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(71) Applicant(s):
Universität Bern
(Incorporated in Switzerland)
Hochschulstraße 4, 3012 Bern, Switzerland
(72) Inventor(s):
Christof Huber
Markus Leuenberger
(74) Agent and/or Address for Service:
Marks & Clerk
Sussex House, 83-85 Mosley Street,
MANCHESTER, M2 3LG, United Kingdom

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(54) Abstract Title: **Process and apparatus for analysis of a gaseous substance**

(57) A process and apparatus for the analysis of a gaseous substance is provided, wherein the analysis is preferably isotopic ratio analysis. The substance to be analysed is contained in a liquid starting substance as a gas or a constituent of a gas, the starting substance is passed through a degassing unit where the gases are separated from the liquid and subsequently removed for analysis. The degassing unit comprises a gas-permeable, but liquid-impermeable, membrane. Also provided is a number of distinct processes for providing a gaseous substance for the analysis of substances.

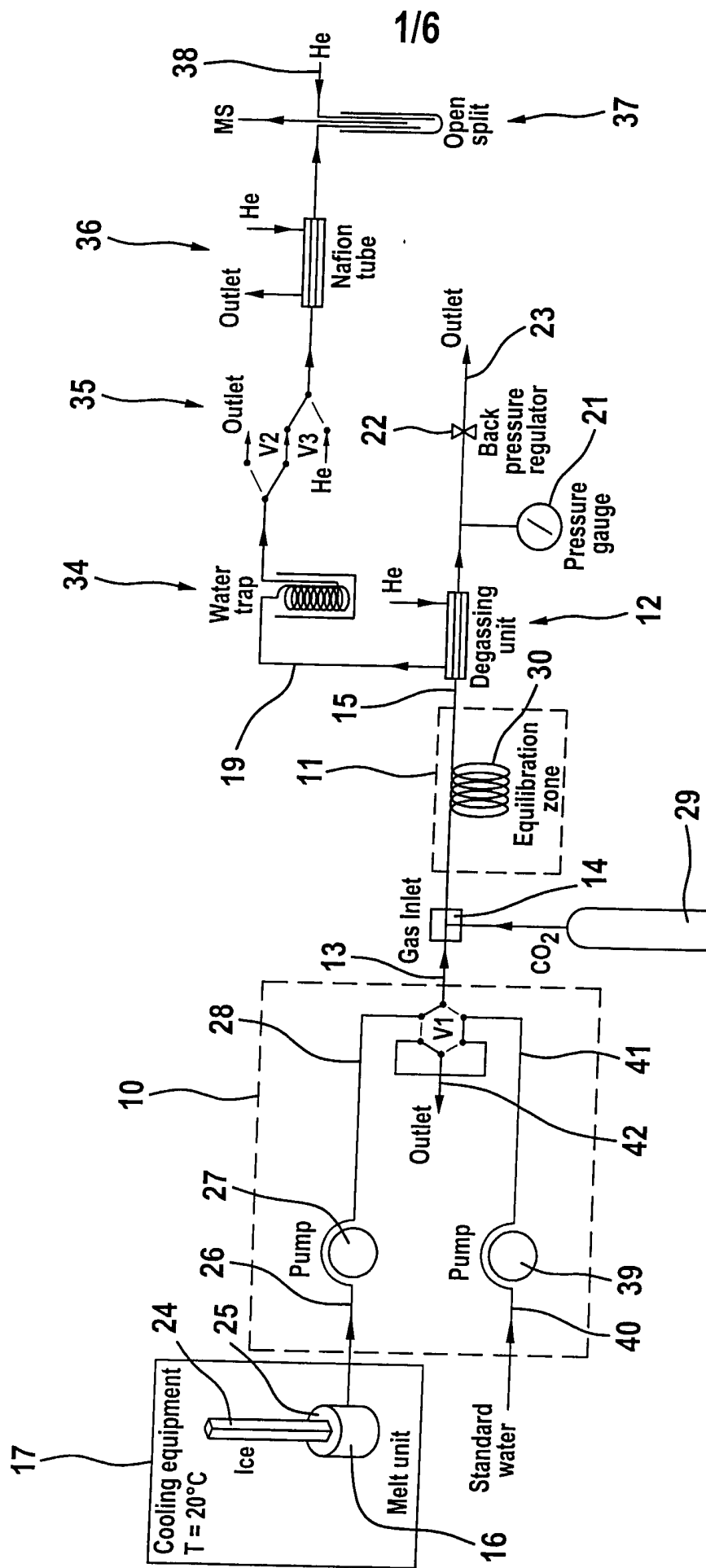


Fig. 1

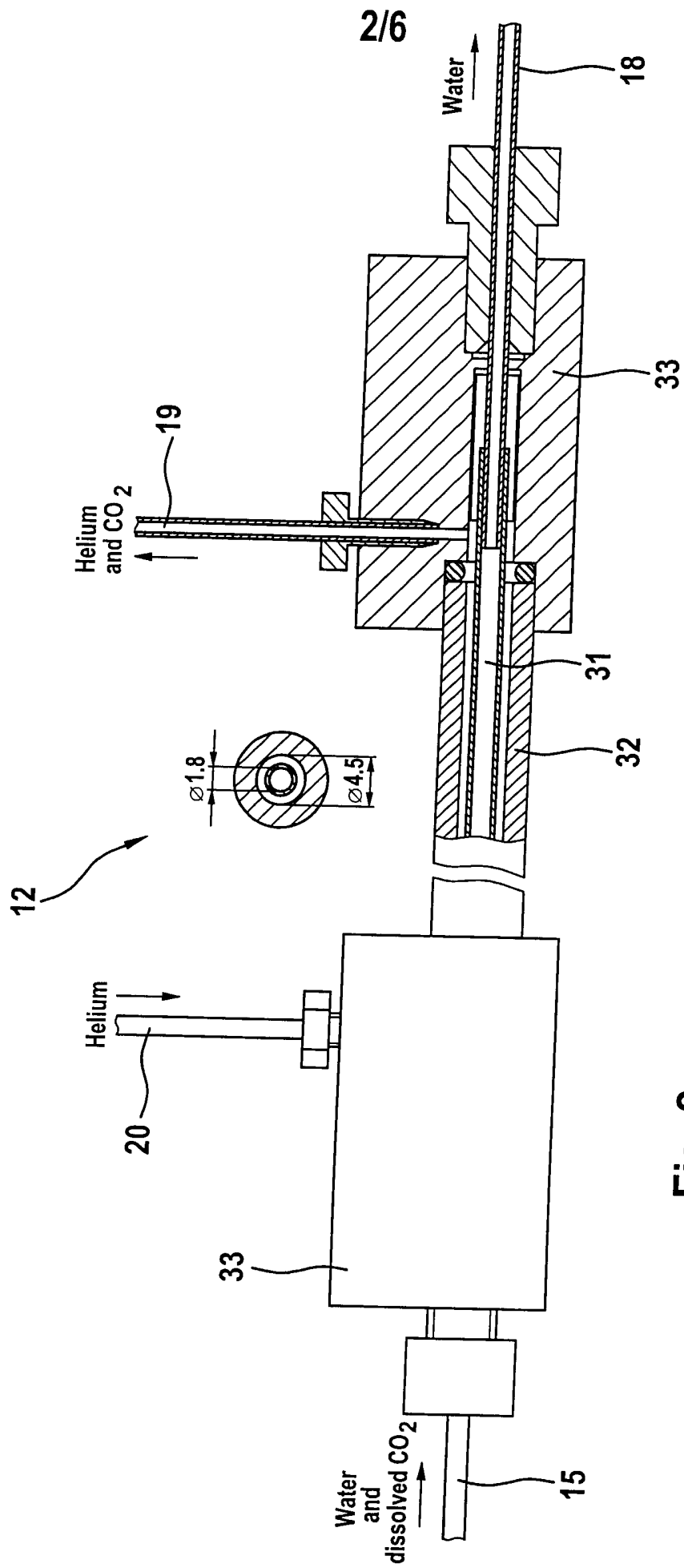


Fig. 2

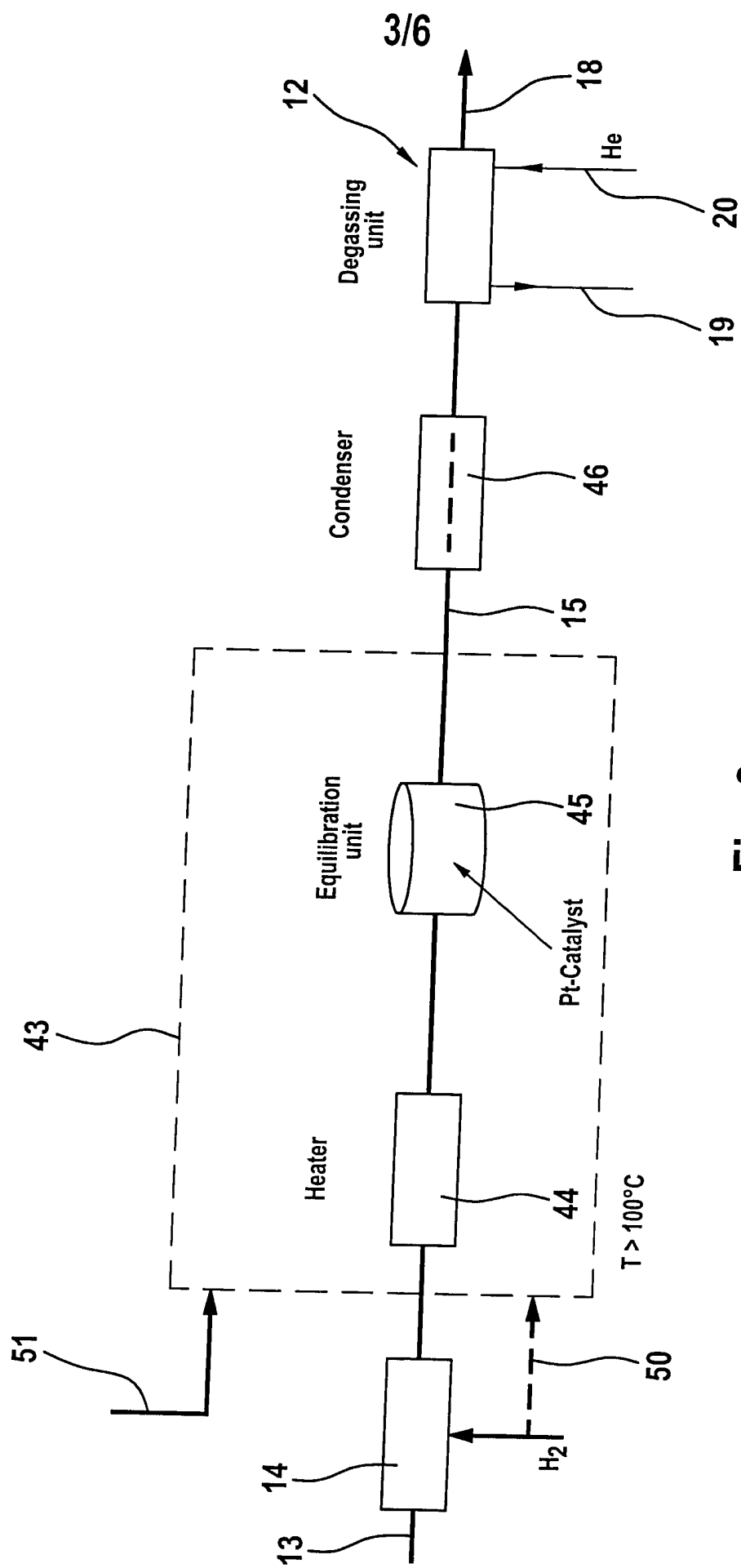


Fig. 3

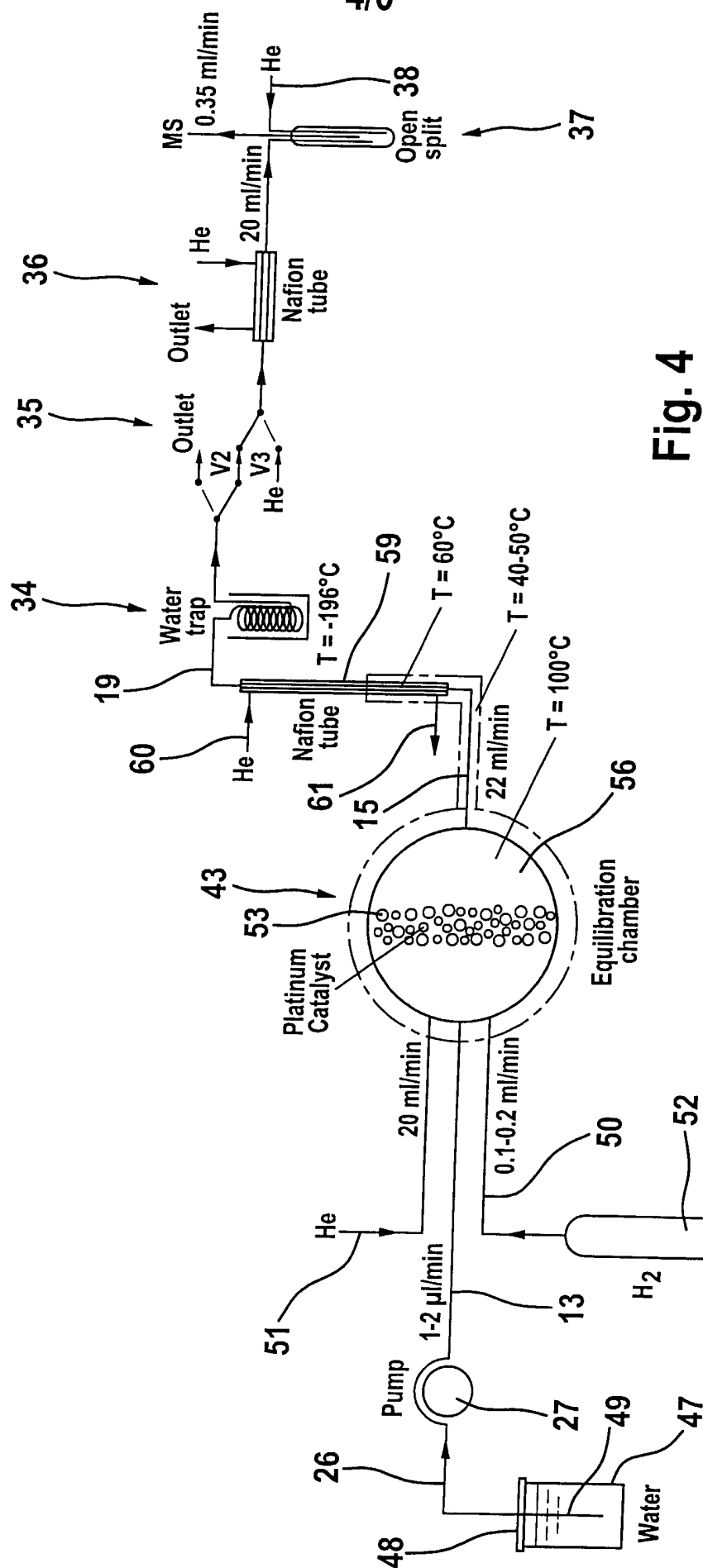


Fig. 4

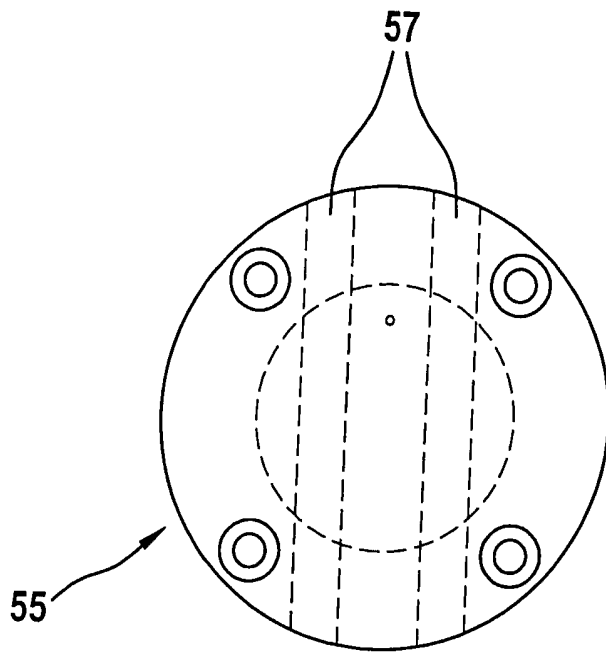


Fig. 5a

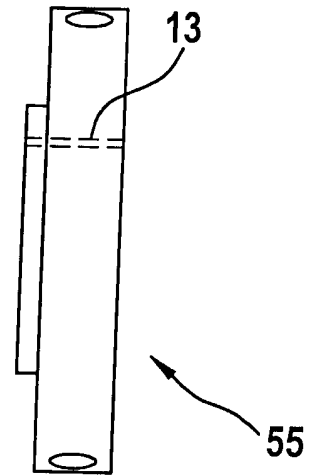


Fig. 5b

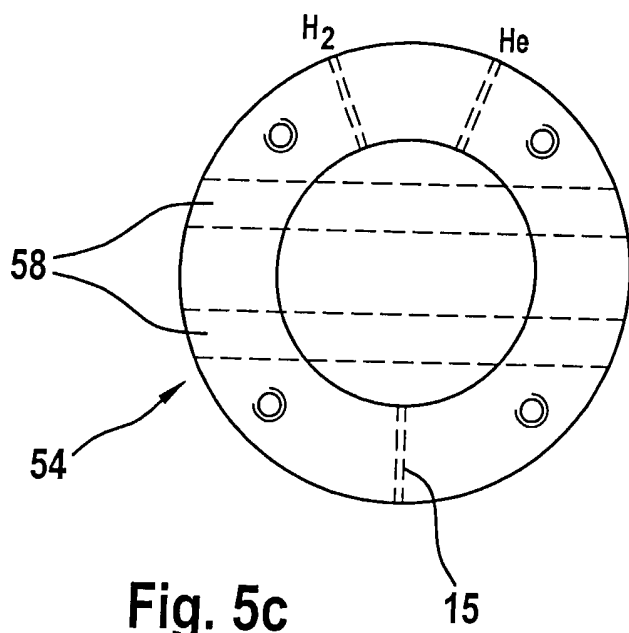


Fig. 5c

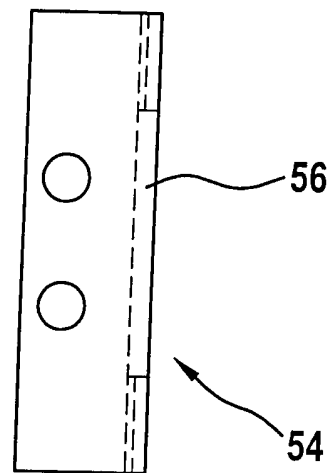


Fig. 5d

Fig. 6 (in particular for Example 1, Table 2 and Example 3, Table1)

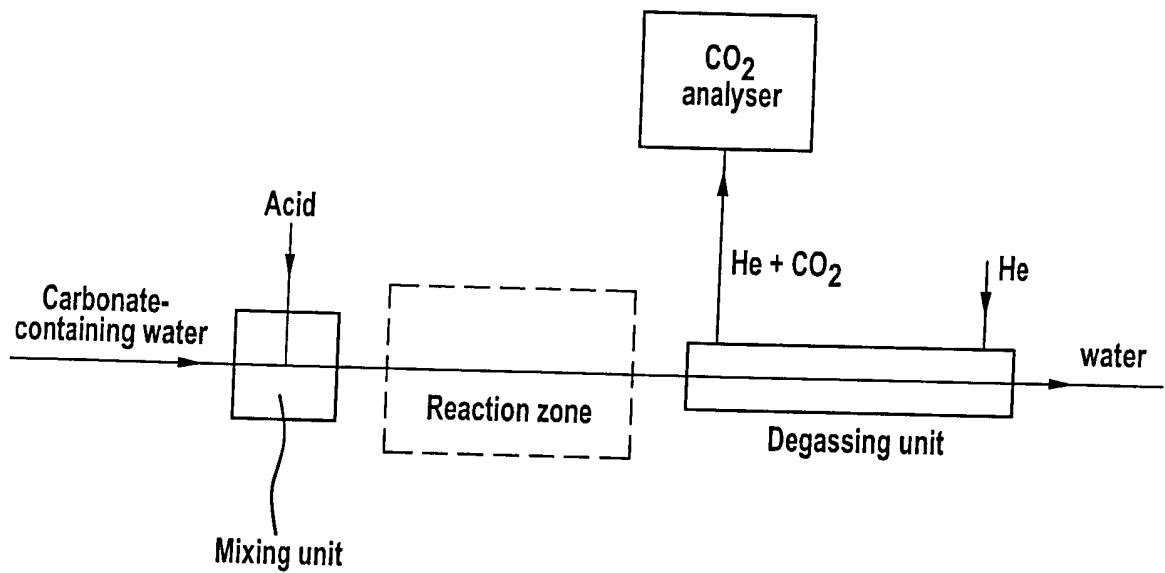
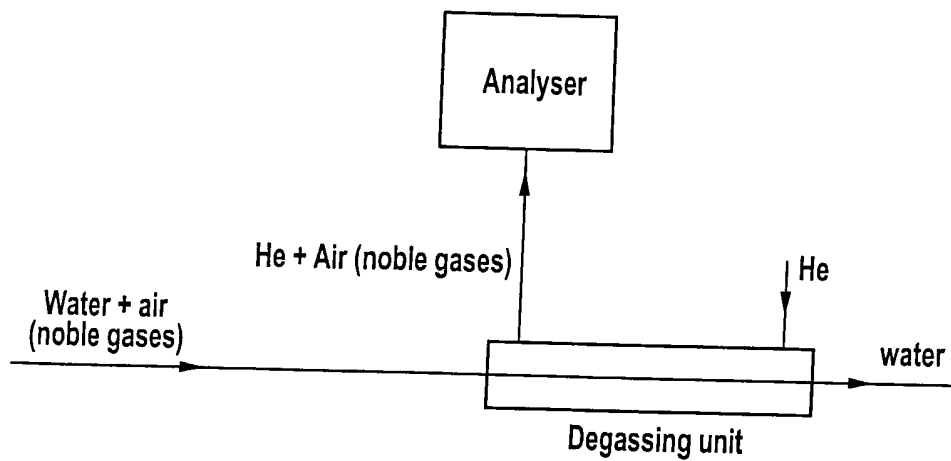


Fig. 7 (in particular for Example 5, Table 2 and Example 6, Table1)



Process and apparatus for providing a gaseous substance for the analysis of chemical elements or compounds

Description:

5

The invention relates to a process and to an apparatus for providing a gaseous substance for the analysis of chemical elements or compounds.

10 The mass spectrometry determination of elemental and of isotopic information are important analytical methods. The use of a mass spectrometer makes it possible to identify individual chemical elements or compounds. A significant application in this context is the
15 determination of the isotopic ratios of individual elements in a starting substance, for example $^{18}\text{O}/^{16}\text{O}$ in water or the determination of different hydrogen isotopes. Since the variations of the isotopic ratios are minimal, extremely precise measurement apparatus
20 and processes are required for the analysis. Therefore, importance attaches not only to the mass spectrometry itself, but also to the preparation of the chemical elements or compounds for the analysis to be carried out.

25

In an existing isotope analysis process, the oxygen of water is not analysed directly. Rather, the isotopic information is transferred to carbon dioxide (CO_2) by the method of equilibration. To this end, a small
30 amount of the water to be analysed is introduced into a vessel, as is an even smaller amount of CO_2 . The proportion of water is higher by a factor of about 10^3 than the proportion of CO_2 . The vessel is shaken and there is mixing of the isotopic information from the
35 oxygen of the water and the CO_2 . Owing to the significantly greater proportion of water, the original isotopic information from the CO_2 is virtually suppressed. The equilibrated CO_2 then contains the isotopic information of the oxygen from the water and

is removed directly or using a carrier gas and fed to an isotope mass spectrometer for analysis. The disadvantage of this system is the necessary provision of the vessels for equilibrating water and CO₂, and also
5 the residence time in the vessels required therefor. This is disadvantageous, especially in the context of relatively large sample sizes.

10 In the example mentioned, the CO₂ added to the water has the function of a reagent substance. After the equilibration, the gaseous CO₂ may be referred to as a reaction product, and the water as a residual substance. The reaction product is required for the analysis.

15 Further processes are conceivable in which a starting substance is not directly analysed, but rather information is passed on therefrom to a gaseous reaction product. It is important that there is a means
20 for rapid and reliable, precise implementation.

It is an object of the present invention to provide a process and an apparatus which allows chemical elements or compounds to be rapidly and precisely prepared for
25 analysis.

The process according to the invention has the following features:

- 30 a) the elements or compounds are contained in a starting substance,
- b) the starting substance is continuously admixed with a reagent substance,
- 35 c) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,

- d) the reaction product is separated from the residual substance,
- 5 e) the reaction product is finally removed for an analysis.

One of the essential features of the novel process compared to the example illustrated at the outset is
10 the continuous combination of the starting substance with the reagent substance. The gaseous reaction product is also formed continuously. Finally the separation of the reaction product from the residual substance likewise takes place continuously. The entire
15 process is therefore continuous and can be carried out without breaks dictated by separate steps.

A preferred field of application is the isotopic or elemental analysis, and also the quantitative
20 determination of elements or compounds in a starting substance. The information contained in the reaction products may therefore also be the elements or compounds themselves. For the sake of simplicity, unless otherwise stated, isotopic information and
25 information on compounds is also referred to as elemental information.

As explained above, the reaction results in the reaction product and the residual substance. Further
30 substances may be formed in addition which are removed. For later analysis, interest attaches to the gaseous reaction product which contains the information about the elements or compounds of the starting substance.

35 For the provision of oxygen on the one hand and hydrogen on the other hand, processes which differ in their detail may be used. For instance, for the provision of oxygen from water, the latter (in particular liquid water) and a suitable gas are

equilibrated. The gas used is preferably CO_2 . The application of the inventive idea to the example mentioned at the outset of an isotopic analysis of the elements contained in water results in the following
5 steps:

- a) oxygen and hydrogen are constituents of the water,
- b) the water is continuously admixed with CO_2 or H_2 as
10 the reagent substance,
- c) at least gaseous CO_2 or H_2 are formed continuously as the reaction product and contain the isotopic information of hydrogen or oxygen of the starting
15 substance, and water or steam are formed as the residual substance,
- d) CO_2 or H_2 are separated from the residual
20 substance,
- e) CO_2 or H_2 are finally removed for analysis. .

The process according to the invention provides for the first time the continuous equilibration of oxygen
25 and/or hydrogen with a suitable gas. Continuous feeding of water is also possible for the first time.

The continuously fed water may be present in gaseous form as steam or in liquid form as a mixture of both
30 phases. The separation of water and equilibration gas is preferably effected continuously, as is the feed of the equilibration gas to the isotopic analysis.

Advantageously, at least one of the elements H, O, C,
35 S, P or N is present in the starting substance. The process according to the invention is preferably used for the preparation of the analysis of these elements or corresponding compounds.

For the provision of hydrogen for isotopic analysis, the water is preferably equilibrated as steam with a suitable gas. Preference is given to using hydrogen as the equilibration gas. In addition to steam, the water
5 may also contain liquid water.

For the equilibration, preference is given to passing the mixture of water or steam and hydrogen over a catalyst and/or heating it. The catalyst contemplated
10 is in particular platinum.

Preference is given to adding a carrier gas to the water or hydrogen (or another equilibration gas) during or before the equilibration. The aim is to increase the
15 gas stream after the equilibration by a factor of about 10^2 .

Advantageously, the water (mainly in the form of steam) is separated from residual gases at a steam-permeable
20 membrane. At this stage of the process, the water should be present as steam. The separation is effected using a NAFION tube known per se.

Generally speaking, the residual substance on
25 separation of gaseous reaction product may be liquid, for example water or an aqueous solution. However, another state is also possible, for instance a gaseous residual substance such as steam. The liquid residual substance makes it possible to use special separating
30 processes, for instance at a membrane which is gas-permeable and liquid-impermeable. When separating, it may be advantageous to entrain and remove the gaseous reaction product from a carrier gas stream on a gas side of the membrane. The residual substance then
35 remains on the liquid side of the membrane. The separation is eased by a pressure differential between the water side and the gas side of the membrane. Preference is given to conducting helium as the carrier gas along the gas side. The pressure on the water side,

for instance in the mixture of water and CO_2 , is about half an atmosphere above the pressure on the gas side (e.g. a mixture of carrier gas and CO_2).

5 The starting substance is preferably a liquid, in particular an aqueous liquid, in which elements or compounds of interest are dissolved, e.g. drinks, in particular wine, mineral water, fruit juice. Useful liquids also include aqueous liquids or solutions such
10 as blood or urine.

When liquid water is used as a starting substance or an aqueous liquid is used, the water may also be provided by continuously melting ice. For instance, it is
15 possible by the process according to the invention to prepare drilled ice cores for an isotopic analysis. When water is continuously provided by constant melting of suitable amounts of ice, the melt water (in liquid form) is continuously aspirated by a pump and passed on
20 for the reaction or equilibration. It is also possible to provide a sample in portions in combination with a continuous further feed. For instance, sample vessels containing liquid water may be connected to a pump. After the sample vessel is emptied, an automatic
25 exchange takes place.

The reagent substance is preferably a gas. In this context, a gas mixture is a gas. However, liquids or solids are also possible.
30

Materials may be dissolved in the water (starting substance), such as carbonates, sulfates, nitrates, etc.

35 The invention further contemplates the reaction of at least one constituent of the reagent substance with at least one constituent of the starting substance, resulting in the gaseous reaction product.

As already stated above, the process according to the invention may be utilised in combination with an equilibration. In the equilibration, at least one constituent of the reagent substance equilibrates with
5 at least one of the elements or compounds of the starting substance. This preferably results in isotopic information or other elemental information being transferred or taken up. The information is then present in the reaction product.

10

In a further alternative of the process according to the invention, the reagent substance changes the pH of the starting substance, which results in the gaseous reaction product being formed. An example of a useful
15 reagent substance is an acid. Some of the reaction product may also already have been present before the reaction. The reaction then increases the proportion of the reaction product in the total amount of reaction product and residual substance.

20

The invention further contemplates the reaction product and the residual substance being in gaseous form and being separated from one another in this state.

25 It is also possible to heat at least one of the substances starting substance, reagent substance, reaction product and residual substance. This may effect a better reaction between starting substance and reagent substance or provide a better means of
30 separating reaction product and residual substance. For the provision of oxygen from water, the mixture of water and CO₂ is advantageously heated. This accelerates the equilibration or reaction. Temperatures of around 50°C are desired.

35

A modification of the process according to the invention relates to applications in which the elements or compounds to be investigated are present as gases or as constituents of gases and are contained in a liquid

starting substance in the widest sense (mixture, solution or the like). The starting substance (with the gases) is passed through a degassing unit. The gases are separated there from the liquid starting substance.

5

In the degassing unit is preferably disposed a membrane which is for separating a gas side from a liquid side and has a reduced pressure on the gas side.

- 10 After leaving the degassing unit, the gases are removed for the analysis. The individual steps are carried out continuously. The starting substance is preferably liquid water or at least one aqueous solution in the sense already described above. The elements or
15 compounds present in the starting substance may be, for example, air or its constituents. The process is of particular interest for the isotopic or quantitative analysis, for instance of air constituents in water. The radon content of the dissolved air may also be
20 determined by the analysis which follows.

The apparatus according to the invention for preparing an analysis of chemical elements or compounds has the following features:

25

- a) a reaction unit for the reaction of a starting substance containing the elements or compounds with a reagent substance,
- 30 b) a means for continuously feeding the starting substance and the reagent substance into the reaction unit,
- c) in a separating unit are provided means for
35 separating a gaseous reaction product from a residual substance,

- d) the separating unit has a first outlet for the residual substance and a second outlet for the reaction product,
- 5 e) a means for passing the reaction product on from the separating unit to an analytical instrument.

A conceivable reaction unit is a chamber provided with feeds which is otherwise closed, in which the reaction
10 of the starting substance with the reagent substance takes place. The starting substance and the reagent substance are introduced into the reaction unit individually or together, for instance using pumps, or using an elevated pressure or pressure drop provided in
15 another way. Preferred analytical instruments are mass spectrometers, isotope mass spectrometers and elemental analysers. Other analytical instruments are also possible.

20 Reaction units and separating units are preferably spatially separated. Means for transferring the reaction product and the residual substance from the reaction unit into the separating unit are then provided.

25 Advantageously, the separating unit has a membrane which is gas-permeable and at the same time liquid-impermeable. Alternatively, and taking into account the substances used and the states of matter present, the
30 separating unit may have a membrane which is permeable to steam or certain gases, but impermeable to other gases.

The impermeabilities specified are dependent upon the
35 quality of the particular membrane. In some cases, residues of the substance to be removed succeed in penetrating the membrane with the gases. If required, additional separating units may be provided which separate the residues mentioned.

In addition, heating equipment may be provided to heat at least one of the substances starting substance, reagent substance, reaction product and residual
5 substance. The heating equipment may also be provided as part of the reaction unit.

In certain cases, the starting substance is present as a solid, for instance as ice. A melt unit for melting
10 the solid starting substance is then advantageously provided. The starting substance is fed from the melt unit to the reaction unit or other units upstream thereof.

15 With regard to the equipment also, the invention independently contemplates the separation of liquid on the one hand and gas on the other hand. The separation is effected as a preparation for the analysis of chemical elements or compounds.

20

The apparatus according to the invention for providing the gaseous substance for the analysis of chemical elements or compounds has the following features:

- 25 a) a degassing unit having a liquid inlet, a liquid outlet and a gas outlet,
- b) in the degassing unit is disposed a gas permeable and liquid impermeable membrane which separates a
30 liquid zone from a gas zone,
- c) the gas zone is coupled to the gas outlet, and the liquid inlet and liquid outlet are coupled to the liquid zone,
- 35 d) from the gas outlet there is a connection to an instrument for the analysis of the elements or compounds.

The instrument contemplated for the analysis is preferably an isotope mass spectrometer (IRMS), an elemental analyser or another analytical instrument. Downstream of the degassing unit, drying units and/or
5 an open split for the exact metering of the gas may be provided. From there, a controlled fraction of the gas enters an ion source of the IRMS.

Advantageously, the degassing unit has a gas inlet
10 coupled to the gas zone. Carrier gas, in particular helium, flows through the gas inlet into the degassing unit to entrain the gas passing through the membrane.

Further features of the invention can also be discerned
15 from the claims and the description. Advantageous implementation examples of the invention are illustrated in more detail with the aid of drawings.

Fig. 1 shows an overview of the individual
20 constituents of the apparatus according to the invention and their combination for the provision of oxygen for isotopic analysis.

Fig. 2 shows an enlarged illustration of a degassing
25 unit.

Fig. 3 shows a basic illustration of the apparatus for providing hydrogen for isotopic analysis.

30 Fig. 4 shows an overview of the individual constituents of an apparatus according to the invention for providing hydrogen for isotopic analysis.

35 Fig. 5a to 5d show details of an equilibration unit for hydrogen:

Fig. 5a shows a plan view of a lid of the equilibration unit.

Fig. 5b shows a side view of the lid of Fig. 5a.

Fig. 5c shows a plan view of a bottom of the
5 equilibration unit.

Fig. 5d shows a side view of the bottom of Fig. 5c.

Fig. 6 shows a schematic diagram of an apparatus
10 according to the invention for providing CO₂ for
the analysis of the carbonate content of a
water sample.

Fig. 7 shows a schematic diagram of an apparatus
15 according to the invention for providing air
for the analysis of the air composition or of
the isotopic composition of the air components.

The key parts of an apparatus according to the
20 invention for providing oxygen or hydrogen from water
for isotopic analysis are a water feed unit 10
(dashed), an equilibration unit 11 (dashed) and a
degassing unit 12.

25 In a water line 13 between the water feed unit 10 and
the equilibration unit 11 is disposed a gas inlet 14.
The equilibration unit 11 is connected to the degassing
unit 12 via a line 15.

30 Upstream of the water feed unit 10 is disposed a melt
unit 16 for melting ice, which is maintained at a
constant cold temperature by cooling equipment 17.
Alternatively, for example, an upstream X-Y sampling
tool (autosampler) may be provided for discrete water
35 samples.

The degassing unit 12 has a water outlet 18, a gas
outlet 19 and a gas inlet 20. Connected to the water
outlet 18 are a pressure gauge 21 and a back pressure

regulator 22. Downstream of the back pressure regulator 22 is disposed a waste line 23.

5 In the cooling equipment 17, an ice rod is provided, for instance from a glaciological drilling, and has a length of 50 - 100 cm and a cross section of 2 x 2 cm or the like. One end of the ice rod 24 is melted by the melt unit 16. The liquid water is pumped out via a drillhole (cross section = 1 cm²) in the middle of a
10 melt head 25. About 25% of the molten water thus enters an intake line 26 of a very uniformly operating pump 27. This is part of the water feed unit 10 and is in particular a peristaltic pump.

15 The water passes from the pump 27 via a pressure line 28 and a four-way valve or a six-way valve V1 into the water line 13.

A CO₂ reservoir 29 is attached to the gas inlet 14. The
20 CO₂ passes through the gas inlet 14 into the water flowing through the water line 13. Specifically, the gas inlet 14 provided is a thin (35 µm), short (15 cm) pressure line (3 bar), from which the CO₂ exits and enters the water line 13 in small bubbles. The gas
25 inlet 14 may therefore be referred to as the bubble generator.

Subsequently, the mixture of water and CO₂ is conducted through the equilibration unit 11. This has a narrow
30 tube 30 or capillary of length 2 m and diameter 0.75 mm (1/16"). The tube 30 is disposed in a water bath maintained at 50°C for accelerating the desired equilibration. The flow rate is preferably set to about 1 ml per minute. This results in a transfer time of
35 about 1 minute.

The equilibrated mixture of water and CO₂ flows through the line 15 into the degassing unit 12. A tubular, gas-permeable membrane of length 5 - 10 cm and internal

diameter 1.8 mm is disposed there in a plexiglas tube of the same length (internal diameter 4.5 mm). Both tubes 31, 32 are accommodated in an aluminium casing 33 for sealing against the surrounding air. The CO₂ contained in the mixture passes through the membrane into the plexiglas tube 32 and is removed from there. To this end, a helium stream is conducted in parallel and in the same direction as (alternatively in the opposite direction to) the mixture of water and CO₂ in the degassing unit 12. The gas inlet 20 is fed from a helium source (not shown). A mixture of helium and CO₂ leaves the gas outlet 19.

The transfer of the CO₂ into the plexiglas tube 32 is dependent upon the pressure differential within and outside the tube 31. This pressure differential is about half an atmosphere. In other words, the pressure in the helium carrier gas is about 0.5 bar less than in the water within the tube 31. The pressure is determined by the cross sections of the lines in question, by the output of the pump 27 and the setting of the back pressure regulator 22. The pressure of the CO₂ before entry into the water line 13 also has an influence.

The mixture of carrier gas and CO₂ is fed from the gas outlet 19 through a first drying unit 34, a changeover valve 35 and a second drying unit 36 to an open split 37. From there, the carrier gas together with CO₂ enters an isotope mass spectrometer (IRMS). Alternatively or additionally, helium may be fed or added in the open split, see feed 38. It is also possible to feed a reference gas.

The first drying unit 34 is designed as a water trap and freezes the water still remaining in the gas out. The cooling is effected by dry ice (-78°C).

The second drying unit 36 is a NAFION tube having a helium counterstream. This drying principle is also known. The aim is to prevent any water content in the gas.

5

The valve 35 consists of two switching valves V2 and V3. In the arrangement shown in Fig. 1, the carrier gas together with CO₂ passes from the first drying unit 34 to the second drying unit 36. When V2 and V3 are
10 switched, the carrier gas together with CO₂ is discharged, while exclusively carrier gas is fed to the second drying unit 36. This allows maintenance work to be carried out on the first drying unit 34 without interrupting the carrier gas stream into the mass
15 spectrometer.

Parallel to pump 27 and line 28, a pump 39 with an intake line 40 and pressure line 41 is connected to the valve V1. Standard water can be fed to the apparatus
20 via the intake line 40 as a comparative sample. In this manner, switching of the valve V1 allows rapid and simple switching between the sample to be analysed and standard water. In Fig. 1, the valve V1 is switched for passing through the sample to be analysed. The standard
25 water is at the same time passed through the valve V1 into a waste stream 42.

In a simpler embodiment, the pressure line 28 is connected directly to the water line 13. The parts
30 having the numbers 40, 39, 41 and 42 are then not provided.

According to Fig. 3, parts of the apparatus illustrated with the aid of Fig. 1 and 2 are modified for the
35 isotopic analysis of hydrogen. The gas inlet 14 is coupled to a hydrogen source. In addition to the thin tube, (similar to tube 30 in Fig. 1) which is not shown, an equilibration unit 43 has a stronger heater 44 which allows heating to above 100°C (even

evaporation). Also, a catalyst 45 is provided downstream of the heater 44, i.e. additionally thereto, which substantially accelerates the process of equilibration of the hydrogen from water with H_2 . The
5 mixture of water (especially steam) and hydrogen (H_2) leaving the equilibration unit 43 via line 15 contains a relatively large amount of water. The latter may be partially separated by an optionally provided condenser 46 upstream of the entrance into the degassing unit 12.

10

The degassing unit 12 may have exactly the same design as in the illustration of Fig. 2 and is only shown in simplified form in Fig. 3.

15 The equilibration unit 43 may also be a reaction chamber with a heater and be charged with a catalyst, in particular of platinum, uranium or zinc. The equilibration of the H_2 is extremely temperature-sensitive. The heater 44 and the catalyst 45 are
20 therefore arranged in very close spatial proximity, in order to be able to carry out the equilibration at a precisely defined temperature.

As a result, the invention enables a rapid and precise
25 feed of hydrogen and/or oxygen isotopes from a water sample or from an ice sample for isotopic ratio determination in a mass spectrometer provided therefor.

Fig. 4 relates to the isotopic analysis of the hydrogen
30 contained in the water. Liquid water may be fed as illustrated in Fig. 1. Alternatively, Fig. 4 shows the provision of a water sample in a vessel 47, consisting in particular of glass, which is sealed in a vapour-tight manner by a rubber membrane 48. The vessel 47 and
35 the rubber membrane 48 are pierced by a hollow needle 49, through which the water passes into the intake line 26. It is also possible to evaporate the water (not shown) before entry into the equilibration unit 43, or equally to feed a vaporous sample.

In this case, the equilibration unit 43 has a special design. As already illustrated with the aid of Fig. 3, heater and catalyst material are integrated. The
5 equilibration unit 43 is a chamber with line 13 as the inlet, a separate hydrogen inlet 50, a carrier gas inlet 51 and line 15 as the outlet for a mixture of carrier gas, steam and hydrogen. For the feed into the equilibration unit 43, the hydrogen is taken from a
10 hydrogen reservoir 52.

The catalyst charge 53 consists of platinum-coated catalyst spheres of diameter 1 millimetre. The carrier gas provided is helium which flows into the
15 equilibration unit 43 at 20 ml/min. In comparison, hydrogen is fed in a stream of 0.1 to 0.2 ml/min. The liquid water in line 13 flows at about 1 to 2 microlitres/minutes. A gaseous mixture leaves the equilibration unit 43 at about 22 ml/min.

20 The equilibration unit 43 is also referred to as a deuterium chamber and in the present case is designed in two sections with a bottom 54 and a lid 55 which form a cavity 56 of about 2 to 5 ml between them.

25 Bottom 54 and lid 55 each have two heating cartridges 57, 58 for heating and evaporating, so that there is a total heating output of about 400 watt.

30 The catalyst charge 53 (about 50 to 100 HOKO beads), or alternatively uranium or zinc, are arranged in a basket of fine stainless steel mesh in the middle of the cavity 56 (not shown).

35 Lid 55 and bottom 54 are held together by four screws and are sealed against each other by an indium wire (not shown).

Downstream of the equilibration unit 43, along line 15, is disposed a NAFION tube. NAFION refers to a special material which is gas-impermeable but water-permeable, especially to steam. The NAFION tube 59 serves in this case as a degassing or drying unit and removes the majority of the water from the mixture of carrier gas, hydrogen and steam. As is customary, a carrier gas counterstream is conducted in the NAFION tube 59, and there is a carrier gas inlet 60 and an outlet 61 for the mixture of stream and carrier gas, in particular helium.

Downstream of the gas outlet 19 of the NAFION tube 59 are provided further apparatus parts in accordance with Fig. 1, such as a cold trap as a drying unit 34, the changeover valve 35, a NAFION tube as a further drying unit 36 and the open split 37. A degassing unit for separating liquid as in Fig. 1 to 3 is not provided in this case.

In this case, the equilibration unit 43 and the cavity 56 are heated to 100°C. The water entering via line 13 immediately evaporates completely. When the hydrogen is fed continuously (inlet 50), an average residence time (exchange time) in the cavity 56 of about 6 seconds at a volume of 2 ml and about 15 seconds at a volume of 5 ml is achieved. Complete HD equilibration is the consequence.

The helium entering via inlet 51 continuously purges the cavity 56 and transports the mixture (helium, hydrogen, steam) into the NAFION tube 59. In this case, line 15 is heated to about 40 - 50°C. The NAFION tube 59 has a length of about 60 centimetres. The first quarter of it is heated to 60°C. This temperature is about 10 to 20°C above the dew point of the gas. The helium counterstream in the NAFION tube 59 flows at about three times the rate of the entering gas stream (steam, hydrogen and helium) and is about 60 to 70 ml/min.

Pressures and temperatures in this case are preferably selected in such a way that no condensate occurs in the region of the NAFION tube 59.

- 5 Downstream of the NAFION tube 59, steam still present is efficiently removed in the cold trap 34. The coolant is preferably liquid nitrogen at a temperature of -196°C.
- 10 One of the features of the implementation example of Fig. 4 is that the mixture of residual substance and reaction product is present exclusively in gaseous form and thus no degassing unit is used. Only steam is removed. It may also be contemplated to feed steam as
- 15 the starting substance.

In both tables at the end of this description, a plurality of examples are in each case systematically listed for the application of the invention in the

20 context of isotopic analyses (Table 1) and elemental analyses (Table 2). The diagrams of Fig. 6 and 7 also refer thereto. Fig. 6 relates in particular to Example 1, Table 2 and Example 3, Table 1. Fig. 7 relates in particular to Example 5, Table 2 and Example 6, Table

25 1. Importance also attaches to the footnotes given under each of the tables.

Example No. 1 of Table 2 relates to the analysis of carbonate-containing water. The carbonate may be

30 present as calcium carbonate, magnesium carbonate or potassium carbonate. The carbonate is present in ionic form, i.e. as carbonate $\text{CO}_3^{(2-)}$, as bicarbonate $\text{HCO}_2^{(-)}$ and also as CO_2 . In neutral water (pH 7), the carbonate:bicarbonate: CO_2 ratio is 90:9:1. The water is

35 continuously conducted by a water pump to a mixing unit in which it is continuously admixed with acid. This changes the pH and forces the equilibrium completely to the CO_2 side in the course of the reaction zone. In the downstream degassing unit, the CO_2 is separated from the

water and conducted with a helium stream into a CO₂ analyser. The CO₂ analysis results in a quantitative carbonate content determination, since the CO₂ content is proportional to the carbonate content.

5

When the CO₂ analyser is replaced by a mass spectrometer, the carbon isotope content of the carbonate ($\delta^{13}\text{C}$) and also the oxygen isotope content of the water may be determined, see Table 1, Example 3.

10

The apparatus shown in Fig. 6 may also be used solely as a degassing unit, see Fig. 7. The apparatus may be used in this form as an isotopic or elemental analysis unit for ground water, ice water, etc., see in particular Table 2, Example 5 and Table 1, Example 6.

15

Example 1 in Table 1 relates to Fig. 1; the examples 2a, 2b in Table 1 relate to Fig. 3 and 4.

20 In the two tables which follow, the starting substance is water or at least an aqueous solution. This also includes blood, urine, etc., and also all further medicinal or pharmaceutical areas of application.

TABLE 1: EXAMPLES OF ISOTOPIC ANALYSES

Example No.	Starting substance gaseous/liquid	Elements of interest	Equilibration substance added gaseous/liquid	Equilibration gas to be removed	Residual liquid substance to be removed from the equilibration gas	Information
1	Water* Liquid	O	Gaseous CO ₂	CO ₂	Water	$\delta^{18}\text{O}$ of H ₂ O
2a ⁺	a) Water* liquid	a) H	a) Gaseous H ₂	a) H ₂	a) Water	δD of H ₂ O
2b ⁺	b) Water* liquid	b) H	b) Gaseous H ₂	b) H ₂	b) Steam	δD of H ₂ O
2c ^o	b) Water* gaseous	b) H	b) Gaseous H ₂	b) H ₂	b) Steam	δD of H ₂ O
3	Carbonate- containing water* (MgCO ₃ or K ₂ CO ₃ or CaCO ₃ + HCO ₃ (-) + CO ₃ (2-) + ...)	C	Acid (e.g. orthophosphoric acid H ₃ O ₄ P)	CO ₂ formed by the reaction	Water containing Mg(2+) K(2+) Ca(2+)	$\delta^{13}\text{C}$ of carbonate plus $\delta^{18}\text{O}$ of H ₂ O

4	Sulfate-containing water* (CaSO ₄ or MgSO ₄ or K ₂ SO ₄ etc.)	S	Acid (e.g. orthophosphoric acid H ₃ O ₄ P)	SO ₂ formed by the reaction	Water containing Ca(2+) Mg(2+) K(2+)	δ ¹⁸ S of sulfur, plus possibly δ ¹⁸ O of H ₂ O
5	Nitrate-containing water* (NaNO ₃)	N	pH-dependent reaction	Nox (NO, NO ₂ , N ₂ O, NH ₃)	Water	δ ¹³ N
6	Ice, ground water*	All isotopes in air	none	Air components	Water	Isotopic composition of the air components

+: With reference to Fig. 3.

&: No degassing unit is used here, since only gaseous substances are present. However, these gaseous substances are conducted through a drying unit (NAFION tube) before analysis, see Fig. 4.

°: According to Fig. 4, when the samples have also been fed in gaseous form. For example, gaseous feed of water vapour in air.

In Examples 3 - 5, salts of the corresponding elements are usually dissolved in water (present as ions) and may partly be released as gas by changing the pH.

*: The term water also covers all aqueous solutions such as blood, urine, etc.

TABLE 2: EXAMPLES OF ELEMENTAL ANALYSES

Example No.	Starting substance gaseous/liquid	Elements of interest	Gaseous/liquid substance added gaseous/liquid	Reaction product to be removed	Residual liquid substance to be removed from the reaction product	Information
1	Carbonate-containing water* (MgCO_3 or K_2CO_3 or $\text{CaCO}_3 + \text{HCO}_3^-$) + $\text{CO}_3^{2-} + \dots$)	C, or sum of CO_3^{2-} , HCO_3^- , CO_2)	Acid (e.g. orthophosphoric acid $\text{H}_3\text{O}_4\text{P}$)	CO_2 formed by the reaction	Water containing Mg^{2+} , K^{2+} , Ca^{2+}	Carbonate content
2	Sulfate-containing water* (CaSO_4 or MgSO_4 or K_2SO_4 etc.)	S	Acid (e.g. orthophosphoric acid $\text{H}_3\text{O}_4\text{P}$)	SO_2 formed by the reaction	Water	Sulfate content
3	Phosphide-containing water* (Ca_3P_2)	P	pH-dependent reaction	PH_3 formed by the reaction	Water containing Ca^{2+} , Mg^{2+} , K^{2+}	Phosphorus content

4	Nitrate-containing water* (NaNO ₃)	N	PH-dependent reaction	Nox (NO, NO ₂ , N ₂ O, NH ₃)	Water	Nitrate content
5	Ice, ground water*	All elements in air	none	Air components	Water	Air composition
6	Water*	Rn#	None	Radon gas	Water	Radon content

+: With reference to Fig. 3

#: Radon as a radioactive noble gas, analytical instrument (α -detector)

5 *: The term water also covers all aqueous solutions such as blood, urine, etc.

CLAIMS

1. Process for providing a gaseous substance for isotopic ratio analysis, having the following features:
 - a) elements or compounds to be analyzed are contained in a liquid starting substance as gases or as constituents of gases,
 - b) the starting substance is passed through a degassing unit.,
 - c) in the degassing unit, the gases are separated from the liquid starting substance,
 - d) after leaving the degassing unit, the gases are removed for isotopic analysis.
2. Process according to claim 1, characterized in that the starting substance is water or at least an aqueous solution.
3. Apparatus for providing a gaseous substance for isotopic ratio analysis, characterized by the following features:
 - a) a degassing unit (12) having a liquid inlet, a liquid outlet and a gas outlet (19),
 - b) in the degassing unit (12) is disposed a gas permeable and liquid impermeable membrane which separates a liquid zone from a gas zone,
 - c) the gas zone is coupled to the gas outlet (19), and liquid inlet and liquid outlet are coupled to the liquid zone,
 - d) the degassing unit (12) has a gas inlet (20) coupled to the gas zone for the introduction of carrier gas,
 - e) from the gas outlet (19) there is a connection to an instrument for isotopic ratio analysis.
4. Apparatus for providing a gaseous substance for the analysis of chemical elements or compounds, characterized by the following features:
 - a) a degassing unit (12) having a liquid inlet, a liquid outlet and a gas outlet (19),
 - b) in the degassing unit (12) is disposed a gas permeable and liquid impermeable membrane which separates a liquid zone from a gas zone,
 - c) the gas zone is coupled to the gas outlet (19), and liquid inlet and liquid outlet are coupled to the liquid zone,

- d) the degassing unit (12) has a gas inlet (20) coupled to the gas zone for the introduction of carrier gas,
 - e) from the gas outlet (19) there is a connection to an instrument for the analysis of the elements or compounds.
5. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in a starting substance,
 - b) the starting substance is admixed continuously with a reagent substance,
 - c) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,
 - d) the gaseous reaction product is separated from the residual substance, specifically at a membrane which is gas-permeable and liquid-impermeable,
 - e) finally, the reaction product is removed for analysis.
6. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in an aqueous, liquid starting substance, for whose production ice is melted continuously,
 - b) the starting substance is admixed continuously with a reagent substance,
 - c) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,
 - d) the gaseous reaction product is separated from the residual substance,
 - e) finally, the reaction product is removed for analysis.
7. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in a starting substance,
 - b) the starting substance is admixed continuously with a reagent substance,
 - c) at least one constituent of the reagent substance equilibrates with at least one of the elements of the starting substance or at least partially takes on its elemental or isotopic information,

- d) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,
 - e) the gaseous reaction product is separated from the residual substance,
 - f) finally, the reaction product is removed for analysis.
8. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in a starting substance,
 - b) the starting substance is admixed continuously with a reagent substance,
 - c) at least one constituent of the reagent substance equilibrates with at least one of the elements of the starting substance such that a gaseous reaction product is formed and a residual substance,
 - d) the gaseous reaction product contains information about the elements or compounds of the starting substance,
 - e) the gaseous reaction product is separated from the residual substance,
 - f) finally, the reaction product is removed for analysis.
9. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in a starting substance,
 - b) the starting substance is admixed continuously with a reagent substance,
 - c) the reagent substance changes the pH of the starting substance, thus forming at least one gaseous reaction product and a residual substance,
 - d) the gaseous reaction product contains information about the elements or compounds of the starting substance,
 - e) the gaseous reaction product is separated from the residual substance,
 - f) finally, the reaction product is removed for analysis.
10. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) the elements or compounds are contained in a starting substance,
 - b) the starting substance is admixed continuously with a reagent substance,

- c) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,
- d) the reaction product and the residual substance are present in gaseous form and are separated from one another in gaseous form,
- e) finally, the reaction product is removed for analysis.

11. Process for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:

- a) the elements or compounds are contained in a starting substance,
- b) the starting substance is present in gaseous form and is thus admixed continuously with a reagent substance,
- c) at least one gaseous reaction product is formed which contains information about the elements or compounds of the starting substance, and a residual substance,
- d) the gaseous reaction product is separated from the residual substance,
- e) finally, the reaction product is removed for analysis.

12. Process for providing a gaseous substance for the isotopic ratio analysis or the mass spectrometric analysis of chemical elements or compounds, having the following features:

- a) the elements or compounds to be analysed are contained in a starting substance,
- b) the starting substance is admixed continuously with a reagent substance,
- c) at least one gaseous reaction product is formed continuously which contains information about the elements or compounds of the starting substance, and a residual substance is formed as part of the reaction,
- d) the gaseous reaction product is separated continuously from the residual substance,
- e) finally, the reaction product is removed continuously for the isotopic ratio analysis or mass spectrometric analysis.

13. Process according to claim 12, characterized in that at least one of the elements H, O, C, S, P or N is contained in the starting substance.
14. Process according to claim 12 or 13, characterized in that the residual substance is liquid on separation from the gaseous reaction product.
15. Process according to claim 14, characterized in that the separation of the reaction product from the residual substance is carried out at a membrane which is gas-permeable and liquid-permeable.
16. Process according to claim 15, characterized in that the gaseous reaction product is entrained and removed by a carrier gas stream on a gas side of the membrane.
17. Process according to any one of claims 12 to 16, characterized in that the starting substance is a liquid.
18. Process according to claim 17, characterized in that the starting substance is an aqueous liquid.
19. Process according to claim 17 or claim 18, characterized in that ice is melted continuously to provide the liquid.
20. Process according to any one of claims 12 to 19, characterized in that the reagent substance is a gas.
21. Process according to any one of claims 12 to 20, characterized in that at least one constituent of the reagent substance equilibrates with at least one of the elements of the starting substance or at least partially takes on its elemental or isotopic information.

22. Process according to any one of claims 12 to 21, characterized in that at least one constituent of the reagent substance reacts with at least one constituent of the starting substance and thus forms the gaseous reaction product.
23. Process according to any one of claims 12 to 22, characterized in that the reagent substance changes the pH of the starting substance, and in that this results in the gaseous reaction product being formed.
24. Process according to any one of claims 12 to 23, characterized in that the reaction product and the residual substance are present in gaseous form and are separated from one another in gaseous form.
25. Process according to claim 12, characterized in that the starting substance is present in gaseous form and is admixed thus with the reagent substance.
26. Process according to any one of claims 12 to 25, characterized in that at least one of the substances selected from the starting substance, reagent substance, reaction product and residual substance is heated.
27. Apparatus for providing a gaseous substance for the analysis of chemical elements or compounds, having the following features:
- a) a reaction unit for the reaction of a starting substance containing the elements or compounds to be analysed with a reagent substance,
 - b) a means for continuously feeding the starting substance and the reagent substance into the reaction unit,
 - c) in a separating unit are provided means for separating a gaseous reaction product from a residual substance,
 - d) the separating unit has a first outlet for the residual substance and a second outlet for the reaction product,
 - e) a means for passing the reaction product on from the separating unit to an analytical instrument.

28. Apparatus according to claim 27, characterized in that the separating unit has a membrane which is gas-permeable and at the same time liquid-impermeable.
29. Apparatus according to claim 27 or 28, characterized by heating equipment for heating at least one of the substances selected from the starting substance, reagent substance, reaction product and residual substance.
30. Apparatus according to any of claims 27 to 29, characterized by a melt unit for melting solid starting substances.

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Claims searched: 1-4

Date of search: 27 April 2006

Patents Act 1977: Search Report under Section 17**Documents considered to be relevant:**

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-4	EP 1177765 A1 (GE MARQUETTE MEDICAL SYSTEMS) See entire document, especially para [0008]-[0009]
X	1-4	US5324938 A (HAMBITZER) See entire document, especially column1 line 37-column 2 line 9
X	1-4	US 5090256 A (ISSENMANN) See entire document, especially column 2 line 58-column 3 line 7 and column 4 line 14-39
X	1-4	US 4713095 A (RICCIARDELLI) See entire document, especially column 1 line 26-61 and column 3 line 57-64

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G1B

Worldwide search of patent documents classified in the following areas of the IPC

B01D; G01N

The following online and other databases have been used in the preparation of this search report

WPI, EPDOC, JAPIO