and the negative phase RF voltages 69.

[0104] Each rod 63, 67 is broken into four segments along the primary ion axis. It is to be noted that the number of segments may be less or more than four. DC bias voltages are applied to each rod segment 63, 67, in addition to the RF voltage. The DC voltage of each segment is determined by a DC voltage 64a applied to the front segment, a DC

voltage 64b applied to the back segment, and a series of resistors 65 located between successive segments. Each rod 63, 67 has a dedicated collection of resistors 65 and capacitors 66 connected in parallel with the resistors 65. Each segment has a dedicated DC contact 64a 64b not directly connected to the DC lead of any other segment. For instance, there are 4 instances of the front electrode contact 64a shown in Figure 6, each dedicated to the front segment of one of the 4 rods. Segments in equivalent positions on each rod have the same DC voltage applied.

[0105] The RF voltages applied to the rods 63, 67 are about 500 V peak-to-peak, used frequencies are in the range of 0.1 - 10 MHz.

[0106] Furthermore, a first DC ring electrode 62 is positioned before the quadrupole and a second DC ring electrode 70 is positioned after the quadrupole, whereas the centers of the central openings of the DC ring electrodes 62, 70 and the center defined by the quadrupole electrodes 63, 67 lie on a common line. The potential difference between the DC ring electrodes 62, 70 is about 35 V.

[0107] Figure 7 shows a second embodiment of the inventive mass spectrometer, including a CI source, RFFD, an interface chamber containing an RF-only quadrupole, an interface chamber containing DC focusing optics, and TOF mass analyzer in an orthogonal configuration.

[0108] A neutral gas flows (flow 31) through a region 32 containing an alpha-particle emitting substance, such as Polonium-210 (^{210}Po) or Americium-241 (^{241}Am) to generate reagent ions, which proceed into an ion molecule reaction region (IMR) 33 of a chamber 39. Neutral analyte molecules 34 enter the IMR through a separate, flow-rate-determining aperture 35 and are ionized in collisions with reagent ions. The IMR region is held at a pressure of about 80 mbar, as determined by the reagent flow rate, analyte flow rate, and the effective speed of the scroll vacuum pump 36 operating on the IMR region. The pumping speed is about 1.5l/s. The axial length of chamber 39 is about 10 cm. A combination of fluid dynamics and electric fields direct the generated ion population 37, which includes reagent ions, CI product ions, and charged, non-covalent complexes, from the IMR region through a nozzle-shaped aperture 38 with a final diameter of 0.5 mm and with adjustable DC voltage into a further chamber 50.

[0109] In some designs, the IMR is a hollow chamber, having a body held at a constant DC voltage (see for example Kercher 2009; Veres 2008). In other designs, the IMR chamber has axial fields, which direct reagent and product ions towards the exit of the IMR. See for example Zheng, 2010; US 7,375,317 B2 (The Texas A&M University System).

[0110] A further scroll vacuum pump 51 attached to the chamber 50 has a pumping speed of about 5 l/s and holds this region at a pressure of about 2 mbar. Within the chamber 50 the RFFD 61 as shown in Figure 6 is arranged. The length of the chamber 50 is about 3 cm. Ion transmission and dissociation of clusters are optimized by tuning the electrode voltages, the entrance and exit aperture voltages, and the pressure within chamber 50.

[0111] The cooled and/or de-clustered population of ions 54 passes from the chamber 50 through an exit aperture 53 having a diameter of about 1.0 mm with adjustable DC voltage into a differential vacuum stage 45, with a pressure of about 0.015 mbar. This stage is pumped by a turbo molecular pump 46 having a pumping speed of 20 l/s and contains an RF-only quadrupole 47. The RF voltages applied to the quadrupole rods are about 600 V peak-to-peak, used frequencies are in the range of 0.1 - 10 MHz.

[0112] The length of the stage 45 is about 11 cm. If the pressure of the stage is high enough, low energy collisions between ions and neutral background gas in the multipole or trap can dampen the energy distribution of the beam, such that ion trajectories are primarily determined by the forces of the ion optics, and total transmission through the stage is increased.

[0113] Through another flow limiting orifice 71 having a diameter of 2.0 mm, the ions pass into a further interface chamber 72, held at a pressure of about $3.5 \cdot 10^{-5}$ mbar by a further turbo molecular pump 73 having a pumping speed of about 1551/s. The further interface chamber 72 comprises a set of DC-voltage focusing lenses 48. Its length is about 3 cm.

[0114] Through a final orifice 74 being a slit of 3x8 mm the ions pass into the TOF mass analyzer, installed and operated in an orthogonal extraction configuration. The main chamber of the mass analyzer is connected with a further turbo molecular pump providing a pumping speed of about 200 l/s.

[0115] Figure 8 shows the essential regions of a mass spectrometer configured for analysis of ambient ions. The device includes in succession an ambient ion interface 81, an interface region 23 and the mass analyzer 24.

[0116] Figure 9 is a schematic representation of an embodiment of a mass spectrometer configured for analysis of ambient ions, where the IMR of the CI source remains installed but chemical ionization is not active. The assembly is identical to that shown in Figure 7 above. However, instead of neutral analyte molecules ambient air 91 including ambient ions enters the chamber 39 through the flow-rate-determining aperture 35. The ion molecule reaction region (IMR) of the chamber 39 is inactive, i. e. no substance flows from region 32 into chamber 39 and ions already present in ambient air will finally be analyzed by the time-of-flight mass analyzer (TOF) 12.

[0117] Figure 10 is a schematic representation of a further embodiment of a mass spectrometer configured for analysis of ambient ions having an inlet including a pumping stage between ambient air and the first interface chamber. The ambient ion interface 81 (inlet) for the ambient air 91 including ambient ions comprises a vacuum chamber 1002, evacuated by a pump 1003 and having a conductance limiting entrance aperture 1001 for feeding the ambient air 91

and a conductance limiting exit aperture 1004 leading into the collisional declustering chamber (CDC) 40. The subsequent stages of the interface exactly correspond to those described above in connection with the embodiment shown in Figure 7.

[0118] Figure 11 is a schematic representation of a further embodiment of a mass spectrometer configured for analysis of ambient ions having an ambient ion interface 81 (inlet) consisting of a conductance limiting tube 1101 extending from ambient air directly into the first interface chamber, i. e. the collisional declustering chamber (CDC) 40. The subsequent stages of the interface exactly correspond to those described above in connection with the embodiment shown in Figure 7.

[0119] The invention is not limited to the embodiments discussed above. Particularly, the number of additional vacuum stages as well as the ion optical elements disposed within these chambers may be different. The operation parameters such as pressures, voltages, frequencies, etc. are related to the particular embodiments and may be chosen differently with other embodiments of the mass spectrometer or in connection with the analysis of different kinds of analyte molecules.

[0120] It is to be noted that the terms "entrance aperture" or "exit aperture" are not considered to be limiting, an "entrance aperture" may as well be the "exit aperture" of the preceding chamber, similarly, an "exit aperture" may be constituted by the "entrance" aperture of the following chamber.

[0121] In summary, it is to be noted that the invention provides a mass spectrometer that allows for improved mass resolution, sensitivity and accuracy in the mass analyzer.

Claims

1. A mass spectrometer including:

a) a chemical ionization source comprising an ion molecule reaction region;
b) a mass analyzer; and
c) an interface, coupling the chemical ionization source to the mass analyzer, whereas the interface comprises
d) a first chamber comprising a radio frequency focusing device, arranged adjacent to a gas conductance limiting exit aperture of an ion molecule reaction region of the chemical ionization source, the chamber defining a collisional declustering region;
e) at least one interface vacuum chamber arranged downstream of the first chamber, the at least one interface vacuum chamber being separated from the first chamber by a further gas conductance limiting aperture; whereas
f) a pressure in the first chamber is 0.01 mbar or more; and whereas
g) the first chamber of the interface is arranged adjacent to a gas conductance limiting exit aperture of the ion molecule reaction region.

2. The mass spectrometer as recited in claim 1, whereas the radio frequency focusing device comprises an ion funnel constituted by a series of ring electrodes to which RF voltages are applied.

3. The mass spectrometer as recited in claim 1, whereas the radio frequency focusing device comprises a tube having a resistive structure to which RF voltages are applied.

4. The mass spectrometer as recited in claim 3, whereas an interior of the tube is separated into at least two chambers by the gas conductance limiting aperture or a plurality of gas conductance limiting apertures.

5. The mass spectrometer as recited in claim 1, whereas the radio frequency focusing device is a multipole defined by a number of electrodes.

6. The mass spectrometer as recited in claim 5, whereas an orientation of the electrodes of the multipole is parallel to a primary ion axis.

7. The mass spectrometer as recited in claim 5, whereas an orientation of the electrodes of the multipole is angled such that an inscribed diameter at an entrance of the multipole is different from an inscribed diameter at an exit of the multipole.

8. The mass spectrometer as recited in one of claims 1 to 7, whereas the radio frequency focusing device creates at least one DC field oriented along a primary ion axis.

9. The mass spectrometer as recited in one of claims 1 to 8, whereas at least one of said at least one interface vacuum chamber includes an RF-only multipole.

10. The mass spectrometer as recited in one of claims 1 to 9, whereas at least one of said at least one interface vacuum chamber includes a mass filtering device that selectively transmits ions having specific values of m/Q.

11. The mass spectrometer as recited in claim 10, comprising a further device capable of fragmenting incoming ions, the further device being arranged downstream of the chamber including the mass filtering device.

12. The mass spectrometer as recited in one of claims 1 to 11, whereas a pressure in the ion molecule reaction region is 1 mbar or more.

13. The mass spectrometer as recited in one of claims 1 to 12, whereas the mass analyzer is a time-of-flight mass analyzer.

14. The mass spectrometer as recited in claim 13, whereas the time-of-flight mass spectrometer is installed in an orthogonal extraction configuration.

15. A method for feeding ions from a chemical ionization source to a mass analyzer, comprising the steps of:

a) feeding ions from the ionization source through a gas conductance limiting aperture into a first chamber comprising a radio frequency focusing device, whereas a pressure in the first chamber is 0.01 mbar or more;
b) transmitting ions from the first chamber through a further gas conductance limiting aperture into an interface vacuum chamber, whereas a pressure in the interface vacuum chamber is substantially lower than a pressure in the first chamber;
c) transmitting ions from the interface vacuum chamber into the mass analyzer.

16. A method for using the mass spectrometer as recited in one of claims 1 to 14, comprising the further steps of

d) replacing the chemical ionization source by an inlet for feeding ambient air, and
e) using the interface and the mass analyzer arranged downstream of the interface for the analysis of ambient ions.

17. The method as recited in claim 16, **characterized by** the following steps:

a) Installing a chemical ionization source in front of the interface and activating the chemical ionization source to produce ions by chemical ionization within a ion molecule reaction region;
b) transmitting said ions through the interface into the mass analyzer and analyzing said transmitted ions by the mass analyzer;
c) removing or rendering inactive the chemical ionization source and installing or configuring an inlet for sampling ambient air, such that ambient air is sampled through said inlet into the interface;
d) transmitting ions of said ambient air into the mass analyzer and analyzing said transmitted ions by the mass analyzer;
e) repeating the sequence of steps a) - d).

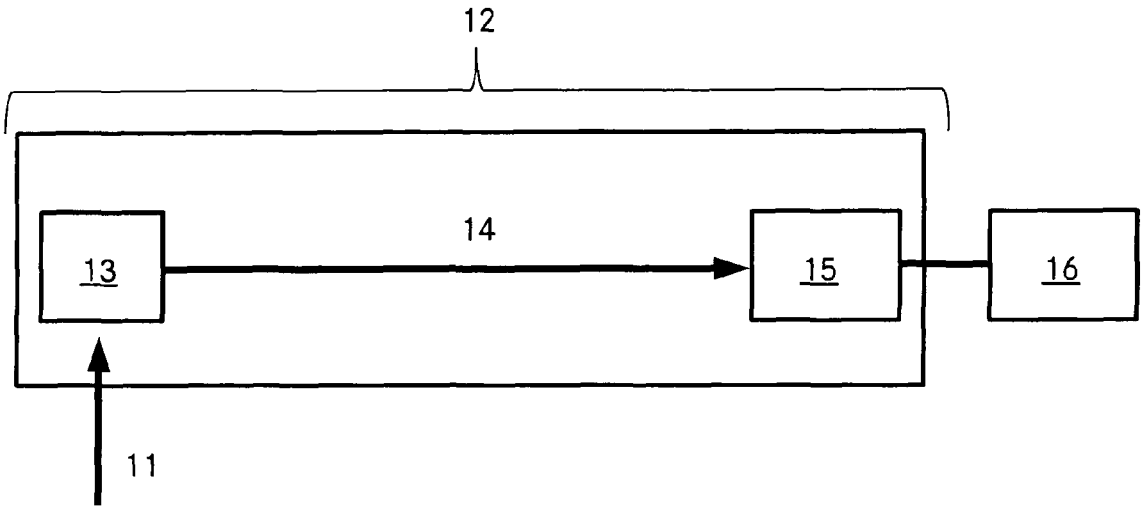

Fig. 1 Prior Art

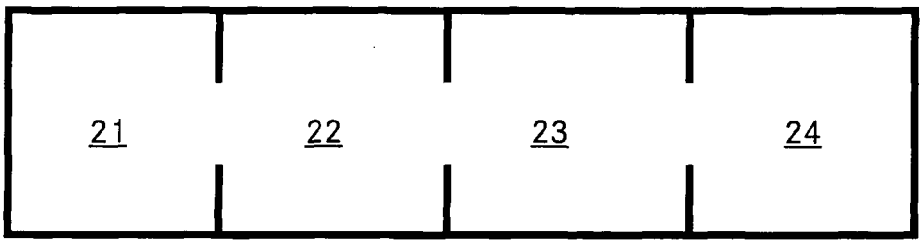

Fig. 2 Prior Art

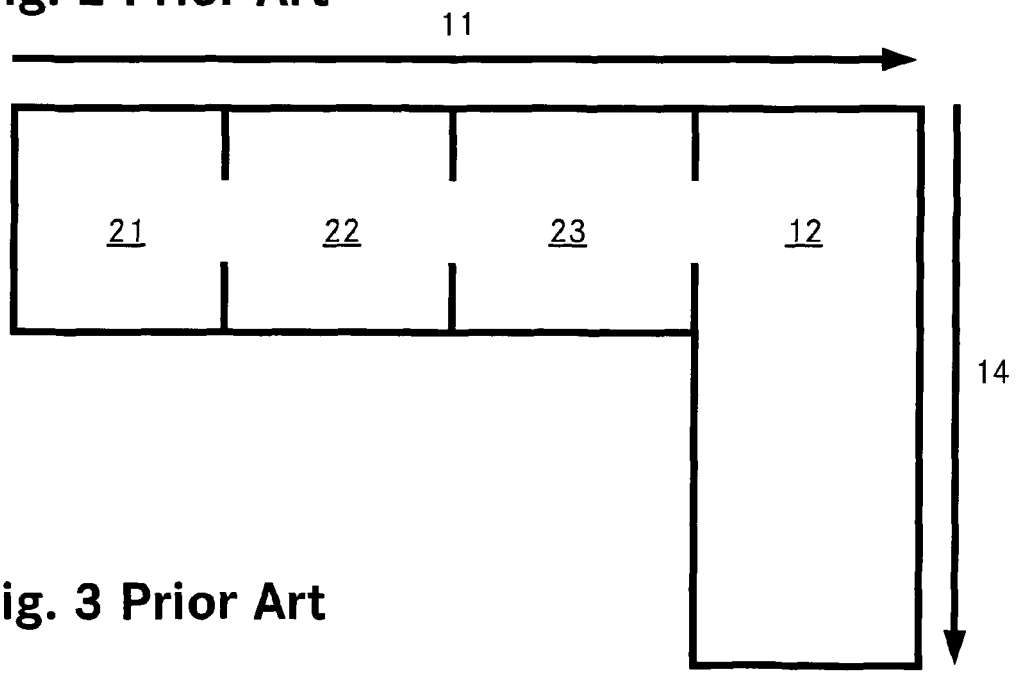

Fig. 3 Prior Art

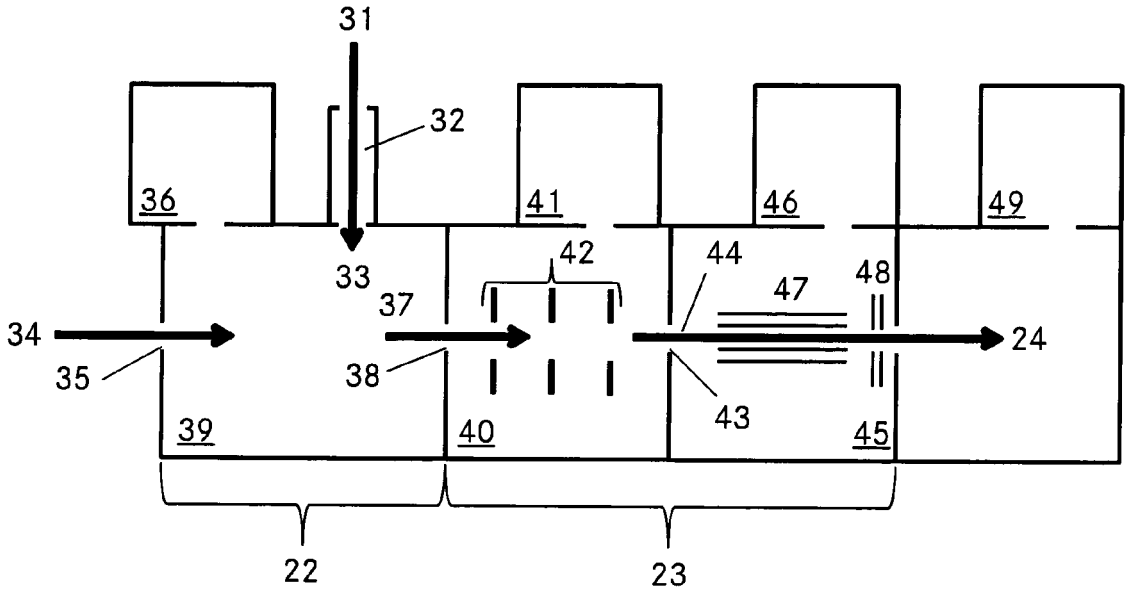

Fig. 4 Prior Art

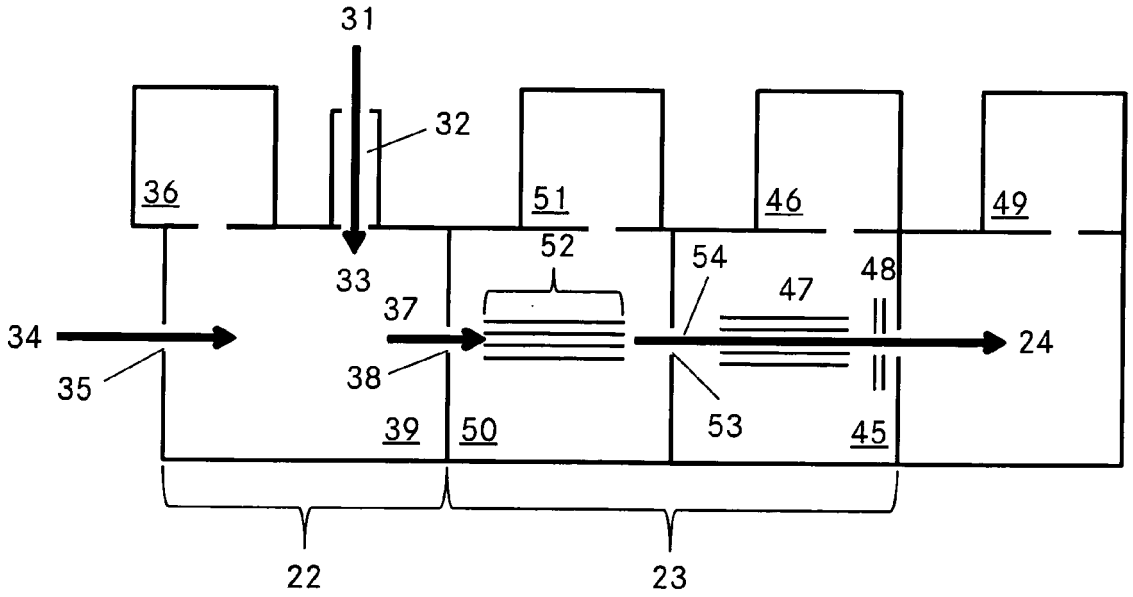

Fig. 5

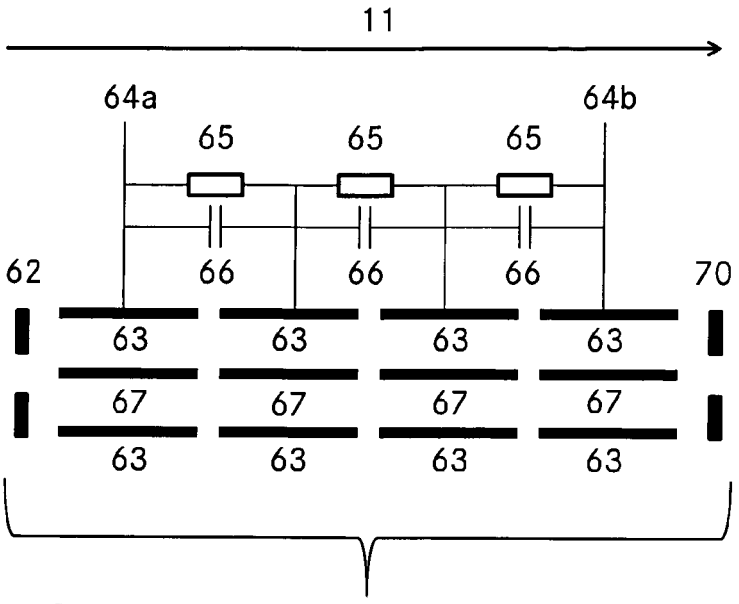

Fig. 6a

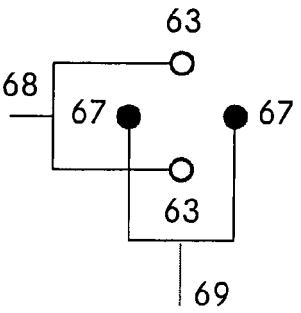

Fig. 6b

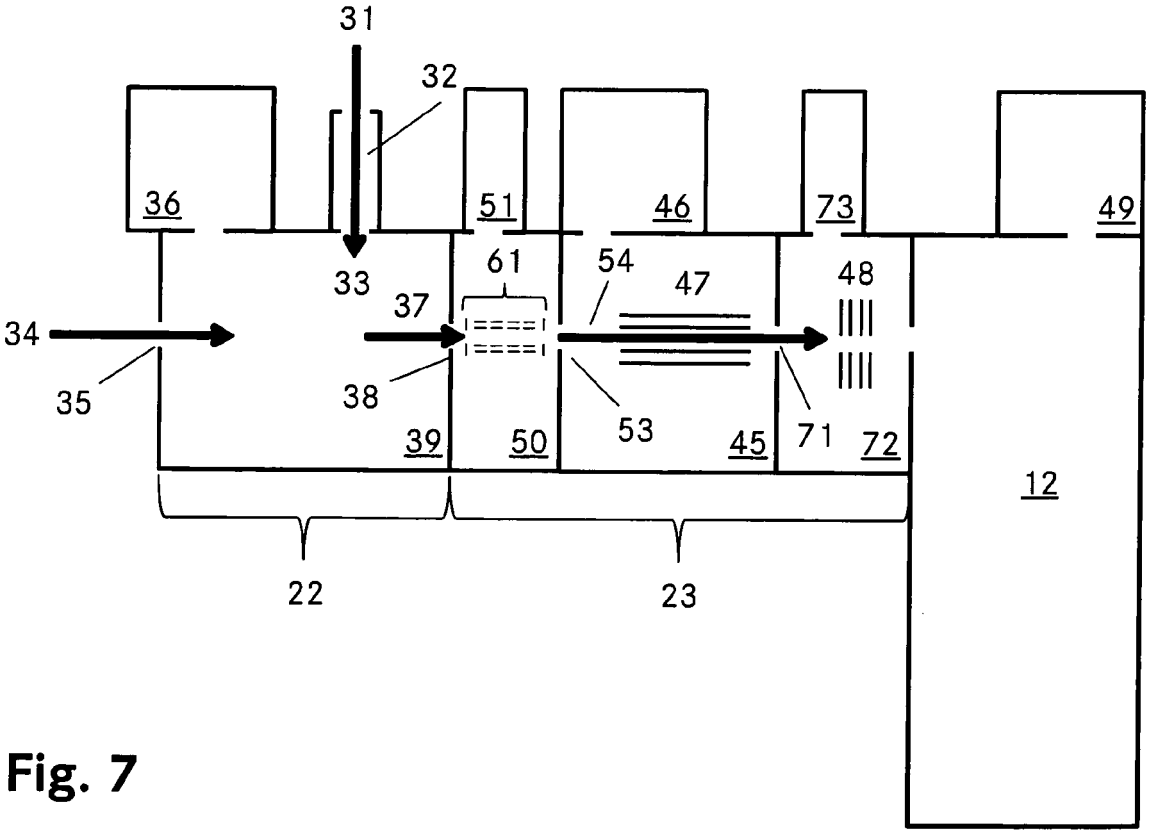

Fig. 7

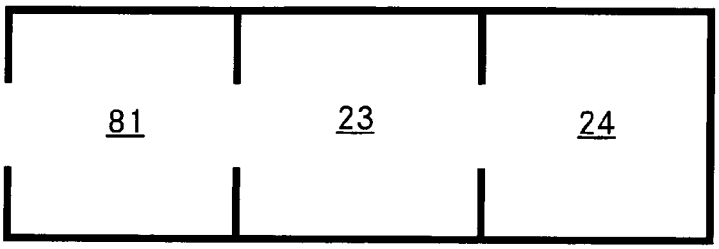
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Fig. 8

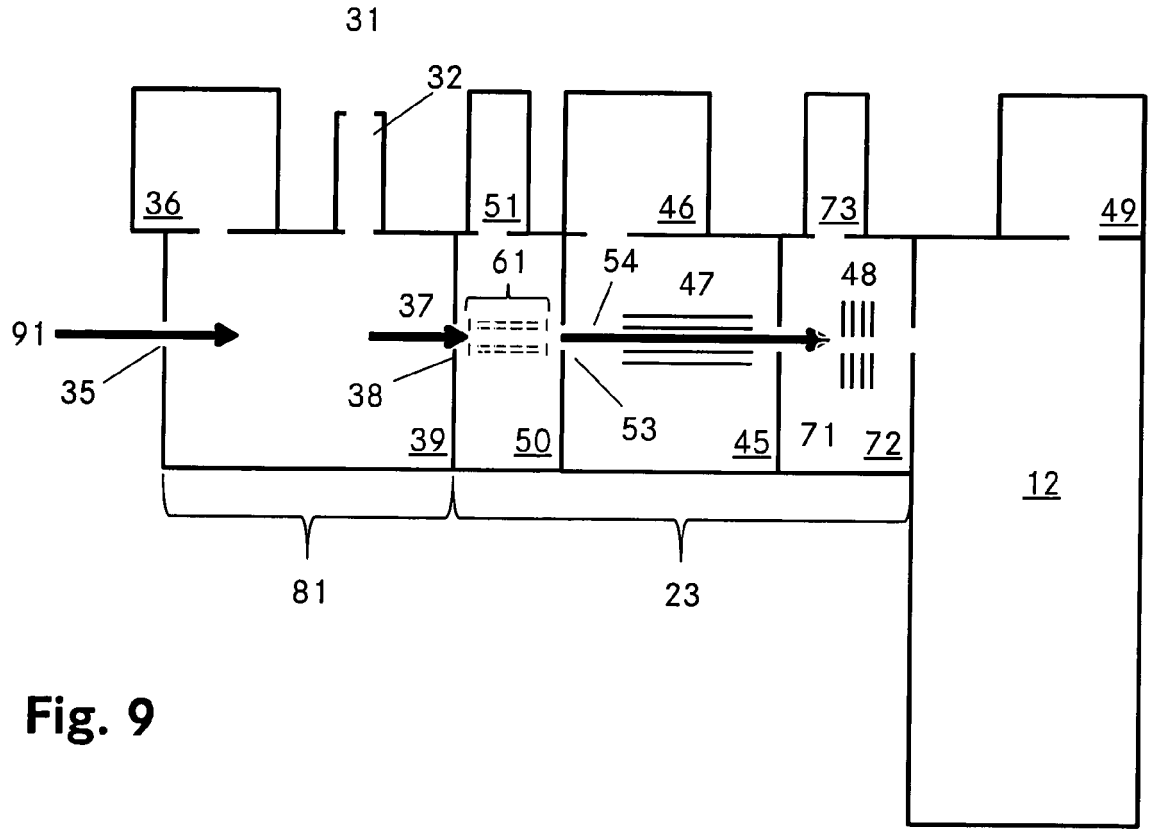
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Fig. 9

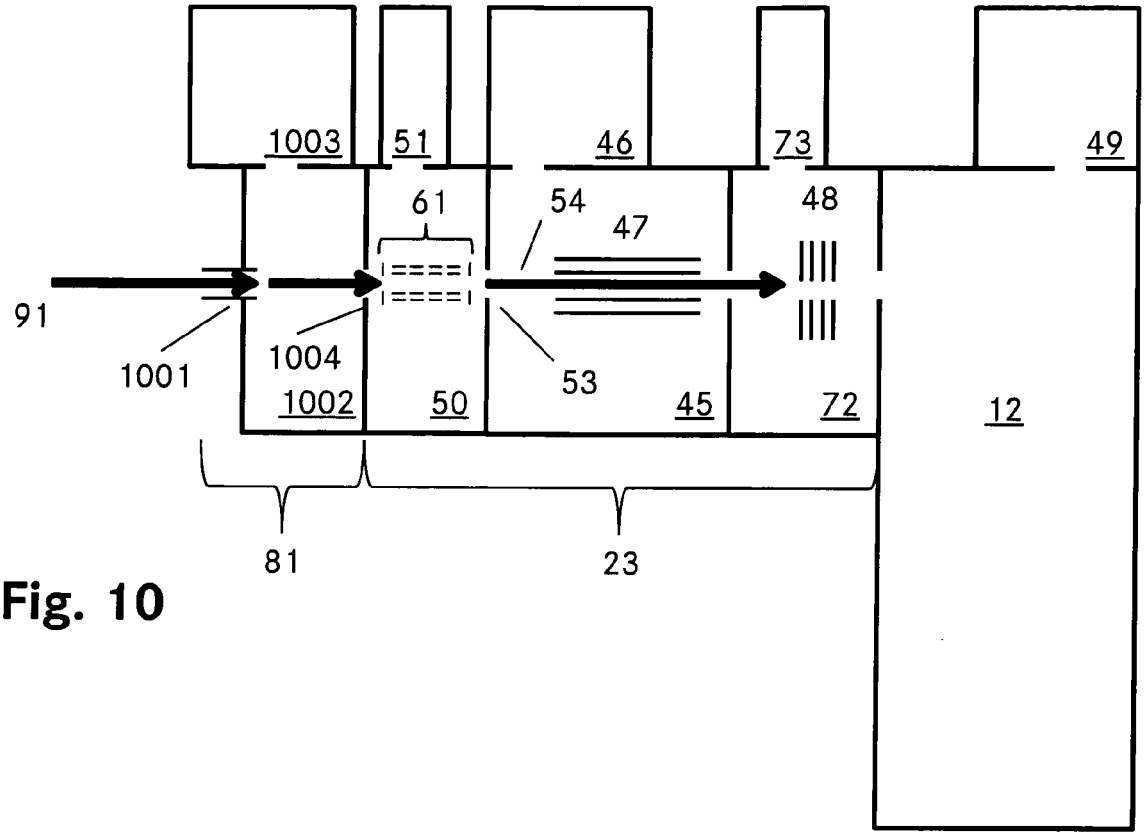
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Fig. 10

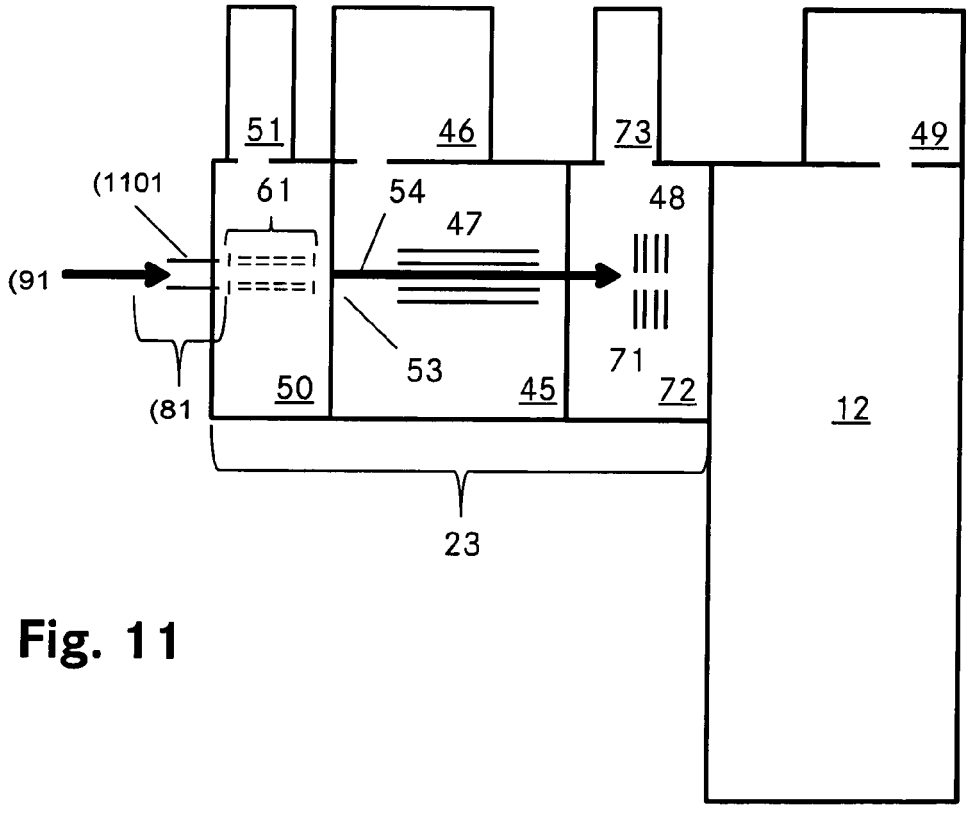
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Fig. 11

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EUROPEAN SEARCH REPORT

Application Number
EP 11 40 5227

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	US 7 034 292 B1 (WHITEHOUSE CRAIG M [US] ET AL) 25 April 2006 (2006-04-25) * column 7, line 54 - line 57 * * column 11, line 27 - line 35 * * column 45, line 11 - line 35 * * figure 28 *	1-15 16,17	INV. H01J49/10 H01J49/14
Y,D	H. JUNNINEN ET AL: "A high-resolution mass spectrometer to measure atmospheric ion composition", ATMOSPHERIC MEASUREMENT TECHNIQUES, vol. 3, 17 August 2010 (2010-08-17), pages 1039-1053, XP55004075, DOI: 10.5194/amt-3-1039-2010 * abstract * * page 1040 *	16,17	

TECHNICAL FIELDS SEARCHED (IPC)
H01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 August 2011	Peters, Volker

CATEGORY OF CITED DOCUMENTS

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EPO FORM 1503 03.82 (P04C01)

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09-08-2011

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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