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(54) **Improvement of a method of mass analyzing a sample.**

(57) In a method of mass analysing a sample, an electrical field condition is produced within a QUISTOR suited to simultaneously trap sample ions over an entire mass range of interest. Sample ions are provided within the QUISTOR whereby ions having masses comprised in a certain mass range are trapped and perform ionmass-specific secular movements therein. Specific ions which have masses of no interest encounter resonance, take up energy and thereby increase their secular movement until they finally leave the trapping field. The ions remaining in the storage field are then mass analysed. The densitiy of the ions remaining in the storage field may be increased until an optimum is reached with respect to receiving a signal during the mass analysation step which is both powerful and highly resolved.

EP 0 362 432 A1

Improvement of a method of mass analyzing a sample

The present invention is directed to a method of mass analyzing a sample according to the preamble of claim 1.

The principles of this method and of devices which allow the performance of this method are discussed a handbook of Dawson: "Quadrupole Mass Spectrometry and its Applications", Amsterdam - Oxford - New York 1976, especially pages 181 to 190 and pages 203 to 219. Further, embodiments of such devices are described in EP-A-0 113 207 and in DE-A-3 533 364.

The devices which allow the performance of the said method are called "Ion Trap" or QUISTOR" ("QUadrupole Ion STORe"). A QUISTOR is comprised of a ring electrode and of end electrodes which together define a storage space. In the book of Dawson, the conditions are discussed in detail which allow a stable trapping of ions within the storage space of a Quistor. These conditions comprise the application of an RF-voltage having a so-called "Trapping Frequency" to the ring electrode of the Quistor. In the book of Dawson, also the phenomenon is discussed that the ions perform an oscillating movement which is called secular movement. The components of this movement in the direction of the rotational axis of the ring electrode (z-direction) and in the directions perpendicular thereto (r-direction) may be treated separately. The secular movement in the z-direction may reach such an amplitude that the ions come into contact with the end cap electrodes of the Quistor and are eliminated thereby (see especially pages 181 ff).

EP-A-0 113 207 also discloses a method which comprises the variation of the magnitude of the storage RF-voltage in order to modify the value of the mass-to-charge ratio of stable trapping conditions so that the trapping conditions vanish successively for ions with growing masses, and the ions become free to leave the ion trap. The ions which leave the Quistor in the direction of the rotational axis of the ring electrode, are registered by means of an electron multiplier in order to evaluate the spectrum of the sample included in the Quistor.

The above mentioned DE-A-3 533 364 also discloses the method to eliminate all ions which are produced when a sample contained in the Quistor is ionized, with the exception of those ions which belong to a watched pollution, by varying concurrently the magnitude of the RF-signal and of a DC-voltage both applied to the ring electrode in such a way that all ions are eliminated which have a mass-to-charge ratio which is different from that of the watched species of ions.

Finally, reference is made to EP Application No. 88 105 847.3, filed on 13.04.1988, which is directed to a method of mass analyzing a sample by means of a Quistor, and to a Quistor designed for performing this method, which method and Quistor will be considered as prior art after the publication of said application. The method and Quistor disclosed in this European Patent Application are incorporated herein by reference.

The method described in EP Application No. 88 105 837.3 consists in generating in addition to the quadrupole storage field an exciting RF-field having a frequency which is different from the frequency of the RF component of the quadrupole storage field and in modifying the electrical field condition defined by said exciting RF-field and said quadrupole storage field in such a way that ions of consecutive masses encounter a resonance of their secular movements with the exciting RF field, thereby taking up energy and increasing the amplitude of their secular movement until they finally leave the storage field. The advantage of this method consists in that a mass selective resonance ejection of the ions which are present in the stability region of the quadrupole storage field takes place. This method is very selective and results in a quantitative elimination of the ions having a specific mass-to-charge ratio.

A mass spectrometer having a Quistor as an ion trap has the special advantage that a Quistor does not need to be exposed to a homogeneous magnetic field. Thus no magnet is needed and the spectrometer may have a simple construction and be easyly handled. On the other hand, it has the drawback that space charge effects limit the performance of the device. It is possible to store about 10^8 to 10^9 ions within the Quadrupole storage field of a Quistor having a ring electrode with an inner diameter of about 2 cm. However, with such a high ion density, the available methods of ion ejection do not allow the separation of different ions with the desired resolution. This is the reason that in a common Quistor, the maximum ion density which still produces a spectrum having an acceptable resolution is about 10^5. It is easy to recognize that with such a low number of ions, the ability to trace pollutions in very low concentrations in the presence of other substances is seriously limited. If the concentration of a pollutant is only 10^{-4} with respect to another substance, it will be necessary to prove the existence of only 10 ions of a special kind in the Quistor.

In some cases it is possible to provide a storage field defining a predetermined mass range in which only ions having masses of interest are stored. However, since only the lower limit of the mass range may be selected, the elimination of ions which have masses of no interest is only possible if all unwanted ions have mass-to-charge ratios which are below that of the traced pollution.

The method decribed in DE-A-3 533 364 allows the selection of the upper limit of the range of trapped ion masses trapped by means of a dc voltage added to the storage field, however, up to now it is not possible to eliminate ions from within the mass range to be investigated.

Therefore, it is the object of the present invention to provide a general method of mass analyzing a sample which allows an enhancement of the ions of interest in the gas sample contained in the Quistor without impairing the selectivity or affecting any other steps of the method.

This object is met by the invention as defined in the characterizing part of Claim 1.

As may easily recognized, the present invention makes use of one of the basic principles described in the elder European Application No. 88 195 847.3 as a means for eliminating all ions from the trap which have a mass-to-charge ratio which is different from that of the ions to be traced. The special advantage of this method consists in that the steps of providing ions and eliminating all those ions therefrom which have a mass-to-charge ratio out of interest may be continued until the number of ions having the mass-to-charge ratio of interest has been increased to a level which is sufficient for an easy detection of the ions, and this irrespective of steps b) and c) being performed simultaneously or alternately.

If the ionisation and elimination steps are performed alternately and if there is only one unwanted ion species present, it is sufficient to excite the ionized sample with an RF signal having only one defined frequency. Thereby, the secular motion of the undesired ions is excited so that these ions take up energy, increase their secular motion and are finally eliminated so that the ion density within the trap is reduced.

A second ionization step produces both ions of the traced pollution and unwanted ions. If then the unwanted ions are again eliminated by exciting their secular motion, the ions having a mass-to-charge ratio of interest remain trapped so that their number in the trap is increased. By repeating these steps, the density of ions of interest may be raised until the limit is reached which produces an optimum relation between signal strength and resolution.

If there is more than one disturbing ion species, an elimination step may be performed for each one of said species before the next ionization step in the above mentioned method. However, preferably, more than ion species is eliminated by the use of a broad-band RF excitation voltage which comprises the secular frequencies of all disturbing ions. In this case, ions having a continous mass range are eliminated.

Puls excitation is another method of eliminating unwanted ions. An appropriate excitation RF-puls may be calculated from the frequencies and amplitudes of the plurality of signals which would be necessary to eliminate the unwanted ions by means of Fourier Transformation.

. As mentioned before, the provision of ions and the elimination of those of the provided ions which have masses out of interest may be performed simultaneously, which means that ion creation and ion ejection takes place in the same time interval. Generally the ejection time should last a little longer than the ionization time to ensure the complete removal of the unwanted ions. The advantage of this method is the shorter time needed to eliminate the unwanted ions as compared to the process making use of alternate steps described above.

Providing the Quistor with ions may be performed in two basically different ways, i.e. either by forming the ions inside the Quistor or by forming them outside thereof and then introducing them into the Quistor as an ion beam. For producing ions, all ionization methods which are common in mass spectrometry may be used, as e.g. Electron Ionisation (EI), Chemical Ionisation (CI), Charge Exchange (CE), Photo Ionisation (PI), Field Desorption (FD), Fast Atom Bombardement (FAB), and Secondary Ion Mass Spectrometry (SIMS).

Special attention should be focussed on ionization methods which use primary ions to produce the sample ions to be traced, as e.g. CI and CE, in combination with the new method of ejecting unwanted ions described herein. With this method, it is possible to select specific primary ions with known thermodynamic data by ejecting all unwanted primary ions. Here again, the elimination of unwanted product ions may be performed during or after the period during which the reaction between the primary ions and the neutral sample takes place which yields the wanted secondary or product ions.

The possibility of eliminating unwanted primary ions by means of the disclosed new method is also very useful in the investigation of ion molecule reactions by mass spectroscopy.

As indicated before, the invention may be performed with mass spectrometers as described in the prior art. These mass spectrometers include an ion trap in form of a Quistor comprising a ring electrode and two end cap electrodes, which ring and end cap electrodes delimit a storage space. The performance of the method requires the connection of an exciting RF-generator to the end cap electrodes which allows the generation of at least one RF signal having a frequency which is equal to the frequency of the secular motion in the direction of the axis of the ring electrode of one species of ions to be eliminated, so that this species of ions which is of no interest may be eliminated by exciting its secular motion. This RF-generator may be designed as a pulse generator producing output signals having a predetermined spectrum. Such RF-pulse generators are common in the art of mass spectroscopy. Indeed, in mass spectrometers, all steps having a rather short duration so that all events may be considered as being pulse like.

As already mentioned, the mass spectrometer described in the elder European Patent Application No. 88 105 847.3 is especially suited to perform the invention. It includes a Quistor which is comprised of a ring electrode and of cap electrodes which deviate from the generally used ideal hyperbolic shape having an angle 1:1,414 of the asymptotes in order to provide field faults which result in non-harmonic oscillations of the ions which are trapped within the Quistor. These non-harmonic oscillations result in very sharp resonances which improve the selectivity of the ion ejection and thus the resolution. Thus, it is of special advantage to use the Quistor described in said European application No. 88 105 847.3 for performing this invention.

Since the claimed method may be performed with any common mass spectrometer having a Quistor as an ion trap and since the principle of the invention is easy to be understood, it is considered as being superfluous to further explain the invention by means of specific examples. Especially in view of the elder Patent Application No. 88 105.847.3 it is evident that the invention makes use of one part of the basic method disclosed in said application as a means for the selective elimination of ions. However, according to the invention, this method is now used for the purpose of enhancing the density of trapped ions having a specified mass-to-charge ratio. This is the reason, why the contents of this elder application has been incorporated into this disclosure by reference.

The method of eliminating ions by exciting their secular motion by means of an RF voltage applied to the end cap electrodes, can be applied in the course of all methods for running mass spectrometers which include a Quistor. In such spectrometers, the ionisation time has commonly a duration in the μs- to ms-range. The RF voltage connected to the ring electrode has a frequency in the range of about 1 MHz and an amplitude of up to some kV. The frequency of the secular motion varies from about 1/100 to about 1/2 of the trapping frequency, and thus varies between about 10 and about 500 kHz. Similarly, the voltage necessary to excite the secular motion is much lower than the voltage of the storage RF-signal, and has a value from about 0,1 to 100 V. The values giving optimum results may be determined by experiments. In any case, the ions of one or more substances of interest may be accumulated until the maximum ion density is reached so that they produce a clear signal and may be definitely detected. The kind and number steps of necessary to eliminate unwanted ions and to reach the maximum density of the ions of interest, allows to estimate the concentration of the pollution. Experiments on samples having known concentrations of the polluting substance may be used to calibrate the device.

Summing up, the man skilled in the art has many possibilities to make use of the invention under a plurality of different conditions and to optimize the different steps or stages of this method to achieve in any case the best results.

Claims

1. In a method of mass analyzing a sample comprising the steps of

a) providing a three-dimensional electrical quadrupole storage field having an RF component, which quadrupole storage field is appropriate to simultaneously trap all sample ions included in a predetermined mass range,

b) providing a plurality of sample ions within said storage field, the ions thereof having a mass which is included in said predetermined mass range being trapped in said storage field and bound to perform ion-mass specific secular movements therein,

c) changing said storage field in such a way that those of said trapped ions which have masses of no interest are free to leave said storage field whereas the ions having masses of interest remain trapped, and

d) mass analyzing said ions remaining trapped,

the improvement which consists in

generating an exciting RF field in step a) in addition to said storage field, which exciting RF field has a frequency which is different from the frequency of said RF component of said storage field, said storage field and said exciting RF field defining a prdetermined field condition,

changing said field condition in step c) in such a way that said ions which have masses of no interest encounter a resonance of their secular movements with said exciting RF field, so that they take up energy, increase thereby their secular movement, and finally leave said storage field, and

continuing steps b) and c) until the densitiy of said ions which remain trapped in said storage field has reached an optimum with respect to the subsequent mass analysis of step d).

2. The method of claim 1, characterized in that steps b) and c) are performed simultaneously.

3. The method of claim 1, characterized in that steps b) and c) are performed alternately.

4. The method of any one of the preceding claims, characterized in that said field condition is generated by means of a QUISTOR of the type having a ring electrode and spaced end cap electrodes, wherein said storage field is defined by U, V_{stor} and f_{stor}, and said exciting RF field is defined by V_{exc} and f_{exc}, and in which said field condition is changed by modifying one or more of U, V_{stor}, f_{stor}, or f_{exc}, wherein

U = amplitude of storage DC voltage between the ring electrode and the end electrodes

V_{stor} = magnitude of storage RF voltage between ring electrode and end electrodes

f_{stor} = frequency of storage RF voltage

V_{exc} = magnitude of exciting RF voltage between the two end electrodes

f_{exc} = frequency of exciting RF voltage.

5. The method of any one of the preceding claims, characterized in that said sample ions are produced outside said storage field and are injected into same by means of an ion beam.

6. The method of any one of claims 1 to 4, characterized in that said sample ions are produced within said storage field.

7. The method of claim 6, characterized in that primary ions are provided within said storage field and said sample ions are produced by interaction with said primary ions, which interaction comprises at least one of the effects of charge transfer and chemical ionisation.

8. The method of any one of the preceding claims, characterized in that said exciting RF field comprises the secular frequencies of a plurality of different ions to be eliminated.

9. The method of claim 8, characterized in that for generating said exciting RF field a broad band RF pulse is produced which includes the frequencies of the secular movements of all of said ions which have masses of no interest.

10. The method of any one of the preceding claims, characterized in that for generating said exciting RF field an RF pulse is produced which includes at least one single frequency which is equal to the frequency of the secular movement of an ion which has a mass of no interest.

11. The method of any one of the preceding claims, characterized by its use for tracing small amounts of polluting substances in air.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 11 6599

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
X	EP-A-0 202 943 (FINNIGAN CORP.) * Page 2, lines 3-10; page 8, line 10 - page 9, line 18; page 10, lines 3-13; figures 1,4,7 *	1-4,6-11	H 01 J 49/42
A,D	EP-A-0 113 207 (FINNIGAN CORP.) * Abstract; figures 1,2 *	1-11	
A,D	GB-A-2 180 687 (BRUKER FRANZEN ANALYTIK GmbH) * Abstract; figures *	7,11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.3)
			H 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-05-1989	WINKELMAN,A.M.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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