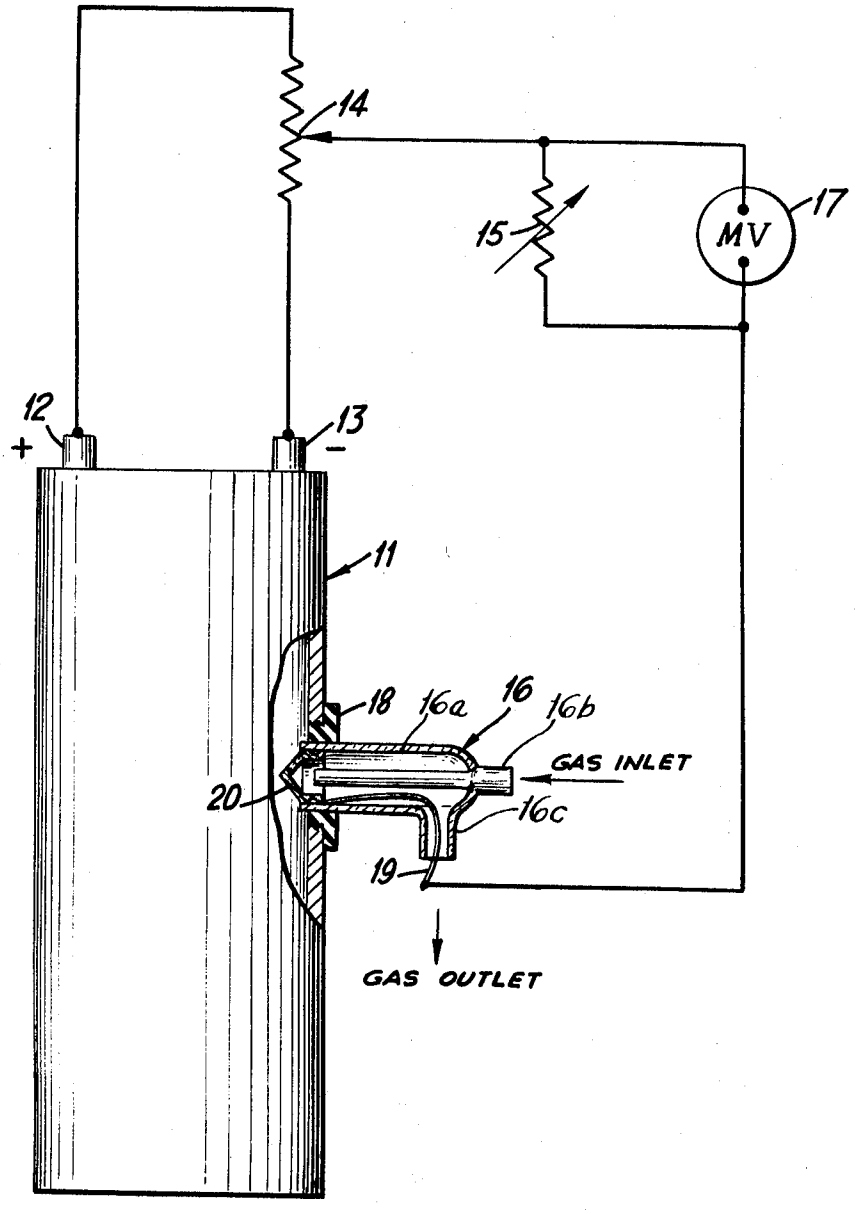
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METHOD AND APPARATUS FOR CONTINUOUSLY DETERMINING THE OXYGEN CONTENT OF GASES

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# METHOD AND APPARATUS FOR CONTINUOUSLY DETERMINING THE OXYGEN CONTENT OF GASES

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## ABSTRACT OF THE DISCLOSURE

In an apparatus for continuously determining the oxygen content in gases there is provided a hollow electrode closed by a graphite base; the outside of said base is exposed to an electrolyte, while its inside is exposed to the flow of a gas whose oxygen content is to be determined. To establish a circuit, the inside of said base is connected to an auxiliary electrode extending into said electrolyte. The intensity of the current flowing in said circuit is a function of the oxygen content of said gas.

This invention relates to a method and apparatus for the continuous determination of oxygen concentration in gases and more particularly to such improved method and apparatus having a relatively short delay of response.

In controlling the combustion of solid, liquid and gaseous fuels in metallurgical, chemical and other technical processes, there is required a reliable method of rapidly, accurately and continuously determining the concentration of oxygen in combustion gases. Analysis of the constituents in fuel combustion is most important to maintain, by preventing excessive fuel consumption, an operation under optimum economical conditions, to permit the elimination of operational failures and to prevent formation of explosive mixtures. Furthermore, in addition to the need for continuously determining the concentration of oxygen in combustion processes, such method is of great value in other productive and research fields such as microbiology, organic chemistry and the like.

There are known at present many types of devices for analyzing and testing gas mixtures for oxygen concentration and for monitoring fuel consumption. In one type of such devices: the operation is based upon the electrical measurement of thermal gas conductivity; in another type of analyzers the operation is based upon the selective absorption of gas in liquids. Further, there are known infra-analyzers and paramagnetic oxygen content analyzers. These known continuous analyzers do not provide necessary selectivity in process-monitoring, they are generally not sufficiently reliable in operation and have a relatively slow response, i.e., a relatively long inertial period or delay.

In addition to the above outlined devices, there have also been utilized electrochemical analyzers of oxygen concentration in gases. Such analyzers operate on the principle of an oxygen electrode in an alkaline medium. However, this type of analyzer does not lend itself to practicable application since the sensing element included therein has a very short lifetime in the presence of acidic gases (such as the carbon dioxide by-product) formed in the process. Furthermore, in this latter type of analyzer the electrical signal provided by the sensing element indicates the rate of gas flow rather than being directly proportional to the oxygen content.

Accordingly, it is an important object of this invention to provide an improved method of continuously automatically monitoring the oxygen content in a gas mixture; said method is selective for oxygen, reliable in operation and substantially reduces the delay in indicating oxygen concentration as compared to known methods used for the same purpose.



It is another object to provide an improved, accurate and more durable apparatus for performing the method set forth hereinbefore.

Briefly stated, in accordance with the invention, there is provided a method for automatically continuously ascertaining the oxygen content in a gas comprising the steps of applying to an electrode immersed in an electrolyte solution having a maximum pH value of substantially 1, a potential from a potential source having a value which is negative with respect to the potential required to evolve hydrogen at the electrode, and subjecting the immersed electrode to the gas to depolarize it with the oxygen in the gas and to produce an electric current flowing from the source to the electrode, the intensity of the current being a function of the oxygen content of the gas.

Also in accordance with the invention, there is provided an apparatus for automatically ascertaining the oxygen content in a gas comprising a given electrolyte having a maximum pH value of substantially 1, a hollow electrode structure closed at one end and comprising a chosen electrode material, immersed at its closed end in the electrolyte. A potential source is included having a value which is negative with respect to the potential required to evolve hydrogen at the chosen electrode material immersed in the given electrolyte, and means are provided for applying the aforesaid potential to the electrode.

For a better understanding of the invention together with other and further objects thereof, reference is had to the following description taken in conjunction with the accompanying drawing.

The drawing shows partly in structural section a preferred, although exemplary embodiment of the invention.

Referring now to the drawing, the apparatus includes a battery **11** which may suitably be of the acidic lead storage type filled with sulfuric acid of a concentration of 30% by weight and having a positive electrode **12** and a negative electrode **13**. Electrode **12** and **13** are respectively connected to the terminals of a potentiometer **14** from which a predetermined voltage is taken off by means of a slider. In an exemplary application, a suitable voltage taken from potentiometer **14** may be 175 millivolts, such voltage being more positive than the potential of negative electrode **13**. The voltage taken from potentiometer **14** is applied over a variable resistor **15** to an indicating electrode generally indicated at **16**. The voltage across the variable resistor **15** is continuously measured by a suitable measuring device **17**, such as a millivoltmeter.

The indicating electrode **16** comprises a hollow, substantially tubular insulating body **16***a* closed at one end by an electrode base **20** and having an opening at the other end to receive a tube **16***b* which functions as a gas inlet. The body **16***a* is further provided with a lateral opening **16***c* which functions as a gas outlet. The electrode base **20** is made of a porous material such as graphite. Within the electrode body **16** there is disposed a silver wire **19** through the potential is applied to electrode base **20**. The indicating electrode **16***a* extends into the interior of battery **11** where it is immersed in the sulfuric acid electrolyte thereof. A rubber bushing **18** is provided forming a seal between the battery wall and the body **16***a*. The graphite body of electrode base **20** may be coated with paraffin to render it hydrophobic.

A basic principle in the operation of the invention is the application of a potential to indicating electrode base **20** which is negative with respect to the potential re-

quired to evolve hydrogen, such potential is hereinafter designated as a "negative" potential.

When the apparatus is connected in circuit, initially the indicating electrode base **20** is depolarized by the oxygen in the gas entering the electrode **16**. Thereafter, current flows from the tapped point on potentiometer **14** through variable resistor **15** to indicating electrode **16**, the intensity of the current flow is measured as a voltage by the millivoltmeter **17**. The source of the "negative" potential and indicating electrode **16** are connected in circuit with a constant, although adjustable resistance; the indicating electrode **16** is supplied with the "negative" potential from electrodes **12** and **13** which, suitably designated as "auxiliary" electrodes, are reversable and regeneratable, and are immersed in the same solution as the indicating electrode **16**. The "negative" potential may also be provided either completely or partly from an external potentiometer to which one or both auxiliary electrodes are connected.

The outside of indicating electrode **16** is in contact with the electrolyte solution of battery **11**, while its inside is in contact with the gas to be analyzed. The material of electrode base **20** is suitably so chosen that in a given electrolyte solution it has a hydrogen evolution voltage which is greater than the potential applied to the indicating electrode **16**.

The indicating electrode base **20** is advantageously associated with a catalyst which accelerates the reaction on the indicating electrode. For this purpose the wire **19** is preferably made of silver.

The apparatus constructed in accordance with the principles of the invention permits a continuous determination of the oxygen content in a gas stream flowing through electrode **16**. With this apparatus, the time necessary to obtain a 90 percent response ranges from a few tenths of one second to, at most, a few seconds. This continuous determination is fully automatic and the obtained electrical signal is sufficiently strong to permit even a direct connection of an indicating device. In such connection, the scale of millivoltmeter **17** is directly calibrated in terms of a gaseous mixture having a known oxygen content and the indicating scale may easily be adjusted to a desired range with a potentiometer.

The invention contemplates the use of a generally acidic electrolyte solution having a pH not exceeding 1. Thus the deleterious effects of acidic gases such as carbon dioxide, which are experienced in known devices are eliminated. Due to the reversibility of auxiliary electrodes **12** and **13**, they are readily regenerated by direct current supplied thereto, either periodically between relatively long time periods, or continuously by connecting them to a potentiometer fed from an external source.

By rendering the indicating electrode base **20** hydrophobic with respect to the electrolyte solution, e.g., by means of a paraffin coating on the graphite body, it is protected from choking or flooding and thus its life expectancy is extended without adversely affecting its function.

The method and apparatus described hereinabove may be advantageously utilized in the determination of oxygen in gases produced by the oxidation of fuels with air or oxygen at high temperatures and with the release of intense heat. They may also be employed in the analysis of the oxygen content in gases produced by flamentation mechanisms in fermentation processes, in chemical syntheses, and in all cases where it is necessary to continuously ascertain the oxygen content in a gas. They may be used to ascertain abrupt changes in oxygen content. The "two-sided" indicating electrode **16**, constructed in accordance with the invention, is particularly advantageously adapted to function as a sensing element in automatic recording instruments and is utilizable in a wide range of oxygen concentrations from as low as a few percents.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

**1.** A method of automatically and continuously ascertaining the oxygen content in a gas comprising the following steps: deriving a potential from a potentiometer connected between the positive and negative electrodes of a storage battery containing an electrolyte having a maximum pH value of substantially 1 in which said positive and negative electrodes are immersed, applying said potential through a variable resistance to an indicating electrode immersed in said electrolyte, said potential being negative with respect to the potential required to evolve hydrogen at said indicating electrode, and exposing said indicating electrode to said gas to depolarize it with the oxygen in said gas and to generate an electric current flowing from said potentiometer to said indicating electrode, the intensity of said current being a function of the oxygen content of said gas.

**2.** A method as defined in claim **1** wherein said indicating electrode includes a hollow body closed at one end by a porous base comprising graphite, said hollow body contains a silver catalyst, at least a portion of said base being immersed in said electrolyte.

**3.** A method as defined in claim **2** wherein said indicating electrode is at least partially hydrophobized.

**4.** An apparatus for automatically and continuously ascertaining the oxygen content in a gas comprising a battery having a positive and negative electrode immersed in an electrolyte having a maximum pH value of substantially 1, an indicating electrode immersed in said electrolyte, said indicating electrode including a hollow body closed at one end by means of a base comprising a porous electrode material, the outside of said base being exposed to said electrolyte by being immersed thereinto, a potentiometer connected between said positive and negative electrodes, means for deriving from said potentiometer a potential having a value negative with respect to the potential required to evolve hydrogen at said electrode material immersed in said electrolyte, a variable resistor, and means for applying said potential to said indicating electrode through said resistor to generate an electric current which, when the inside of said base is in contact with said gas, has an intensity which is a function of the oxygen-content in said gas.

**5.** An apparatus as defined in claim **4** including a catalyst contained within said indicating electrode for accelerating the reaction thereon.

**6.** An apparatus as defined in claim **5** wherein said catalyst includes silver.

**7.** An apparatus as defined in claim **4** wherein said electrode material is graphite.

**8.** An apparatus as defined in claim **4** wherein said base is at least partially rendered hydrophobic.

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