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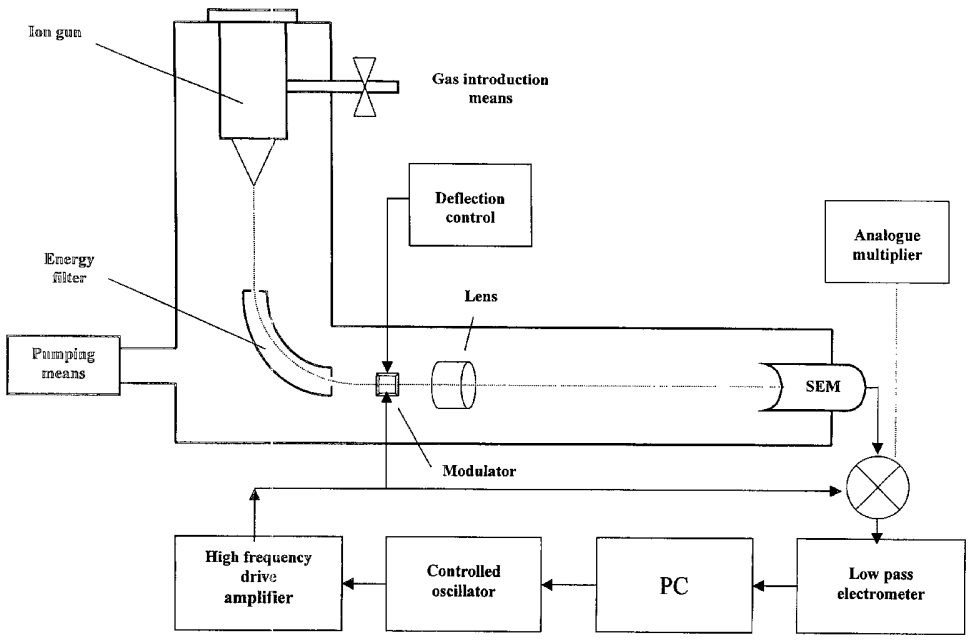
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(54) Title: TIME-OF-FLIGHT MASS SPECTROMETER WITH AN ION SOURCE EMITTING CONTINUOUSLY



(57) Abstract: The present invention relates to an advanced time-of-flight mass spectrometer. Due to the application of an analogue multiplier (12) no higher harmonics appear in the time-of-flight spectra obtained. The mass spectrometer according to the invention also has an extremely high resolution.

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TIME-OF-FLIGHT MASS SPECTROMETER WITH AN ION SOURCE EMITTING CONTINUOUSLY

The present invention relates to time-of-flight (TOF) mass spectrometry, in particular to such type of a TOF mass spectrometer (TOFMS) that operates with an ion source emitting continuously in time. The present invention specifically deals with a new concept of eliminating certain deficiencies of TOFMS of this type in order to provide an apparatus useful in practice.

TOF mass spectroscopy is a special branch of mass spectroscopy; it is used to determine the chemical composition of a given sample. The sample to be analyzed can equally be gaseous, liquid or solid. For the analysis, a tiny part of the sample should be ionized and admitted into the vacuum chamber of a mass spectrometer apparatus which consequently separates the ions with respect to their mass/charge ratios. Most of the ions are single-charged, so the spectrum finally obtained is simply referred to as a mass spectrum. Separation of the ions can take place either in space, ie. ions of different mass/charge ratios arrive at various locations, or in time, ie. ions of different mass/charge ratios arrive at the same location, however, at different times. The present invention is based on the latter type of ion separation technique. To reach the mass separation needed, all mass spectrometer apparatuses exploit electric and/or magnetic fields. That is why there is a need for generating ions from the sample; it is the charge of the ions that is able to interact with the fields applied.

Numerous publications deal with TOF mass spectrometry, note eg. the paper by B.A. Mamyrin entitled *Time-of-flight mass spectrometry (concepts, achievements and prospect)* published in International Journal of Mass Spectrometry 206 (2001) pp. 251 to 266, which gives a concise overview on development of measuring techique used in the field of TOF mass spectroscopy.

The operating principle of TOFMS apparatuses is as follows: in an ion source ions are generated which due to the acceleration effect of an electric field applied reach the same level of kinetic energy. As the ions have velocities inversely proportional to the square root of their mass/charge ratios, it takes

them a definite time to fly over a given distance; the time of their flight is proportional to the square root of their mass/charge ratio. Hence, the time of the flight serves as the mass information sought.

The time of the flight can be determined basically in two ways.

The first possibility is that the launch of the ions takes place in a pulsed manner. Here the time of their flight can be determined as a difference between the time of arrival recorded and the time of launch. The pulsed type launch of ions can be carried out with either a pulsed ionization or gating of a continuously emitting ion source in a pulsed manner. The width of the launching pulse, however, should be short in time because when the difference between the times of flight of two ions with neighbouring mass numbers is smaller than the width concerned, the spectrometer is not able to discriminate the two ions, ie. the spectrometer's resolution is limited by the width of the launching pulse. For recent apparatuses of the pulsed type the magnitude of the width of the launching pulse is about 10 ns. Various developments of the pulsed type apparatuses are disclosed eg. in US Patent Nos. 6,011,259; 5,973,322; 5,955,730; 5,869,829; and 5,969,350 to mention without limitation only few of the documents.

The second possibility is that the generation of ions takes place continuously and stationarily in time, ie. not in a pulsed manner. The obtained flow of ions is modulated in intensity by a cosine function of time at the beginning of the drift tube, and the frequency of the modulating signal is increased uniformly and continuously. Just before the detection, ie. at the end of the drift tube, the flow of ions is again subjected to a modulation in intensity. Both of the modulators are driven by the same signal. Furthermore, the magnitude of the current signal detected and its phase relative to that of the modulating signal are recorded for all the frequencies used for modulation. The TOF spectra are generated from the signal so detected by utilizing a Fourier transformation.

US Patent No. 4,707,602 discloses a method and a TOF apparatus operating in the Fourier mode, ie. with a continuously emitting ion source instead

of pulses of ions. The apparatus claimed contains an evacuable envelope, an ion source with a substance to be analysed emitting continuously, a drift tube of sub-atmospheric pressure, ion accelerating means in the form of a grid assembly and steering plates, detector means for detecting flow of ions, a modulator for modulating the flow of ions at a given modulation frequency, a frequency generator for providing uniform changes in the modulation frequency and transforming means for generating a mass spectrum of the substance under study from the signals recorded by the detector.

The apparatus of US-4,707,602 exhibits essentially two major advantegous features opposed to a TOFMS operating with a pulsed excitation of ions. On the one hand, the excitation is characterized by a duty cycle (percentage of the time when the excitation is active) of about 0,25, while that of an apparatus of a pulsed ion emission is only about 10^{-4}. On the other hand, the difficulties emerging due to the space charge present within the flow of ions become much easier to handle as the space charge density of a flow of ions, due to a longitudinal spread-out, is much lower than what is observed in ion bunches present in apparatuses exploiting a pulsed type of ion emission.

Besides the above advantages, a TOFMS of the present type also exhibits some limitations and disadvantages with regard to the measurement and interpretability of data. The difficulties basically relate to the modulation of the intensity of the flow of ions.

One of the disadvantages is that due to the modulation higher harmonics appear naturally in the TOF spectra because the modulation is a nonlinear process. The higher harmonics, nevertheless, should be filtered out as they make the interpretation of data difficult or in certain cases can even lead to a misinterpretation thereof. For example, driving the modulator of the apparatus described in US-4,707,602, ie. the grid assembly with a pure cosine waveform does not guarantee automatically that the intensity of the flow of ions will also follow a pure cosine waveform. Hence, the TOF spectra obtained will contain higher harmonics that should be dealt with. It is noted that neither an effort nor a hint for realizing a modulation of pure cosine type is mentioned in US-4,707,602.

Another disadvantage emerges in terms of the time resolution of the apparatus. The time resolution is roughly equal to the period associated with the highest modulation frequency applied. One of the aims in a measurement is to reach the highest possible time resolution. This requires increasing the modulation frequency up to as high as possible. However, the longitudinal extension of the modulator (ie. its dimension in the direction of the flow of ions) has a crucial effect on the maximal value of the modulation frequency of the flow of ions. If the effective wavelengths for the flow of ions are defined by the distances being covered during one period of the modulating signal at a given beam voltage by various ion species having definite mass/charge ratios, the shortest wavelength observable is just equal to the longitudinal extension of the modulator. This means that shorter wavelengths (and higher modulation frequencies) of the flow of ions require smaller longitudinal extension of the modulator. The apparatus of US-4,707,602 equipped with steering plates as part of the modulator exhibits relatively large longitudinal dimension which leads to a time resolution that should be improved.

The object of the present invention is therefore to eliminate, or at least to reduce the deficiencies of known TOFMS apparatuses used in Fourier mode, ie. to provide such an advanced TOFMS apparatus that is able on the one hand to operate at a modulation frequency being sufficient for ensuring a high resolution of the obtained mass spectra, and on the other hand to record TOF spectra free from undesirable higher harmonics being preclusive of interpreting the data.

Our investigations led us to the conclusion that the aimed object can be reached by utilizing (i) an analogue multiplier assuring a modulation of a pure cosine type during processing of the current signals detected, and (ii) a new type of modulator with small longitudinal extension. A rigorous mathematical basis in support of the use of an analogue multiplier can be found in the paper of Gy. Hars and I. Maros entitled *Time-of-flight (TOF) mass spectrometer without pulses of any kind, with continuous ion introduction* published in International Journal of Mass Spectrometry 225 (2003) pp. 101 to 114.

The aimed object of the present invention is reached in a first aspect by constructing of a TOFMS wherein the electronics comprises an analogue multiplier, and the output of the frequency generator is connected simultaneously (i) to the modulator and (ii) to a first input of the analogue multiplier, optionally via the broad band power amplifier; the output of the detector is connected to a second input of the analogue multiplier, optionally via the signal preamplifier; the output of the analogue multiplier is connected to a data acquisition channel of the controlling and processing unit, optionally via the low pass filter.

The aimed object of the present invention is reached in a second aspect by preparing a modulator that is built up of a deflection unit and a pass unit separated by a certain distance; the deflection unit is prepared from two narrow sheet members each having a slit in the middle formed congruently, the sheet members are arranged one after the other in a transverse position relative to the path of the flow of ions and bound together via adjacent sides thereof, wherein one of the adjacent sides is insulating and the other one carries a pair of metallic deflection strips extending along the longitudinal edges of the slit formed therein, while the remaining free sides of the sheet members are metallic; the pass unit is prepared in the form of a single member made of a thin metal sheet having a slit in the middle being congruent with the slits of the sheet members of the deflection unit; and the metallic regions of the deflection unit and the pass unit are equally grounded.

Preferably, the modulator has a longitudinal extension comparable to the distance covered by the flow of ions during a period associated with the upper limit for the predefined range of frequencies.

The invention and its operating principle will be explained in detail via a particular embodiment with reference to the accompanied drawings and to an example, wherein

Figure 1 shows a schematic block diagram of an advanced time-of-flight mass spectrometer (TOFMS) according to the invention equipped with an analogue multiplier;

Figure 2a is the longitudinal sectional view of the modulator used in the TOFMS according to the invention;

Figure 2b shows front views of each building member of the modulator;

Figure 3 is a further embodiment of the TOFMS apparatus according to the invention as used in the Example;

Figure 4 is a plot of the current signal (in arbitrary units) versus the modulation frequency (in units of kHz) detected by the detector;

Figure 5 is the fast Fourier transform (FFT) of Fig. 4; and finally

Figures 6 and 7 are exemplary mass spectra derived from Fig. 5 by expressing the intensity on a linear and on a logarithmic scale, respectively, taken on ambient air.

Referring to Fig. 1, a TOFMS apparatus according to the invention comprises an ion source 2 operating continuously within a vacuum chamber 1, various ionoptical elements (not shown), an electrostatic reflector or an energy filter 3, a detector 4 preferably in the form of a secondary electron multiplier (SEM) and an electronics connected to the vacuum chamber 1 from the outside for control. The pressure of the residual gas in the vacuum chamber 1 is maintained below about 10^{-6} mbar by means of a *per se* known pumping assembly (not shown) connected from the outside to the vacuum chamber 1. As a result of the continuous operation of the ion source 2 a flow of ions 7 of a substance to be analyzed is generated. As it is known, the substance can be either combined with the ion source 2 or introduced to the ion source 2 from the outside in a manner (eg. through an introduction means) known in literature. In between the energy filter 3 and the detector 4 a special modulator 5 (to be discussed later) with small longitudinal extension is placed in order to accelerate and modulate the flow of ions 7 therethrough. Behind the modulator 5 a free drift space 6 is formed.

The electronics comprises a signal preamplifier 11, an analogue multiplier 12, a low pass filter 13, a controlling and processing unit 10 preferably in the form of a personal computer (PC), a frequency generator 9 of programmed frequency, preferably in the form of an oscillator, for sweeping over a predefined

range of frequencies and a broad band power amplifier 8 for driving the modulator 5 at different modulation frequencies. The cut-off frequency of the low pass filter 13 is about several kHz. The frequency bandwidth of the broad band power amplifier 8 is equal to the highest modulation frequency applied. The latter ranges from about 1 MHz up to about several hundreds of MHz.

As for the electronics, the output of the detector 4 is connected directly to the input of the signal preamplifier 11. The output of the signal preamplifier 11 is directly connected to an input of the analogue multiplier 12. To a second input of the analogue multiplier 12 the modulating signal generated by the frequency generator 9 and optionally amplified by the broad band power amplifier 8 is fed. The output of the analogue multiplier 12 is connected to a data acquisition channel of the controlling and processing unit 10 via the low pass filter 13. At the same time a control output of the controlling and processing unit 10 is connected directly to the frequency control input of the frequency generator 9. The output of the frequency generator 9 is connected to the modulator 5 via the broad band power amplifier 8 in order to drive it.

The TOFMS apparatus according to the invention operates as follows.

The flow of ions 7 generated by the ion source 2 travels through the energy filter 3, the modulator 5, and the drift space 6 and finally reaches the detector 4. The modulator 5 modulates the flow of ions 7 in intensity at a given frequency generated by the frequency generator 9. The modulated flow of ions 7 reaching the detector generates an electric signal therein. The signal which is a mixture of the first harmonic and many higher harmonics is led out from the vacuum chamber 1 and after having been subjected to a preamplification by means of the signal preamplifier 11, it is fed into the analogue multiplier 12, instead of a customarily used demodulator. Furthermore, contrary to the known processing methods wherein at this stage a second modulation or, if one prefers a demodulation takes normally place, the signal is subjected to an analogue multiplication with the driving signal also applied to the modulator 5. Since after a proper adjustment the analogue multiplier 12 can be considered as an electronic device generating a pure cosine waveform, the multiplication results in an output

signal of a pure cosine waveform, which means that all the higher harmonics are cancelled out or filtered from the signal. As a next step, this output signal is fed via the low pass filter 13 into the controlling and processing unit 10, which stores it for further processing and instructs the frequency generator 9 to generate the next driving signal of a higher frequency.

After the available frequency range has been swept over in given (preferably uniform) steps, the signal data acquisited are processed in a traditional way (ie. by being subjected to eg. a fast Fourier transformation) in order that a mass spectrum be generated. Some illustrative spectra can be seen in Figs. 5 to 7.

As it was mentioned earlier another major limiting factor is the time during which a certain ion travels through the modulator. Obviously, when this duration becomes equal to the period of the modulating voltage applied, no deflection will occur. This means that in order to reach a sufficiently high modulation frequency the modulator must have a very small dimension in parallel with the flow of ions.

Figures 2a and 2b show a preferred embodiment of the modulator 5 used in the TOFMS apparatus according to the invention. It is basically built up of two components, a deflection unit 5a and a pass unit 5b, which are parallel to each other and arranged downstream in this order in the path of the flow of ions 7 perpendicular to the path. Furthermore, the two units are apart from each other by a distance ranging about 10 to 30 mm.

The deflection unit 5a comprises two identical, generally circular members. Each member is made of a two-sided sheet of printed circuit board with a (deflection) slit 15 in the middle. The pass unit 5b is a single member made of a thin metal sheet with a (pass) slit 18 in the middle. It has also a circular shape in general and is grounded. The slits 15, 18 are aligned essentially congruently, their width and length is about 1 mm and about 10 mm, respectively.

In Fig. 2b the sides (denoted by A to F) of the members can be seen. Here hatching represents metallization of a certain area, while the areas without hatching denote insulator regions. As can be seen from the figure, one of the

sides of the first member of the deflection unit 5a is fully metallized forming a screening plate 16, while the other side of the same member is without metallization, ie. it is left insulator. One of the sides of the second member of the deflection unit 5a is again fully metallized, so it also forms a screening plate 16, while a pair of deflection strips 14 extending parallel on both edges of the slit 15 is formed on the other side of the second member. In order to prepare the deflection unit 5a the two members at issue are combined together by means of bonding the insulator side B and the side C carrying the deflection strips 14 together keeping the slits 15 aligned. The outer sides A and D of the deflection unit 5a, ie. the screening plates 16 are grounded and serve to prevent the build-up of a stray electric field which in turn would distort the path of the flow of ions 7 approacing to and departing from the pair of deflection strips 14. The deflection strips 14 are narrow, ie. they are about 1 to 2 mm in width, and formed with a small surface area in order that their capacity relative to that of the screening plates 16 grounded be as small as possible for facilitating high frequency applications.

Finally an example is presented to demonstrate the practical aspects of the improved technique according to the invention.

Here, the operation of the apparatus is demonstrated for ambient air introduced intentionally into the apparatus. The background pressure was kept as low as 10^{-6} mbar, the air introduced represents 7×10^{-6} mbar. The expected minor components are the usual water vapor and some carbon dioxide present at 18 and 44 atomic mass units (AMU), respectively.

Referring to Fig. 3, an embodiment of the apparatus according to the invention consists of the following major parts: a vacuum chamber with pumping means for providing low pressure therein, a source of ions embodied in the form of a gas introduction means and an ion gun for ionizing the molecules/atoms of the gas to be analyzed, an energy filter, an Einzel lens, a SEM detector, a modulator according to the invention with deflection control, an analogue multiplier (type 796), a high frequency drive amplifier, a controlled oscillator, a broad band low pass electrometer and a personal computer for controlling the

setup and processing the data obtained. The Einzel lens serves to prevent beam divergency and to focus the flow of ions onto the detector. During measurements the vacuum is kept in the order of 10^{-6} mbar.

The ion gun provides a primary ion current of 100 nA at the beam voltage of 1 kV. The modulator in its original concept is simply a pair of deflection plates followed by an aperture as shown earlier in Fig. 2a. The intensity of the ion flow can easily be modulated by deflecting and conducting it through an aperture as it was already mentioned earlier.

The actual measurement is carried out by increasing the modulation frequency from 1 MHz up to 8 MHz uniformly in 4096 steps. Followed by low pass filtering, the output of the analogue multiplier is recorded for each frequency. A single cycle lasts for 3 ms, so the measurement takes about 13 seconds. The data collected are shown in Fig. 4 as a function of the modulation frequency.

After finishing with acquisition of data points a fast Fourier transformation (FFT) algorithm is effected in order to withdraw information on the composition of the sample, here of air introduced intentionally. The FFT transformation of Fig. 4 results in Fig. 5, which contains 4096 points and is symmetrical due to the properties of the Fourier transformation. For the sake of easier understanding the horizontal axis is converted into AMU units. Figures 6 and 7 show spectra of air investigated up to 150 AMU with the intensity expressed on a linear and on a logarithmic scale, respectively. In the figures at issue the peaks of nitrogen and oxygen at 28 and 32 AMU, respectively, clearly show up. The nitrogen peak is roughly five times higher, which is the expected ratio, similar to natural air. Due to the application of the analogue multiplier electronics according to the invention, however, no higher harmonic peaks appear in the spectra, since the modulation applied is almost a perfect cosine one, in contrast to ion beam modulation carried out in the vacuum chamber.

CLAIMS

1. An advanced time-of-flight mass spectrometer comprising

a vacuum chamber (1) for containing elements of the spectrometer at sub-atmospheric pressure equipped with a pumping means;

an ion source (2) arranged within the vacuum chamber (1) emitting a continuous flow of ions (7) of a substance to be analyzed;

an energy filter (3), a modulator (5) for modulating the flow of ions (7) in intensity at uniformly distributed frequencies within a predefined range of frequencies, a field-free drift space (6) and a detector (4) for detecting the flow of ions (7) and generating a current signal in response, wherein all these elements are arranged along the path of the flow of ions (7) within the vacuum chamber (1) one after the other in the given order; and

an electronics containing a controlling and processing unit (10) provided with at least a control output and a data acquisition channel, a frequency generator (9) for sweeping over the predefined range of frequencies connected to the control output of the controlling and processing unit (10) and optionally a signal preamplifier (11), a low pass filter (13) and a broad band power amplifier (8),

characterized in that

the electronics comprises an analogue multiplier (12), and

the output of the frequency generator (9) is connected simultaneously (i) to the modulator (5) and (ii) to a first input of the analogue multiplier (12), optionally via the broad band power amplifier (8);

the output of the detector (4) is connected to a second input of the analogue multiplier (12), optionally via the signal preamplifier (11);

the output of the analogue multiplier (12) is connected to a data acquisition channel of the controlling and processing unit (10), optionally via the low pass filter (13).

2. The time-of-flight mass spectrometer according to Claim 1, **characterized in** that the frequency bandwidth of the broad band power

amplifier (8) and that of the signal preamplifier (11) are equal to the upper limit for the predefined range of frequencies.

3. The time-of-flight mass spectrometer according to Claim 2, **characterized in** that the upper limit for the predefined range of frequencies ranges from about 1 MHz up to several hundreds of MHz.

4. The time-of-flight mass spectrometer according to any of the preceding Claims, **characterized in** that ionoptical elements are arranged for focusing the flow of ions (7) onto the detector (4) at the beginning of the drift space (6) in the path of the flow of ions (7).

5. The time-of-flight mass spectrometer according to Claim 4, **characterized in** that the ionoptical elements are made in the form of an Einzel lens.

6. The time-of-flight mass spectrometer according to any of the preceding Claims, **characterized in** that the modulator (5) has a longitudinal extension comparable to the distance covered by the flow of ions (7) during a period associated with the upper limit for the predefined range of frequencies.

7. The time-of-flight mass spectrometer according to any of the preceding Claims, **characterized in** that

the modulator (5) is built up of a deflection unit (5a) and a pass unit (5b) separated by a certain distance;

the deflection unit (5a) is prepared from two narrow sheet members each having a slit (15) in the middle formed congruently, the sheet members are arranged one after the other in a transverse position relative to the path of the flow of ions (7) and bound together via adjacent sides (B; C) thereof, wherein one of the adjacent sides (B; C) is insulating and the other one carries a pair of metallic deflection strips (14) extending along the longitudinal edges of the slit (15) formed therein, while the remaining free sides (A; D) of the sheet members are metallic;

the pass unit (5b) is prepared in the form of a single member made of a thin metal sheet having a slit (18) in the middle being congruent with the slits (15) of the sheet members of the deflection unit (5a); and

the metallic regions of the deflection unit (5a) and the pass unit (5b) are equally grounded.

8. The time-of-flight mass spectrometer according to Claim 7, **characterized in** that the distance between the deflection unit (5a) and the pass unit (5b) ranges from about 10 mm to about 30 mm.

9. The time-of-flight mass spectrometer according to Claim 7 or 8, **characterized in** that the width and the length of the slits (15, 18) is about 1 mm and about 10 mm, respectively.

10. The time-of-flight mass spectrometer according to any of the preceding Claims, **characterized in** that the deflection strips (14) are formed narrow and with a small surface area relative to the metallic free sides (A; D) of the sheet members.

11. The time-of-flight mass spectrometer according to Claim 10, **characterized in** that the deflection strips (14) are about 1 mm to 2 mm in width.

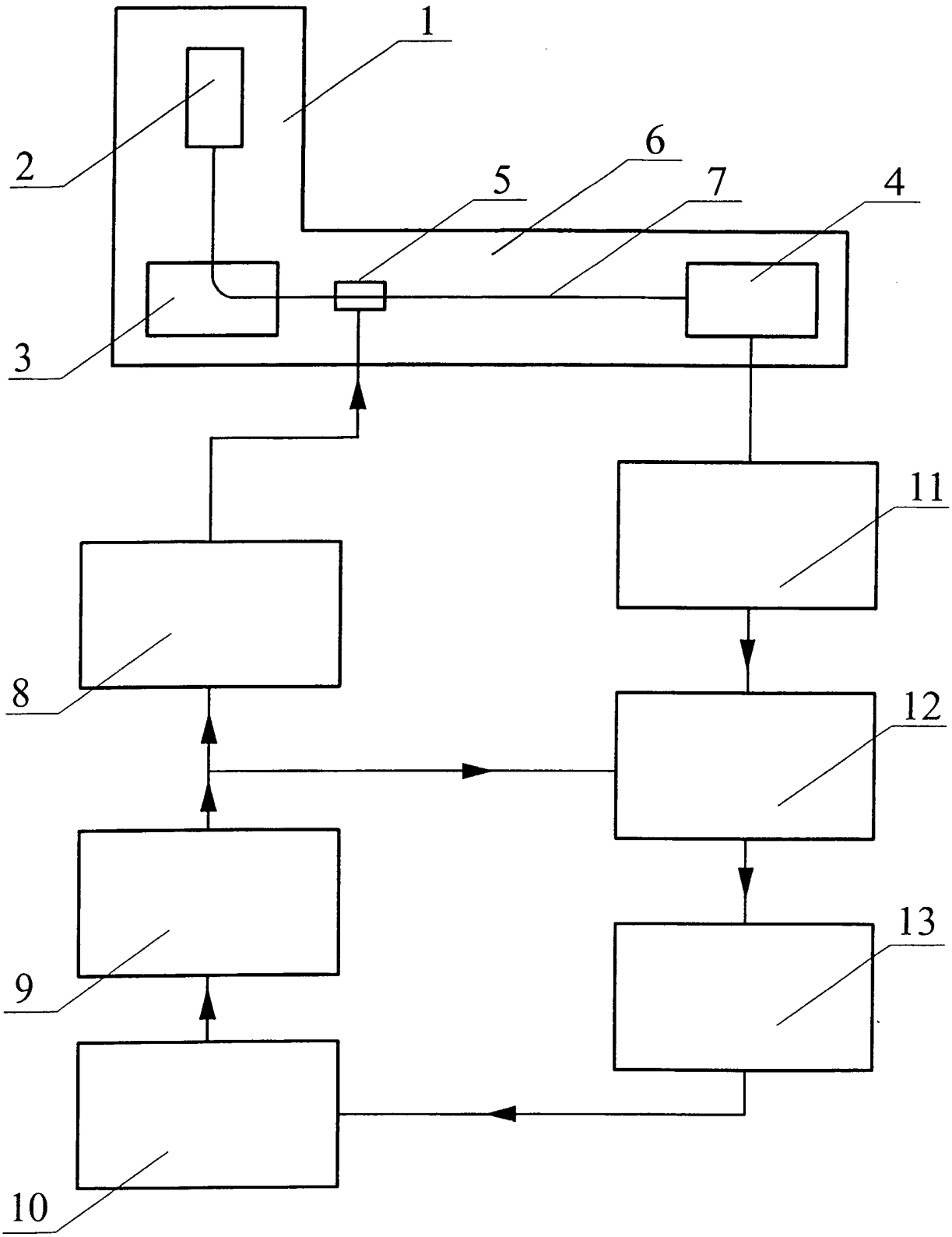


Figure 1

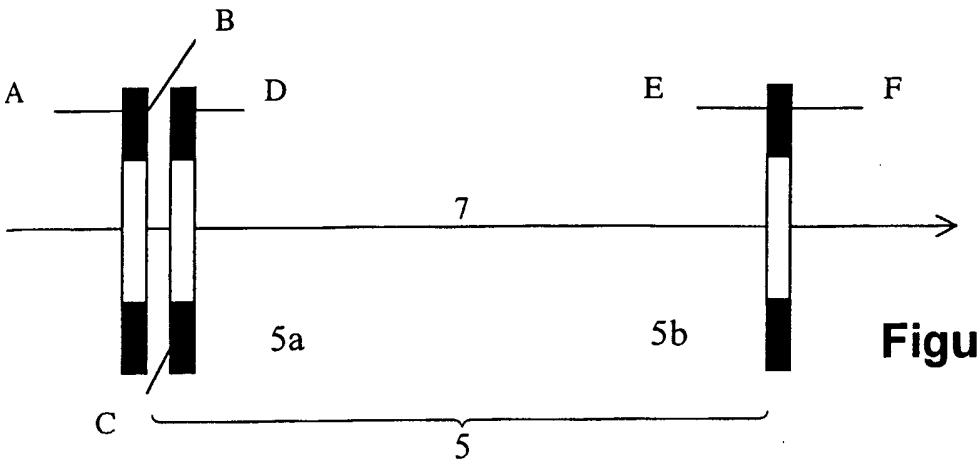


Figure 2a

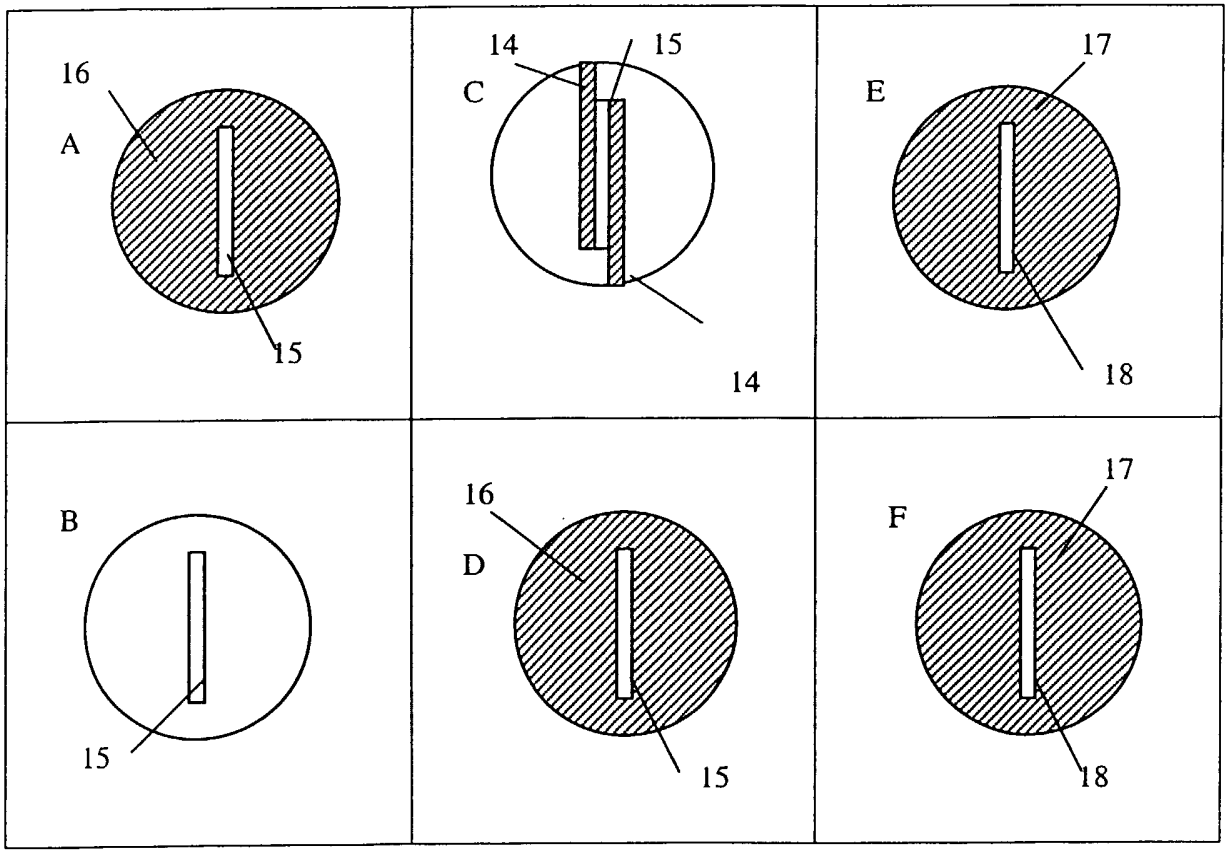


Figure 2b

Figure 3

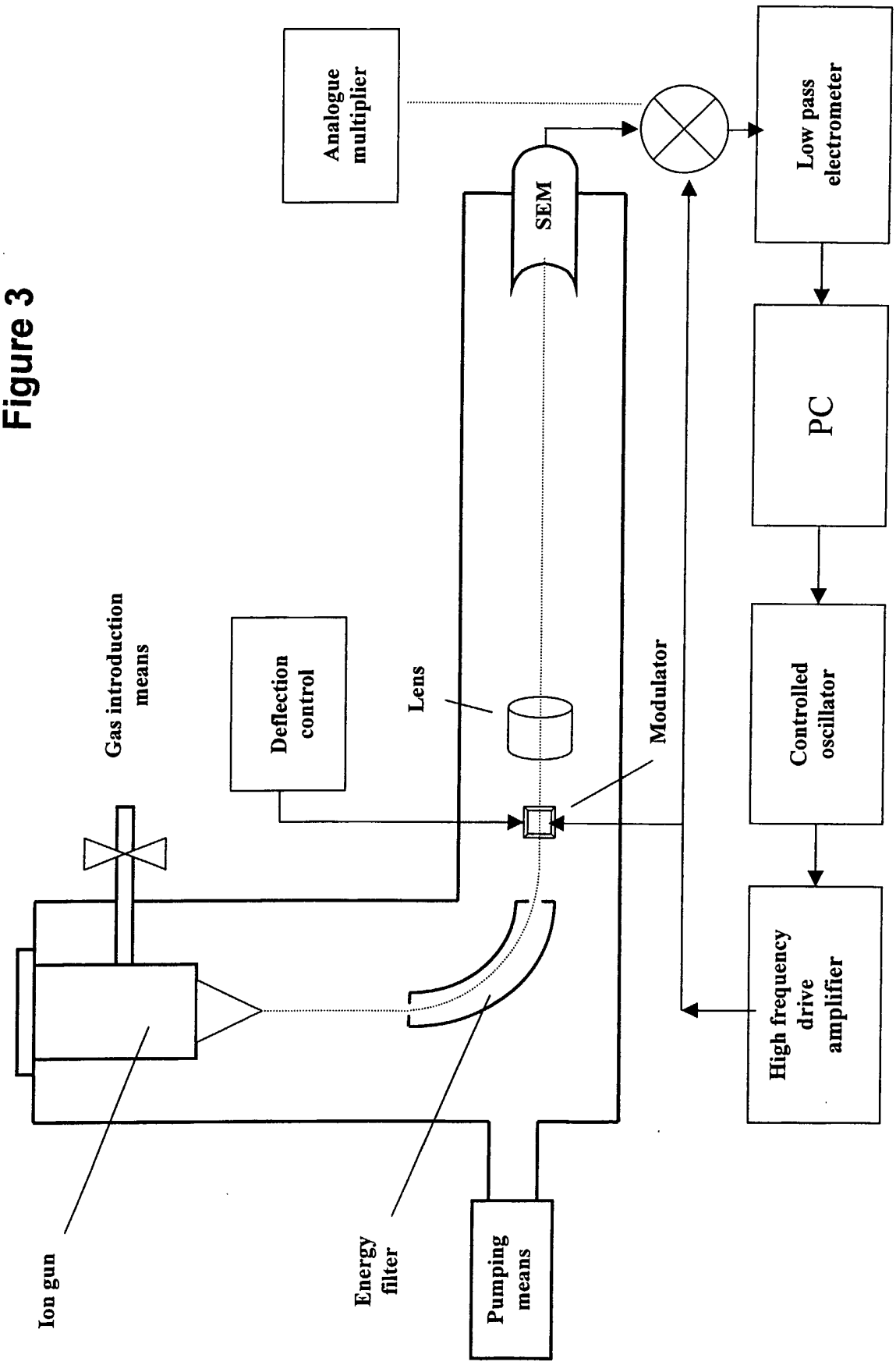

Analogue multiplier
Low pass electrometer
SEM
PC
Controlled oscillator
High frequency drive amplifier
Modulator
Lens
Deflection control
Gas introduction means
Ion gun
Energy filter
Pumping means

Figure 4

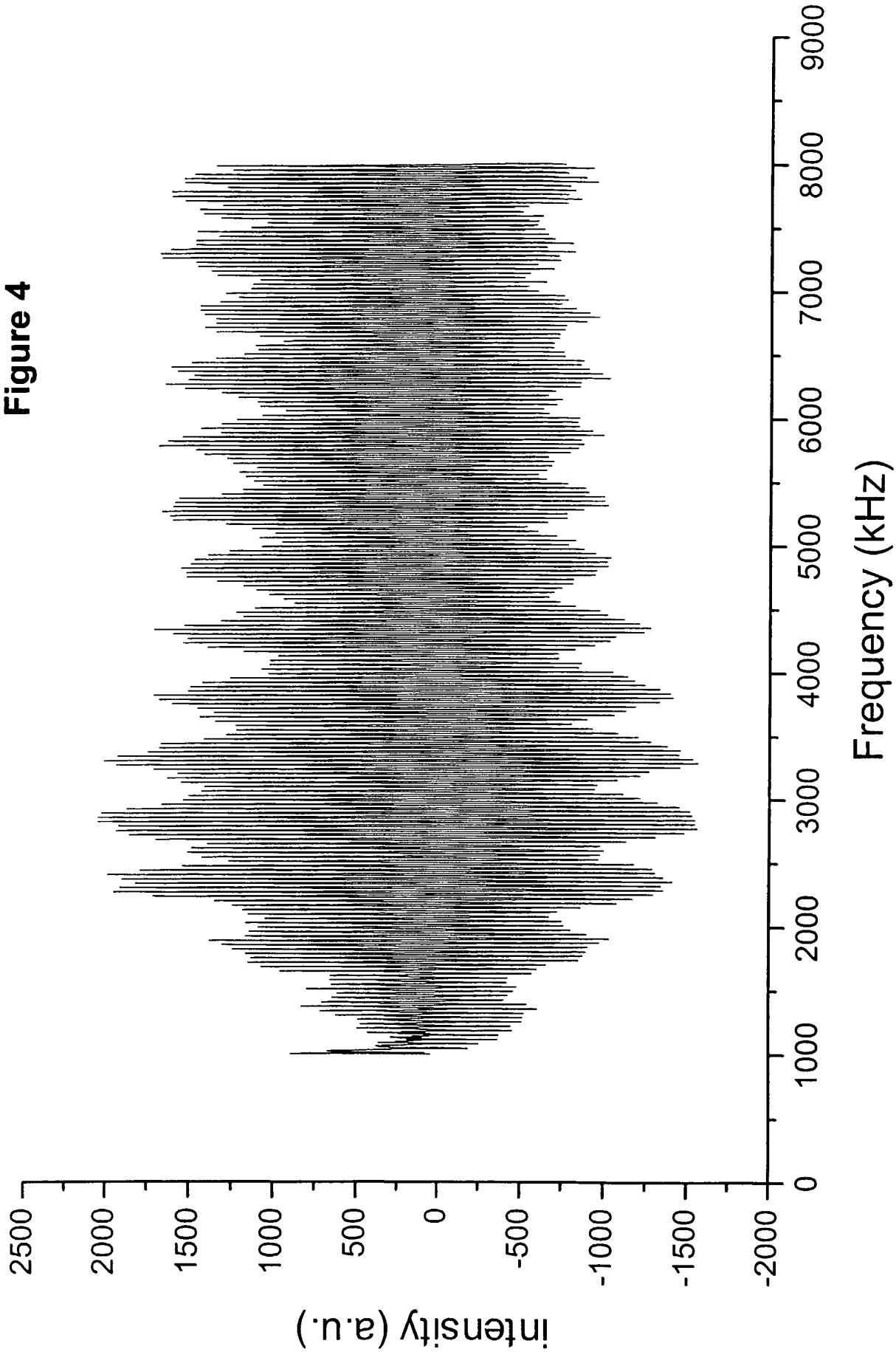

intensity (a.u.)
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
Frequency (kHz)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000

Figure 5

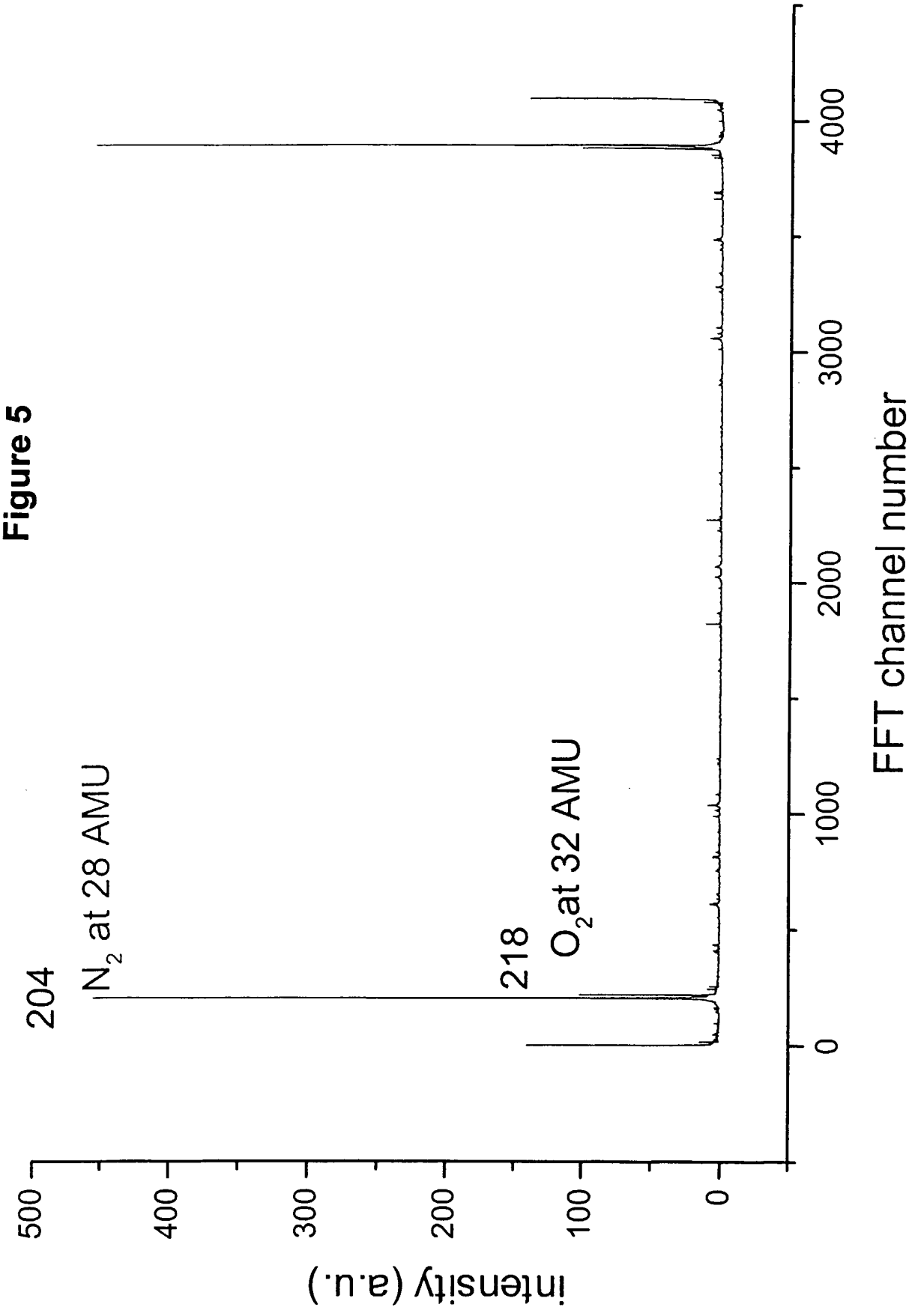

204
N_2 at 28 AMU
218
O_2at 32 AMU
intensity (a.u.)
FFT channel number
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200
300
400
500
0
1000
2000
3000
4000

Figure 6

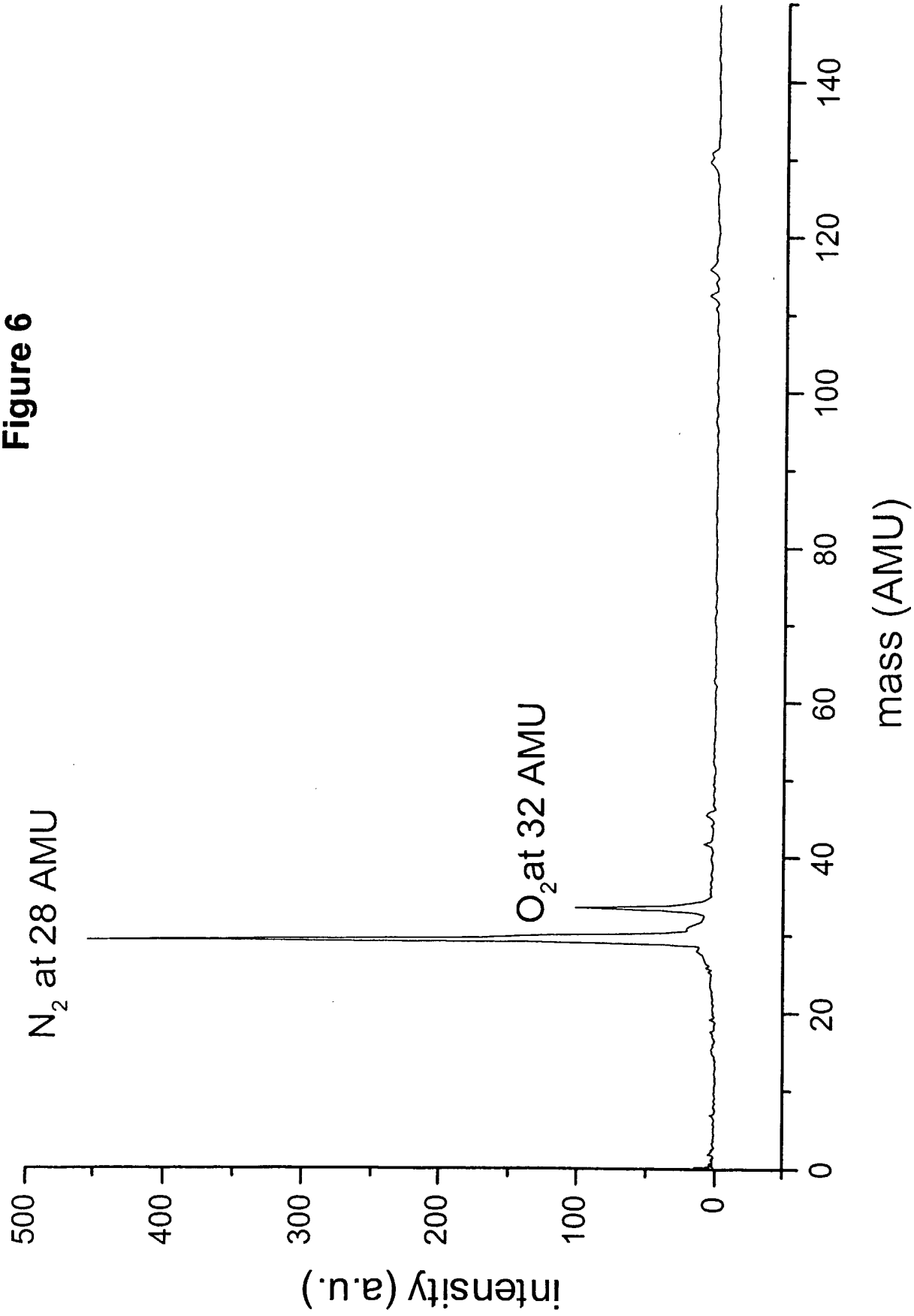
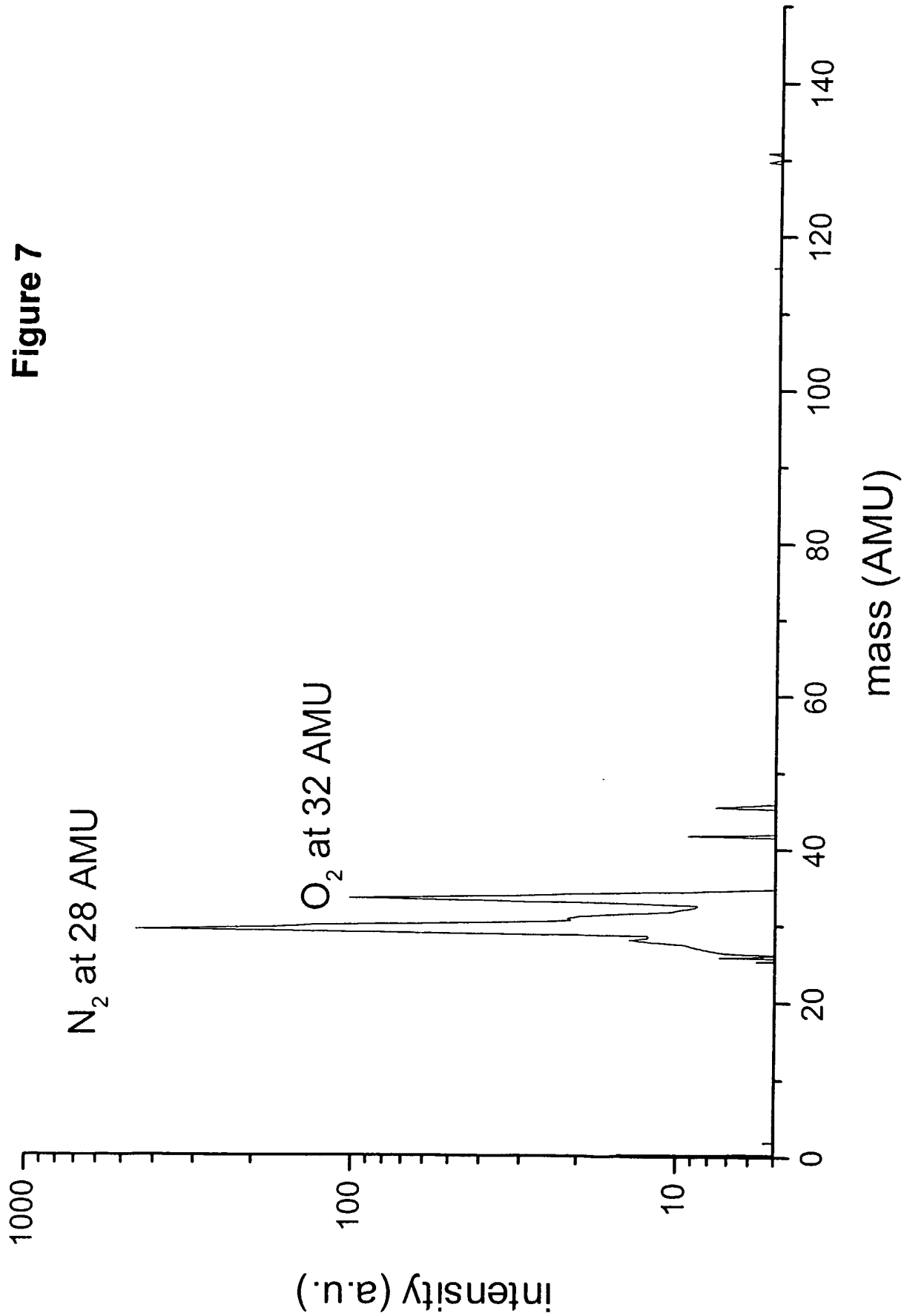

intensity (a.u.)
500
400
300
200
100
0
0
20
40
60
80
100
120
140
mass (AMU)
N_2 at 28 AMU
O_2at 32 AMU

Figure 7


intensity (a.u.)
1000
100
10
0
20
40
60
80
100
120
140
mass (AMU)
N2 at 28 AMU
O2 at 32 AMU

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/HU 03/00037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01J49/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	HARS G ET AL: "Time-of-flight (TOF) mass spectrometer without pulses of any kind, with continuous ion introduction" INTERNATIONAL JOURNAL OF MASS SPECTROMETRY, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 225, no. 2, 15 February 2003 (2003-02-15), pages 101-114, XP004403424 ISSN: 1387-3806 page 102, left-hand column, last paragraph -page 103, right-hand column page 107, right-hand column, paragraph 3 ---	1-8
A	WO 98 08244 A (MILLBROOK INSTR LIMITED ;STEELE TIMOTHY ANDREW (GB); ECCLES ADRIAN) 26 February 1998 (1998-02-26) abstract ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2003	15/09/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hulne, S

INTERNATIONAL SEARCH REPORT

Intern I Application No
PCT/HU 03/00037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 707 602 A (KNORR FRITZ J) 17 November 1987 (1987-11-17) cited in the application abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No
PCT/AU 03/00037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9808244 A	26-02-1998	DE 69703624 D1	04-01-2001
		DE 69703624 T2	28-06-2001
		EP 0919067 A2	02-06-1999
		WO 9808244 A2	26-02-1998
US 4707602 A	17-11-1987	US 4633083 A	30-12-1986