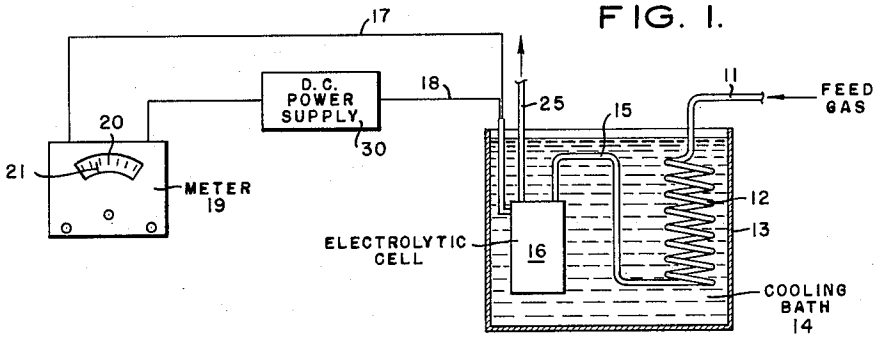
Sept. 1, 1964 L. M. JOHNSON ETAL 3,147,202

DETERMINATION OF MOISTURE BY ELECTROLYSIS

Filed March 18, 1960

FIG. 1.



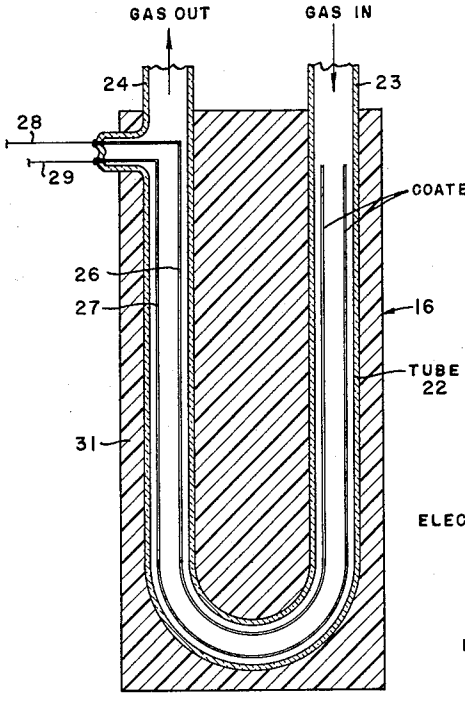


FIG. 2.

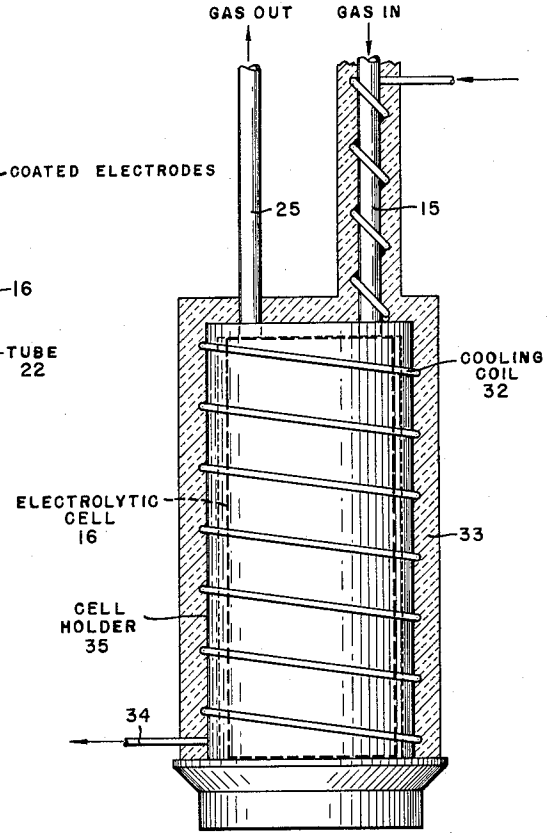


FIG. 3.

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United States Patent Office

3,147,202

Patented Sept. 1, 1964

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DETERMINATION OF MOISTURE BY ELECTROLYSIS

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Filed Mar. 18, 1960, Ser. No. 16,036

5 Claims. (Cl. 204—1)

The present invention is directed to a method for determination of moisture in a fluid such as a gas or a gasiform material. More particularly, the invention is concerned with a method for determination of moisture in which a coulometric method is employed. In its more specific aspects, the invention is concerned with the determination of moisture in fluids containing oxygen and hydrogen and in which the moisture is present in parts per million.

The present invention may be briefly described as a method for determination of moisture in a fluid containing a reactive gas such as oxygen and hydrogen in which the fluid is passed into contact with a hydroscopic substance which is electrically conductive only when wet which, in turn, is in contact with electrodes across which a D.C. potential is imposed and moisture is decomposed to hydrogen and oxygen and in which a signal is displayed indicating the amount of moisture. The particular feature of the present invention is adjusting the temperature of the gasiform fluid, the electrodes, and the hydroscopic substance to a temperature below that at which substantial recombination of hydrogen and oxygen occurs in significant amounts in the determination of moisture in said environment.

In the practice of the present invention, the water determination is electrolytic and may be conducted in apparatus such as described in the Keidel Patent 2,830,945, issued April 15, 1958. While water may be determined electrolytically, such determination is attendant with difficulties when hydrogen or oxygen is present because of inaccurate results which have been obtained. The inaccurate results have led to the necessity of applying a correction factor in the electrolytic determination of moisture in fluid such as gas and gasiform material which contain hydrogen or oxygen. It has now been discovered in determination of moisture electrolytically in a fluid containing hydrogen or oxygen that the inaccurate results are obtained because of recombination of hydrogen and oxygen in the presence of the electrodes employed in the electrolytic determination of moisture. In accordance with this invention, it is now possible to determine moisture in hydrogen- and oxygen-containing fluids with extreme accuracy. By virtue of adjusting the temperature of the fluid, the electrodes, and the hydroscopic substance to a temperature below that at which substantial recombination of hydrogen occurs in significant amounts, it is possible to obtain a correct determination of the moisture content of the fluid.

The present invention will be further illustrated by reference to the drawing in which:

FIG. 1 is a schematic view of an apparatus by way of which the present invention may be conducted;

FIG. 2 is a sectional view of the electrolytic cell of FIG. 1; and

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FIG. 3 illustrates a preferred embodiment of apparatus for conducting the method of the present invention.

Referring now to the drawing and particularly to FIG. 1, numeral **11** designates a charge line by way of which a hydrogen- or oxygen-containing stream containing moisture is led into a coil **12** arranged in a cooling bath **13** which may contain cool fluid **14** such as water or any other cooling fluid maintained at a temperature below that at which recombination of hydrogen and oxygen would occur in the apparatus employed in the present invention. Coil **12** connects by line **15** into an electrolytic cell **16**, which may be of the type as described in the Keidel patent supra. In electrolytic cell **16**, the moisture in the feed gas introduced by line **11** is decomposed to oxygen and hydrogen and a signal is transmitted by electrical signal leads **17** and **18** to a meter **19** in which the moisture content is indicated in parts per million on scale **20** in indicator **21**.

In accordance with the present invention, the feed gas, the electrodes, and hydroscopic substance in cell **16** are cooled to a temperature below that at which hydrogen and oxygen recombine in cell **16**. This temperature is below about 50° F. and preferably is in the range from about 0° to about 50° F. Therefore, the temperature of the feed gas must be reduced from a temperature in the range from about 60° F. to about 150° F. to below 50° F. to obtain the improved results.

The feed gas may be substantially pure hydrogen or substantially pure oxygen containing small amounts of water ranging up to about 100 parts per million or more. Ordinarily the feed gas will contain less than 500 parts per million of moisture and smaller amounts. By cooling the feed gas, the electrodes and the hydroscopic substance in accordance with the present invention, the water content of the feed gas is determined accurately and displayed on meter **19**. The feed gas contains at least about 50% of oxygen or hydrogen.

Referring now to FIG. 2, a sectional view of the cell **16** is shown. Cell **16** is comprised essentially of a tube **22** which is provided with an inlet **23** which connects to line **15** and an outlet **24** which connects to line **25** of FIG. 1. Arranged in the tube **22** are platinum electrodes **26** and **27**, which are suitably connected to a power source of direct current. Energy is supplied to electrodes **26** and **27** by way of leads **28** and **29**. The gas is introduced by inlet **23** and is removed by outlet **24** connecting to line **25**. As the gas flows through tube **22**, power is supplied through leads **28** and **29**, which connect to leads **17** and **18**, connecting in series with the meter **19**. As shown in FIG. 1, the power supply **30** (D.C.) shown in lead **18** causes electrolysis of the moisture when absorbed by the hydroscopic substance which coats the electrodes **26** and **27**. As a result thereof, a signal is transmitted to meter **19** and the signal which is indicative of the water content is displayed on a scale **20**.

In FIG. 2, the hydroscopic substance is phosphorus pentoxide but other hydroscopic substances such as potassium carbonate, potassium hydroxide, sodium carbonate, sodium hydroxide, and barium hydroxide may be employed. As shown in FIG. 2, the tube **22** may be embedded in a plastic material **31** for protection of the tube **22**.

Referring now to FIG. 3, an electrolytic cell such as **16** having a line **15** conducting gas thereto and line **25** conducting gas therefrom is provided. In this particular

instance, the line **15** is cooled by circulating a cooling fluid through a cool coil **32** which is employed to trace line **15** and which is extended around a cell holder **35** containing the cell **16**. The cell holder **35** and the coil **32** may be suitably insulated by insulation means **33** which surrounds the cell holder **35**, the line **15**, and the coil **32**. The cooling solution is discharged from the coil **32** by line **34**.

In order to illustrate the invention further, a number of runs were made on a hydrogen-containing gas employing apparatus such as illustrated in the drawing. In these operations, the electrolytic cell temperature was varied from above 100° F. to below 50° F. The results obtained are shown in the following table.

Table I

Cell No.	Cell Temperature	H_2O in H_2 (p.p.m.)	H_2O in H_2, Instrument Reading (p.p.m.)
A	About 85° F.	<1	18
A	Above 100° F.	<1	50
B	About 85° F.	<1	6
B	Below 50° F.	<1	<1
B	Below 50° F.	181	180

It will be noted from the data shown in Table I that when the temperature of the cell and the gas was above 50° F., the instrument reading in p.p.m. varied 50-fold greater than the actual water content whereas when the temperature was below 50° F., accurate results were obtained.

Other runs were made at cell and gas temperatures of 23° F., 41° F., 2° F., 40° F., and 5° F. on hydrogen streams which contained varying amounts of water. These results are shown in the following Table II.

Table II

Cell Temperature (° F.)	H_2O in H_2 (p.p.m.)	Inst. Reading H_2O in H_2 (p.p.m.)
23	19.9	24.3
	64.9	66.5
	115	120
	181	180
	204	208
	262	267
	<1	5.0
41	<1	3.6
	19.6	23.4
	63.2	67
	112	116
	174	179
	208	212
	268	273
	742	725
	922	907
2	<1	0.7
	19.9	17.4
	63.2	60.0
	111.7	111.0
	175.0	177.0
	208.5	207.0
	273.5	267.0
	750	720
	944	820
40	<1	3.7
	63.2	65.0
	176.3	177.0
	266	267
	742	700
	906	905
2	732	715
5	916	912

It will be seen that the instrument reading when the temperature was below 50° F. correspond closely with the actual water content of the hydrogen stream.

In order to illustrate further the practice of the present invention, determinations were made of water in oxygen-containing streams with a cell and gas temperature of 40° F. These results are shown in Table III.

Table III

Cell Temperature (° F.)	H_2O in O_2 (p.p.m.)	Measured H_2O in O_2 (p.p.m.)
40	<1	3.5
	40.2	44.0
	78.8	90.0
	110.5	111.0
	147.0	145.5
	162.5	162.0
	214	204
	860	830
	505	490
	264	262.5
	180	177.0
	86.8	90.0
	29.6	33.0
	118	114

Examination of the data in Table III shows that accurate results are obtained in analyzing moisture-containing oxygen streams. A number of runs were made at temperatures above 50° F. In these operations at elevated temperatures, inaccurate results were obtained.

In the several operations employed to exemplify the invention, phosphorous pentoxide was employed as the hydroscopic substance.

It will be seen from the number of runs made that extremely accurate determinations of moisture in hydrogen- and oxygen-containing streams may be effected.

The present invention is quite advantageous and useful in that it is now possible to determine accurately the amount of moisture in hydrogen- and oxygen-containing streams. Such streams are encountered in the steel industry and in the petroleum industry. Particularly in the petroleum industry, it is frequently necessary to control carefully the amount of moisture in hydrogen streams which are employed in catalytic conversion of hydrocarbons such as in hydroforming and hydrofining operations. Also, in the steel industry where reduction operations are conducted, it is extremely important to determine the moisture content of hydrogen-containing streams.

As will be seen from the foregoing description and the numerous examples, the present invention is based on a discovery that the electrolytic determination of moisture may be made extremely accurate if conducted at temperatures below about 50° F.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and secure by Letters Patent is:

1. In the determination of moisture in a gasiform fluid passed into contact with a hydroscopic substance which is electrically conductive only when wet, which substance is in contact with electrodes across which direct current is imposed and moisture is decomposed to hydrogen and oxygen, said fluid containing a substantial amount at least about 50% of a reactive gas selected from the group consisting of oxygen and hydrogen, the improvement which comprises establishing and maintaining the temperature of said fluid, said electrodes and said substance during said determination of moisture at a value below about 50° F. at which substantial recombination of hydrogen and oxygen in significant amounts is suppressed therein.

2. A method in accordance with claim 1 in which the reactive gas is oxygen.

3. A method in accordance with claim 1 in which the reactive gas is hydrogen.

4. In the determination of moistuure in a gasiform fluid at a temperatuure substantially above 50° F. which is to be passed into contact with a hydroscopic substance which is electrically conductive only when wet, which substance is in contact with electrodes across which direct current is imposed and moisture is decomposed to hydrogen and oxygen, said fluid containing at least 50% of a reactive gas selected from the group consisting of oxygen and hydrogen, the improvement which comprises lower-

ing the temperature of said fluid, said electrodes and said substance to a temperature below about 50° F. at which substantial recombination of hydrogen and oxygen in significant amounts is suppressed therein and carrying out the electrolytic determination of the moisture content of said fluid while maintaining said lowered temperature.

5. In the electrolytic determination of the water content of a gasiform fluid containing as a major portion one of the atomic constituents of water, wherein the contained water is electrolytically decomposed into hydrogen and oxygen the improvement which comprises establishing and maintaining the electrolytic reaction at a temperature less than 50° F. at which substantial recombination of hydrogen and oxygen in significant amounts is suppressed therein.

References Cited in the file of this patent

UNITED STATES PATENTS

2,830,945 Keidel ---------- Apr. 15, 1958

OTHER REFERENCES

Keidel; "Analytical Chemistry," volume 31, No. 12 (December 1959), pages 2043–2048.

Mellor; "Treatise on Inorganic and Theoretical Chemistry," volume 1 (1922), page 325.