

[54] METHOD OF ANALYZING OXYGEN

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[52] U.S. Cl. 23/232 E
[51] Int. Cl. G01n 27/26
[58] Field of Search 23/232 E, 232 R, 230 R

[56] References Cited

UNITED STATES PATENTS			
2,083,521	6/1937	Miller	23/232 E
2,260,821	10/1941	Bendy	23/232 E
3,149,921	9/1964	Warner	23/232 E
3,342,558	9/1967	Reinecke.....	23/232 E

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[57] **ABSTRACT**
A method of analyzing oxygen capable of measuring the concentration of oxygen in a sample gas with accuracy and a minimum fluctuation with time, even when said sample gas contains combustible gases together with oxygen, which comprises:
dividing the sample gas into two parts;
removing oxygen from the one part of the two divided sample gas;
adding a predetermined amount of oxygen of a known concentration to the one part of the sample gas from which oxygen has been removed and another part of the sample gas, respectively;
converting the oxygen concentration in each part of the sample gas thus treated into electromotive force electrochemically by means of an oxygen concentration cell comprising a solid electrolyte; and
determining and indicating the difference between said respective electromotive forces.

22 Claims, 6 Drawing Figures

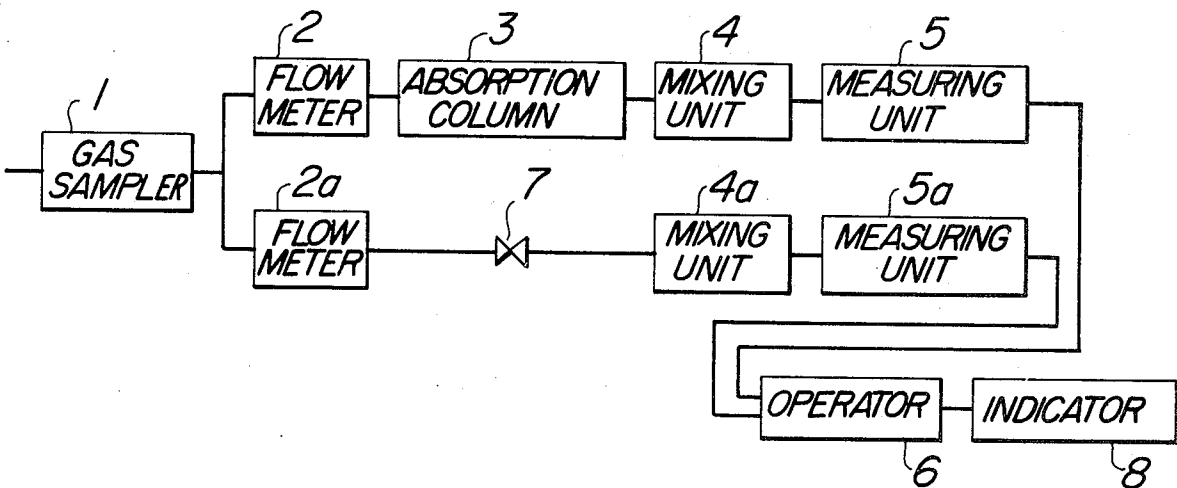


FIG. 1

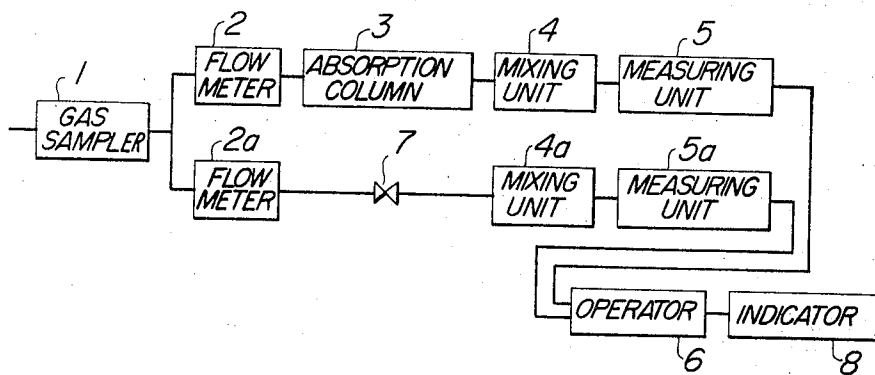


FIG. 2

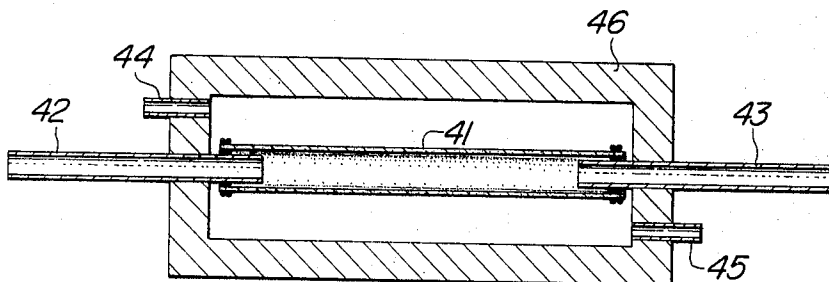


FIG. 3

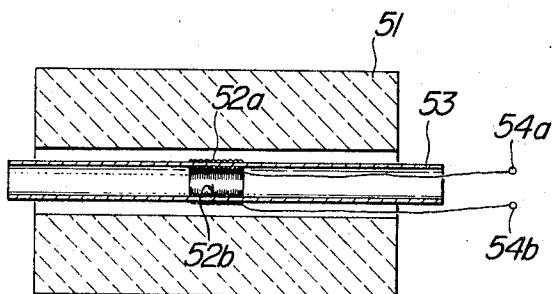


FIG. 5

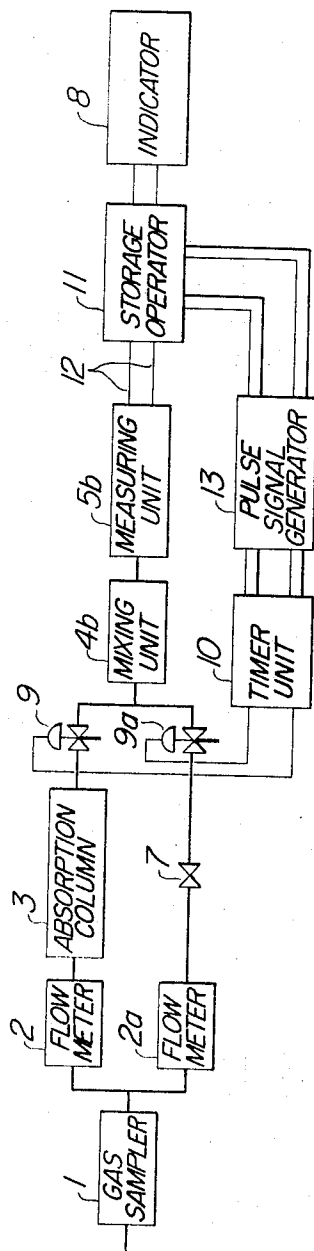


FIG. 4

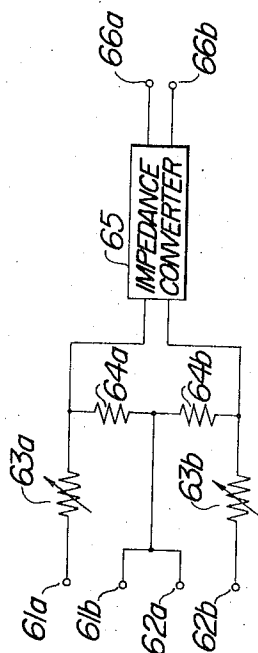
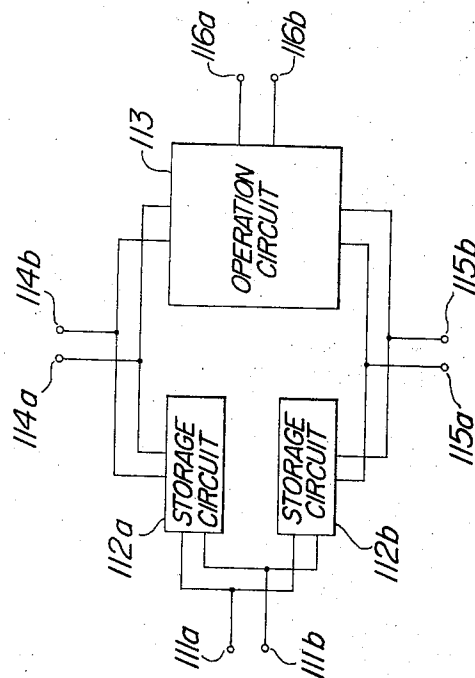


FIG. 6



METHOD OF ANALYZING OXYGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of analyzing oxygen, more particularly to improvements in the method of analyzing oxygen utilizing an oxygen concentration cell comprising a solid electrolyte.

2. Description of the Prior Art

For measuring continuously the concentration of a small amount of oxygen present in a gas, there has been utilized an liquid electrolyte or the oxidation-luminescence of yellow phosphorous. However, the former has had the disadvantage that the reproducibility and accuracy of the analysis value are poor, while the latter has suffered the disadvantage that the measuring operation is laborious and in addition, the analysis value changes with the yellow phosphorus decreasing, though the starting analysis value is accurate.

It is well known to make an oxygen concentration cell by a solid electrolyte consisting of a solid solution of at least one oxide selected from the group consisting of zirconium oxide (ZrO_2), hafnium oxide (HfO_2), cerium oxide (CeO_2), and thorium oxide (ThO_2), and at least one oxide selected from the group consisting of magnesium oxide (MgO), calcium oxide (CaO), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), neodymium oxide (Nd_2O_3), barium oxide (BaO), strontium oxide (SrO), selenium oxide (Se_2O_3), ytterbium oxide (Yb_2O_3) and samarium oxide (Sm_2O_3). Theoretically, the electromotive force (EMF) of such solid electrolyte at a temperature T ($^{\circ}K$) for an oxygen partial pressure ratio P_2/P_1 across its opposite surfaces is given as follows:

$$EMF = RT/4F \ln P_2/P_1$$

wherein R is the gas constant and F is the Faraday constant.

Based on the above equation, it is possible to determine an unknown oxygen partial pressure P_2 by measuring the EMF and the temperature while exposing the solid electrolyte to a known oxygen partial pressure P_1 at its one surface and to the unknown oxygen partial pressure P_2 at its opposite surface.

Therefore, it is possible to determine an unknown oxygen concentration, based on the partial pressure thus determined.

In the event when combustible gases, such as carbon monoxide, hydrogen or methane, coexist in a sample gas with oxygen, however, these combustible gases consume oxygen through oxidation reactions respectively, as the temperature of the oxygen concentration cell is high and platinum electrodes plated to said cell act as catalyst for the oxidation reactions, so that the true oxygen concentration in the sample gas cannot be measured. Thus, the conventional method of analyzing oxygen utilizing solid electrolytes and applying the above-described principle have been applicable to the measurement of oxygen concentrations in only such sample gases in which the amounts of the coexisting combustible gases are negligible.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved method for analyzing oxygen utilizing an oxygen concentration cell comprising a solid electrolyte.

It is another object of the invention to provide a method for analyzing oxygen capable of measuring the concentration of oxygen in a sample gas with accuracy even when combustible gases are coexisting in said sample gas.

It is a further object of the invention to provide a method for analyzing oxygen which can be used continuously with a minimum fluctuation of analysis value with the passage of time.

The foregoing objects and other objects as well as the characteristic features of the present invention will become more apparent and more readily understandable by the following description and the appended claims when read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow sheet of an embodiment of the present invention,

FIG. 2 is a sectional view of the oxygen mixing unit according to the invention,

FIG. 3 is a sectional view of the oxygen partial pressure measuring unit according to the invention,

FIG. 4 is a circuit diagram of an operator used with the embodiment shown in FIG. 1,

FIG. 5 is a flow sheet of another embodiment of the invention, and

FIG. 6 is a circuit diagram of a storage operator used with the embodiment shown in FIG. 5.

Like parts are designated by like numerals throughout the drawings.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, a sample gas is collected by a gas sampler 1 and the collected sample gas is divided into two parts by conventional means. One of the two parts of the sample gas is passed, via a cock and a first flow meter 2, through oxygen removing means, e.g. an oxygen absorption column 3 which is filled with 0.5 - 3.0 mm diameter fine particles, flakes or a sponge of a metal such, for example, as aluminum, calcium, magnesium, lithium, silic titanium, zinc and/or tungsten, whose reaction energy with oxygen is larger than the reaction energy between oxygen and a combustible gas, such as carbon monoxide hydrogen and/or methane, which might be contained in the sample gas, and which is maintained at a temperature of $250^{\circ} - 700^{\circ}C.$, whereby oxygen present in said part of the sample gas is removed therefrom. Thereafter, the sample gas emerging from the oxygen absorption column 3 is passed through means for adding a predetermined amount of oxygen of a known concentration, e.g. a first oxygen mixing unit 4, in which a predetermined amount of oxygen is added to the sample gas, and introduced into means for converting oxygen concentration into electromotive force, e.g. a first oxygen partial pressure measuring unit 5 utilizing an oxygen concentration cell comprising a solid electrolyte.

The first oxygen mixing unit 4, as shown in FIG. 2, is composed of an enclosure 46 having an oxygen inlet port 44 and an oxygen outlet port 45, a small diameter

tube 41 disposed in said enclosure 46, and a sample gas inlet conduit 42 and a sample gas outlet conduit 43 extending into said enclosure 46 and hermetically connected to the opposite ends of said tube 41 respectively, said tube 41 being made of an oxygen-permeable material capable of passing constantly 0.001 - 0.05 cc/min.cm² of oxygen therethrough under normal state (1 atm., 0°C.), e.g. a film of silver, silicon rubber, ethylene tetrafluoride resin, natural rubber or polyethylene, or a sintered metal, a porous glass or a porous ceramic having numerous ultra-fine interconnected pores capable of passing oxygen at the rate specified above. Oxygen of a known concentration is introduced into the enclosure 46 from the inlet port 44 and discharged therefrom from the outlet port 45, after passing around the tube 41. During passage in the enclosure 46, a predetermined amount of oxygen penetrates into the tube 41 through the film or ultra-fine interconnected pores of said tube, though the quantity is very small, and is added to the sample gas passing in said tube 41. Air is usually used as oxygen to be added to the sample gas.

The first oxygen partial pressure measuring unit 5, as shown in FIG. 3, is composed of an electric furnace 51 maintained at a constant temperature of 500° - 1,000°C., a tube 53 consisting of a solid electrolyte and having opposed electrodes 52a, 52b plated on the inner and outer surfaces thereof, and lead wires 54a, 54b connecting said electrodes 52a, 52b respectively to external means for determining an electromotive force difference, e.g. the operator 6, for feeding the potentials of said electrodes to said operator 6 as inputs of said operator. The arrangement is such that the sample gas and a reference gas of a known oxygen concentration, which is usually air, may be passed along the inner and outer surfaces of the tube 53 respectively. It should be understood that the tube 53 may be in a U-shape (not shown).

Another part of the sample gas, as shown in FIG. 1, is passed, via a cock, a second flow meter 2a and a flow regulator 7, through a second oxygen mixing unit 4a without removing oxygen therefrom, and after having a predetermined amount of oxygen of a known concentration added in the oxygen mixing unit 4a, introduced into a second oxygen partial pressure measuring unit 5a.

The second oxygen mixing unit 4a and second oxygen partial pressure measuring unit 5a are of the same constructions as those of the first oxygen mixing unit 4 and first oxygen partial pressure measuring unit 5 respectively. The lead wires 54a, 54b of the first oxygen partial pressure measuring unit 5 are respectively connected with input terminals 61a, 61b of the operator 6, and the lead wires of the second oxygen partial pressure measuring unit 5a with input terminals 62a, 62b of said operator 6.

It is apparent from above description and FIG. 1 that there is provided two sets of steps in this embodiment and the set of steps are carried out in parallel with each other for the sample gas: the step of adding the predetermined amount of oxygen of known concentration and the step of converting the oxygen concentration into electromotive force.

As shown in FIG. 4, the circuit of the operator 6 is arranged such that the input terminals 61a, 61b connected with the first oxygen partial pressure measuring unit 5 and the input terminals 62a, 62b connected with

the second oxygen partial pressure measuring unit 5a are connected with each other through variable resistors 63a, 63b and fixed resistors 64a, 64b in such a manner that the polarities of the interconnected input terminals are opposite to each other, and a resultant potential difference is fed to indicator means e.g. an indicator 8, from output terminals 66a, 66b through an impedance converter 65.

With x representing the quantity of oxygen in the sample gas, y representing the equivalent quantity of oxygen for reaction with combustible gas present, if any, in the sample gas, and c representing the quantity of oxygen added to the sample gas in the oxygen mixing unit, an electromotive force corresponding to the value measured at the first oxygen partial pressure measuring unit 5, i.e., the quantity $-y+c$ of oxygen is applied to the input terminals 61a, 61b and an electromotive force corresponding to the value measured at the second oxygen partial pressure measuring unit 5a, i.e., the quantity $x-y+c$ of oxygen is applied to the input terminals 62a, 62b. The difference between these two inputs, i.e., $(x-y+c) - (-y+c) = x$, is calculated in the operator 6, and the calculated electromotive force appears on the indicator 8, indicating the true quantity of oxygen in the sample gas.

It should be understood that another part of the sample gas passing through the flow regulator 7 may be introduced directly into the second oxygen partial pressure measuring unit 5a, without passing it through the second oxygen mixing unit 4a. In this case, an electromotive force corresponding to the quantity $x-y$ of oxygen is applied to the input terminals 62a, 62b, so that the value $(x-y) - (-y+c) = x-c$ is calculated in the operator 6. This value is also useful because the value of c is known. In other words, it is not always essential to add oxygen to the sample gas passing in the second flow passage.

For prolonging the useful life of the oxygen removing means, by maintaining the response time of each flow passage constant, it is preferable that the sample gas is passed in the first and second flow passages at the same rate of about 300 - 1,000 cc/min and it is also preferable that the oxygen of a known concentration is added in a quantity large enough for the combustible gas present, if any, in the sample gas to be completely oxidized, e.g. in a quantity of about 5 - 30 ppm.

Referring to FIG. 5, there is shown another embodiment of the present invention in which the first and second oxygen mixing units 4, 4a and the first and second oxygen partial pressure measuring units 5, 5a in the embodiment shown in FIG. 1 are replaced by a single oxygen mixing unit 4b and a single oxygen partial pressure measuring unit 5b respectively.

In the embodiment of FIG. 5, a sample gas similarly divided into two parts and passing in the first and second flow passages as in the embodiment shown in FIG. 1 is introduced into the oxygen mixing unit 4b alternately from first and second valves 9, 9a. The oxygen mixing unit 4b and oxygen partial pressure measuring unit 5b are identical in construction with the first and second oxygen mixing units 4, 4a and the first and second oxygen partial pressure measuring units 5, 5a of the first embodiment, respectively.

The first valve 9 and second valve 9a are alternately opened and closed by the function of a separately provided timer unit 10 which can be set at predetermined times. A three-way valve may be employed so as to

achieve the measurement with a minimum time lag by keeping the sample gas being discharged constantly from the discharge port of said valve and introducing the sample gas into the measuring system at any desired time.

According to the embodiment shown in FIG. 5, it is possible to use the single oxygen mixing unit 4b and single oxygen partial pressure measuring unit 5b commonly for both parts of the divided sample gas by alternately opening and closing the first valve 9 and second valve 9a, so that the number of units can be reduced to a half of that of the embodiment shown in FIG. 1.

The electromotive forces respectively corresponding to the quantities of oxygen present in the two parts of sample gas passing alternately through the oxygen partial pressure measuring unit 5b, are transmitted to a storage operator 11, shown in FIG. 5, through lead wires 12. On the other hand, the storage operator 11 is connected electrically to a pulse signal generator 13 connected to the aforesaid timer unit 10, by first pulse signal input terminals 114a, 114b and second pulse signal input terminals 115a, 115b shown in FIG. 6. It is apparent from the above description and FIG. 5 that there is provided one set of steps in this embodiment and this set of steps is carried out alternately for each part of the sample gas: the step of adding the predetermined amount of oxygen of known concentration and the step of converting the oxygen concentration into electromotor force.

The circuit of the storage operator 11, as shown in FIG. 6, includes a pair of input terminals 111a, 111b, first and second storage circuits 112a, 112b and an operation circuit 113, and operates in response to a pulse signal in synchronism with a predetermined time set by the timer unit 10 shown in FIG. 5.

With the first valve 9 open, an electromotive force corresponding to the quantity $-y+c$ of oxygen is applied to the input terminals 111a, 111b, similar to the case of the first flow passage in the embodiment of FIG. 1, and is stored in the first storage circuit 112a. On the other hand, with the second valve 9a open, an electromotive force corresponding to the quantity $x-y+c$ of oxygen is applied to the input terminals 111a, 111b, similar to the case of the second flow passage in the embodiment of FIG. 1, and stored in the storage circuit 112b. A calculation of $(x-y+c) - (-y+c) = x$ is performed in the operation circuit 113 which is similar to the operator 6 in the embodiment of FIG. 1, and the calculated electromotive force is transmitted to the indicator 8 from the output terminals 116a, 116b, and thus, the true concentration of oxygen in the sample gas is indicated on said indicator 8.

In the embodiment of FIG. 5, similar to the embodiment of FIG. 1, the sample gas passing through the second valve 9a may be introduced directly into the oxygen partial pressure measuring unit 5b, without passing it through the oxygen mixing unit 4b.

EXAMPLES

The oxygen concentrations in two kinds of highly pure nitrogen gas which were respectively contained in highly stable bombs and containing as impurities 2.9 ppm oxygen gas and 6.5 ppm hydrogen gas, and 3.0 ppm oxygen gas and 8.0 ppm hydrogen gas, were analyzed by the method of the present invention, by using the oxidation-luminescence of yellow phosphorous (A) and by using the liquid electrolyte (B). The results of

analysis are shown in Tables 1 and 2 given below for comparison.

Table 1.

Run No.	Present invention	Conventional method	
		A	B
1	2.9	2.9	2.3
2	2.9	2.8	2.7
3	2.9	2.7	2.9
4	2.9	2.6	3.3
5	2.9	2.5	3.9
6	2.9	2.3	4.1
7	2.8	2.2	3.5
8	2.9	2.0	3.1
9	2.9	1.9	2.8
10	2.9	1.8	2.4

Table 2

Run No.	Present invention	Conventional method	
		A	B
1	3.0	3.0	3.0
2	3.0	3.0	3.0
3	3.0	2.9	2.7
4	3.0	2.8	2.8
5	2.95	2.8	2.6
6	2.95	2.6	2.6
7	3.0	2.5	3.0
8	3.0	2.3	3.2
9	3.0	2.3	4.0
10	3.05	2.0	3.5
11	3.05	2.0	3.4
12	3.05	1.9	2.9

Note: The oxygen concentrations in Tables 1 and 2 are in terms of ppm.

As may be seen from Tables 1 and 2, the method for analyzing oxygen of the present invention is capable of indicating the concentration of oxygen in a sample gas with accuracy and with a minimum fluctuation, even when other combustible gases are coexisting in said sample gas.

The concentrations of very small amounts of oxygen contained in various kinds of commercial nitrogen gases were measured by the method of the invention, with the results shown in Table 3 given below:

Table 3

Nominal concentrations of impurities		Analysis value by the method of the invention
O ₂	H ₂	
2.6	6.2	2.5
6.2	0.5	6.3
6.3	9.0	6.2
8.0	15.0	7.8
12.4	15.0	12.2
12.6	20.0	12.5

Note: The concentrations in Table 3 are in terms of ppm.

Further, the concentration of oxygen contained in a gas which consisted of 5.2 ppm oxygen, 8.0 ppm hydrogen and the balance being nitrogen, and contained in a highly stable bomb, was measured by the method of the invention over an extended period of time, to examine the fluctuation of analysis value with the passage of time. The results are shown in Table 4 given below:

Table 4

Number of days after which analysis was performed	Analysis value of oxygen by the method of the invention
0	5.2
2	5.0
4	5.1
6	5.3
8	5.4
10	5.1
20	5.3
30	5.4
40	5.5
50	5.3
60	5.2
70	5.0
80	5.2

Note: The analysis values in Table 4 are in terms of ppm.

It will be understood from the foregoing description that, with the method for analyzing oxygen of the present invention, the concentration of oxygen in a sample gas can be measured with accurate and with a minimum fluctuation of analysis value, continuously, even when combustible gases are present in said sample gas, and thus, the method of the invention is of great industrial value.

While several examples have been herein disclosed, it is obvious that various changes can be made without departing from the spirit and scope of the invention as set forth in the appended claims. Further, it is to be understood that all matter hereinbefore set forth is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. A method of analyzing oxygen, which comprises:

- dividing a sample gas into two parts;
- removing oxygen from the one part of the divided sample gas;
- adding a predetermined amount of oxygen of a known concentration to the one part of the sample gas from which oxygen has been removed and another part of the sample gas, respectively;
- converting the oxygen concentration in each part of the sample gas thus treated into electromotive force electrochemically by means of an oxygen concentration cell comprising a solid electrolyte; and
- determining and indicating the difference between said respective electromotive forces.

2. A method of analyzing oxygen as recited in claim 1, wherein two sets of said steps (c) and (d) are carried out in parallel with each other for each part of the sample gas.

3. A method of analyzing oxygen as recited in claim 2, wherein said step (b) is carried out in such a way that the sample gas is contacted with a metal whose reaction energy with oxygen is larger than the reaction energy between oxygen and a combustible gas.

4. A method of analyzing oxygen as recited in claim 3, wherein said metal is fine particles, flakes or a sponge of at least one metal selected from the group consisting of aluminum, calcium, magnesium, lithium, silicon, titanium, zinc and tungsten.

5. A method of analyzing oxygen as recited in claim 2, wherein said step (c) is carried out in such a way that the sample gas and oxygen of a known concentration are contacted with each other through a quantitative oxygen permeable material.

6. A method of analyzing oxygen as recited in claim 5, wherein said quantitative oxygen permeable material is a film.

7. A method of analyzing oxygen as recited in claim 5, wherein said film is made of at least one material selected from the group consisting of silver, silicon rubber, ethylene tetrafluoride resin, natural rubber and polyethylene.

8. A method of analyzing oxygen as recited in claim 5, wherein said quantitative oxygen permeable material is porous material having numerous interconnected ultra-fine interconnected pores therein.

9. A method of analyzing oxygen as recited in claim 8, wherein said porous material is made of at least one member selected from the group consisting of metals, glass and ceramics.

10. A method of analyzing oxygen as recited in claim 1, wherein one set of said steps (c) and (d) are carried out alternately for each part of the sample gas.

11. A method of analyzing oxygen as recited in claim 10, which further comprises:

- introducing each part of the sample gas into said step (c) alternately therethrough, and
- storing the electromotive forces into which the oxygen concentration in each part of the sample gas has been converted in said step (d).

12. A method of analyzing oxygen as recited in claim 10, wherein said step (b) is carried out in such a way that the sample gas is contacted with a metal whose reaction energy with oxygen is larger than the reaction energy between oxygen and a combustible gas.

13. A method of analyzing oxygen as recited in claim 12, wherein said metal is fine particles, flakes or a sponge of at least one metal selected from the group consisting of aluminum, calcium, magnesium, lithium, silicon, titanium, zinc and tungsten.

14. A method of analyzing oxygen as recited in claim 10, wherein said step (c) is carried out in such a way that the sample gas and oxygen of a known concentration are contacted with each other through a quantitative oxygen permeable material.

15. A method of analyzing oxygen as recited in claim 14, wherein said quantitative oxygen permeable material is a film.

16. A method of analyzing oxygen as recited in claim 15, wherein said film is made of at least one material selected from the group consisting of silver, silicon rubber, ethylene tetrafluoride resin, natural rubber and polyethylene.

17. A method of analyzing oxygen as recited in claim 14, wherein said quantitative oxygen permeable material is a porous material having numerous interconnected ultra-fine interconnected pores therein.

18. A method of analyzing oxygen as recited in claim 17, wherein said porous material is made of at least one member selected from the group consisting of metals, glass and ceramics.

19. A method of analyzing oxygen which comprises:

- dividing a sample gas into two parts,
- removing oxygen from the one part of the divided sample gas,
- adding a predetermined amount of oxygen of a known concentration to the one part of the sample gas from which oxygen has been removed,
- converting the oxygen concentration in each part of the sample gas thus treated into electromotive

force electrochemically by means of an oxygen concentration cell comprising a solid electrolyte, and

e. determining and indicating the difference between said respective electromotive forces.

20. A method of analyzing oxygen as recited in claim 19, wherein two sets of said steps (c) and (d) are carried out in parallel with each other for each part of the sample gas.

21. A method for analyzing oxygen as recited in claim 19, wherein one set of said steps (c) and (d) are

carried out alternately for each part of the sample gas.

22. A method for analyzing oxygen as recited in claim 21, which further comprises:

introducing each part of the sample gas into said step (c) alternately therethrough, and

storing the electromotive forces into which the oxygen concentration in each part of the sample gas has been converted in said step (d).

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