Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2269385 C 2008/02/19

(11)(21) 2 269 385

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1999/04/19

(41) Mise à la disp. pub./Open to Public Insp.: 1999/10/20

(45) Date de délivrance/Issue Date: 2008/02/19

(30) Priorité/Priority: 1998/04/20 (GB9808319.9)

(51) Cl.Int./Int.Cl. *H01J 49/26* (2006.01), *G01N 30/72* (2006.01), *H01J 49/30* (2006.01)

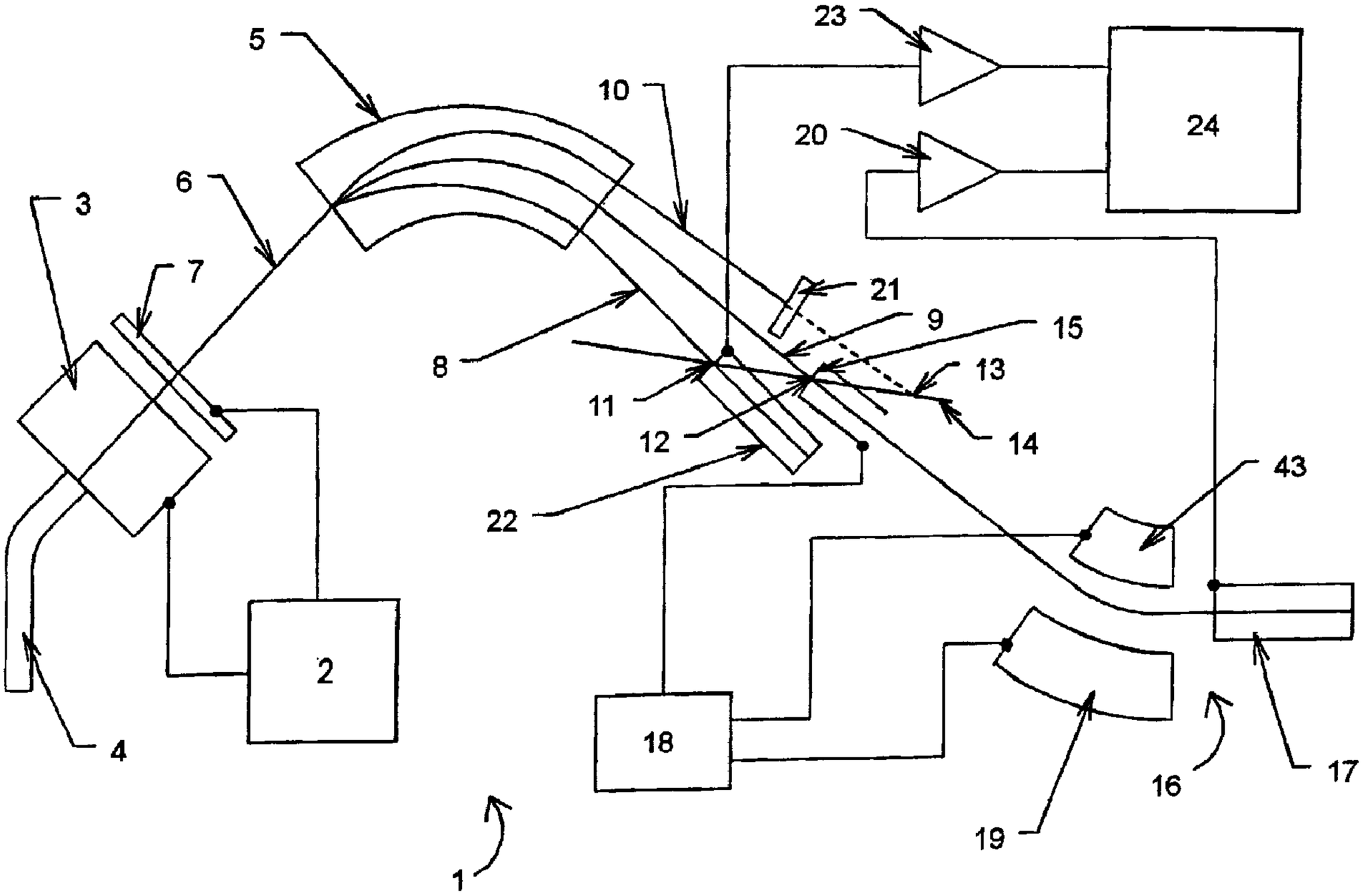
(72) Inventeur/Inventor:
MERREN, THOMAS OLIVER, GB

(73) Propriétaire/Owner:
MICROMASS UK LIMITED, GB

(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : SPECTROMETRE DE MASSE A DETECTION SIMULTANEE POUR LA MESURE DU RAPPORT ISOTOPIQUE

(54) Title: SIMULTANEOUS DETECTION ISOTOPIC RATIO MASS SPECTROMETER



(57) Abrégé/Abstract:
The invention comprises a mass spectrometer 1 and a method of mass spectrometry that is especially useful for the measurement of the isotopic composition of hydrogen in the presence of a helium carrier gas. Interference to the accurate measurement of the

(11)(21) 2 269 385

(13) C

(57) Abrégé(suite)/Abstract(continued):
small HD^+ peak at mass-to-charge ratio 3 by the much larger He^+ peak at mass-to-charge ratio 4 is reduced by provision of an energy filter 35 in the ion detector assembly used to collect HD^+ ions. This prevents ions of He^+ which have lost energy through scattering, etc giving rise to a signal from the HD^+ detector and distorting the deuterium hydrogen isotopic ratio measurement. Such a mass spectrometer 1 is typically used in conjunction with a continuous flow inlet system 4 based on an elemental analyzer that converts hydrogen present in a sample to gaseous hydrogen in a flow of helium carrier gas. Another embodiment of the invention provides a similar mass spectrometer useful for carbon or oxygen isotopic determinations in carbon dioxide gas.

Abstract

Simultaneous Detection Isotopic Ratio Mass Spectrometer

The invention comprises a mass spectrometer 1 and a method of mass spectrometry that is especially useful for the measurement of the isotopic composition of hydrogen in the presence of a helium carrier gas. Interference to the accurate measurement of the small HD^+ peak at mass-to-charge ratio 3 by the much larger He^+ peak at mass-to-charge ratio 4 is reduced by provision of an energy filter 35 in the ion detector assembly used to collect HD^+ ions. This prevents ions of He^+ which have lost energy through scattering, etc giving rise to a signal from the HD^+ detector and distorting the deuterium hydrogen isotopic ratio measurement. Such a mass spectrometer 1 is typically used in conjunction with a continuous flow inlet system 4 based on an elemental analyzer that converts hydrogen present in a sample to gaseous hydrogen in a flow of helium carrier gas.

Another embodiment of the invention provides a similar mass spectrometer useful for carbon or oxygen isotopic determinations in carbon dioxide gas.

[Fig. 1]

Simultaneous Detection Isotopic Ratio Mass Spectrometer

This invention relates to a magnetic sector mass spectrometer that is capable of simultaneously detecting two or more mass dispersed ion beams, and which is particularly useful for the determination of the isotopic composition of hydrogen.

The accurate determination of isotopic composition by mass spectrometry is usually carried out by means of a magnetic sector mass analyzer that has a plurality of collectors disposed along its mass-dispersed focal plane. In such a spectrometer each collector is positioned to receive only ions of a given mass-to-charge ratio and is provided with means for reading out the number of ions which it receives during a given time period. Consequently, the ratio of the signals generated by the arrival of several ion beams of different mass-to-charge ratio is unaffected by variations in parameters such as the sample flow rate into the ionization source and the ion source efficiency which affect both beams equally, so that, for example, the isotopic composition of an element in a sample can be determined very accurately. An example of a conventional multi-collector array for a magnetic sector mass spectrometer is given by Stacey, et. al. in Int. J. Mass Spectrom. and Ion Phys. 1981 vol 39 pp 167-180.

In the case when an isotope is present only in a small proportion relative to another isotope having an adjacent mass-to-charge ratio, the property known as abundance sensitivity of the mass spectrometer becomes critically important. Abundance sensitivity is a measure of an interfering signal at any given mass-to-charge ratio M due to the presence of a larger signal at M$\pm$1. Unless special precautions are taken the larger peak typically has a "tail", usually greatest on the low mass side of the peak, which often extends to adjacent masses and causes an uncertainty in the true zero of the signal at that mass.

A major cause of the low mass tail is thought to be scattering of the ions composed in the major peak due to collisions with neutral gas molecules in the spectrometer housing. Typically these collisions result in a loss in energy so that the ions that have undergone

them appear on the low mass side of the true position on the mass-to-charge axis of a resultant spectrum.

Various arrangements are known to improve the abundance sensitivity of a spectrometer. Firstly, the ion optical arrangements of the analyzer, such as the magnetic sector angle, poleface inclination and curvature and the positions and sizes of the entrance and exit slits can be selected to produce high dispersion to minimise the overlap at the detector between beams comprising ions which differ in mass-to-charge ratio of 1 unit. Examples of this approach include Wollnik, Int. J. Mass Spectrom. and Ion Phys. 1979 vol 30 pp 137-154, Prosser, Int J. Mass Spectrom. and Ion Proc. 1993 vol 125 (2-3) pp 241-266 and Prosser and Scrimegour, Anal. Chem. 1995 vol 67 pp 1992-1997. This approach can be successfully adopted with a simultaneous collection spectrometer, but increasing mass dispersion does not necessarily improve the abundance sensitivity as it may merely result in the centroids of adjacent mass peaks being spaced further apart while the width of the peaks is correspondingly increased. An alternative approach is to provide an electrostatic lens or retarding electrode arrangement between the exit aperture of the analyzer and the detector itself. This electrode may be biased so that it provides a potential barrier which ions must surmount to reach the detector. If correctly set, ions which have lost energy and which are therefore comprised in the unwanted low mass tail of a peak will have insufficient energy to surmount the barrier and will be prevented from reaching the detector. Such devices are taught by Kaiser and Stevens, Report No ANL-7393 of Argonne National Laboratory (Pub. Nov. 1997), Merrill, Collins and Peterson, 27th An. Confr. on Mass Spectrometry and Allied Topics, June 1979, Seattle, pp 334, Freeman, Daly and Powell in Rev. Sci. Instrum. 1967 vol 38 (7) pp 945-948. This method has not typically been applied to simultaneous collection mass analyzers because the retardation of the wanted ions as they surmount the potential barrier amplifies the relative contribution of any component of velocity they may have perpendicular to their direction of travel and can actually result in a greater overlap between adjacent mass peaks.

An improvement on the provision of a retarding electrode is the use of an energy analyzing device between a magnetic sector analyzer and the ion detector. The three-stage mass spectrometer of White, Rourke and Sheffield described in Appld.

Spectroscopy 1958 (2) pp 46-52 comprised two magnetic sector analyzers followed by an electrostatic energy analyzer and was intended to provide improved abundance sensitivity. However, the restriction imposed on the extent of the mass-to-charge focal plane by the final electrostatic analyzer precluded the use of a multicollector detector at this location. Instead, the "low mass" ion beam was deflected into an auxiliary electron multiplier as it left the second magnetic sector and only the high mass ion beam entered the energy analyzer. Thus, when used for its intended purpose of the isotopic analysis of uranium, the ^{238}U ion beam would pass into the energy analyzer and the ^{235}U beam would be intercepted after the second magnet. As the ^{238}U beam was 140x more intense than the ^{235}U beam in the examples given, the presence of the energy analyzer does not prevent ^{238}U ions which have lost energy striking the ^{235}U collector because the collector is situated upstream of the energy analyzer. This prior art therefore teaches that an energy filter should be used to filter the most abundant ion beam, but as the authors make clear, when used in the simultaneous collection mode the improvement in abundance sensitivity arises from the presence of the two magnetic sector analyzers and not from the electrostatic analyzer. It is clear that energy filtration of the most intense ion beam subsequent to it passing the collector used for the less abundant beam can have no effect on the interference to the signal at that collector from ions in the most abundant beam that have lost energy.

An isotopic-ratio multicollector spectrometer having a 90° spherical sector energy analyzer is described by Zhang in Nucl. Instrum. and Methods in Phys. Research 1987 vol B26 pp 377-380. This instrument is similar to that described by White, Rourke and Sheffield in that the energy filter is arranged to filter the highest mass ion beam only (ie, the ^{238}U beam in the example given) while collectors for other ion beams are disposed before the entrance slit of the energy analyzer in such a way that they intercept only lower mass ion beams. Consequently, as in the earlier instrument, if used in a simultaneous collection mode this instrument cannot reduce interference to the less abundant ^{235}U, ^{236}U and ^{237}U beams. The example given suggests that to obtain an improvement in abundance sensitivity the instrument is used in a conventional single-collector mode and the magnetic field is scanned.

US patent 5220167 and International Application WO 97/15944 teach use of an electrostatic lens disposed between the exit of a magnetic sector mass analyzer and an array of collectors in an isotopic ratio mass spectrometer in order to increase the separation between beams of different mass-to-charge ratios at the detector. Such an arrangement does not improve the abundance sensitivity, as explained above.

GB patent application 2230896 teaches the disposition of a retarding lens and a quadrupole mass filter to receive one of the ion beams in a simultaneous collection mass spectrometer to eliminate ions of different mass-to-charge ratios which have lost energy due to scattering from that beam. US patent 5545894 describes a hydrogen isotopic ratio mass spectrometer in which isobaric interferences are reduced by passing ions of hydrogen, deuterium, tritium and helium into a detection device which comprises a thin foil through which the ions must pass. Atomic ions of H, D, and T exit the foil as negative ions and may be separated by scanning an electrostatic energy analyzer disposed downstream of the foil.

It is an object of the present invention to provide a simultaneous collection isotopic ratio mass spectrometer that has higher abundance sensitivity than prior types of similar size and cost. It is another object to provide such a mass spectrometer suitable for the determination of hydrogen isotopic ratios in the presence of helium gas. It is another object of the invention to provide methods of determining isotopic composition using such a simultaneous collection mass spectrometer, and still another object to provide improved methods of determining the isotopic composition of hydrogen in the presence of helium gas.

From a first aspect the present invention provides an isotopic-ratio multiple-collector mass spectrometer for the determination of hydrogen isotopic ratios in the presence of helium gas comprising:

an ionization source for generating ions having an initial kinetic energy from a sample comprising hydrogen isotopes in the presence of helium gas;

a magnetic sector analyzer that disperses the ions according to their momentum into a plurality of ion beams each of which substantially comprises ions of a different mass to charge ratio and focuses each of the beams to different position in a focal plane, wherein in use the plurality of beams comprises at least a first ion beam comprising the minor isotope HD^+, a second ion beam comprising He^+ ions that is more intense than the first ion beam, and a third ion beam comprising the major isotope H_2^+;

first ion detection means disposed to receive ions in the first ion beam having a mass to charge ratio of 3;

second ion detection means disposed to receive ions in the third ion beam having a mass to charge ratio of 2;

a beam stop disposed in the path of the second ion beam to discharge ions in the second ion beam, the second ion beam comprising ions having a mass to charge ratio of 4; and

means for determining from signals generated by the first and the second ion detection means the ratio of the number of HD^+ ions having a mass to charge ratio of 3 to the number of H_2^+ ions having a mass to charge ratio of 2;

wherein the first ion detection means comprises an ion-energy filter that allows only ions having substantially the initial kinetic energy to pass to a collection electrode and thereby to generate the signal from the first ion detection means.

From a second aspect the present invention provides a method for determining hydrogen isotopic ratios in the presence of helium using a multiple collector mass spectrometer comprising the steps of:

generating from a sample ions which have an initial kinetic energy;

dispersing the ions according to their momentum by means of a magnetic sector analyzer thereby producing a plurality of ion beams each of which substantially comprises ions of a different mass to charge ratio and focusing each of the plurality of ion beams to a different position in a focal plane, the plurality of ion beams comprising a first ion beam comprising the minor isotope HD^+, a second ion beam comprising He^+ ions that is more intense than the first ion beam and a third ion beam comprising the major isotope H_2^+;

receiving ions comprised in the first ion beam that have a mass to charge ratio of 3 in first ion detection means;

receiving ions having a mass to charge ratio of 2 in the third ion beam in second ion detection means;

intercepting the second beam by disposing a beam stop in its path, the second beam comprising ions having a mass to charge ratio of 4; and

determining from signals generated by the first and second ion detection means the ratio of the number of HD^+ ions having a mass to charge ratio of 3 to the number of H_2^+ ions having a mass to charge ratio of 2;

wherein the ions are energy filtered after they have entered the first ion detection means to allow only ions having the initial kinetic energy to reach a collection electrode and thereby to generate the signal from the first ion detection means.

The first ion beam comprises the minor isotope HD^+ (mass-to-charge ratio 3) and the second, more intense, ion beam comprises the He^+ ions (mass-to-charge ratio 4) which are not to be determined but are unavoidably generated in the ion source. A beam stop is provided in the path of the second ion beam to discharge the He^+ Ions. The second ion detection means is disposed to receive the major isotope H_2^+ at mass-to-charge ratio 2. According to the invention an energy filter is provided in the first ion detection means which is disposed to receive ions of mass-to-charge ratio 3 so that only ions having approximately the initial kinetic energy at which they are formed in the ion source will reach a collector electrode and generate a signal. This arrangement largely eliminates the interference to the signal at mass-to-charge ratio 3 which would otherwise result from He^+ ions (mass-to-charge ratio 4) which have lost energy through collisions with neutral gas molecules during their journey from the ion source to the focal plane; such ions may enter the first ion detection means at mass-to-charge 3 rather than pass through the focal plane at the mass-to-charge ratio 4 position, so that the abundance sensitivity of the spectrometer at mass-to-charge ratio 3 is improved by preventing these ions reaching the collection electrode.

In another preferred embodiment a spectrometer of the invention further comprises an inlet system capable of generating gaseous samples of hydrogen, HD and deuterium from a solid or liquid sample, for example the arrangement taught in European Patent No EP 0419167 B1. Such a continuous flow introduction system unavoidably introduces large

quantities of helium gas into the ion source and in a conventional mass spectrometer the accuracy of the HD/H_2 isotope ratio determined may be impaired due to the detection of scattered He^+ ions by the HD^+ detector. However, the improved abundance sensitivity of a spectrometer according to the invention results in a substantial reduction in the interference to the very small signal at mass-to-charge ratio 3 due to HD^+ from scattered He^+ ions and improves the accuracy of the HD^+/H_2^+ ratio determination.

The invention overcomes the limitation on the extent of the mass-dispersed focal plane, and hence the number of ion beams that can be simultaneously monitored, imposed by the energy filter of the prior spectrometer described above because each filter is required to transmit only ions of one particular mass-to-charge ratio.

Preferably the energy filter comprised in the first detector comprises a small cylindrical sector analyzer which focuses ions having the correct initial ion energy into a collector electrode which comprises a Faraday bucket of the type conventionally employed in the isotopic-ratio multi-collector mass spectrometer. Other types of energy filters may also be employed, however.

A preferred method is a method as described above wherein hydrogen isotopic ratios are determined in the presence of helium gas. In the method of the present invention the first ion beam comprises HD^+, the second ion beam comprises He^+ and the second ion detection means is disposed to receive the major isotopic component H_2^+. The second ion beam is intercepted by a beam stop disposed in its path. In a further preferred method, a continuous flow of a gaseous hydrogen and HD is generated from a sample in a flow of Helium carrier gas, for example by the method taught in European Patent No 0419167 B1.

In further preferred methods the ions entering the first ion detection means are energy filtered by passing them through a cylindrical sector electrostatic energy analyzer which focuses those ions having approximately the initial ion energy into a collector electrode which comprises a Faraday bucket of the type conventionally employed in isotopic ratio multi-collector mass spectrometers.

Preferred embodiments of the invention, given by way of example only, will now be described in greater detail with reference to the figures, wherein:

figure 1 is a schematic drawing of a mass spectrometer according to the invention suitable for the determination of hydrogen isotopic ratios in the presence of helium;

figure 2 is a schematic drawing of a mass spectrometer arrangement suitable for the determination of the isotopic composition of carbon dioxide; and

figure 3 is part of a scanned mass spectrum obtained with apparatus according to figure 1 illustrating the abundance sensitivity of that apparatus.

Referring first to figure 1, an isotopic-ratio multi-collector mass spectrometer generally indicated by 1 comprises a vacuum housing (not shown) and an ion source 3 for generating positive ions from a sample. A gaseous sample comprising hydrogen isotopes in an excess of helium carrier gas is introduced into the ion source 3 through the inlet pipe 4. A magnetic sector analyzer 5 receives the ion beam 6 produced by the ion source 3 which comprises ions having an initial energy determined by the potential maintained between the ion source 3 and an analyzer entrance slit 7. A power supply 2 maintains a potential difference (typically about 4 kV) between the ion source 3 and the entrance slit 7. The magnetic sector analyzer 5 disperses the ions in the beam 6 according to their mass-to-charge ratios and produces a plurality of beams 8, 9, and 10 comprising ions of mass-to-charge ratios 2, 3 and 4 respectively. These are focused by the analyzer 5 at different positions (11, 12, 13 respectively) in the focal plane 14 of the analyzer.

A first ion beam 9 comprising ions of mass-to-charge ratio 3 (HD^+) is focused at position 12 on focal plane 14 and enters a first ion detection means comprising a detector entrance slit 15, an energy filter 16 and a collection electrode 17. The energy filter 16 comprises a pair of cylindrical electrodes 19, 43 maintained respectively positive and negative with respect to the potential of detector entrance slit 15 by means of a power supply 18, as in a conventional cylindrical sector analyzer. The radius and sector angle of the filter 16, and the potentials applied to the electrodes 19 and 43, are selected to deflect ions having the correct initial ion energy that pass through the detector entrance slit 15

into the collection electrode 17. The collection electrode 17 preferably comprises a conventional Faraday bucket collector of the type conventionally employed in multiple-collector mass spectrometers, for example those taught in European Patent Application No 0762472 A1. The filter 16 is also arranged so that an ionic image of the detector entrance slit 15 is created on the collection electrode 17 as a result of its focusing action. Ions that strike the collection electrode 17 generate an electrical current that flows through the input resistance of an amplifier 20 to generate a signal from the first ion detection means.

The energy filter 16 prevents ions that have lost energy since their formation (as a consequence of collisions with neutral gas molecules) from reaching the collection electrode 17 even when they have passed through the detector entrance slit 15. The trajectory through the energy filter 16 of these ions will have a smaller radius so that the ions will either strike the inner electrode of the filter or will exit in such a way that they do not strike the collection electrode 17. Typically these ions will be scattered He^+ ions, present in large numbers, which because of their low energy are deflected along a smaller radius trajectory in the magnetic sector analyzer 5 than ions of the correct energy and pass through the detector entrance slit 15 instead of being confined in the second beam 10 which does not pass through slit 15. Consequently, the interference to the small signal representing HD^+ from the scattered helium ions is greatly reduced (that is, the abundance sensitivity is improved) in comparison with a similar sized conventional mass spectrometer.

As explained, in this embodiment the He^+ ions (mass-to-charge ratio 4) exit from the magnetic sector analyzer 5 in the second beam 10 which is intercepted by a beam stop 21. H_2^+ ions at mass-to-charge ratio 2 exit from the magnetic sector analyzer 5 in the beam 8 and are received by a second ion detection means 22 disposed in the focal plane 14 at position 11. Because this beam is invariably far more intense than the HD^+ beam 9, and is separated from the He^+ beam 10 by a greater distance, it is unnecessary to provide an energy filter and the detector 22 comprises only a conventional Faraday bucket collector. An amplifier 23 amplifies the signal generated by the detector 22.

A digital computer 24 with a suitable input device receives the signals from the two amplifiers 20 and 23 (which represent the ion intensities of the HD^+ and H_2^+ ions respectively) and determines their ratio, thereby providing an accurate measurement of the ratio of H and D in the sample gas. As in a conventional isotopic ratio spectrometer, a reference sample may be introduced into the ion source alternately with the sample to calibrate the system and provide a highly accurate determination.

Figure 3 illustrates the effectiveness of the invention in improving the abundance sensitivity of the spectrometer in relation to the HD^+ peak. In figure 3 the vertical axis represents the signal generated by the first ion detection means (15, 16, 17 figure 1) and the horizontal axis is the magnetic field strength of the analyzer 5. The spectrum was obtained by scanning the field strength so that the beam of ions of mass-to-charge ratio 3 was scanned across the detector entrance slit 15. Peak 25 represents the HD^+ ions, while the very large peak 26 is part of the He^+ peak at mass-to-charge ratio 4, for a typical sample introduced into the source. It is clear that a complete baseline separation exists between the peaks, despite the size of the He^+ peak.

Referring next to figure 2, a spectrometer 27 arranged for the determination of the isotopic composition of carbon dioxide is illustrated. Three ion detection means are provided to simultaneously monitor the major isotope at mass-to-charge ratio 44 and the two minor isotopes at mass-to-charge ratios 45 and 46. The magnetic sector analyzer 5 generates three beams 28, 29, 30 which are focussed at points 31, 32 and 33 in the focal plane 14 as illustrated. Beams 28, 29, 30 comprise ions of mass-to-charge ratio 44, 45 or 46 respectively. The most intense beam 28 (the second beam) is received in the second ion detection means 34 which comprises a conventional Faraday bucket while the first ion detection means receives the minor beam 29 and comprises an entrance slit located at point 33, an energy filter 35 and a collection electrode 36. The other minor isotope beam 30 is received in a third ion detection means comprising a detector entrance slit at point 33, a second analysing channel in the energy analyzer 35, and another collection electrode 37. As in the figure 1 embodiment the collection electrodes 36 and 37 may comprise conventional Faraday bucket collectors.

The energy filter 35 comprises two outer electrodes 38, 39 and an inner electrode 40 which are shaped to provide two separate cylindrical annular channels through which the beams 29 and 30 respectively travel. As in the figure 1 embodiment the sector angles, radius and image and object distances of each part of the analyzer are selected to focus the beam passing through it into the appropriate collector electrode. In practice it is not necessary to achieve very accurate focusing because the energy loss associated with the unwanted scattered ions from the major beam 28 is typically quite large and the energy filtering does not need to be very sharp in order to reject them. Consequently, the outer electrodes 38 and 39 may be of the same radius to facilitate construction.

The signals from the three collectors 34, 36 and 37 are fed to separate amplifiers 41, 42 and 43 and digital computer 24 is programmed to calculate the appropriate isotopic ratios from the three signals for mass-to-charge ratios 44, 45 and 46 as in a conventional mass spectrometer.

The provision of energy filtration of the minor isotopic beams substantially eliminates interference with the signals from their detectors due to ions in the major beam at mass-to-charge ratio 44 which have lost energy through collisions, and greatly improves the abundance sensitivity of the spectrometer.

Claims:

1. An isotopic-ratio multiple-collector mass spectrometer for the determination of hydrogen isotopic ratios in the presence of helium gas comprising:

an ionization source (3) for generating ions (6) having an initial kinetic energy from a sample comprising hydrogen isotopes in the presence of helium gas;

a magnetic sector analyzer (5) that disperses said ions (6) according to their momentum into a plurality of ion beams (8,9,10) each of which substantially comprises ions of a different mass to charge ratio and focuses each of said beams to different position (11,12,13) in a focal plane (14), wherein in use said plurality of beams (8,9,10) comprises at least a first ion beam (9) comprising the minor isotope HD^+, a second ion beam (10) comprising He^+ ions that is more intense than said first ion beam, and a third ion beam (8) comprising the major isotope H_2^+;

first ion detection means (15,16,17) disposed to receive ions in said first ion beam (9) having a mass to charge ratio of 3;

second ion detection means (22) disposed to receive ions in said third ion beam (8) having a mass to charge ratio of 2;

a beam stop (21) disposed in the path of said second ion beam (10) to discharge ions in said second ion beam, said second ion beam (10) comprising ions having a mass to charge ratio of 4; and

means (20,23,24) for determining from signals generated by said first (15,16,17) and said second (22) ion detection means the ratio of the number of HD^+ ions having a mass to charge ratio of 3 to the number of H_2^+ ions having a mass to charge ratio of 2;

wherein said first ion detection means (15,16,17) comprises an ion-energy filter (16) that allows only ions having substantially said initial kinetic energy to pass to a collection electrode (17) and thereby to generate said signal from said first ion detection means (15,16,17).

2. A mass spectrometer as claimed in claim 1, further comprising a continuous flow inlet system that generates from a sample to be analyzed and for delivery to said ionization source (3) a flow of H_2, HD and D_2 in a helium carrier gas.

3. A mass spectrometer as claimed in claim 1 or claim 2, wherein said ion-energy filter (16) comprises a cylindrical sector analyzer that focuses ions having said initial kinetic energy into a collection of electrodes (17).

4. A mass spectrometer as claimed in any one of claims 1, 2 or 3, wherein said collection electrode (17) comprises a Faraday bucket collector electrode.

5. A method of determining hydrogen isotopic ratios in the presence of helium gas using a multiple collector mass spectrometer comprising the steps of:

generating from a sample ions (6) which have an initial kinetic energy;

dispersing said ions (6) according to their momentum by means of a magnetic sector analyzer (5) thereby producing a plurality of ion beams (8,9,10) each of which substantially comprises ions of a different mass to charge ratio and focusing each of said plurality of ion beams (8,9,10) to a different position in a focal plane (14), said plurality of ion beams (8,9,10) comprising a first ion beam (9) comprising the minor isotope HD^+, a second ion beam (10) comprising He^+ ions that is more intense than said first ion beam and a third ion beam (8) comprising the major isotope H_2^+;

receiving ions comprised in said first ion beam (9) that have a mass to charge ratio of 3 in first ion detection means (15,16,17);

receiving ions having a mass to charge ratio of 2 in said third ion beam (8) in second ion detection means (22);

intercepting said second beam (10) by disposing a beam stop (21) in its path, said second beam (10) comprising ions having a mass to charge ratio of 4; and

determining from signals generated by said first (15,16,17) and second (22) ion detection means the ratio of the number of HD^+ ions having a mass to charge ratio of 3 to the number of H_2^+ ions having a mass to charge ratio of 2;

wherein the ions are energy filtered after they have entered said first ion detection means (15,16,17) to allow only ions having said initial kinetic energy to reach a

collection electrode (17) and thereby to generate said signal from said first ion detection means (15,16,17).

6. A method as claimed in claim 5, further comprising converting hydrogen isotopes present in a sample to H_2, HD and D_2 in a flow of helium gas by a continuous flow inlet system prior to the generation of said ions (6).

7. A method as claimed in claim 5 or claim 6, wherein said energy filtering is carried out by a cylindrical sector analyzer which focuses ions having said initial kinetic energy into a collector electrode (17).

8. A method as claimed in any one of claims 5, 6 or 7, wherein said collector electrode (17) comprises a Faraday bucket collector electrode.

20208-1731

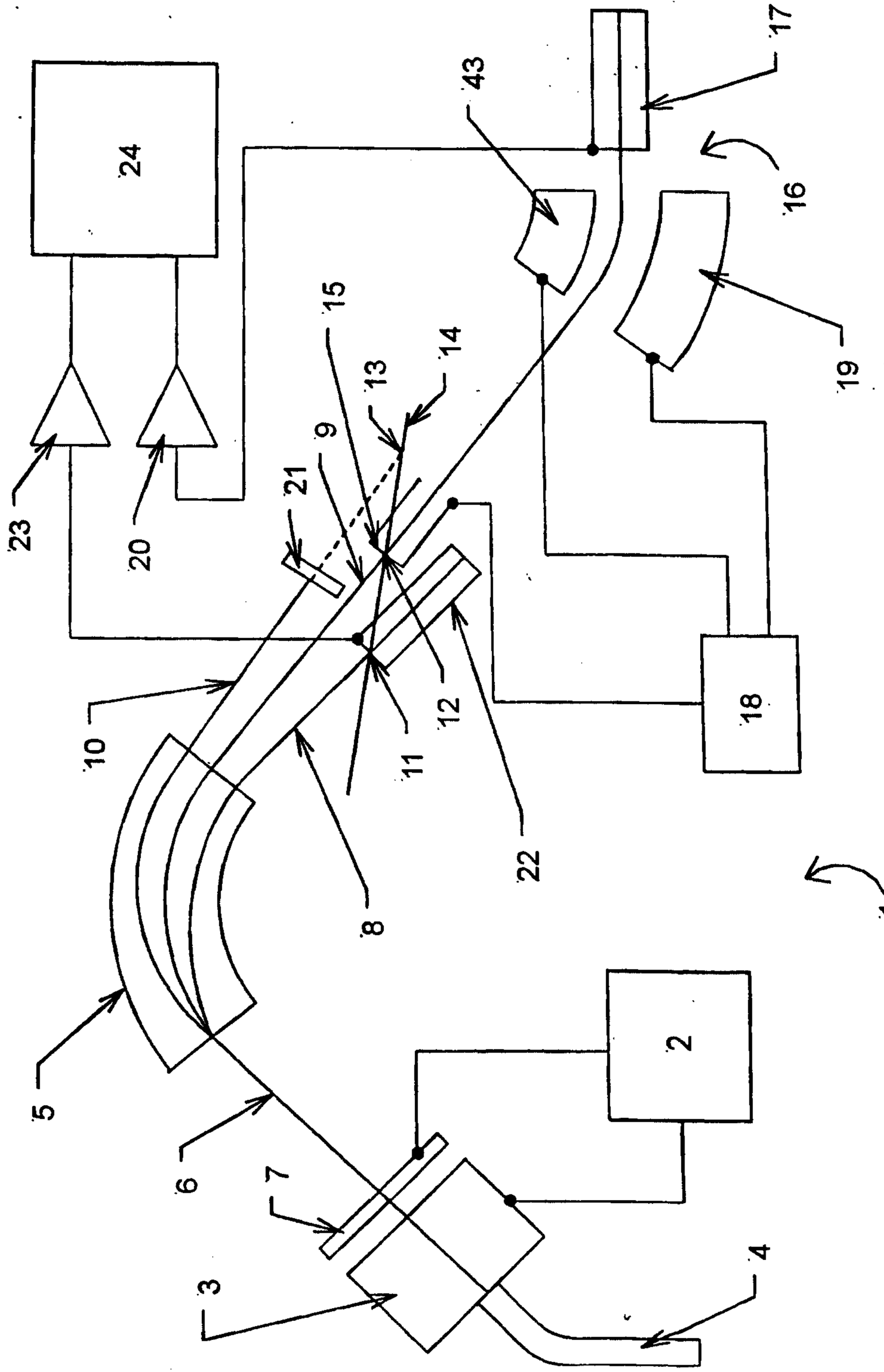


FIGURE 1

20208-1731

FIGURE 2

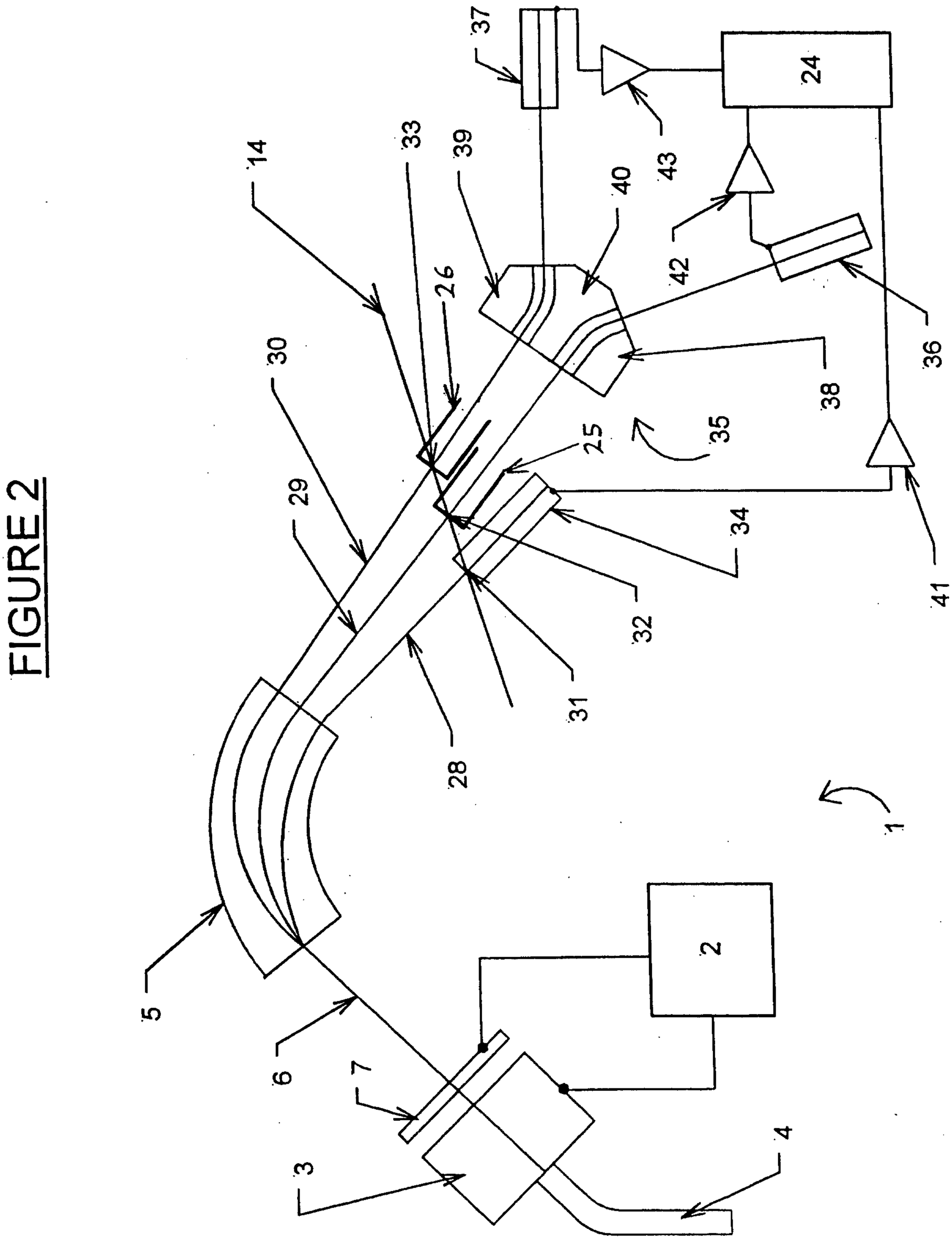
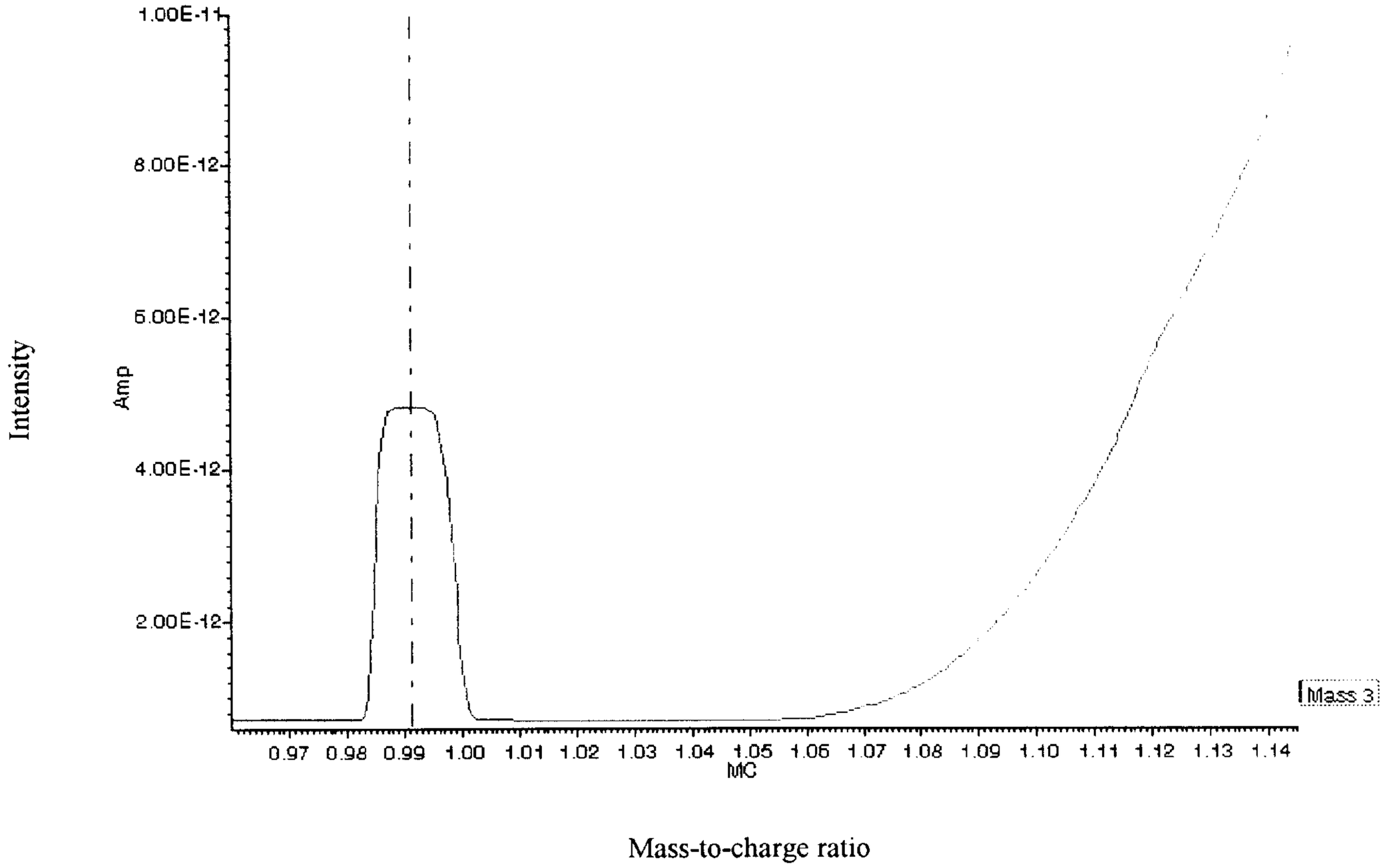
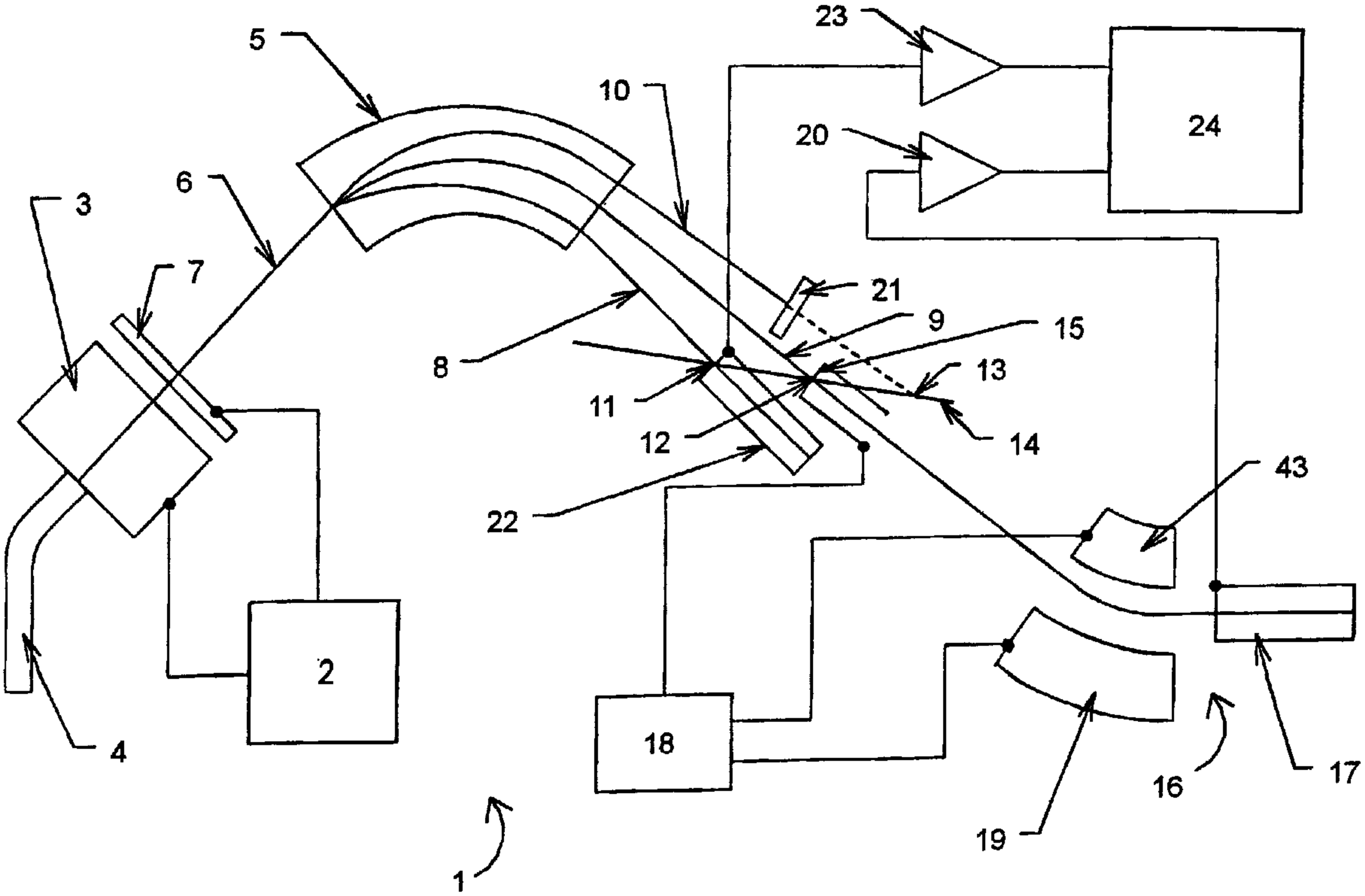


FIGURE 3


Intensity
Amp
1.00E-11
8.00E-12
6.00E-12
4.00E-12
2.00E-12
0.97 0.98 0.99 1.00 1.01 1.02 1.03 1.04 1.05 1.06 1.07 1.08 1.09 1.10 1.11 1.12 1.13 1.14
MC
Mass 3
Mass-to-charge ratio


5
6
3
7
10
8
11
12
22
23
20
24
21
9
15
13
14
43
2
4
18
19
16
17
1