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(54) GAS ANALYSIS DEVICE AND GAS ANALYSIS METHOD

GASANALYSEVORRICHTUNG UND GASANALYSEVERFAHREN

DISPOSITIF ET PROCÉDÉ D'ANALYSE DE GAZ

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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 quadrupole 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 quadrupole 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 quadrupole 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.

[0004] WO 2018/056419 A1 relates to the accurate quantitative analysis of the Ar element contained in a sample gas in an elemental analysis device combing a heating oven and a mass spectrometer for performing quantitative analysis of an element in a vacuum atmosphere.

[0005] Davies et al. (S. Davies, J.A. Rees, D.L. Seymour; Threshold ionization mass spectrometry (TIMS): a complementary quantitative technique to conventional mass resolved mass spectrometry; Vacuum, vol. 101; 2014; pp. 416-422) disclose applications of the threshold ionization mass spectrometry (TIMS) technique to a variety of problems which have proved to be difficult to tackle using more conventional mass analysis and to demonstrate the complimentary effectiveness of the technique.

[0006] Yu et al. (Y. Yu, J. Hu, Z. Wan, J. Wu, H. Wang, B. Cao; Mass separation of deuterium and helium with conventional quadrupole mass spectrometer by using varied ionization energy; Review of scientific instruments, vol. 87; no. 3; 2016) relates to the mass separation of deuterium and helium with conventional quadrupole mass spectrometer by using varied ionization energy.

[0007] US 5 294 797 A discloses a method for generating ions from thermally unstable, nonvolatile, large molecules, particularly for a mass spectrometer such as a time-of-flight mass spectrometer.

[0008] WO 2004/098743 A2 describes a non-radioactive atmospheric pressure device for ionization of analytes.

[0009] US 6 919 562 B1 relates to an apparatus and methods that enable the interaction of low-energy electrons and positrons with sample ions.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0010] Patent document 1: WO2018 / 056419 A

SUMMARY OF THE INVENTION

PROBLEMS SOLVED BY THE INVENTION

[0011] A main object of this invention is make it possible for a quadrupole 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

[0012] 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 quadrupole 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.

[0013] 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 quadrupole 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.

[0014] 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.

[0015] 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.

[0016] 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.

[0017] 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 quadrupole 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 quadrupole 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.

[0018] As mentioned above, the applicant of this invention successfully invented the present claimed invention based on the knowledge obtained through the above-mentioned experiments.

[0019] More specifically, the gas analysis device in accordance with this invention comprises a mixed gas generation mechanism that comprises a heating furnace that is configured to heat a crucible where a sample is put while introducing a carrier gas to be an object substance not to be measured, to generate a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and to discharge a mixed gas comprising the carrier gas and the sample gas, a quadrupole mass spectrometer that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism is introduced and that is configured to conduct 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 is configured to adjust the pressure in the measurement space, wherein the pressure control mechanism is configured to adjust the pressure in the measurement space so as to make the energy that is given to the object substance not to be measured in the measurement space equal or less than the lower limit value of the ionization energy of the object substance not to be measured and more than or equal to the lower limit value of the ionization energy of the subject substance to be measured, wherein when the pressure in the measurement space is decreased, a speed of an electron to ionize the substance is fast and the energy given to the substance increases and when the pressure in the measurement space is increased, a speed of an electron to ionize the substance is slow and the energy given to the substance decreases.

[0020] 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 quadrupole 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 quadrupole mass spectrometer.

[0021] 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 quadrupole mass spectrum so that it is possible to conduct the quantitative analysis on the object substance to be measured more accurately.

[0022] 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 make the energy given to the object substance not to be measured equal to or less than the lower limit value of 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.

[0023] In accordance with this arrangement, all of the signals of the object substances not to be measured detected by the quadrupole 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.

[0024] In addition, concretely the pressure control mechanism comprises a chamber to which the quadrupole mass spectrometer is connected and that has an internal space that communicates with the measurement space of the quadrupole 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.

[0025] 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.

[0026] 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.

[0027] 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 an 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.

[0028] 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.

[0029] 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.

[0030] 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, a quadrupole 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 a pressure in the measurement space, wherein the energy that is given to the object substance not to be measured in the measurement space is made equal to or less than the lower limit value of the ionization energy of the object substance not to be measured and more than or equal to the lower limit of the ionization energy of the object substance to be measured by adjusting the pressure in the measurement space, wherein when the pressure in the measurement space is decreased, a speed of an electron to ionize the substance is fast and the energy given to the substance increases and when the pressure in the measurement space is increased, a speed of an electron to ionize the substance is slow and the energy given to the substance decreases.

[0031] 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 ± 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

[0032] 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

[0033]

[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

[0034] A gas analysis device in accordance with this invention will be explained with reference to drawings.

[0035] 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.

[0036] <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 quadrupole 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 quadrupole mass spectrometer (20).

[0037] 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.

[0038] 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).

[0039] 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.

[0040] 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.

[0041] 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).

[0042] Since the quadrupole mass spectrometer (20) has the same configuration as that of the quadrupole mass spectrometer (20) shown in Fig. 6, detailed explanation will be omitted.

[0043] The pressure control mechanism (30) comprises a chamber (31) having an internal space that communicates with the measurement space (S) of the quadrupole 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).

[0044] The chamber (31) comprises four ports. Each of the introducing line (L3), the quadrupole mass spectrometer (20), the pressure sensor (P) and the exhaust pump (34) is connected to each of the four ports respectively.

[0045] 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).

[0046] 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 quadrupole mass spectrometer (20) that communicates with the internal space of the chamber (31).

[0047] 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 quadrupole 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 (34)a and a dry pump (34)b are arranged in serial.

[0048] 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).

[0049] 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).

[0050] 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 quadrupole 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.

[0051] 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).

[0052] 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.

[0053] 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).

[0054] In accordance with this arrangement, in case that quantitative analysis is conducted on the mixed gas by the quadrupole 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 quadrupole mass spectrometer (20) to relatively easily conduct the quantitative analysis on the object substance to be measured.

[0055] 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 quadrupole mass spectrometer (20) to detect at least the detection signal of the object substance to be measured.

[0056] <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).

[0057] 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.

[0058] 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.

[0059] The dehydration unit (16) may use, for example, at least one selected among magnesium peroxide and diphosphorus pentoxide as the dehydration agent.

[0060] 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 quadrupole 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.

[0061] More specifically, if the quadrupole 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 quadrupole 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.

[0062] 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 (11)a, 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.

[0063] <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.

[0064] 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 quadrupole mass spectrometer (20) according to the lower limit value of the object substance not to be measured.

EXPLANATION OF CODES

[0065]

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	quadrupole 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 (100) comprising

a mixed gas generation mechanism (10) that comprises a heating furnace (11) that is configured to heat a crucible (11a) where a sample is put while introducing a carrier gas to be an object substance not to be measured, to generate a sample gas that contains an object substance to be measured by vaporizing at least a part of the sample and to discharge a mixed gas comprising the carrier gas and the sample gas,
a quadrupole mass spectrometer (20) that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism (10) is introduced and that is configured to conduct 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 (30) that is configured to adjust a pressure in the measurement space, wherein
the pressure control mechanism (30) is configured to adjust the pressure in the measurement space so as to make the energy that is given to the object substance not to be measured in the measurement space equal or less than the lower limit value of the ionization energy of the object substance not to be measured and more than or equal to the lower limit value of the ionization energy of the object substance to be measured, wherein when the pressure in the measurement space is decreased, a speed of an electron to ionize the substance is fast and the energy given to the substance increases and when the pressure in the measurement space is increased, a speed of an electron to ionize the substance is slow and the energy given to the substance decreases.

2. The gas analysis device (100) described in claim 1, wherein

the mixed gas generation mechanism (10) is configured to generate the mixed gas containing multiple object substances not to be measured, and
the pressure control mechanism (30) is configured to adjust the pressure in the measurement space so as to make the energy given to the object substance not to be measured equal to or less than the lower limit value of 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.

3. The gas analysis device (100) described in claim 1 or 2, wherein
the pressure control mechanism (30) comprises a chamber (31) to which the quadrupole mass spectrometer (20) is connected and that has an internal space that is configured to communicate with the measurement space of the quadrupole mass spectrometer (20), an introducing line (L3) that is configured to introduce at least a part of the mixed gas generated by the mixed gas generation mechanism (10) into the internal space of the chamber (31) and

a pressure regulating valve that is arranged in the introducing line (L3) and that is configured to adjust the pressure of the internal space of the chamber (31).

4. The gas analysis device (100) described in either of claim 1 through 3, wherein

the carrier gas is He gas, and
the sample gas contains D_2 as being the object substance to be measured.

5. The gas analysis device (100) described in either of claim 1 through 4, wherein

the heating furnace (11) is an impulse furnace, and
the crucible (11a) is a graphite crucible.

6. The gas analysis device (100) described in claim 5, wherein

the sample gas contains D_2 to be the object substance to be measured and CO to be an object substance not to be measured, and
the mixed gas generation mechanism (10) further comprises an oxidization unit (14) that is configured to oxidize the mixed gas discharged from the heating furnace (11), a decarbon-dioxide unit (15) that is configured to decarbon-dioxide the mixed gas discharged from the oxidization unit (14) and a dehydration unit (16) that is configured to dehydrate the mixed gas discharged from the decarbon-dioxide unit (15).

7. The gas analysis device (100) described in claim 6, wherein
the oxidization unit (14) uses the Schutze reagent as an oxidizing agent.

8. The gas analysis device (100) described in claim 6 or 7, wherein
the decarbon-dioxide unit (15) uses at least one selected among soda lime, sodium hydroxide and activated alumina impregnated with sodium hydroxide as the decarbon-dioxide agent.

9. The gas analysis device (100) described in either of claim 6 through 8, wherein
the dehydration unit (16) uses at least one selected from magnesium peroxide or diphosphorus pentoxide as a dehydrating agent.

10. A gas analysis method that uses

a mixed gas generation mechanism (10) that comprises a heating furnace (11) that heats a crucible (11a) 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 quadrupole mass spectrometer (20) that has a measurement space into which the mixed gas generated by the mixed gas generation mechanism (10) 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 (30) that adjusts a pressure in the measurement space,
wherein the energy that is given to the object substance not to be measured in the measurement space is made equal or less than the lower limit value of the ionization energy of the object substance not to be measured and more than or equal to the lower limit of the ionization energy of the object substance to be measured by adjusting the pressure in the measurement space,
wherein when the pressure in the measurement space is decreased, a speed of an electron to ionize the substance is fast and the energy given to the substance increases and when the pressure in the measurement space is increased, a speed of an electron to ionize the substance is slow and the energy given to the substance decreases.

11. The gas analysis method described in claim 10, wherein
the mixed gas generation mechanism (10) 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.

Patentansprüche

1. Gasanalysevorrichtung (100), umfassend:

einen Mischgasgenerierungsmechanismus (10), der einen Wärmofen (11) umfasst, der dafür eingerichtet ist, einen Tiegel (11a) zu erwärmen, in dem sich eine Probe befindet, während ein Trägergas als eine nicht zu messende Objektsubstanz eingeleitet wird, ein Probengas zu generieren, das eine zu messende Objektsubstanz enthält, indem mindestens ein Teil der Probe verdampft wird, und ein Mischgas abzugeben, das das Trägergas und das Probengas umfasst,

ein Quadrupol-Massenspektrometer (20), das einen Messraum aufweist, in den das durch den Mischgasgenerierungsmechanismus (10) generierte Mischgas eingeleitet wird, und das dafür eingerichtet ist, eine quantitative Analyse der zu messenden Objektsubstanz durch Zuführen von Energie zu der zu messenden Objektsubstanz und der nicht zu messenden Objektsubstanz in dem Messraum durchzuführen, und

einen Drucksteuerungsmechanismus (30), der dafür eingerichtet ist, einen Druck in dem Messraum einzustellen, wobei

der Drucksteuerungsmechanismus (30) dafür eingerichtet ist, den Druck in dem Messraum so einzustellen, dass die Energie, die der nicht zu messenden Objektsubstanz in dem Messraum zugeführt wird, maximal so groß wie der untere Grenzwert der Ionisierungsenergie der nicht zu messenden Objektsubstanz und mindestens so groß wie der untere Grenzwert der Ionisierungsenergie der zu messenden Objektsubstanz ist, wobei, wenn der Druck in dem Messraum verringert wird, eine Geschwindigkeit eines Elektrons zum Ionisieren der Substanz schnell ist und die der Substanz zugeführte Energie zunimmt, und wenn der Druck in dem Messraum erhöht wird, eine Geschwindigkeit eines Elektrons zum Ionisieren der Substanz langsam ist und die der Substanz zugeführte Energie abnimmt.

2. Gasanalysevorrichtung (100) nach Anspruch 1,

wobei der Mischgasgenerierungsmechanismus (10) dafür eingerichtet ist, das Mischgas zu generieren, das mehrere nicht zu messende Objektsubstanzen enthält, und

der Drucksteuerungsmechanismus (30) dafür eingerichtet ist, den Druck in dem Messraum so einzustellen, dass die Energie, die der nicht zu messenden Objektsubstanz zugeführt wird, maximal so groß ist wie der untere Grenzwert der nicht zu messenden Objektsubstanz, die den unteren Grenzwert der Ionisierungsenergie aufweist, der der niedrigste unter den mehreren nicht zu messenden Objektsubstanzen ist, die in den Messraum eingeleitet werden.

3. Gasanalysevorrichtung (100) nach Anspruch 1 oder 2, wobei der Drucksteuerungsmechanismus (30) umfasst: eine Kammer (31), mit der das Quadrupol-Massenspektrometer (20) verbunden ist und die einen Innenraum aufweist, der dafür eingerichtet ist, mit dem Messraum des Quadrupol-Massenspektrometers (20) zu kommunizieren, eine Zuleitung (L3), die dafür eingerichtet ist, mindestens einen Teil des durch den Mischgasgenerierungsmechanismus (10) generierten Mischgases in den Innenraum der Kammer (31) einzuleiten, und ein Druckregelventil, das in der Zuleitung (L3) angeordnet ist und das dafür eingerichtet ist, den Druck des Innenraums der Kammer (31) einzustellen.

4. Gasanalysevorrichtung (100) nach einem der Ansprüche 1 bis 3, wobei

das Trägergas He-Gas ist und
das Probengas D_2 als die zu messende Objektsubstanz enthält.

5. Gasanalysevorrichtung (100) nach einem der Ansprüche 1 bis 4, wobei

der Wärmofen (11) ein Impulsofen ist und
der Tiegel (11a) ein Graphittiegel ist.

6. Gasanalysevorrichtung (100) nach Anspruch 5, wobei

das Probengas D_2 als die zu messende Objektsubstanz und CO als eine nicht zu messende Objektsubstanz enthält und

der Mischgasgenerierungsmechanismus (10) des Weiteren umfasst: eine Oxidationseinheit (14), die dafür eingerichtet ist, das von dem Wärmofen (11) abgegebene Mischgas zu oxidieren, eine Entkohlendioxidierungseinheit (15), die dafür eingerichtet ist, das von der Oxidationseinheit (14) abgegebene Mischgas zu entkohlendixodieren, und eine Dehydratisierungseinheit (16), die dafür eingerichtet ist, das von der Entkohlendioxidierungseinheit (15) abgegebene Mischgas zu dehydratisieren.

7. Gasanalysevorrichtung (100) nach Anspruch 6, wobei die Oxidationseinheit (14) das Schütze-Reagens als ein Oxidationsmittel verwendet.

8. Gasanalysevorrichtung (100) nach Anspruch 6 oder 7, wobei die Entkohlendioxidierungseinheit (15) mindestens eines, das unter Natronkalk, Natriumhydroxid und mit Natriumhydroxid imprägniertem aktiviertem Aluminiumoxid ausgewählt ist, als das Entkohlendioxidierungsmittel verwendet.

9. Gasanalysevorrichtung (100) nach einem der Ansprüche 6 bis 8, wobei
die Dehydratisierungseinheit (16) mindestens eines, das aus Magnesiumperoxid und Diphosphorpentoxid ausgewählt ist, als ein Dehydratisierungsmittel verwendet.

10. Gasanalyseverfahren, verwendend:

einen Mischgasgenerierungsmechanismus (10), der einen Wärmofen (11) umfasst, der einen Tiegel (11a) erwärmt, in dem sich eine Probe befindet, während ein Trägergas als eine nicht zu messende Objektsubstanz eingeleitet wird, ein Probengas generiert, das eine zu messende Objektsubstanz enthält, indem mindestens ein Teil der Probe verdampft wird, und ein Mischgas abgibt, das das Trägergas und das Probengas umfasst, ein Quadrupol-Massenspektrometer (20), das einen Messraum aufweist, in den das durch den Mischgasgenerierungsmechanismus (10) generierte Mischgas eingeleitet wird, und das eine quantitative Analyse der zu messenden Objektsubstanz durch Zuführen von Energie zu der zu messenden Objektsubstanz und der nicht zu messenden Objektsubstanz in dem Messraum durchführt, und einen Drucksteuerungsmechanismus (30), der einen Druck in dem Messraum einstellt,
wobei, durch Einstellen des Drucks in dem Messraum, die Energie, die der nicht zu messenden Objektsubstanz in dem Messraum zugeführt wird, maximal so groß wie der untere Grenzwert der Ionisierungsenergie der nicht zu messenden Objektsubstanz und mindestens so groß wie der untere Grenzwert der Ionisierungsenergie der zu messenden Objektsubstanz ist,
wobei, wenn der Druck in dem Messraum verringert wird, eine Geschwindigkeit eines Elektrons zum Ionisieren der Substanz schnell ist und die der Substanz zugeführte Energie zunimmt, und wenn der Druck in dem Messraum erhöht wird, eine Geschwindigkeit eines Elektrons zum Ionisieren der Substanz langsam ist und die der Substanz zugeführte Energie abnimmt.

11. Gasanalyseverfahren nach Anspruch 10, wobei der Mischgasgenerierungsmechanismus (10) das Mischgas generiert, das die zu messende Objektsubstanz und die nicht zu messende Objektsubstanz enthält, deren Massenzahl in einen Bereich von ±4 der Massenzahl der zu messenden Objektsubstanz fällt und deren Ionisierungsenergie einen unteren Grenzwert aufweist, der größer ist als der untere Grenzwert der Ionisierungsenergie der zu messenden Objektsubstanz.

Revendications

1. Dispositif d’analyse de gaz (100) comprenant un mécanisme de génération de gaz mixte (10) qui comprend un four de chauffage (11) qui est conçu pour chauffer un creuset (11a) dans lequel un échantillon est placé tout en introduisant un gaz porteur qui est une substance objet qui ne doit pas être mesurée, pour générer un gaz échantillon qui contient une substance objet à mesurer en vaporisant au moins une partie de l’échantillon et pour évacuer un gaz mixte comprenant le gaz porteur et le gaz échantillon,

un spectromètre de masse quadripolaire (20) doté d’un espace de mesure dans lequel le gaz mixte généré par le mécanisme de génération de gaz mixte (10) est introduit et qui est conçu pour effectuer une analyse quantitative de la substance objet à mesurer en donnant de l’énergie à la substance objet à mesurer et à la substance objet à ne pas mesurer dans l’espace de mesure, et
un mécanisme de contrôle de pression (30) conçu pour ajuster une pression dans l’espace de mesure, dans lequel
le mécanisme de contrôle de pression (30) est conçu pour ajuster la pression dans l’espace de mesure de manière à ce que l’énergie qui est donnée à la substance objet à ne pas mesurer dans l’espace de mesure soit égale ou inférieure à la valeur limite inférieure de l’énergie d’ionisation de la substance objet à ne pas mesurer et supérieure ou égale à la valeur limite inférieure de l’énergie d’ionisation de la substance objet à mesurer,
dans lequel, lorsque la pression dans l’espace de mesure diminue, la vitesse d’un électron pour ioniser la substance est rapide et l’énergie donnée à la substance augmente, et lorsque la pression dans l’espace de mesure augmente, la vitesse d’un électron pour ioniser la substance est lente et l’énergie donnée à la substance diminue.

2. Dispositif d’analyse de gaz (100) selon la revendication 1, dans lequel

le mécanisme de génération de gaz mixte (10) est conçu pour générer le gaz mixte contenant de multiples substances objets à ne pas mesurer, et
le mécanisme de contrôle de pression (30) est conçu pour ajuster la pression dans l’espace de mesure de manière à ce que l’énergie donnée à la substance objet à ne pas mesurer soit égale ou inférieure à la valeur limite inférieure de la substance objet à ne pas mesurer ayant la valeur limite inférieure de l’énergie d’ionisation qui est la plus faible parmi les multiples substances objets à ne pas mesurer introduites dans l’espace de mesure.

3. Dispositif d’analyse de gaz (100) selon la revendication 1 ou 2, dans lequel
le mécanisme de contrôle de pression (30) com-

prend une chambre (31) à laquelle le spectromètre de masse quadripolaire (20) est relié et qui possède un espace interne conçu pour communiquer avec l'espace de mesure du spectromètre de masse quadripolaire (20), une conduite d'introduction (L3) qui est conçue pour introduire au moins une partie du gaz mixte généré par le mécanisme de génération de gaz mixte (10) dans l'espace interne de la chambre (31) et une vanne de régulation de pression qui est agencée dans la conduite d'introduction (L3) et conçue pour ajuster la pression de l'espace interne de la chambre (31).

4. Dispositif d'analyse de gaz (100) selon l'une ou l'autre des revendications 1 à 3, dans lequel le gaz porteur est du gaz He, et
le gaz échantillon contient du D2 en tant que substance objet à mesurer.

5. Dispositif d'analyse de gaz (100) selon l'une des revendications 1 à 4, dans lequel le four de chauffage (11) est un four à impulsion, et
le creuset (1la) est un creuset en graphite.

6. Dispositif d'analyse de gaz (100) selon la revendication 5, dans lequel

le gaz échantillon contient du D2, qui est la substance objet à mesurer, et du CO qui est une substance objet à ne pas mesurer, et
le mécanisme de génération de gaz mixte (10) comprend en outre une unité d'oxydation (14) qui est conçue pour oxyder le gaz mixte évacué du four de chauffage (11), une unité de décarbonatation (15) conçue pour décarbonater le gaz mixte évacué de l'unité d'oxydation (14) et une unité de déshydratation (16) conçue pour déshydrater le gaz mixte évacué de l'unité de décarburation (15).

7. Dispositif d'analyse de gaz (100) selon la revendication 6, dans lequel
l'unité d'oxydation (14) utilise le réactif de Schutze comme agent oxydant.

8. Dispositif d'analyse de gaz (100) selon la revendication 6 ou 7, dans lequel
l'unité de décarbonatation (15) utilise au moins un agent de décarbonatation choisi parmi la chaux sodée, l'hydroxyde de sodium et l'alumine activée imprégnée d'hydroxyde de sodium.

9. Dispositif d'analyse de gaz (100) selon l'une ou l'autre des revendications 6 à 8, dans lequel
l'unité de déshydratation (16) utilise au moins un agent de déshydratation choisi parmi le peroxyde de magnésium ou le pentoxyde de diphosphore.

10. Procédé d'analyse de gaz qui utilise

un mécanisme de génération de gaz mixte (10) qui comprend un four de chauffage (11) qui chauffe un creuset (11a) dans lequel un échantillon est placé tout en introduisant un gaz porteur qui est une substance objet qui ne doit pas être mesurée, génère un gaz échantillon qui contient une substance objet à mesurer en vaporisant au moins une partie de l'échantillon et évacue un gaz mixte comprenant le gaz porteur et le gaz échantillon, un spectromètre de masse quadripolaire (20) doté d'un espace de mesure dans lequel le gaz mixte généré par le mécanisme de génération de gaz mixte (10) est introduit et qui effectue une analyse quantitative de la substance objet à mesurer en donnant de l'énergie à la substance objet à mesurer et à la substance objet à ne pas mesurer dans l'espace de mesure, et un mécanisme de contrôle de pression (30) qui ajuste une pression dans l'espace de mesure,
dans lequel l'énergie qui est donnée à la substance objet à ne pas mesurer dans l'espace de mesure est rendue égale ou inférieure à la valeur limite inférieure de l'énergie d'ionisation de la substance objet à ne pas mesurer et supérieure ou égale à la limite inférieure de l'énergie d'ionisation de la substance objet à mesurer en ajustant la pression dans l'espace de mesure,
dans lequel, lorsque la pression dans l'espace de mesure diminue, la vitesse d'un électron pour ioniser la substance est rapide et l'énergie donnée à la substance augmente, et lorsque la pression dans l'espace de mesure augmente, la vitesse d'un électron pour ioniser la substance est lente et l'énergie donnée à la substance diminue.

11. Procédé d'analyse de gaz selon la revendication 10, dans lequel
le mécanisme de génération de gaz mixte (10) génère le gaz mixte contenant la substance objet à mesurer et la substance objet à ne pas mesurer dont le numéro de masse se situe dans une plage de ± 4 du numéro de masse de la substance objet à mesurer et dont la valeur limite inférieure de l'énergie d'ionisation est supérieure à la valeur limite inférieure de celle de la substance objet à mesurer.

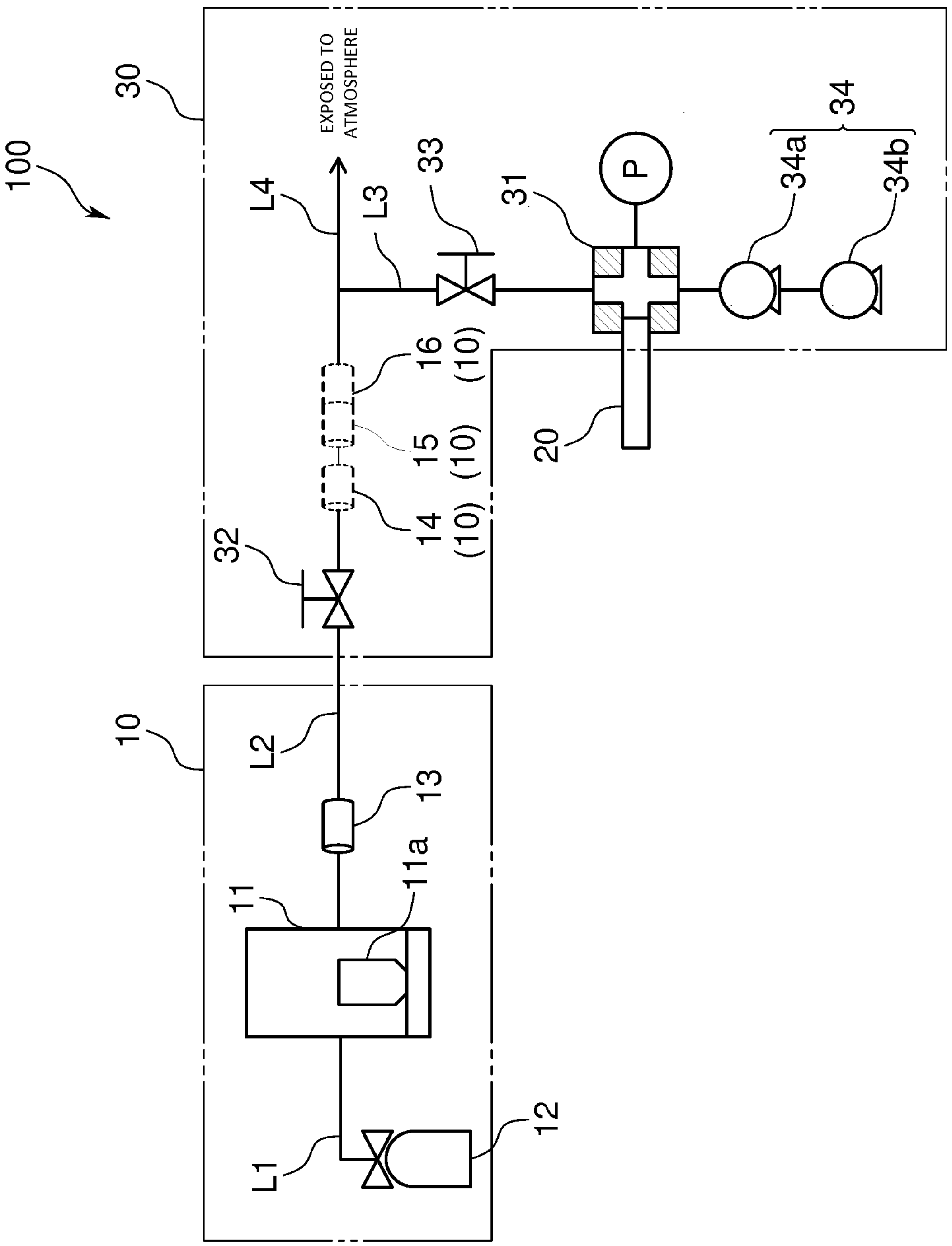

100
10
11
11a
12
13
L1
L2
30
32
14
(10)
15
(10)
16
(10)
L3
L4
EXPOSED TO ATMOSPHERE
33
31
P
20
34
34a
34b

FIG.1

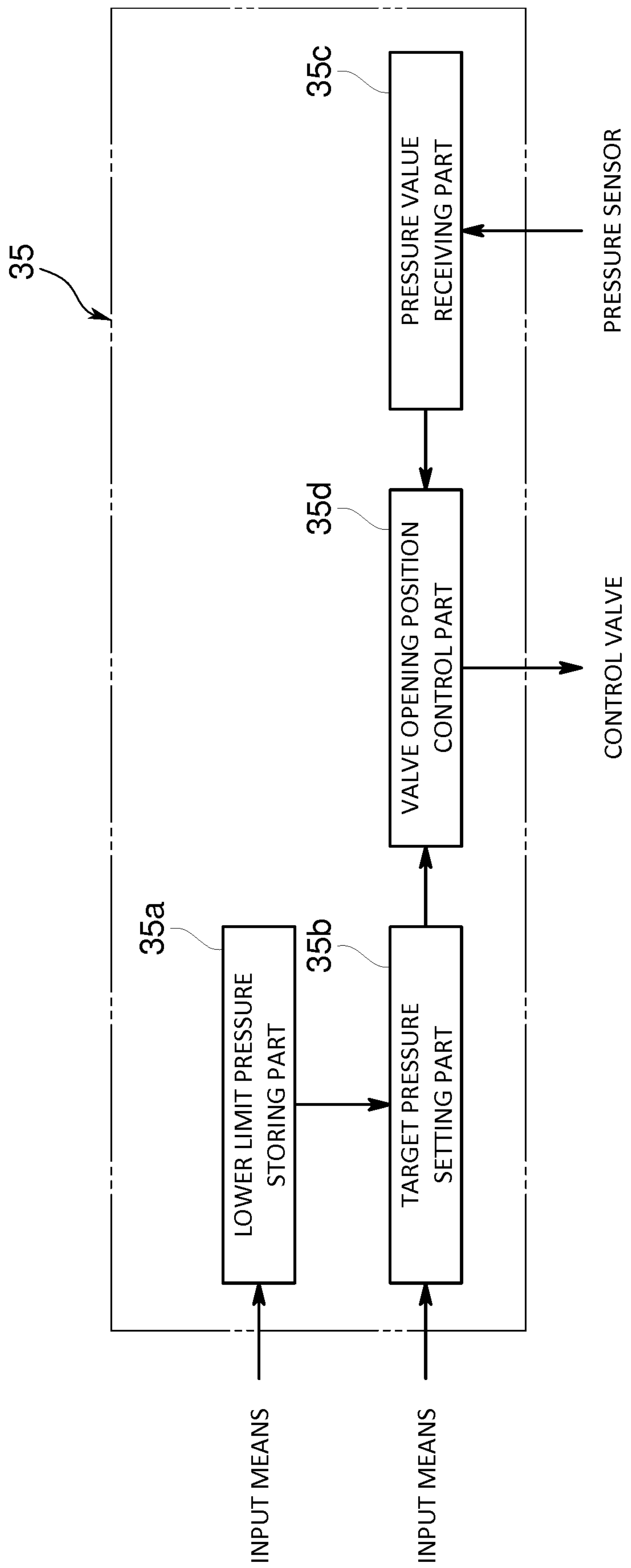

35
35a
LOWER LIMIT PRESSURE STORING PART
35b
TARGET PRESSURE SETTING PART
35c
PRESSURE VALUE RECEIVING PART
35d
VALVE OPENING POSITION CONTROL PART
INPUT MEANS
INPUT MEANS
PRESSURE SENSOR
CONTROL VALVE

FIG.2

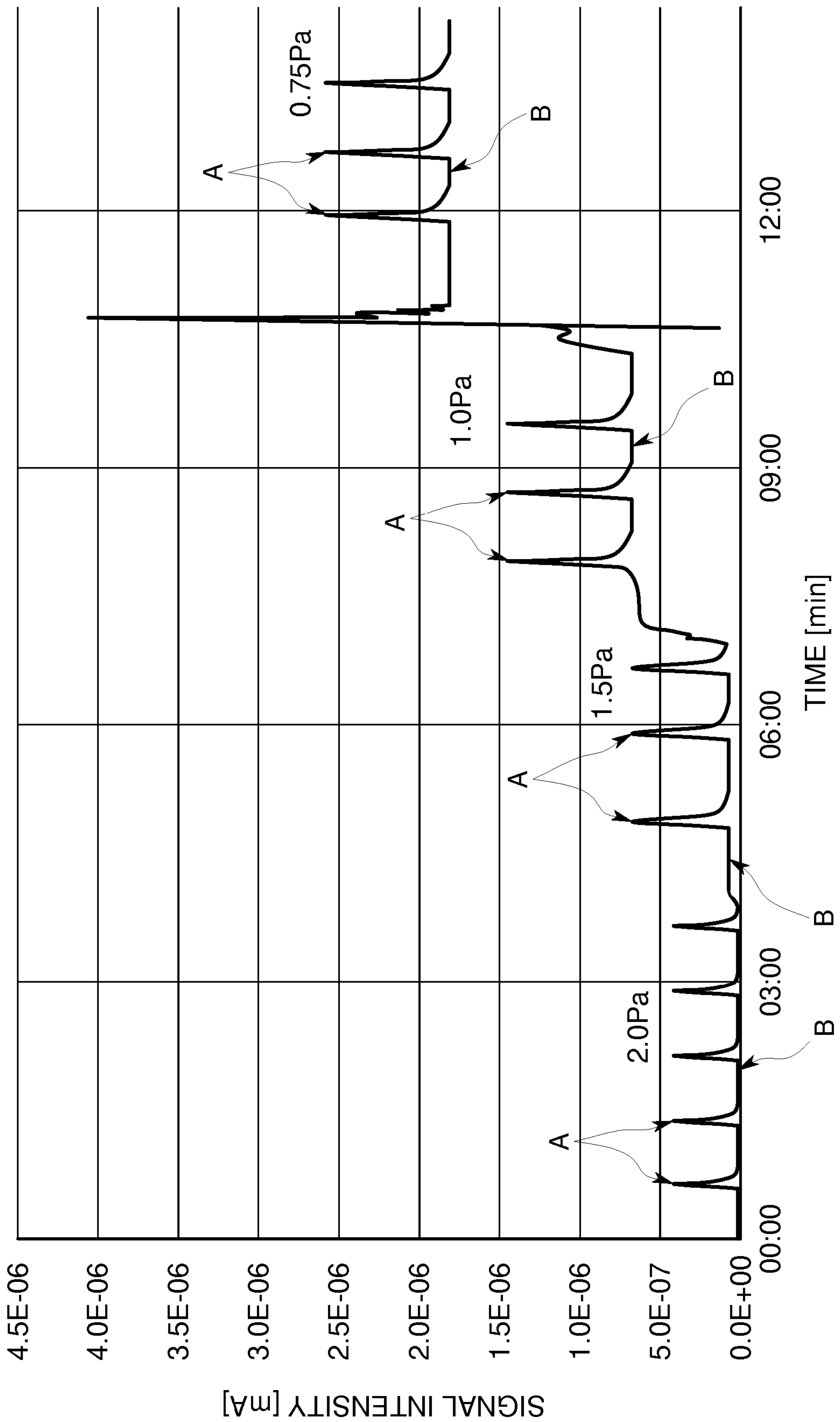

SIGNAL INTENSITY [mA]
4.5E-06
4.0E-06
3.5E-06
3.0E-06
2.5E-06
2.0E-06
1.5E-06
1.0E-06
5.0E-07
0.0E+00
00:00
03:00
06:00
09:00
12:00
TIME [min]
2.0Pa
1.5Pa
1.0Pa
0.75Pa
A
B

FIG.3

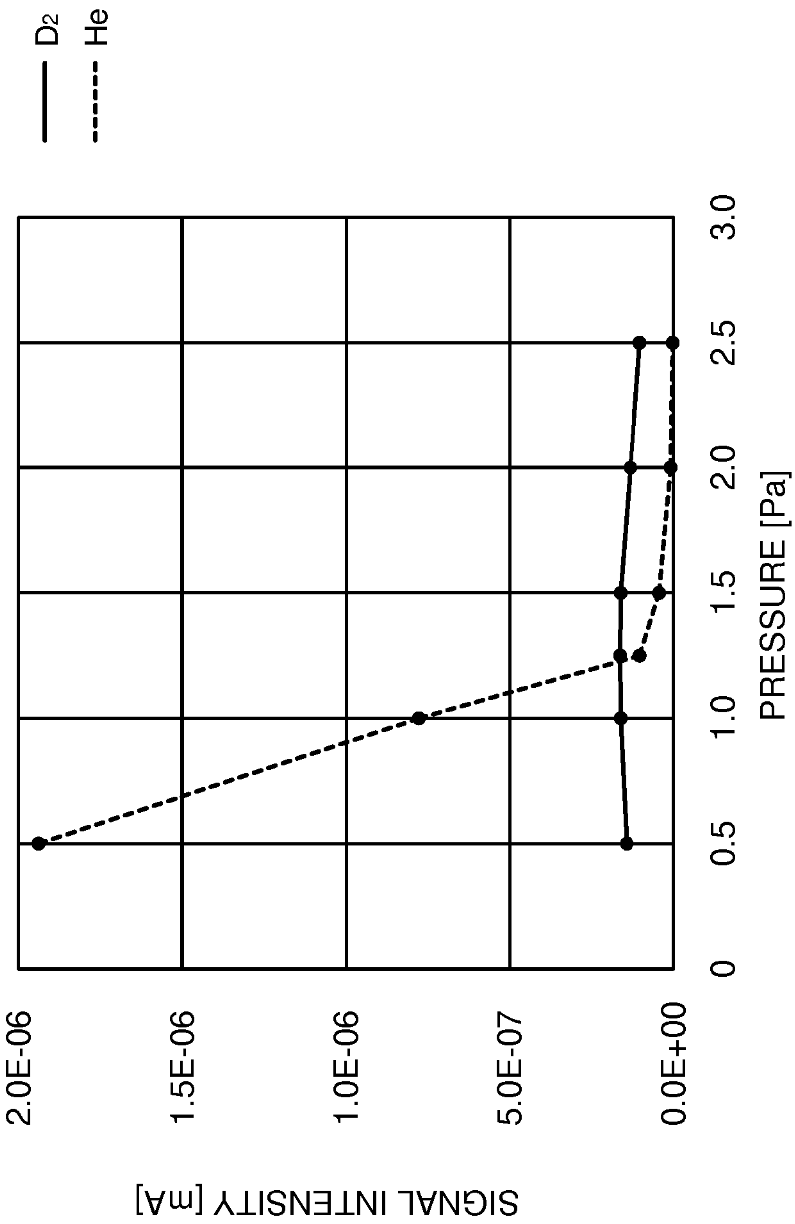

D2
He
SIGNAL INTENSITY [mA]
2.0E-06
1.5E-06
1.0E-06
5.0E-07
0.0E+00
PRESSURE [Pa]
0
0.5
1.0
1.5
2.0
2.5
3.0

FIG.4

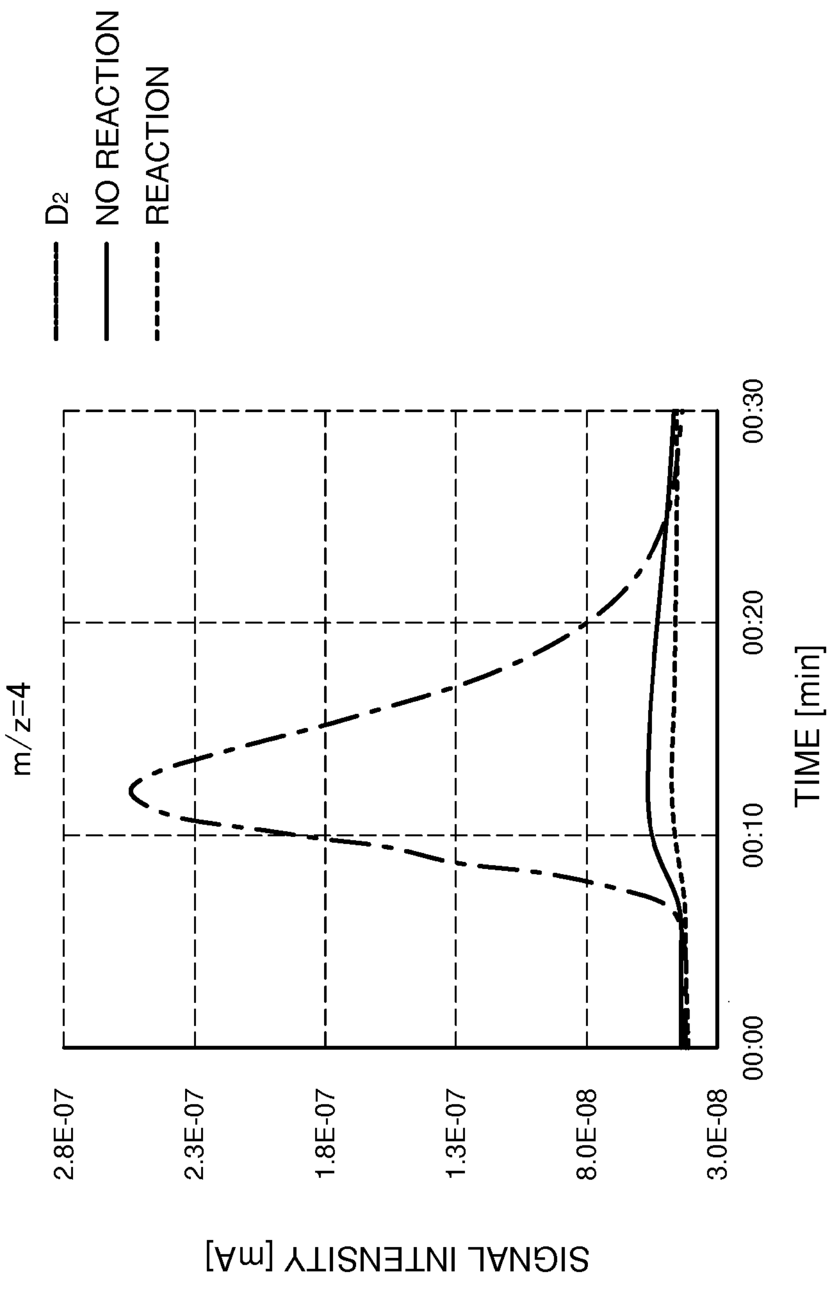

m/z=4
D2
NO REACTION
REACTION
2.8E-07
2.3E-07
1.8E-07
1.3E-07
8.0E-08
3.0E-08
SIGNAL INTENSITY [mA]
00:00
00:10
00:20
00:30
TIME [min]

FIG.5

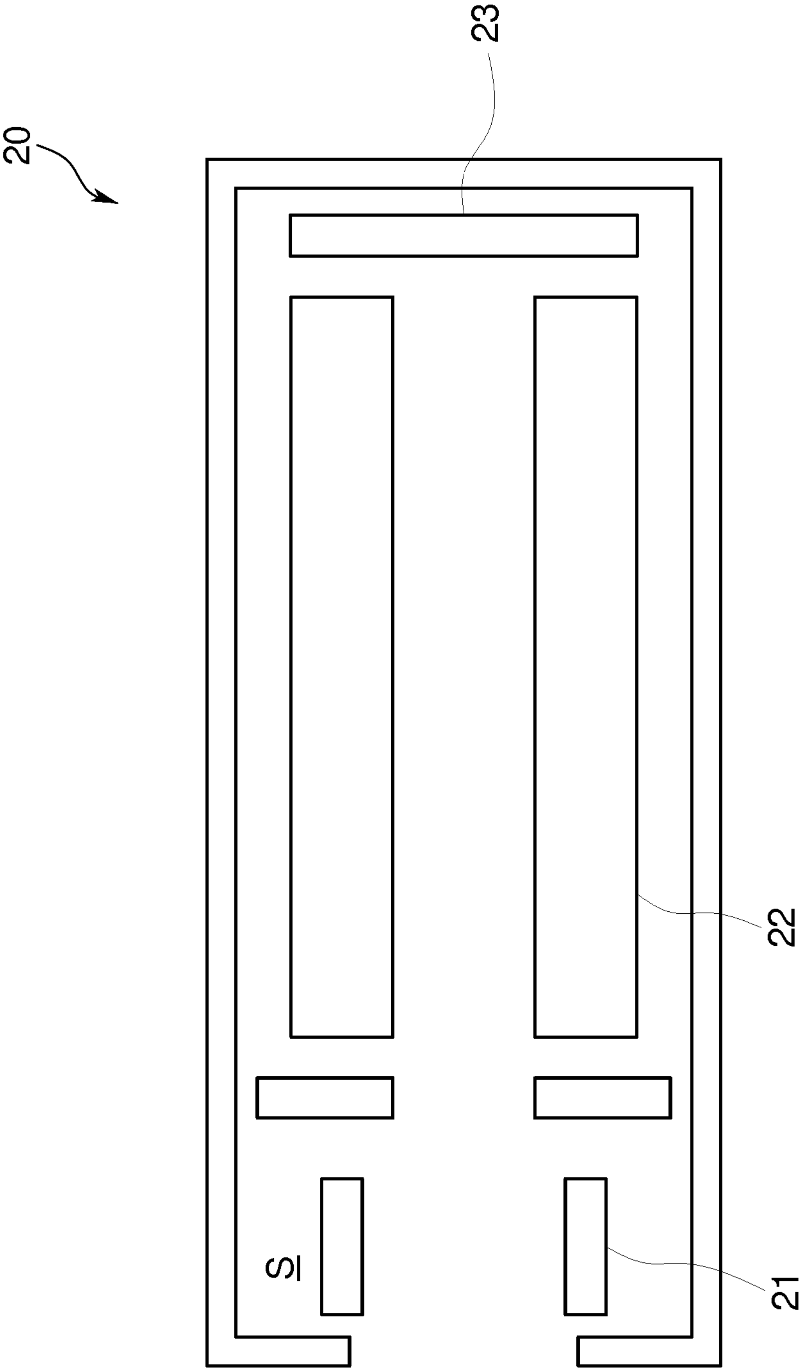
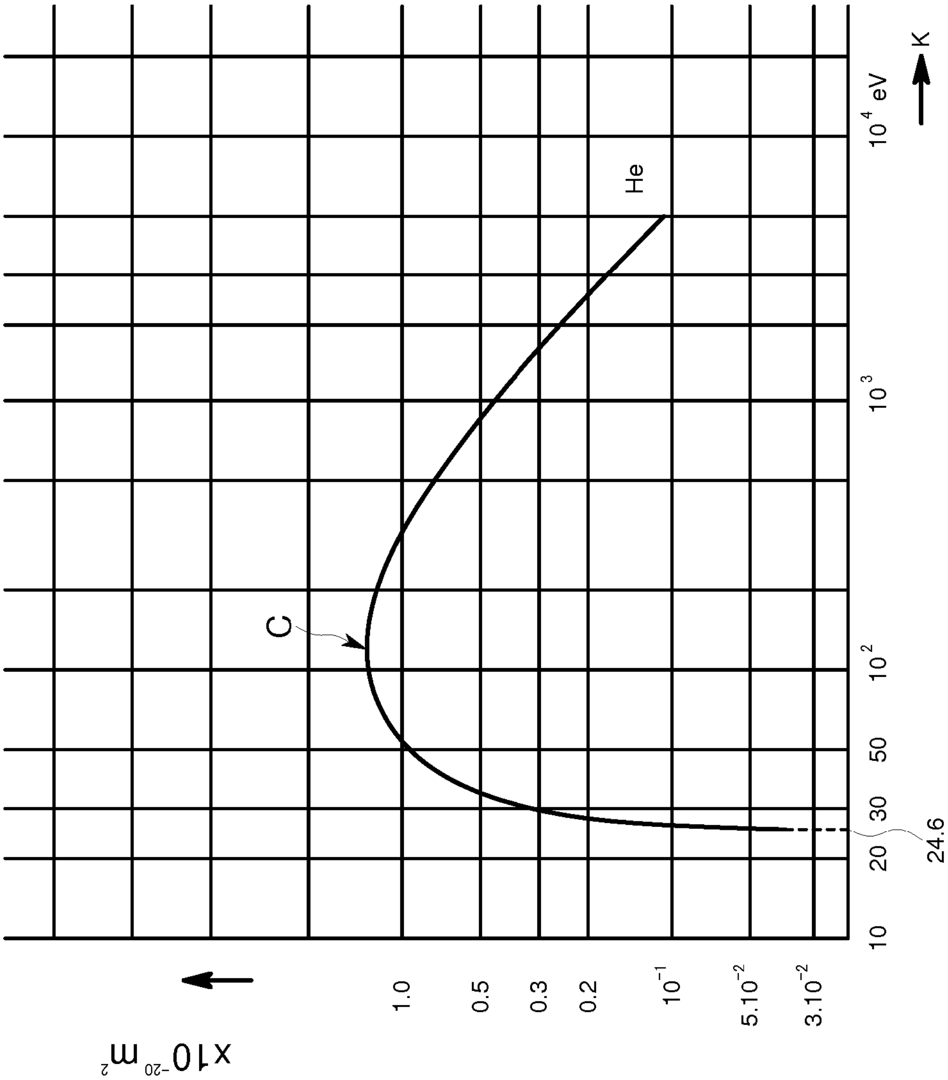


FIG.6



x10^{-20} m^2
1.0
0.5
0.3
0.2
10^{-1}
5.10^{-2}
3.10^{-2}
10
20
30
50
10^2
10^3
10^4 eV
K
He
C
24.6

FIG.7

REFERENCES CITED IN THE DESCRIPTION

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