(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 644 344 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
29.04.2020 Bulletin 2020/18

(51) Int Cl.:
H01J 49/14 *(2006.01)* ***H01J 49/04*** *(2006.01)*

(21) Application number: **19196202.6**

(22) Date of filing: **09.09.2019**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **26.10.2018 JP 2018201795**

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(54) GAS ANALYSIS DEVICE AND GAS ANALYSIS METHOD

(57) A gas analysis device of this invention is to conduct a quantitative analysis on a mixed gas containing an object substance to be measured and an object substance not to be measured whose mass number is the same or near that of the object substance to be measured by the use of a quadruple mass spectrometer. The gas analysis device comprises a mixed gas generation mechanism that comprises a heating furnace that heats a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, generates a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and discharges a mixed gas comprising the carrier gas and the sample gas, a quadruple mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that conducts a quantitative analysis on the object substance to be measured by giving energy to the object substance to be measured and the object substance not to be measured in the measurement space, and a pressure control mechanism that adjusts pressure in the measurement space, and the pressure control mechanism adjusts the pressure in the measurement space so as to change the energy that is given to the object substance not to be measured in the measurement space according to the lower limit value of ionization energy of the object substance not to be measured.

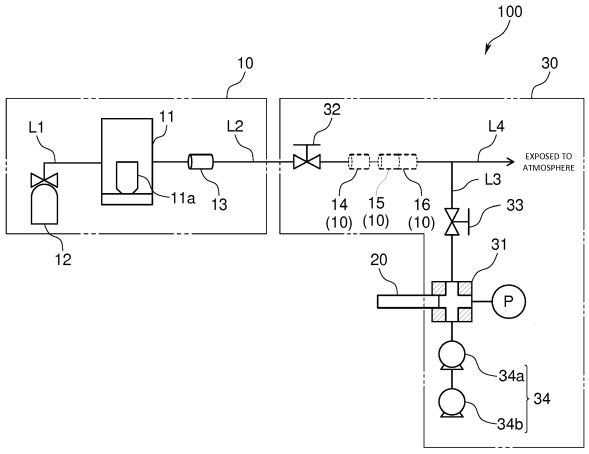

FIG.1

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Description

FIELD OF THE ART

[0001] This invention relates to a gas analysis device and a gas analysis method.

BACKGROUND ART

[0002] A quadruple mass spectrometer 20 has, as shown in Fig. 6, a measurement space (S) into which a gas containing an object substance to be measured is introduced, and an ionization unit 21, a quadrupole unit 22 and a detection unit 23 are arranged inside of the measurement space (S). The quadruple mass spectrometer 20 has a principle wherein the ionization unit 21 applies voltage to the gas introduced into the measurement space (S) and gives and ionizes energy to the substance contained in the gas. Then, the detection unit 23 detects the ionized object substance to be measured that passes the quadrupole unit 22, and conducts a quantitative analysis on the object substance to be measured based on a detection signal (refer to the patent document 1)

[0003] If the quantitative analysis is conducted on the object substance to be measured of the mixed gas (hereinafter also called as the mixed gas) containing the object substance not to be measured whose mass number is the same as or near the mass number of the object substance to be measured by the use of the quadruple mass spectrometer, the detection signal of the object substance to be measured is detected in a state of being overlapped with the detection signal of the object substance not to be measured. Then, the detection signal of the object substance not to be measured becomes an obstruction so that it becomes difficult to conduct the quantitative analysis on the object substance to be measured.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0004] Patent document 1: WO2018 / 056419 A

SUMMARY OF THE INVENTION

PROBLEMS SOLVED BY THE INVENTION

[0005] A main object of this invention is make it possible for a quadruple mass spectrometer to relatively accurately conduct a quantitative analysis on an object substance to be measured of a mixed gas containing an object substance not to be measured whose mass number is the same as or near that of the object substance to be measured.

MEANS TO SOLVE THE PROBLEMS

[0006] In order to solve the above-mentioned problem, the applicant of this invention repeated the experiment to conduct a quantitative analysis on an object substance to be measured contained in the mixed gas by the use of the quadrupole mass spectrometer. As a result of the repeated experiments to conduct the quantitative analysis on the object substance to be measured contained in the mixed gas while changing the pressure in the measurement space of the quadruple mass spectrometer, the applicant found a phenomenon that almost no detection signal of the object substance not to be measured alone is detected when the pressure in the measurement space becomes more than or equal to a predetermined pressure.

[0007] Concretely, the experiment was conducted; while introducing a He gas (the object substance not to be measured) whose mass number is 4 as being the carrier gas into the measurement space of the quadruple mass spectrometer, D_2 (the object substance to be measured) whose mass number is 4 is introduced intermittently at multiple times into the carrier gas, and a signal of He and a signal of D_2 are detected while applying a predetermined voltage to the gas by the ionization unit. This experiment was conducted while decreasing the pressure in the measurement space step by step in an order of 2.0Pa, 1.5Pa, 1.0Pa and 0.75Pa, then a graph shown in Fig. 3 is obtained. In the graph shown in Fig. 3, a vertical axis indicates signal intensity and a horizontal axis indicates elapsed time.

[0008] According to the graph shown in Fig. 3, it is proved that a signal (a detection signal shown by "A" in Fig. 3) is detected for D_2 in spite of pressure drop. Almost no signal (a detection signal shown by "B" in Fig. 3) is detected for He in case that the pressure is 2.0Pa, however, an extremely big signal is detected for He in case that the pressure is decreased to 1.0Pa.

[0009] There exists energy (ionization energy) necessary for ionization in a substance. He is taken as an example, and will be concretely explained. A relation between the energy (a horizontal axis) given to He and a number of ions (a vertical axis) per unit area is a graph shown in Fig. 7. More specifically, the lower limit value of the ionization energy of He is 24.6 eV, and if the energy of the lower limit value is given, ionization starts and ionization is quickly promoted only when the energy increases just a little around the lower limit value. Then, ionization of He is promoted until the ionization energy that is more than or equal to a predetermined value (a value indicated by "C" in Fig. 7) is given, and tends to be gradually suppressed when the given energy becomes more than or equal to the predetermined value. The ionization energy differs for each substance and the above-mentioned tendency also shows the same for other substances.

[0010] The lower limit value of the ionization energy of D_2 is 15.467 eV so that it is smaller than the lower limit

value (24.6 eV) of the above-mentioned He. Then, in case that the energy given to He and D_2 in the measurement space is more than or equal to 15.467 eV and less than 24.6 eV, only the signal of D_2 is detected. In other words, in the graph shown in Fig. 3, in case that the pressure in the measurement space is set 2.0Pa, the reason why only the signal of D_2 is detected can be estimated that the energy given to the object substance to be measured and the object substance not to be measured in the measurement space is more than or equal to 15.267 eV and less than 24.6 eV. In addition, in the graph shown in Fig. 3, when the pressure in the measurement space becomes less than or equal to 1.0 Pa, the signal intensity of He rapidly increases. This reason can be estimated that the pressure in the measurement space rises and the energy given to He in the measurement space becomes more than or equal to 24.6 eV so that ionization is rapidly promoted.

[0011] More specifically, when the pressure in the measurement space is increased, the energy given to the substance in the measurement space becomes smaller. When the pressure in the measurement space is decreased, the energy given to the substance in the measurement space becomes bigger. In a state wherein the pressure in the measurement space of the quadruple mass spectrum is low (in a state wherein a vacuum degree is high), since a number of the substance existing in the measurement space becomes small, it becomes difficult for the substances to collide each other. This makes a state wherein a speed of an electron to ionize the substance is fast, in other words, a state wherein the energy given to the substance becomes big. Meanwhile, in a state wherein the pressure in the measurement space of the quadruple mass spectrum is high (in a state wherein the vacuum degree is low), since the number of the substance existing in the measurement space becomes big, it becomes easy for the substances to collide each other. This makes a state wherein the electron to ionize the substance is prevented from moving so that the speed of the electron is slow, in other words, a state wherein the energy given to the substance becomes small.

[0012] As mentioned above, the applicant of this invention successfully invented the present claimed invention based on the knowledge obtained through the above-mentioned experiments.

[0013] More specifically, the gas analysis device in accordance with this invention comprises a mixed gas generation mechanism that comprises a heating furnace that heats a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, generates a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and discharges a mixed gas comprising the carrier gas and the sample gas, a quadruple mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that conducts a quantitative analysis on the object substance to be measured by giving energy to the object substance to be measured and the object substance not to be measured in the measurement space, and a pressure control mechanism that adjusts pressure in the measurement space, and is characterized by that the pressure control mechanism adjusts the pressure in the measurement space so as to change the energy that is given to the object substance not to be measured in the measurement space according to the lower limit value of ionization energy of the object substance not to be measured.

[0014] In accordance with this arrangement, since the pressure in the measurement space can be adjusted by the pressure control mechanism, it is possible to adjust the energy given to the object substance not to be measured in the measurement space so as to be near the lower limit value of the ionization energy of the object substance not to be measured. Then, it is possible to lessen a signal of the object substance not to be measured detected by the quadruple mass spectrometer in such a degree as not to cause obstruction in conducting the quantitative analysis on the object substance to be measured. As a result of this, even though the object substance not to be measured (concretely, the object substance not to be measured whose mass number falls within a range of ± 4 of the mass number of the object substance to be measured) whose mass number is near the mass number of the object substance to be measured is contained in the mixed gas, it becomes possible to conduct the quantitative analysis on the object substance to be measured accurately by the use of the quadruple mass spectrometer. "Change in accordance with the lower limit value of the object substance not to be measured" includes not only a case wherein change with referring to the lower limit value alone of the object substance not to be measured but also a case wherein change with referring to a difference between the lower limit value of the object substance not to be measured and the lower limit value of the object substance to be measured.

[0015] If the pressure control mechanism is so configured to adjust the pressure in the measurement space so as to make the energy given to the object substance not to be measured in the measurement space equal to or less than the lower limit value of the ionization energy of the object substance not to be measured, almost no signal of the object substance not to be measured is detected by the quadruple mass spectrum so that it is possible to conduct the quantitative analysis on the object substance to be measured more accurately.

[0016] In addition, in case that the mixed gas generation mechanism generates the mixed gas containing multiple object substances not to be measured, it is preferable that the pressure control mechanism adjusts the pressure in the measurement space so as to change the energy given to the object substance not to be measured having the lower limit value of the ionization energy that is the lowest among the multiple object substances not to be measured introduced into the measurement space

according to the lower limit value of the object substance not to be measured.

[0017] In accordance with this arrangement, all of the signals of the object substances not to be measured detected by the quadruple mass spectrum become small in such a degree as not to cause obstruction in conducting the quantitative analysis on the object substance to be measured. Then, even though the mixed gas contains multiple object substances not to be measured whose mass number is near that of the object substance to be measured, it is possible to conduct the quantitative analysis on the object substance to be measured relatively accurately by the use of the quadrupole mass spectrum.

[0018] In addition, concretely the pressure control mechanism comprises a chamber to which the quadruple mass spectrometer is connected and that has an internal space that communicates with the measurement space of the quadruple mass spectrometer, an introducing line that introduces at least a part of the mixed gas generated by the mixed gas generation mechanism into the internal space of the chamber and a pressure regulating valve that is arranged in the introducing line and that adjusts the pressure of the internal space of the chamber.

[0019] In accordance with this arrangement, since the flow rate of the fluid flowing in the introducing line is adjusted by the pressure control valve, it is possible to adjust the pressure in the measurement space of the quadrupole mass spectrum.

[0020] In addition, in case that the carrier gas is a He gas and the sample gas contains D_2 as being the object substance to be measured, although both the mass number of He and the mass number of D_2 are four, it becomes possible to conduct the quantitative analysis on D_2 as being the object substance to be measured relatively accurately.

[0021] Furthermore, the heating furnace may be an impulse furnace, and the crucible may be a graphite crucible. In this case, a gas containing D_2 to be the object substance to be measured and CO to be the object substance not to be measured is generated as the sample. As a result of this, the mixed gas generation mechanism may further comprise an oxidization unit that oxidizes the mixed gas discharged from the heating furnace, a decarbon-dioxide unit that decarbon-dioxides the mixed gas discharged from the oxidization unit and a dehydration unit that dehydrates the mixed gas discharged from the decarbon-dioxide unit.

[0022] In case that the quantitative analysis is conducted on the mixed containing D_2 and CO by the quadrupole mass spectrum, the detection signal (a solid line in Fig. 5) of CO is detected in an overlapped state with the detection signal (a dashed line in Fig. 5) of D_2 in the detection CH ($m/z = 4$) as shown in Fig. 5. However, in accordance with the mixed gas generation mechanism, the mixed gas discharged from the heating furnace is introduced into the quadrupole mass spectrum in a state wherein CO is generally removed by each reaction so that it becomes difficult to detect the detection signal of CO as shown by a dotted line in Fig. 5. As this result, it becomes possible to conduct the quantitative analysis on D2 as being the object substance to be measured relatively accurately.

[0023] Concretely, the oxidization unit may use the Schutze reagent as an oxidizing agent, the decarbon-dioxide unit may use at least one selected among soda lime, sodium hydroxide and activated alumina impregnated with sodium hydroxide as the decarbon-dioxide agent, and the dehydration unit may use at least one selected from magnesium peroxide or diphosphorus pentoxide as a dehydrating agent.

[0024] In addition, a gas analysis method in accordance with this invention is a gas analysis method that uses a mixed gas generation mechanism that comprises a heating furnace that heats a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, generates a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and discharges a mixed gas comprising the carrier gas and the sample gas, and a quadruple mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that conducts the quantitative analysis on the object substance to be measured by giving energy to the object substance to be measured and the object substance not to be measured in the measurement space, and is characterized by that the energy that is given to the object substance not to be measured in the measurement space is changed according to the lower limit value of ionization energy of the object substance not to be measured by adjusting the pressure in the measurement space.

[0025] In addition, the mixed gas generation mechanism may generate the mixed gas containing the object substance to be measured and the object substance not to be measured whose mass number falls within a range of $\pm$ 4 of the mass number of the object substance to be measured and the lower limit value of whose ionization energy is bigger than the lower limit value of that of the object substance to be measured.

EFFECT OF THE INVENTION

[0026] In accordance with the gas analysis device having this arrangement, it becomes possible to conduct relatively accurately the quantitative analysis on the object substance to be measured of the mixed gas containing the object substance not to be measured whose mass number is the same as or near the mass number of the object substance to be measured by the use of the quadrupole mass spectrum.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

[Fig. 1] A diagram schematically showing a whole

configuration of a gas analysis device of a first embodiment.

[Fig. 2] A block diagram showing a pressure control unit of the gas analysis device in accordance with the first embodiment.

[Fig. 3] A graph showing a relation between a detection signal (signal intensity) and an elapsed time (analysis time) of D_2 and He.

[Fig. 4] A graph showing a relation between a detection signal (signal intensity) and pressure in a chamber (pressure in measurement space) of D_2 and He.

[Fig. 5] A graph showing a relation between a detection signal (signal intensity) and an elapsed time (analysis time) of m/z = 4 obtained by introducing the mixed gas generated by the mixed gas generation mechanism into the measurement space of the quadrupole mass spectrum of the gas analysis device in accordance with the second embodiment.

[Fig. 6] A diagram schematically showing an internal configuration of a quadrupole mass spectrometer.

[Fig. 7] A graph showing a relation between energy given to He and an ion number per area.

MODE FOR EMBODYING THE INVENTION

[0028] A gas analysis device in accordance with this invention will be explained with reference to drawings.

[0029] The gas analysis device in accordance with this embodiment heats and melts a sample such as steel or ceramics and conducts a quantitative analysis on an object substance to be measured contained in a sample gas that is produced during the sample is heated and melted.

[0030] <Embodiment 1> The gas analysis device 100 in accordance with this embodiment comprises, as shown in Fig. 1, a mixed gas generation mechanism 10 that generates a mixed gas that contains an object substance to be measured and an object substance not to be measured, a quadruple mass spectrometer 20 that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism 10 is introduced, and a pressure control mechanism 30 that adjusts pressure in the measurement space of the quadruple mass spectrometer 20.

[0031] The object subject to be measured in this embodiment is concretely D_2. In addition, the object subject not to be measured is concretely He that has the same mass number (4) as that of D_2 and that has the lower limit value (24.6 eV) of ionization energy that is bigger than the lower limit value (15.467 eV) of the ionization energy of D_2. The object substance to be measured is not limited to D_2. In addition, the object substance not to be measured is not limited to He as far as the mass number of the object substance not to be measured falls within a range of ± 4 of the mass number of the object substance to be measured and the lower limit value of whose ionization energy is bigger than the lower limit value of that of the object substance to be measured.

[0032] The mixed gas generation mechanism 10 comprises a heating furnace 11, an upstream line L1 extending to an upstream side from the heating furnace 11, a carrier gas supplier 12 to be connected to a starting end of the upstream line L1 and a downstream line L2 extending to a downstream side from the heating furnace 11.

[0033] The heating furnace 11 is, so called, an impulse furnace, and houses a crucible 11a that puts the sample into inside of the furnace 11. The heating furnace 11 produces Joule het by flowing the impulse current in the crucible 11a, and produces the sample gas by vaporizing at least a part of the sample put into the crucible 11a. The sample used in this embodiment is the sample that generates the sample gas containing D_2 as being the object substance to be measured by heating the sample in the heating furnace 11. The crucible 11a may be a graphite crucible. In addition, the heating furnace 11 may also be a high frequency induction heating furnace. In this case, the crucible 11a may be a ceramic crucible.

[0034] The upstream line L1 introduces the carrier gas supplied from the carrier gas supplier 12 into the heating furnace 11. The carrier gas in this embodiment uses a He gas to be the object substance not to be measured. The carrier gas is not limited to the He gas, and may be an Ar gas.

[0035] The downstream line L2 discharges the mixed gas comprising the sample gas and the carrier gas from the heating furnace 11. A dust filter 13 to remove dust such as soot contained in the mixed gas is provided in the middle of the downstream line L2.

[0036] Since the quadruple mass spectrometer 20 has the same configuration as that of the quadruple mass spectrometer 20 shown in Fig. 6, detailed explanation will be omitted.

[0037] The pressure control mechanism 30 comprises a chamber 31 having an internal space that communicates with the measurement space (S) of the quadruple mass spectrometer 20, an introducing line L3 that bifurcates from the downstream line L2 and that introduces at least a part of the mixed gas flowing in the downstream line L2 into the internal space of the chamber 31, an exhaust line L4 that bifurcates from the downstream line L2 and that exhausts remaining mixed gas flowing in the downstream line L2, a flow rate control valve 32 that is arranged in the upstream side from the bifurcating point of the downstream line L2, a pressure control valve 33 arranged in the introducing line L3 and an exhaust pump 34 and a pressure sensor (P) to be connected to the chamber 31.

[0038] The chamber 31 comprises four ports. Each of the introducing line L3, the quadruple mass spectrometer 20, the pressure sensor (P) and the exhaust pump 34 is connected to each of the four ports respectively.

[0039] The flow rate control valve 32 is, so called, a needle valve. The flow rate control valve 32 adjusts a flow rate of the mixed gas exhausted from the exhaust line L4 whose terminal end is exposed to the atmosphere.

Then, the flow rate control valve 32 controls the flow rate of the mixed gas introduced into the introducing line L3.

[0040] The pressure control valve 33 is, so called a needle valve. The pressure control valve 33 adjusts pressure in the internal space of the chamber 31. Then, the pressure control valve 33 adjusts pressure in the measurement space (S) of the quadruple mass spectrometer 20 that communicates with the internal space of the chamber 31.

[0041] The pressure sensor (P) measures the pressure in the internal space of the chamber 31. Then, the pressure sensor (P) measures the pressure in the measurement space (S) of the quadruple mass spectrometer 20 that communicates with the internal space of the chamber 31. In addition, the exhaust pump 34 exhausts the mixed gas introduced into the internal space of the chamber 31. Concretely, a turbo pump 34a and a dry pump 34b are arranged in serial.

[0042] In addition, the pressure control mechanism 30 further comprises a pressure control unit 35 to be connected to the pressure control valve 33 and the pressure sensor (P). The pressure control unit 35 is, as shown in Fig. 2, so-called a computer comprising a CPU, a memory, an A/D converter and a D/A converter. The pressure control unit 35 executes programs stored in the memory and produces functions as a lower limit pressure storing part 35a, a target pressure setting part 35b, a pressure value receiving part 35c and a valve opening position control part 35d.

[0043] The lower limit pressure storing part 35a stores the pressure (hereinafter also called as the lower limit pressure) in the measurement space (S) wherein the energy that is given to the object substance not to be measured in the measurement space (S) and that is previously obtained for the object subject not to be measured becomes nearly less than or equal to the lower limit value (for example, the lower limit value, less than or equal to the lower limit value). A name of the object substance not to be measured and the lower limit value are linked and stores in the lower limit pressure storing part 35a.

[0044] The lower limit pressure can be mastered by conducting an experiment; the object substance not to be measured (the carrier gas) is introduced into the measurement space (S) of the quadruple mass spectrometer 20, the predetermined voltage is applied to the gas introduced into the measurement space (S) by an ionizing unit while the pressure is varied step by step and the object substance to be measured is introduced to the object substance not to be measured for each step. Concretely, the lower limit pressure of He as being the object substance not to be measured in this embodiment may be selected from the pressure bigger than 1.5 Pa and smaller than or equal to 2.0 Pa. If referring to the graph shown in Fig. 4 obtained by an experiment wherein an interval between the pressure fluctuations is further shorten than that of the experiment obtained by the graph shown in Fig. 3, it turns out that the lower limit of He is smaller than the lower limit of D_2 at least when the pressure in the measurement space (S) is 1.25 Pa. Then, then lower limit pressure may be selected from the pressure less than or equal to 1.25 Pa.

[0045] In this embodiment, for example, He and 1.25 Pa are linked and stored in the lower limit pressure storing part 35a. In case that it is not possible to specify a single value as the value of the lower limit pressure, the lower limit pressure may be stored as a range in the lower limit pressure storing part 35a.

[0046] In cast that an input signal indicating a name of the object substance not to be measured contained in the mixed gas is received through an input means such as a key board by an operator, the target pressure setting part 35b sets the lower limit pressure linked with the object substance not to be measured stored in the lower limit pressure storing part 35a as the target pressure. In case that the range of the lower limit pressure is stored in the lower limit pressure storing part 35a, the pressure selected in the range of the lower limit pressure (for example, the center value of the range) may be set as the target pressure. In this embodiment, in case that the input signal indicating He is received, 1.25 Pa is set as the target pressure.

[0047] The pressure value receiving part 35c receives the pressure value measured by the pressure sensor (P). In addition, the valve opening position control part 35d adjusts the valve opening position of the pressure control valve 33 so as to make the pressure value received by the pressure value receiving part 35c approach the target pressure value set by the target pressure setting part 35b.

[0048] In accordance with this arrangement, in case that quantitative analysis is conducted on the mixed gas by the quadruple mass spectrometer 20, the pressure in the measurement space (S) is adjusted so as to be less than or equal to near the lower limit value. Accordingly, the detection signal of the object substance not to be measure is not detected or only the degree of unobtrusive detection signal for the quantitative analysis on the object substance to be measured is detected. Accordingly, it is possible for the quadruple mass spectrometer 20 to relatively easily conduct the quantitative analysis on the object substance to be measured.

[0049] The lower limit pressure storing part 35a stores the lower limit pressure of the object substance not to be measured alone in this embodiment, however, the lower limit pressure of the object substance to be measured may be stored. In this case, the target pressure setting part 35b may set the value more than or equal to the lower limit pressure of the object subject to be measured as the target pressure. With this arrangement, it is possible for the quadruple mass spectrometer 20 to detect at least the detection signal of the object substance to be measured.

[0050] <Embodiment 2> This embodiment is a modified embodiment of the mixed gas generation mechanism 10 of the gas analysis device 100 in accordance with the above-mentioned first embodiment. Concretely, the mixed gas generation mechanism 10 in accordance with

this embodiment is further provided with an oxidization unit 14 that oxidizes the mixed gas discharged from the heating furnace 11, the decarbon-dioxide unit 15 that decarbon-dioxides the mixed gas discharged from the oxidization unit 14 and the dehydration unit 16 that dehydrates the mixed gas discharged from the decarbon-dioxide unit 15 (shown by dotted lines in Fig. 1) in the downstream line L2. Concretely, the oxidization unit 14, the decarbon-dioxide unit 15 and the dehydration unit 16 are arranged in the downstream line L2 in the downstream side of the flow rate control valve 32 and in the upstream side from the bifurcated point between the introducing line L3 and the exhaust line L4.

[0051] The oxidization unit 14 may use, for example, the Schutze reagent (concretely, the Schutze reagent whose main component is iodine pentoxide) as an oxidizing agent.

[0052] The decarbon-dioxide unit 15 may use, for example, at least one selected among soda lime, sodium hydroxide, and activated alumina impregnated sodium hydroxide as the decarbon-dioxide agent.

[0053] The dehydration unit 16 may use, for example, at least one selected among magnesium peroxide and diphosphorus pentoxide as the dehydration agent.

[0054] The gas analysis device 100 in accordance with this embodiment is suitable for conducting the quantitative analysis on D_2 of the mixed gas containing D_2, CO, N_2 and He by the use of the quadruple mass spectrometer 20. Concretely, in case that the impulse furnace is used as the heating furnace 11 and the graphite crucible is used as the crucible 11a, since the mixed gas containing CO and N_2 is generated, the gas analysis device 100 is suitable for conducting the quantitative analysis on the object to be measured contained in the mixed gas.

[0055] More specifically, if the quadruple mass spectrometer 20 conducts the quantitative analysis on the mixed gas containing D_2, CO, N_2 and He, the detection signal solid line in Fig. 5) of CO is detected in an overlapped state with the detection signal of D_2 (dashed line in Fig. 5) in detection channel CH of m/z = 4. Then, it becomes difficult to conduct the quantitative analysis on D_2. However, in accordance with the gas analysis device 100 of this embodiment, the mixed discharged from the heating furnace 11 is introduced into the quadruple mass spectrometer 20 in a state wherein CO is generally removed, and almost no detection signal of CO is detected in the detection channel CH of m/z = 4 as shown in dotted line in Fig. 5.

[0056] If the sample gas containing D_2 as being the object substance to be measured is generated by putting Sn together with the sample into the crucible 11a of the heating furnace 11 in accordance with this embodiment and heating the crucible 1 1a, in case of conducting the quantitative analysis on D_2 as being the object substance to be measured, it is difficult to be affected by the detection signal of N_2.

[0057] <Other embodiment The quantitative analysis is conducted on the mixed gas containing one object substance not to be measured in each of the above-mentioned embodiments, however, the quantitative analysis may be conducted on the mixed gas containing multiple object substances not to be measured. Each of the object substances not to be measured is a substance whose mass number falls within a range of ± 4 of the mass number of the object substance to be measured and the lower limit value of whose ionization energy is bigger than the lower limit value of that of the object substance to be measured.

[0058] In this case, the pressure control mechanism 30 may adjust the pressure so as to change the energy that is given to the object substance not to be measured having the lowest lower limit value among the multiple object substances introduced into the measurement space (S) of the quadruple mass spectrometer 20 according to the lower limit value of the object substance not to be measured.

[0059] In addition, the present claimed invention is not limited to the above-mentioned embodiments, and may be variously combined or modified without departing from a spirit of the invention.

EXPLANATION OF CODES

[0060]

100 ...	gas analysis device
10 ...	mixed gas generation mechanism
11 ...	heating furnace
11a ...	crucible
14 ...	oxidization unit
15 ...	decarbon-dioxide unit
16 ...	dehydration unit
20 ...	quadruple mass spectrometer
30 ...	pressure control mechanism
L3 ...	introducing line
31 ...	chamber
32 ...	flow rate control valve
33 ...	pressure control valve
34 ...	exhaust pump

Claims

1. A gas analysis device comprising
a mixed gas generation mechanism that comprises a heating furnace that heats a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, generates a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and discharges a mixed gas comprising the carrier gas and the sample gas,
a quadruple mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that conducts a quantitative analysis on the ob-

ject substance to be measured by giving energy to the object substance to be measured and the object substance not to be measured in the measurement space, and
a pressure control mechanism that adjusts pressure in the measurement space, wherein
the pressure control mechanism adjusts the pressure in the measurement space so as to change the energy that is given to the object substance not to be measured in the measurement space according to the lower limit value of ionization energy of the object substance not to be measured.

2. The gas analysis device described in claim 1, wherein
the pressure control mechanism adjusts the pressure in the measurement space so as to make the energy given to the object substance not to be measured in the measurement space equal to or less than the lower limit value of the ionization energy of the object substance not to be measured.

3. The gas analysis device described in claim 1 or 2, wherein
the mixed gas generation mechanism generates the mixed gas containing multiple object substances not to be measured, and
the pressure control mechanism adjusts the pressure in the measurement space so as to change the energy given to the object substance not to be measured having the lower limit value of the ionization energy that is the lowest among the multiple object substances not to be measured introduced into the measurement space according to the lower limit value of the object substance not to be measured.

4. The gas analysis device described in either of claim 1 through 3, wherein
the pressure control mechanism comprises a chamber to which the quadruple mass spectrometer is connected and that has an internal space that communicates with the measurement space of the quadruple mass spectrometer, an introducing line that introduces at least a part of the mixed gas generated by the mixed gas generation mechanism into the internal space of the chamber and a pressure regulating valve that is arranged in the introducing line and that adjusts the pressure of the internal space of the chamber.

5. The gas analysis device described in either of claim 1 through 4, wherein
the carrier gas is He gas, and
the sample gas contains D_2 as being the object substance to be measured.

6. The gas analysis device described in either of claim 1 through 5, wherein
the heating furnace is an impulse furnace, and
the crucible is a graphite crucible.

7. The gas analysis device described in claim 6, wherein
the sample gas contains D_2 to be the object substance to be measured and CO to be the object substance not to be measured, and
the mixed gas generation mechanism further comprises an oxidization unit that oxidizes the mixed gas discharged from the heating furnace, a decarbon-dioxide unit that decarbon-dioxides the mixed gas discharged from the oxidization unit and a dehydration unit that dehydrates the mixed gas discharged from the decarbon-dioxide unit.

8. The gas analysis device described in claim 7, wherein
the oxidization unit uses the Schutze reagent as an oxidizing agent.

9. The gas analysis device described in claim 7 or 8, wherein
the decarbon-dioxide unit uses at least one selected among soda lime, sodium hydroxide and activated alumina impregnated with sodium hydroxide as the decarbon-dioxide agent.

10. The gas analysis device described in either of claim 7 through 9, wherein
the dehydration unit uses at least one selected from magnesium peroxide or diphosphorus pentoxide as a dehydrating agent.

11. A gas analysis method that uses
a mixed gas generation mechanism that comprises a heating furnace that heats a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, generates a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and discharges a mixed gas comprising the carrier gas and the sample gas, and a quadruple mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that conducts a quantitative analysis on the object substance to be measured by giving energy to the object substance to be measured and the object substance not to be measured in the measurement space, wherein
the energy that is given to the object substance not to be measured in the measurement space is changed according to the lower limit value of ionization energy of the object substance not to be measured by adjusting the pressure in the measurement space.

12. The gas analysis method described in claim 11,

wherein
the mixed gas generation mechanism generates the mixed gas containing the object substance to be measured and the object substance not to be measured whose mass number falls within a range of ±4 of the mass number of the object substance to be measured and the lower limit value of whose ionization energy is bigger than the lower limit value of that of the object substance to be measured.

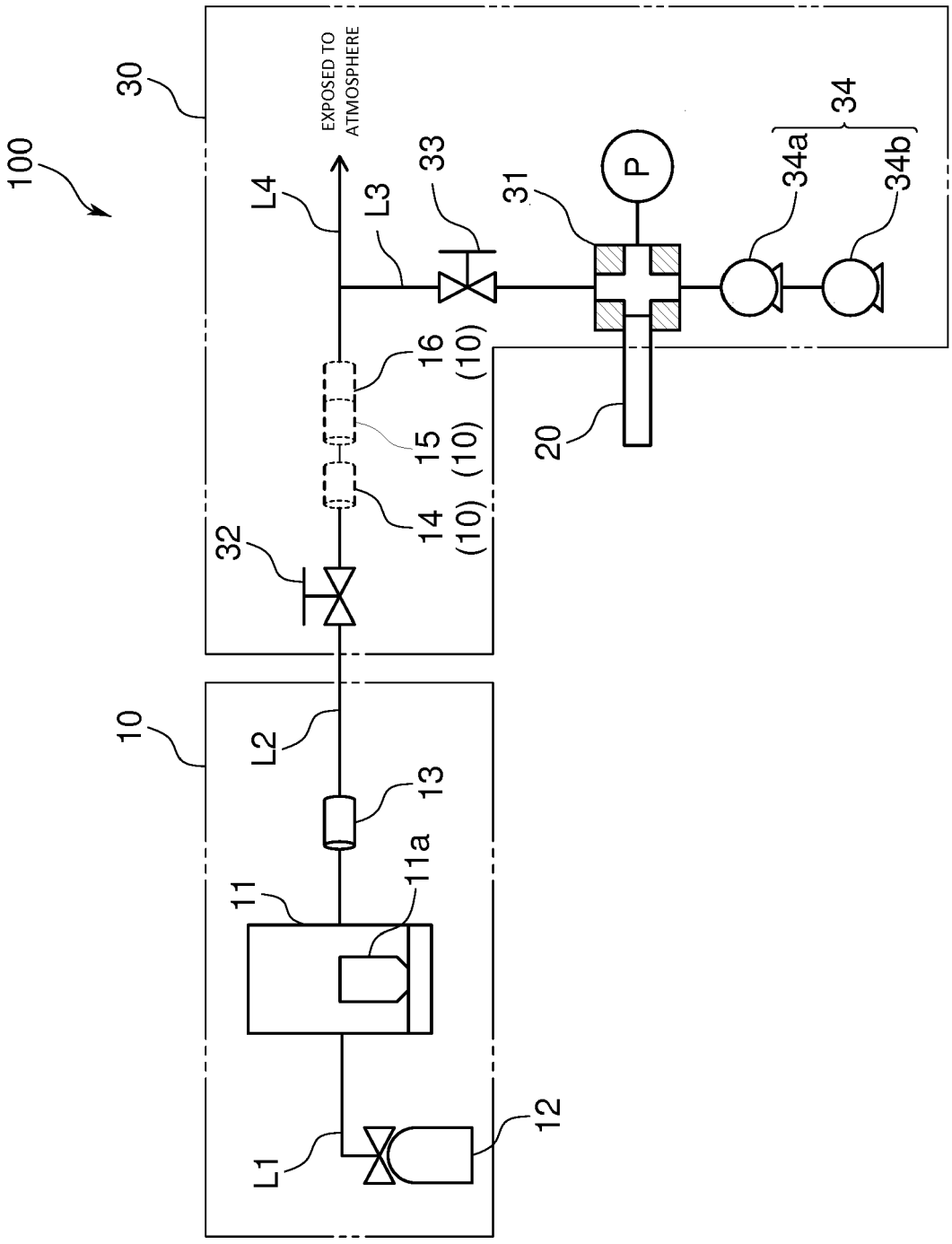

100
30
EXPOSED TO ATMOSPHERE
L4
L3
33
31
P
34
34a
34b
16 (10)
15 (10)
14 (10)
20
32
10
L2
13
11a
11
12
L1

FIG.1

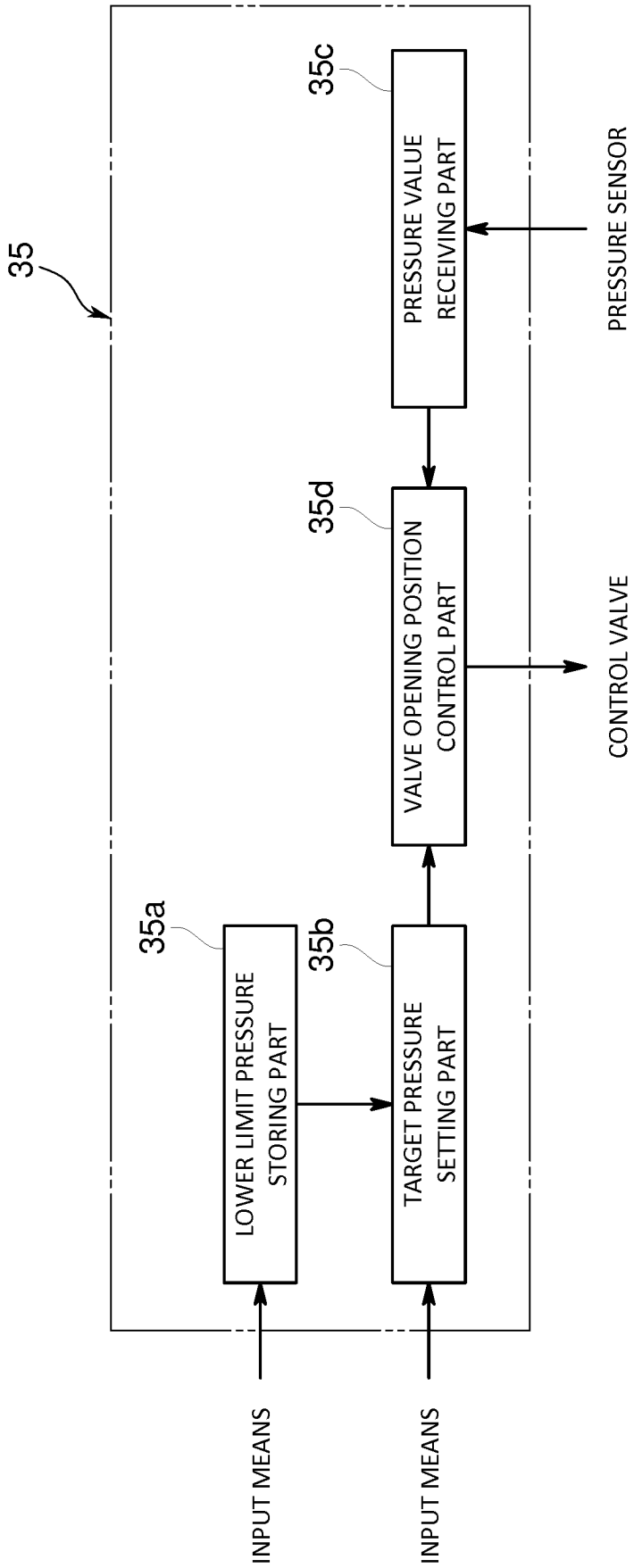
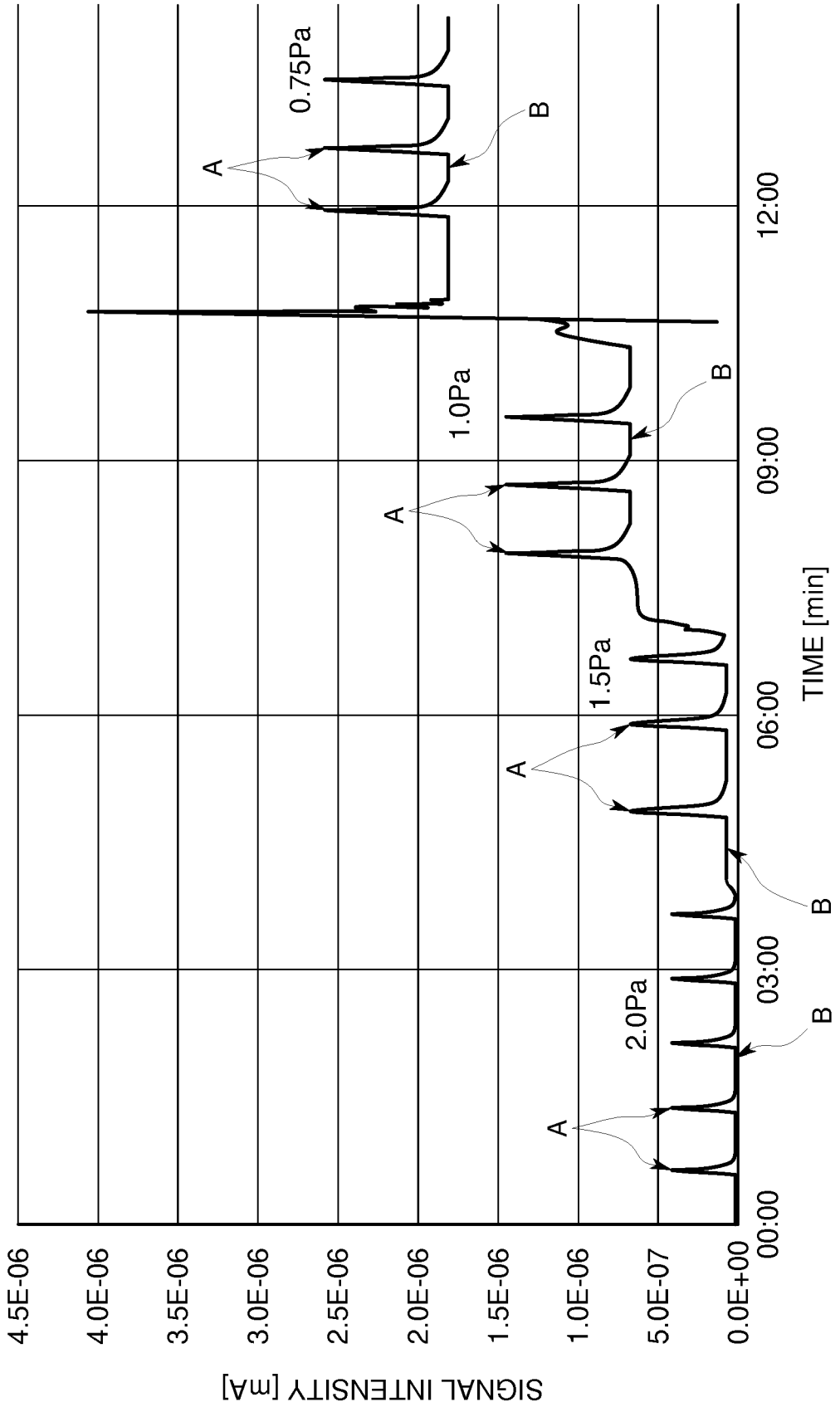

35
35a
LOWER LIMIT PRESSURE STORING PART
35b
TARGET PRESSURE SETTING PART
35c
PRESSURE VALUE RECEIVING PART
35d
VALVE OPENING POSITION CONTROL PART
INPUT MEANS
INPUT MEANS
PRESSURE SENSOR
CONTROL VALVE

FIG.2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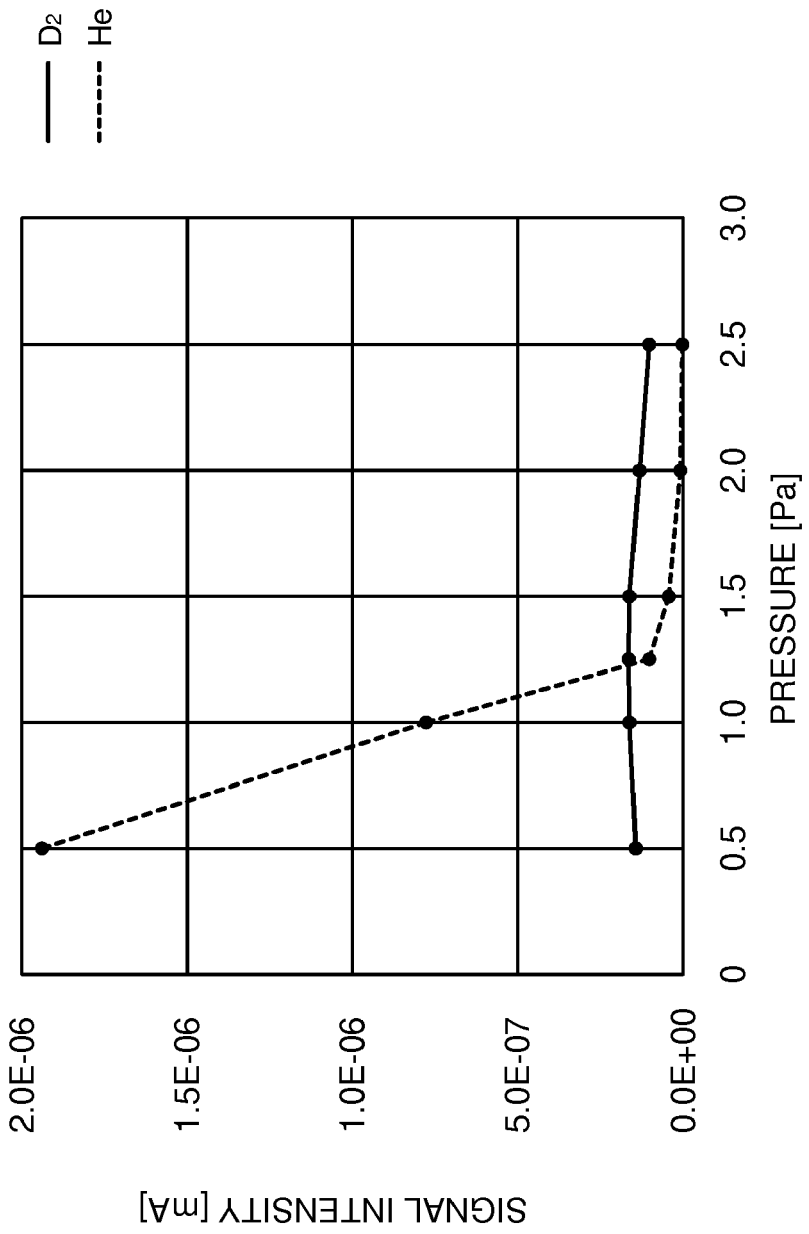
3.5E-06
3.0E-06
2.5E-06
2.0E-06
1.5E-06
1.0E-06
5.0E-07
0.0E+00
00:00
03:00
06:00
09:00
12:00
TIME [min]
0.75Pa
1.0Pa
1.5Pa
2.0Pa
A
B

FIG.3


D2
He
SIGNAL INTENSITY [mA]
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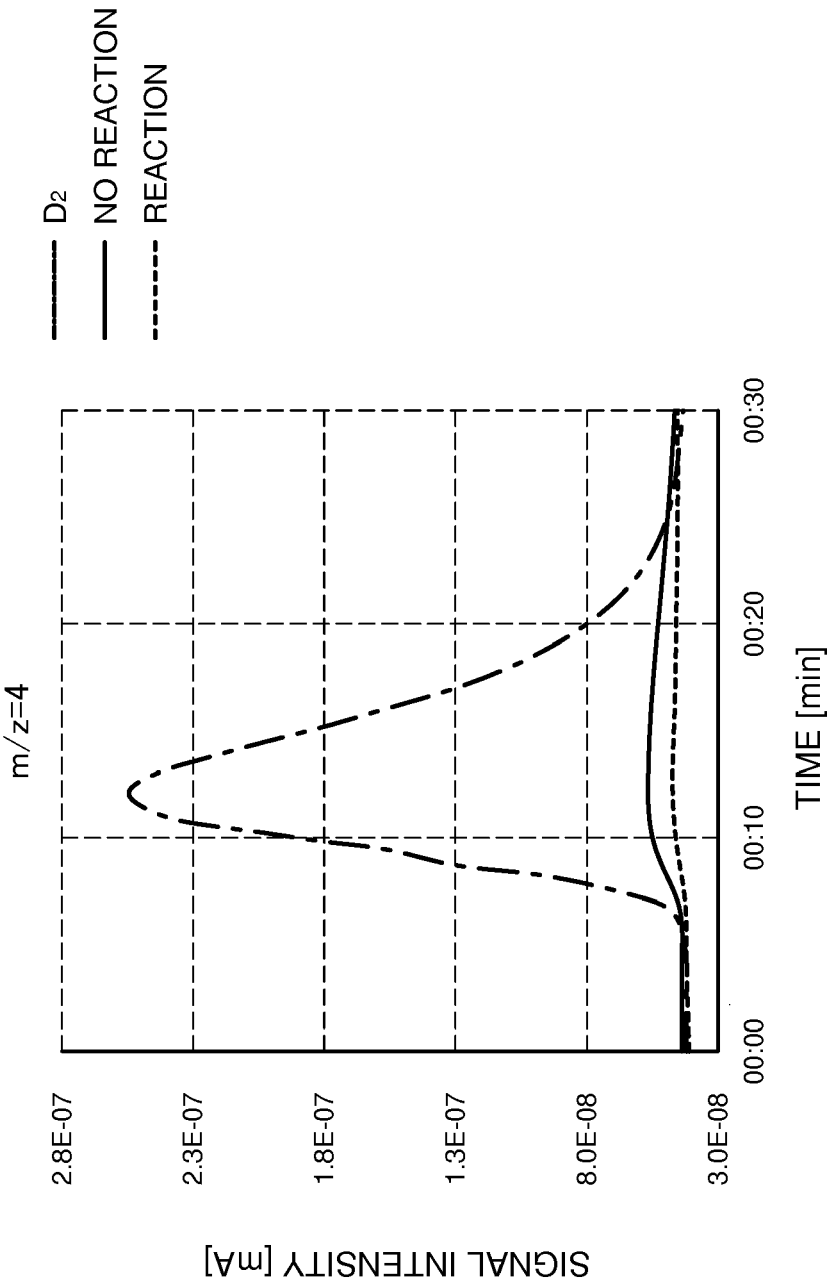
1.5E-06
1.0E-06
5.0E-07
0.0E+00
0
0.5
1.0
1.5
2.0
2.5
3.0
PRESSURE [Pa]

FIG.4


D2
NO REACTION
REACTION
m/z=4
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2.3E-07
1.8E-07
1.3E-07
8.0E-08
3.0E-08
SIGNAL INTENSITY [mA]
00:00
00:10
00:20
00:30
TIME [min]

FIG.5

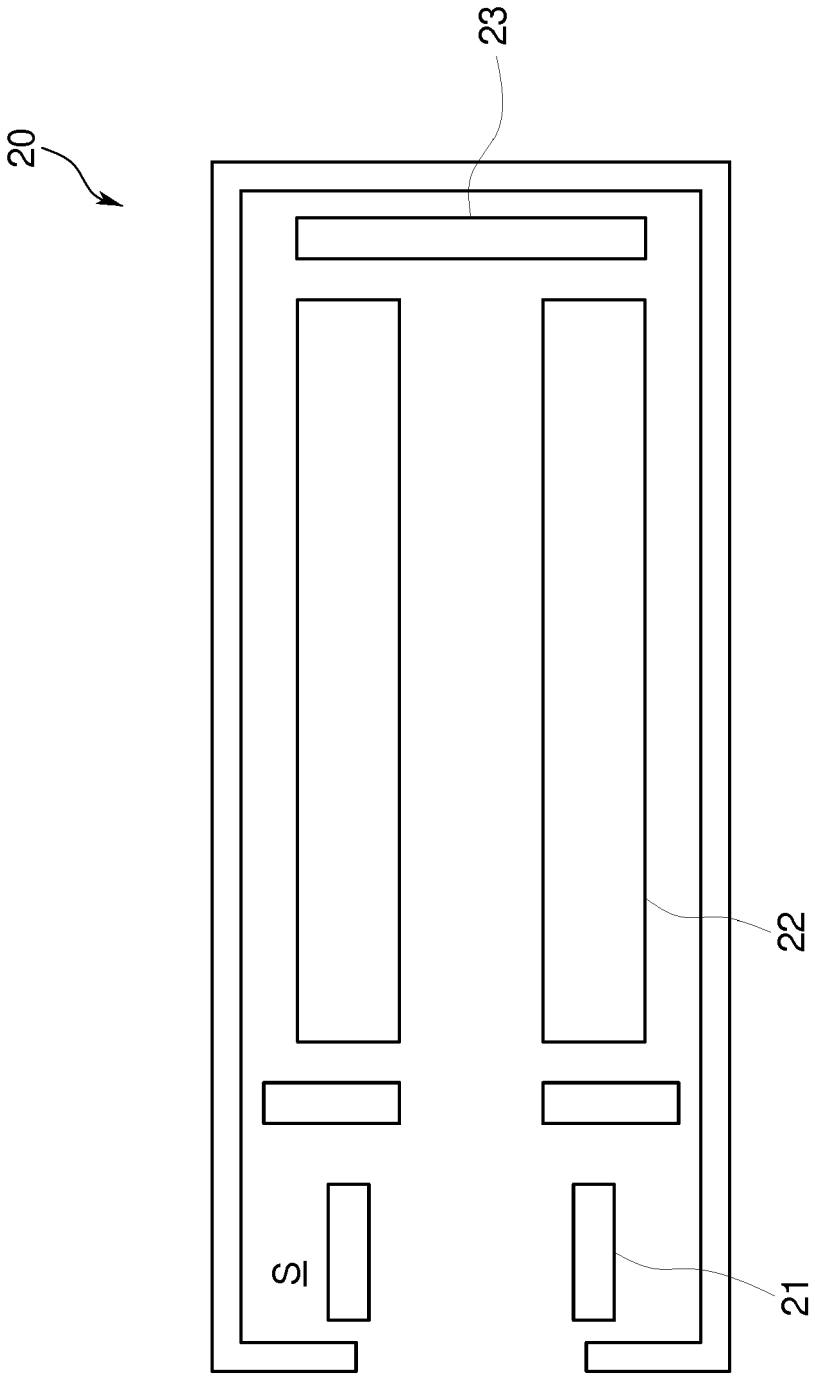

FIG.6

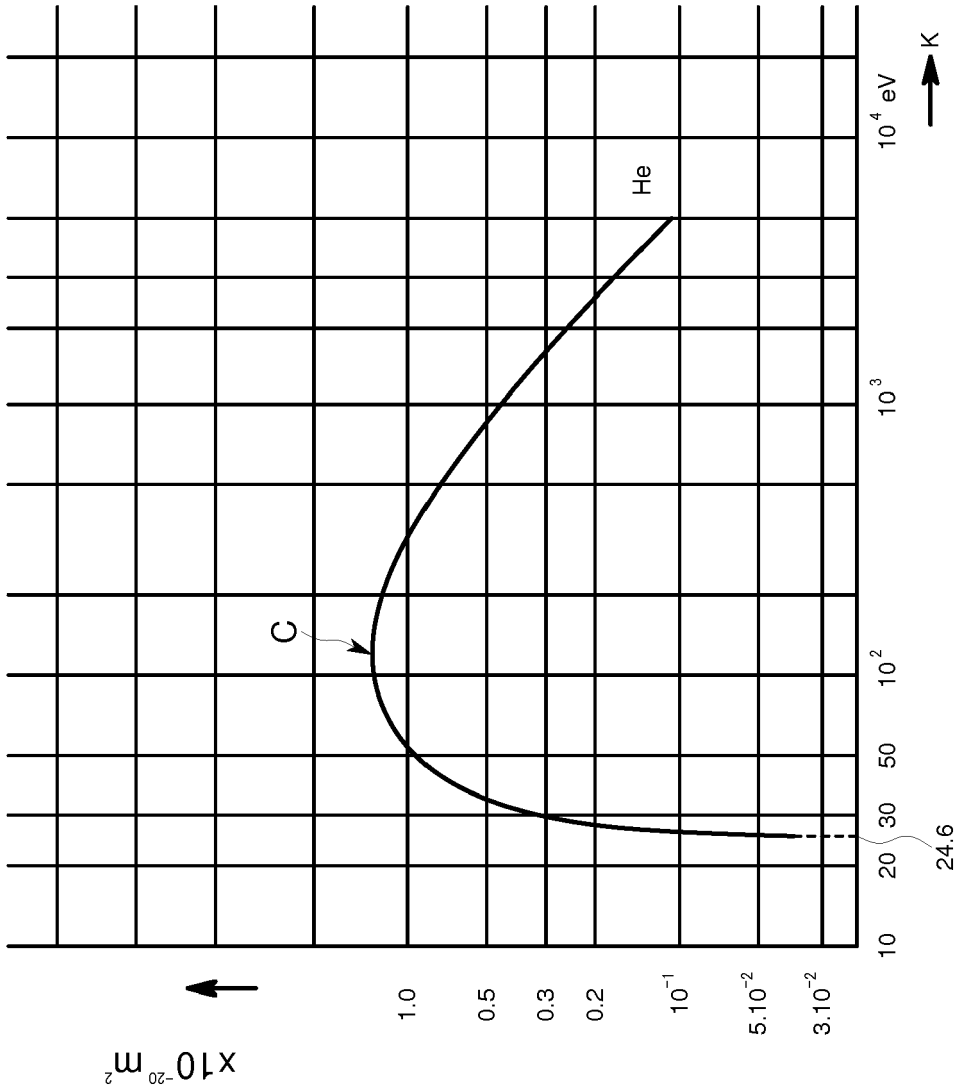
x10⁻²⁰ m²
1.0
0.5
0.3
0.2
10⁻¹
5.10⁻²
3.10⁻²
10
20
30
50
10²
10³
10⁴ eV
K
24.6
He
C

FIG.7

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Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 19 19 6202

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20 February 2020	Dietsche, Rainer

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EUROPEAN SEARCH REPORT

Application Number
EP 19 19 6202

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