April 5, 1966 J. R. GLASS ETAL 3,244,602

METHOD AND APPARATUS FOR DETERMINING WATER CONTENT IN GASEOUS MEDIA

Filed Oct. 2, 1961 4 Sheets-Sheet 1

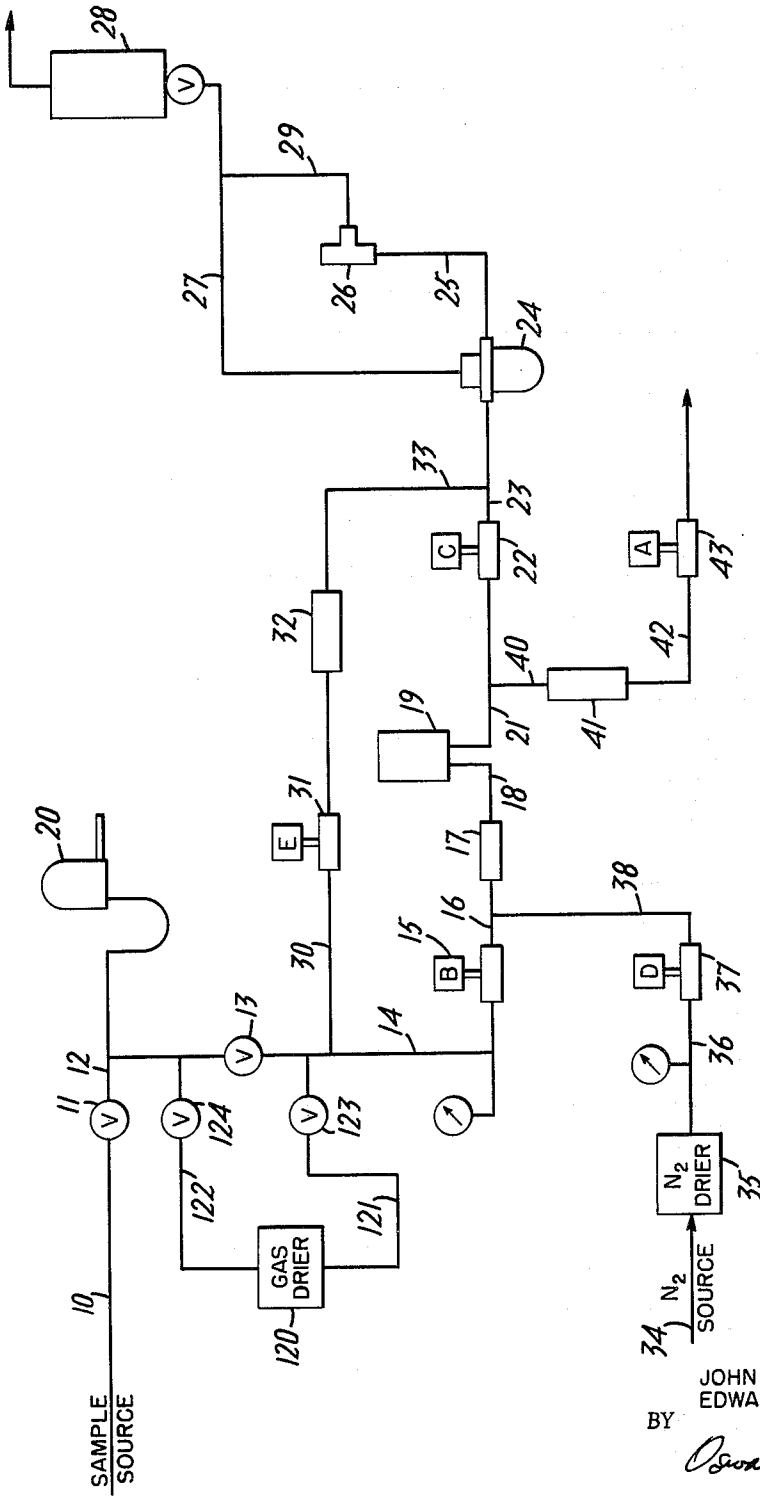


FIG. 1

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Filed Oct. 2, 1961 4 Sheets-Sheet 2

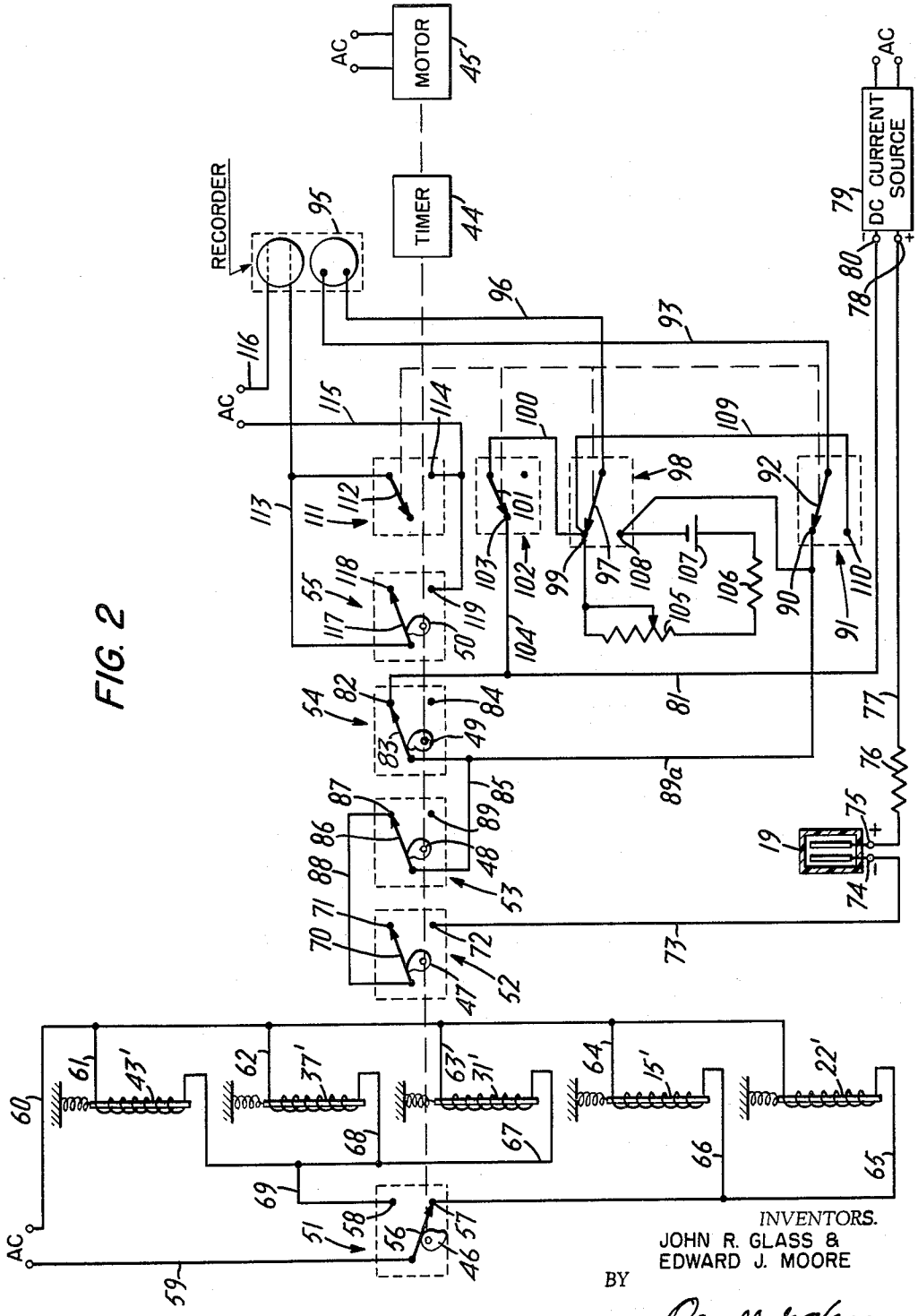


FIG. 2

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METHOD AND APPARATUS FOR DETERMINING WATER CONTENT IN GASEOUS MEDIA
Filed Oct. 2, 1961 4 Sheets-Sheet 3

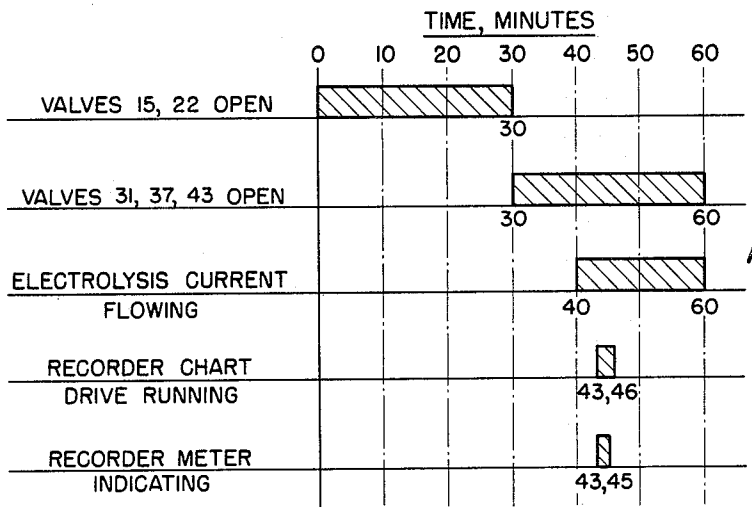


FIG. 3A

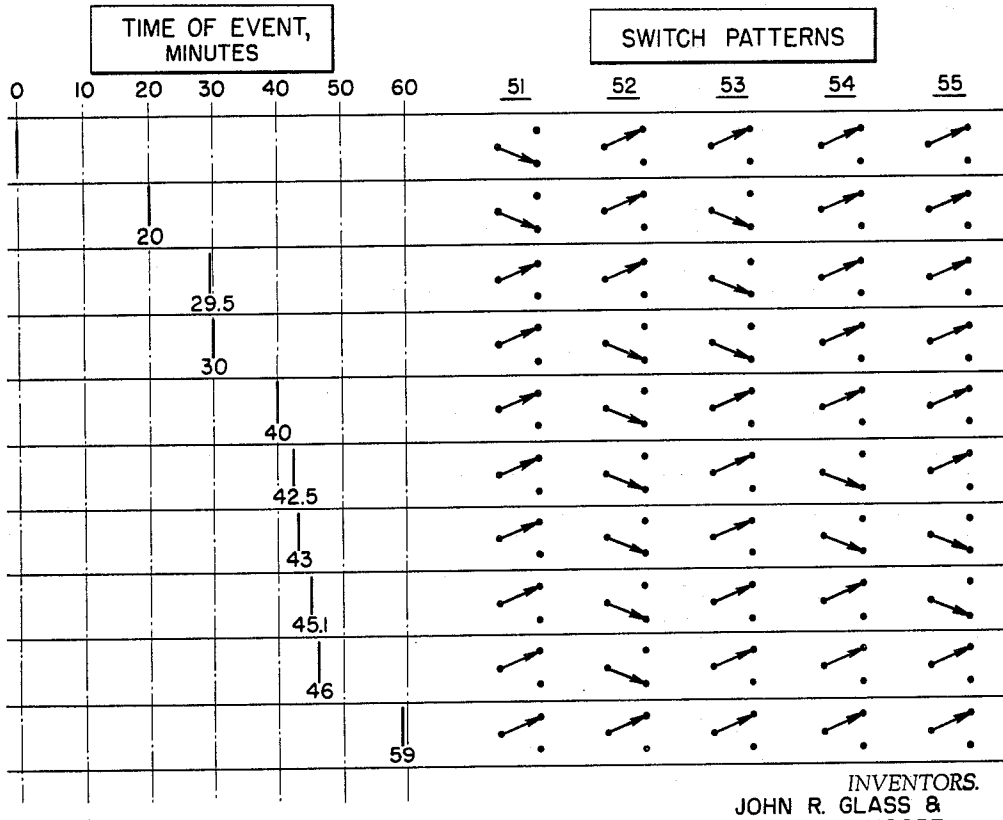


FIG. 3B

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Filed Oct. 2, 1961 4 Sheets-Sheet 4

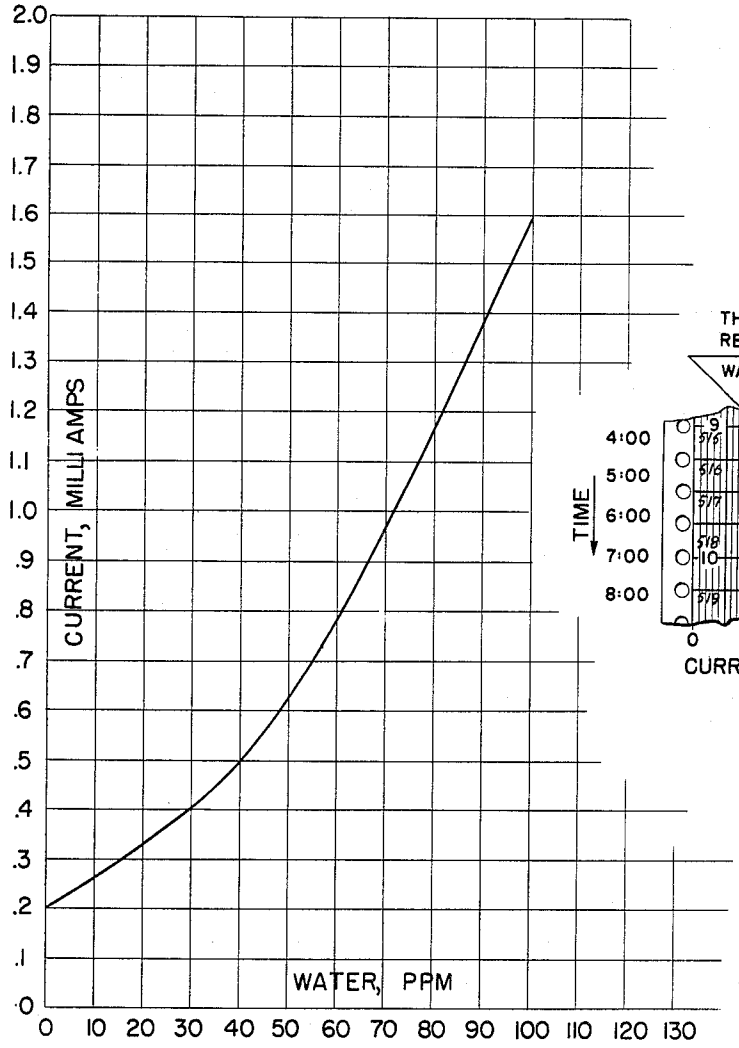


FIG. 5

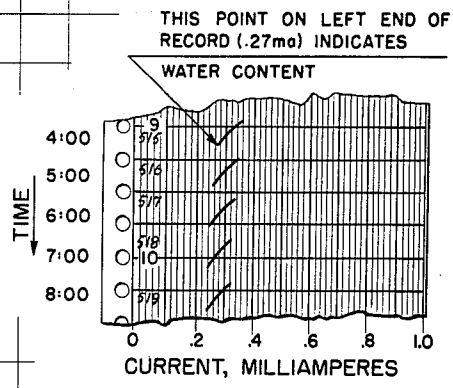


FIG. 4

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United States Patent Office

3,244,602

Patented Apr. 5, 1966

3,244,602

METHOD AND APPARATUS FOR DETERMINING WATER CONTENT IN GASEOUS MEDIA

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Filed Oct. 2, 1961, Ser. No. 142,098
2 Claims. (Cl. 204—1)

This invention relates to a method and apparatus for determining the water content of a gaseous specimen and, more particularly, to a method and apparatus for semicontinuously measuring small concentrations of water in a gaseous stream, although it is not limited to such use.

In many chemical and other processes, the water content in a gaseous stream has a significant effect upon the process and efforts have been made heretofore to devise apparatus for continuously determining the water content in such streams so that appropriate corrective action may be taken, if necessary. In one form of device that has been developed for this purpose, the gaseous stream is passed through a special electrolytic cell in which all entering water is continuously and quantitatively absorbed and electrolyzed to hydrogen and oxygen. Since the quantity of electricity required to electrolyze water is known, the water content of the stream is determined by measuring the electrolysis current.

While apparatus of this general character is effective for some purposes, it has been found that the readings which it gives with certain gaseous streams, notably those containing hydrogen, are not accurate. The reason for this is believed to be that the oxygen released by the electrolysis tends to recombine with the hydrogen present in the stream to form water which is again electrolyzed, so that the water content readings obtained are high.

It is an object of the present invention, accordingly, to provide an improved method and apparatus for measuring the water content of gaseous media which is free from the above-mentioned deficiencies of the prior art.

A further object of the invention is the provision of an electrolytic method and apparatus for semicontinuously determining the water content of a gaseous specimen stream in which no opportunity is afforded for the gaseous products of the electrolysis to combine with gaseous components of the specimen stream to form water.

A still further object is to provide a new and improved method and apparatus for measuring water content in a gas which produces highly accurate results and is relatively safe, simple, inexpensive, highly sensitive and stable, and which can be operated by nonskilled personnel.

Broadly speaking, these and other objects of the invention are attained by utilizing an electrolytic moisture determining cell alternately to absorb moisture from a gaseous sample and to electrolyze moisture thus absorbed. In the case of a gaseous sample stream, the stream is caused to flow through the cell only during the moisture absorbing part of the operating cycle. During the part of the cycle devoted to electrolysis of the absorbed moisture, the sample stream is temporarily diverted from the cell so that there are no sample stream gas components present that might combine with the products of the electrolysis to form water. Preferably, an inert gas such as nitrogen is flowed through the cell during electrolysis to carry off the hydrogen and oxygen thus produced. In this manner, it is possible to obtain highly accurate moisture content determinations even with gaseous samples containing a gas such as hydrogen that might combine with the products of the electrolysis to form water. By alternately absorbing moisture from a gaseous sample and electrolyzing it in this manner, determinations of water content may be made semicontinuously.

Various other objects and advantages will appear from the following detailed description of a typical embodiment of the invention taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a simple flow diagram of a typical system according to the invention for determining the water content of a gaseous sample stream;

FIG. 2 is a schematic diagram of a simplified electrical control circuit for the water content determining system of FIG. 1;

FIGS. 3A and 3B are typical timing and switch pattern diagrams, respectively, for certain of the operations carried out by the circuit of FIG. 2;

FIG. 4 is a typical water content record that might be produced by apparatus shown in FIGS. 1 and 2; and

FIG. 5 is a representative calibration chart for a water analyzer system of the type shown in FIGS. 1 and 2.

Referring first to FIG. 1, a gaseous sample stream, which may comprise, for example, gaseous hydrocarbon material in admixture with hydrogen from a petroleum refinery process stream, is supplied to the conduit **10** of water content determining apparatus embodying the invention. From the conduit **10**, the sample stream passes through a valve **11**, a conduit **12**, a valve **13**, a conduit **14**, a solenoid operated valve **15**, a conduit **16**, a filter **17** and a conduit **18** to a water analysis cell **19** for determining the water content of the gaseous stream supplied thereto.

A pressure relief valve **20** may be connected to the conduit **12** between the valves **11** and **13** to prevent the pressure in the system from accidentally rising to an unsafe value. The filter **17** may be of any known type and it serves to prevent solid particles suspended in the gaseous sample from reaching the cell **19**.

The cell **19** is preferably of the type disclosed in prior Patent No. 2,830,945 to Keidel and further described in an article entitled "Determination of Water by Direct Amperometric Measurement" by F. A. Keidel which appears at page 2043 of "Analytical Chemistry," volume 13, No. 12, December 1959. In a cell of this character, a hygroscopic electrically conductive material absorbs moisture from any gas passing therethrough and the cell can be energized electrically to electrolyze the moisture thus absorbed.

For proper operation of the water analysis cell **19**, it is desirable that the sample flow therethrough be maintained at a predetermined arbitrary value. To this end, the output from the cell **19** is fed through a conduit **21**, a solenoid operated valve **22** and a conduit **23** to conventional flow regulating apparatus which may comprise, for example, a pressure responsive flow regulator **24**, a conduit **25**, a conventional flow restrictor device **26**, and conduit **27** for sensing the pressure at the output of the flow restrictor device and supplying it to the regulator **24** to control the flow through the same. The flow regulator **24** functions automatically in the well known manner to maintain the pressure drop across the restrictor **26** at a value sufficient to preserve a predetermined sample flow rate through the water analysis cell **19**. The rate of flow can be measured in any conventional manner as by a flow meter **28** connected by a conduit **29** to receive the output of the restrictor **26**.

In order to maintain a constant rate of sample flow through the system when the solenoid operated valves **15** and **22** are closed and the water sample collected by the water analysis cell **19** is being electrolyzed, a by-pass is provided which includes a conduit **30** connected to the conduit **14**, a solenoid operated valve **31**, a flow restricting orifice **32**, and a conduit **33** connected to the conduit **23**. The flow restricting orifice **32** serves to restrict the sample flow through the by-pass so that the pressure of

gas in the sample line will remain constant throughout the operating cycle.

As will be described in greater detail hereinafter, after a water sample has been collected by the water analysis cell **19** and the solenoid operated valves **15** and **22** have been closed, it is desirable to flush out the cell **19** with an inert gas and preferably to maintain the flow of inert gas through the cell **19** while the water sample collected thereby is being electrolyzed. For this purpose, inert gas is supplied from a suitable source through a conduit **34**, a conventional gas dryer **35**, a conduit **36**, a solenoid operated valve **37** and a conduit **38** which is connected to the conduit **16**. After passing through the cell **19**, the inert gas is vented from the system over a path including a conduit **40** connected to the conduit **21**, a conventional flow restrictor device **41** which may be a commercially available filter device or finely divided inert material packed in a housing, a conduit **42** and a solenoid operated valve **43**.

In accordance with the invention, a sample stream from the source is passed through the cell **19** for a sufficient period of time to permit any water contained therein to be absorbed by the hygroscopic material in the cell **19**. The solenoid valves **15** and **22** are then closed, and the valves **31**, **37** and **43** are opened. The opening of the valve **31** permits the sample stream to flow through the by-pass described above, thus maintaining the same rate of flow through the system, while the opening of the valves **37** and **43** permits inert gas to pass through the cell **19** and to flush out all traces of the sample stream previously flowed therethrough. Electric current is then passed through the cell **19** to electrolyze the water sample absorbed by the hygroscopic material therein and the electrolysis current is measured and taken as an indication of the water content present in the sample stream.

While the steps outline briefly above may be carried out by hand, automatic operation is preferred, a control system of the type shown in FIG. 2 being employed for this purpose. Referring to FIG. 2, the several operations may be controlled in sequence by a conventional timer **44** driven by a synchronous motor **45** connected to the electrical power mains (not shown). The timer **44** may be of the type having a plurality of cams **46**, **47**, **48**, **49** and **50** on a common shaft which are adapted to actuate the switches **51**, **52**, **53**, **54** and **55**, respectively, in predetermined sequence as outlined in greater detail below.

The switch **51** has a movable contact arm **56** which normally engages a fixed contact **57** and is adapted to be moved by the cam **46** into engagement with a second contact **58**. The movable contact arm **56** is connected by a conductor **59** to one side of the power mains, the other side being connected by a conductor **60** to the solenoid **22'** and through the conductors **61**, **62**, **63** and **64** to one side of each of the solenoids **43'**, **37'**, **31'** and **15'**, for actuating the valves **22**, **43**, **37**, **31** and **15**, respectively. The other terminals of the solenoids **15'** and **22'** are connected by the conductors **65** and **66** to the fixed switch contact **57**, while the other terminals of the solenoids **31'**, **37'** and **43'** are connected by the conductors **67**, **68** and **69** to the fixed contact **58**. It will be understood, therefore, that when the movable switch contact **56** is in engagement with the fixed contact **57**, the solenoids **15'** and **22'** will be energized and the valves **15** and **22** (FIG. 1) will be opened, while the solenoids **31'**, **37'** and **43'** will not be energized so that the valves **31**, **37** and **43** will be closed.

The switches **52** and **53** serve to control the supply of electric current to the cell **19** to electrolyze any water removed from the sample stream thereby. To this end, the switch **52** has a movable contact arm **70** which at the beginning of each cycle is normally in engagement with a fixed contact **71** but is adapted at the proper time to be moved by operation of the cam **47** into engagement with a fixed contact **72**. The contact **72** is connected by a conductor **73** to one terminal **74** of the cell **19**, the other terminal **75** of which is connected in series with a current limiting resistor **76** and a conductor **77** to one terminal **78** of a conventional low impedance electrical current source **79**. The other terminal **80** of the current source **79** is connected by a conductor **81** to the fixed contact **82** of the switch **54** which serves to connect a recorder for the electrolysis current in and out of the cell circuit during part of the operating cycle as described in detail below.

The switch **54** also has a movable contact **83** which, at the beginning of each cycle, engages a fixed contact **82** but is adapted to be moved by the cam **49** at the proper time into engagement with the fixed contact **84**. The movable contact arm **83** of the switch **54** is connected by a conductor **85** to the movable contact arm **86** of the switch **53**, which, at the beginning of an operating cycle, is normally in engagement with a fixed contact **87**. The fixed contact **87** is connected by a conductor **88** to the movable contact arm **70** of the switch **52**. The movable contact arm **86** of the switch **53** is adapted to be moved by operation of the cam **48** at the proper time in the cycle out of engagement with the contact **87** and into engagement with a fixed contact **89**.

The movable contact arms **83** and **86** of the switches **54** and **53**, respectively, are also connected by a conductor **89*a*** to one terminal **90** of a switch **91** having a movable contact arm **92** connected by a conductor **93** to one terminal of a conventional current recording device **95**. The other terminal of the recorder **95** is connected by a conductor **96** to the movable contact arm **97** of a switch **98** which normally engages a fixed contact **99**. The contact **99** is connected by a conductor **100** to the movable contact arm **101** of a switch **102** which normally engages a fixed contact **103** connected by the conductor **104** to the conductor **81**.

In order to provide a suitable reference reading, say zero, on the recorder **95** corresponding to dry gas, a circuit including an adjustable resistor **105**, a fixed resistor **106** and a battery or other source of D.C. voltage **107** may be connected between the fixed contact **99** and a second fixed contact **108** on the switch **98**, the contact **108** also being connected to the conductor **89*a***. The fixed contact **99** on the switch **98** is also connected by a conductor **109** to a fixed contact **110** on the switch **91**, so that the connections between the recorder **95** and the reference voltage source can be reversed to enable the magnitude of the latter to be measured, if desired.

The switches **91**, **98** and **102** are connected for ganged operation with a switch **111** having a movable contact arm **112** connected by a conductor **113** to one terminal of the drive motor circuit for the recorder **95**. The switch **111** also has a fixed contact **114** connected by a conductor **115** to one side of the power mains, the other side of the power mains being connected by a conductor **116** to the other terminal of the recorder drive motor circuit.

The timer switch **55** serves to turn on the recorder **95** at the proper time in the operating cycle. To this end, it has a movable contact **117** which, at the beginning of each cycle, is in engagement with a fixed contact **118** but is adapted to be moved by the cam **50** at the appropriate time into engagement with a second fixed contact **119**. The movable contact arm **117** is connected to the conductor **113** and the fixed contact **119** is connected to the conductor **115** so that when the two are in engagement, the drive motor for the recorder **95** is connected to the power mains.

In connection with the establishment of a reference reading (e.g., zero) on the recorder **95** for the condition when dry gas is passing through the cell **19**, as mentioned above, provision should be made for drying the gaseous sample stream before passing it through the cell **19**. Thus, a conventional gas dryer **120** (FIG. 1) may be connected by conduits **121** and **122** and valves **123** and

124 on opposite sides of the valve 13 so that by closing the latter the sample stream may be dried before it is fed to the water analysis cell 19.

In a typical operation, let it be assumed that the timer 44 is just beginning a cycle so that the valves 15 and 22 (FIG. 1) are open, while the valves 31, 37 and 43 are closed. Under these conditions, with the valve 13 open and the valves 123 and 124 closed, the sample stream, which may be, for example, a gaseous hydrocarbon at a pressure of say 10 lbs. per square inch and containing small amounts of moisture, will flow at a uniform rate through the water analysis cell 19. After say twenty minutes of the cycle have elapsed, the contact arm 86 of the switch 53 is repositioned into engagement with the fixed contact 89 (FIG. 3B). When a further period, say 9.5 minutes has elapsed, the timer 44 (FIG. 2) will have driven the cam 46 to the point where it causes the movable contact arm 56 to disengage the fixed contact 57 and to engage the fixed contact 58. This will cause the solenoids 15′ and 22′ to be deenergized, closing the valves 15 and 22, respectively, (FIG. 1) and the solenoids 31′, 37′ and 43′ to be energized, opening the valves 31, 37 and 43. These actions are shown graphically on the timing diagrams in FIGS. 3A and 3B.

Under these conditions, the fluid stream no longer flows through the cell 19 but is diverted through the bypass including the open solenoid valve 31. In its place, dry inert gas which may be, for example, nitrogen is flushed through the cell 19 at a rate of say 10 cubic centimeters per minute for a predetermined period which may be the remainder of the cycle.

A short time, say a half minute later, the movable contact 70 of the switch 52 is repositioned into engagement with the fixed contact 72 (FIGS. 2 and 3B).

After the cell 19 has been flushed with nitrogen for say, ten minutes, the timer 44 (FIG. 2) will have moved the cam 48 so that the movable contact arm 86 of the switch 53 is in engagement with the fixed contact 87. This in effect connects the conductor 81 to the conductor 73 so that the cell is now energized from the source 79 and electrolysis begins. This event is indicated on the timing chart of FIG. 3A. It will be noted, however, that the connection between the movable contact arm 83 and the fixed contact 82 of the switch 54 short circuits the recorder 95 so that it does not begin to record at this time.

After the electrolysis has proceeded for a predetermined period, say 2.5 minutes, the cam 49 causes the movable contact arm 83 of the switch 54 to disengage the fixed contact 82 and to engage the contact 84. This breaks the short circuit across the terminals of the recorder 95 so that it is now connected in series with the cell 19. Shortly thereafter, (e.g., at 43 minutes after the start of the cycle) the timer 44 will have moved the cam 50 to the position where the movable contact arm 117 of the switch 55 is in engagement with the contact 119. This connects the conductors 113 and 115 so that power is now supplied to the drive motor of the recorder 95 and a record strip therein (not shown) begins to move as a function of time (see FIGS. 3A and 3B).

Several minutes later (e.g., at 45.1 minutes after the beginning of the cycle), the timer 44 causes the cam 49 to move the contact arm 83 into engagement with the contact 82, again shorting out the recorder 95. This is followed (at say 46 minutes) by disengagement of the contact arm 117 and the contact 119, so that the recorder drive motor is deenergized. Then, just before the end of the cycle (at say 59 minutes—see FIG. 3B) the contact arm 70 of the switch 52 (FIG. 2) is disengaged from the contact 72, so that the electrolysis current is cut off. The cycle then repeats so that a series of records of the electrolysis current at different times are made.

A typical graph, such as might be produced by the recorder 95 is shown in FIG. 4 in which the several discontinuous curves represent the records made during successive times when the recorder 95 is on.

If the electrolysis current is plotted against time, integration of the area under the curve will give a value proportional to coulombs consumed. However, it is simplier to take as a measure of the water content the current at a fixed time, say five minutes, after electrolysis is initiated (i.e., the point on the left end of each of the curves recorded on the graph in FIG. 4).

FIG. 5 illustrates a typical calibration curve for the water detecting apparatus described above in which the moisture in a gaseous sample, in parts per million is plotted as a function of the electrolysis current.

If it is desired to establish a predetermined reference on the recorder 95 corresponding to dry gas, the valve 13 (FIG. 1) may be closed and the valves 123 and 124 opened so that the sample is passed through the gas dryer 120 and dried before being supplied to the cell 19.

With dry gas passing through the cell 19 for one or more cycles of operation as described above, the adjustable resistor 105 (FIG. 2) is adjusted to give a predetermined reference reading, say zero, on the record made by the recorder 95.

The ganged switches 111, 102, 98 and 91 which serve to start the recorder drive and to connect the recorder 95 to the bucking voltage appearing at the fixed contacts 99 and 108 of the switch 98 afford means for checking the constancy of the bucking voltage prior to or after any fluid sample test.

While the flow rate through the water detection system described above is not critical, desirably it should be of the order of 100 cubic centimeters per minute. If it is solwer, less water will be picked up and, if faster, more water will be picked up.

The timing cycle described above is typical for a flow rate of 100 cubic centimeters per minute and a pressure of approximately 10 lbs. per square inch gauge for the sample stream. With higher pressures for the sample stream, the sensitivity of the apparatus will be higher and the operating cycle may be made shorter.

The system will operate effectively at any temperature between the freezing and boiling points of water. However, the sample gas pressure, temperature and flow rate should preferably be maintained constant. Moreover, the apparatus may be used effectively for determining the water content of other gaseous streams such as oxygen streams, for example.

From the foregoing, it will be understood that the invention provides a highly effective method and apparatus for accurately determining the presence of small quantities of moisture in fluid streams. By virtue of the fact that absorption of moisture from a sample stream and electrolysis of such absorbed moisture are carried out sequentially, instead of simultaneously as in the prior art, there is no opportunity for oxygen generated during electrolysis to recombine with any hydrogen in the sample fluid stream passing through the cell to form water which might result in spurious readings.

While specific operations and operating cycles, as well as apparatus for carrying them out, have been described above by way of example, the invention is not intended to be limited thereto. On the contrary, it encompasses all modifications in form and detail falling within the scope of the following claims.

We claim:

1. In a method for determining the water content of a specimen gas containing hydrogen, the steps of passing such gas at a predetermined rate through a confined space in the presence of a hygroscopic material, then blowing through said confined space a gas substantially dry and nonreactive with hydrogen to remove said specimen gas from said confined space while simultaneously bypassing succeeding portions of said specimen gas through an alternate route at the same rate of flow, said

water being retained in said confined space by said hygroscopic material, then decomposing the water retained by said hygroscopic material by electrolysis for a predetermined period of time to indicate a function of said electrolysis.

2. In a method for determining the water content of a specimen gas containing oxygen, the steps of passing such gas at a predetermined rate through a confined space in the presence of a hygroscopic material, then blowing through said confined space a gas substantially dry and nonreactive with oxygen to remove said specimen gas from said confined space while simultaneously bypassing succeeding portions of said specimen gas through an alternate route at the same rate of flow, said water being retained in said confined space by said hygroscopic material, then decomposing the water retained by said hygroscopic material by electrolysis for a predetermined period of time to indicate a function of said electrolysis.

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