Oct. 5, 1971 D. I. AGEIKIN ET AL 3,610,023

GAS ANALYSIS A METHOD OF AND A GAS ANALYZER FOR ACCOMPLISHING SAME

Filed Nov. 14, 1969 3 Sheets-Sheet 1

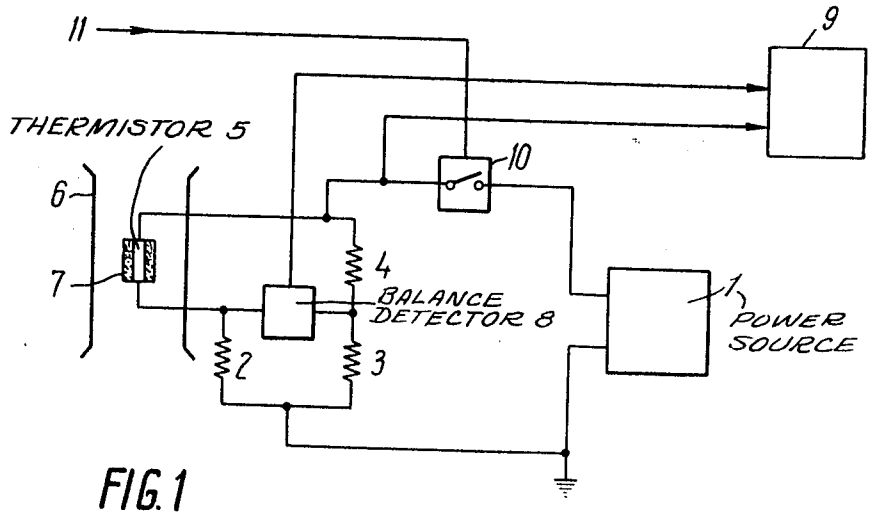


FIG. 1

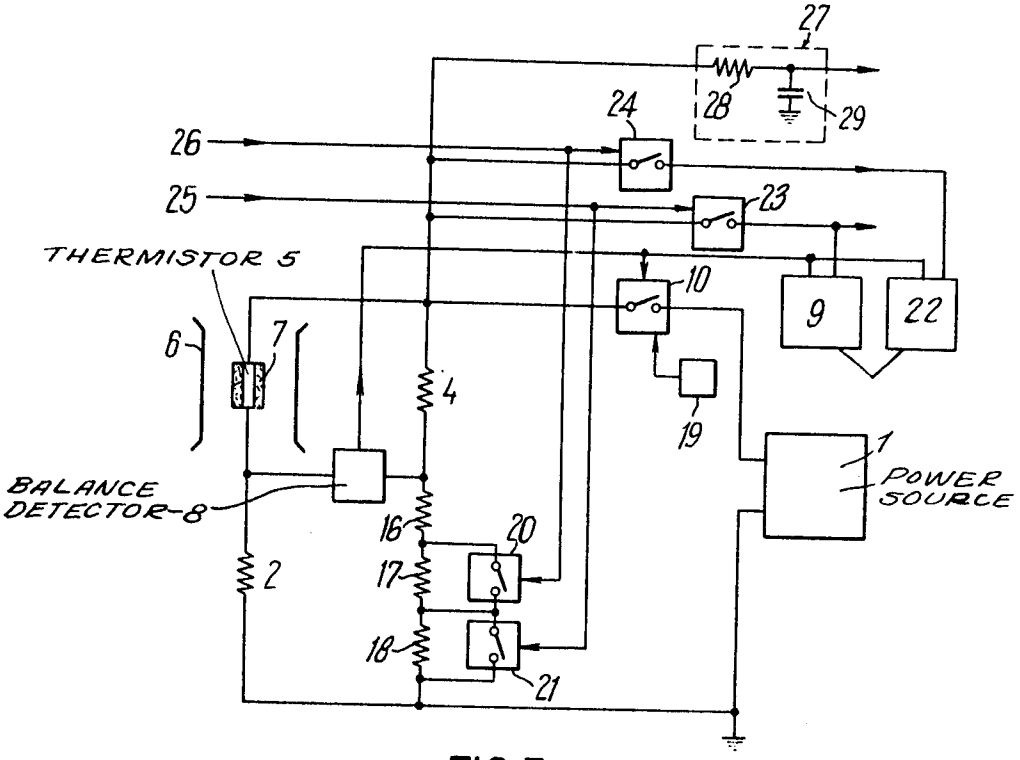


FIG. 3

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Filed Nov. 14, 1969 3 Sheets-Sheet 2

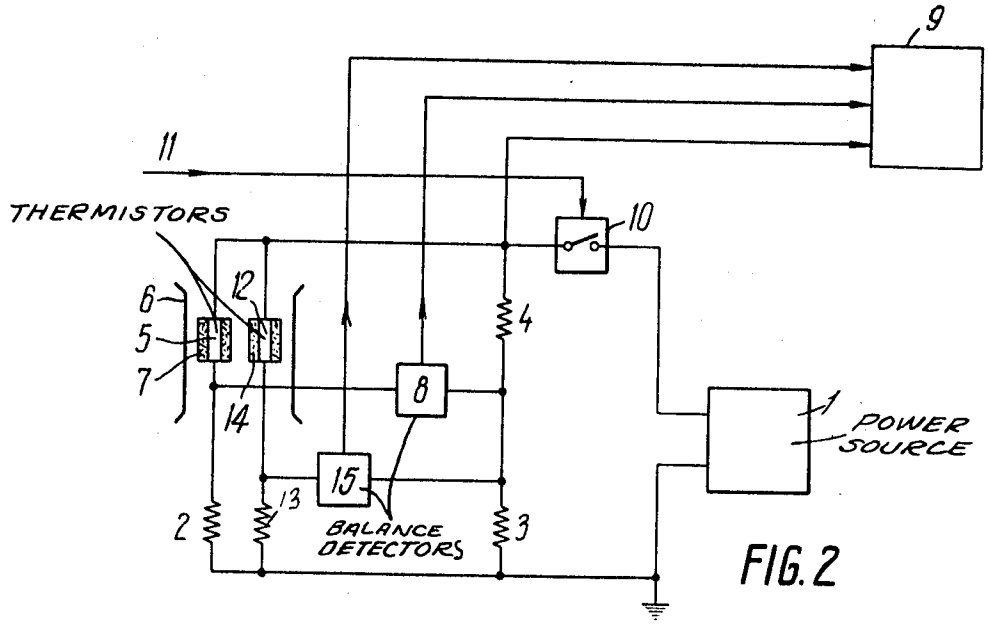


FIG. 2

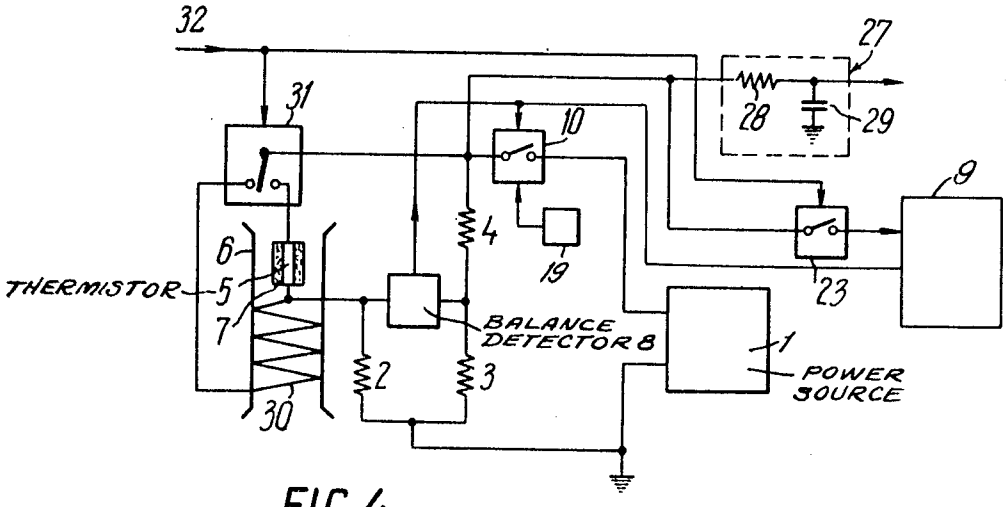


FIG. 4

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Filed Nov. 14, 1969 3 Sheets-Sheet 3

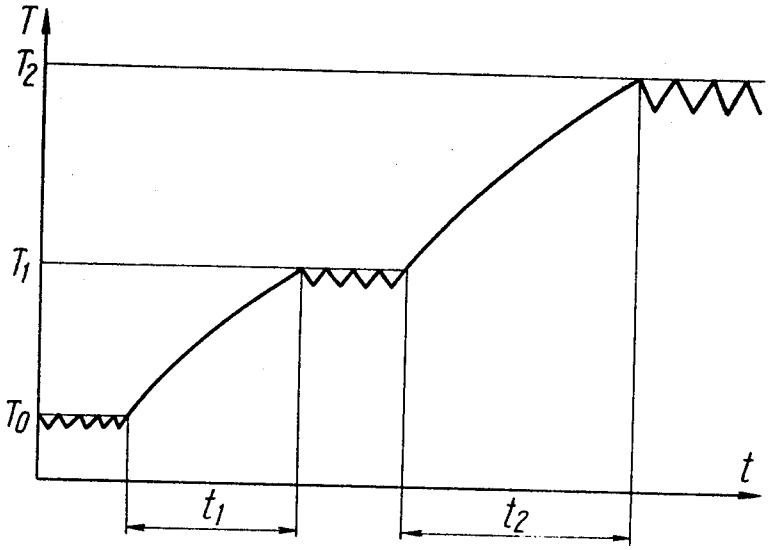


FIG. 6

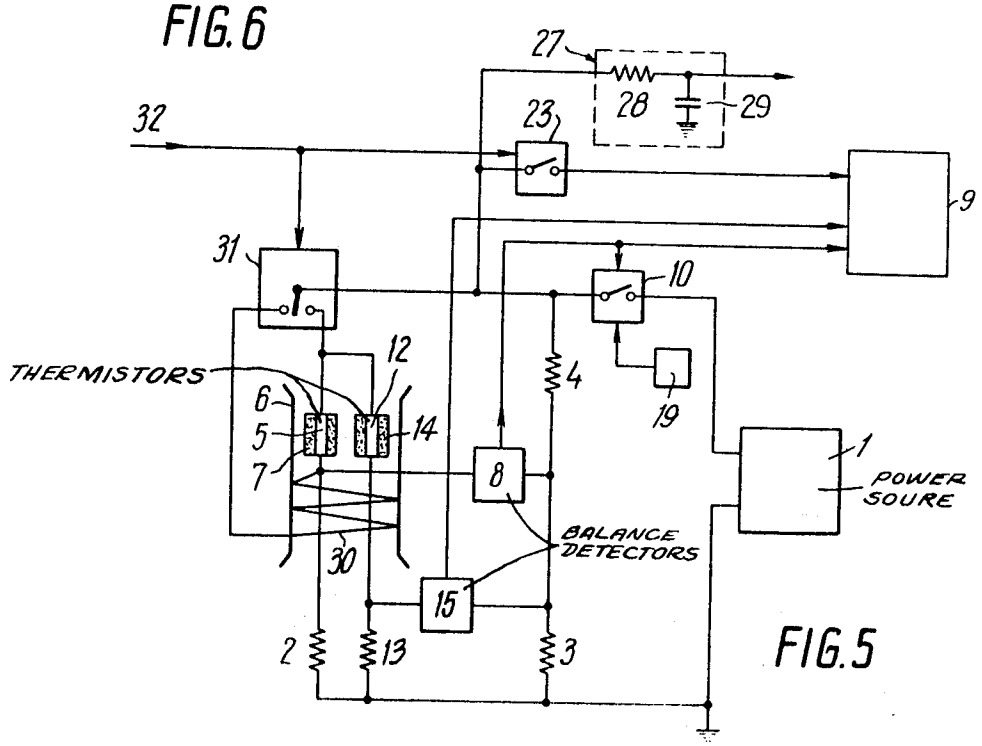


FIG. 5

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GAS ANALYSIS, A METHOD OF AND A GAS ANALYZER FOR ACCOMPLISHING SAME

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U.S. Cl. 73—27 6 Claims

ABSTRACT OF THE DISCLOSURE

A method and a facility for measuring gas composition based on the measurement of time required to heat a sorbent introduced into the gas mixture to be analyzed up to a specified temperature at which intensive desorption of the mixture component sorbed by the sorbent takes place.

The sorbent coats the thermistor incorporated into an arm of a measuring bridge whose supply circuit includes a key and the measuring diagonal includes a balance detector. The thermistor heating time is measured between the moment of power supply to the bridge and of the signal reception from the balance detector. The modifications of the facility include differential connection of two thermistors coated with different sorbents, and stabilization of the initial temperature of the thermistors.

This invention relates to methods of gas analysis and to gas analyzers for accomplishing same.

There are known chromatographic methods of gas analysis, which involve sorption of the gas being analyzed, followed by desorbing the gas by passing a neutral gas through the sorbent bed, and determining the composition of the gas being analyzed from data on the content of its components in the neutral gas directed to a detector. These known methods are useful for carrying out analyses of complex mixtures of various gases.

However, the known methods are disadvantageous in that they cannot be accomplished in a facile manner, as evidenced by the fact that gas analyzers intended for embodying said methods are elaborate instruments comprising pumps, a gas cylinder, programmers, thermostats, and intricate detectors, so that the practical application of said methods is confined to cases where it is desired to effect an ultimate analysis of complex gas mixtures.

Another disadvantage of the known gas analysis methods consists in that the shape of output signals is inconvenient for feeding said signals to automatic devices, and the chromatogram obtained should be subjected to analysis and decoding.

Also known are gas analyzers, which incorporate at least one measuring bridge whose arms are formed by resistors and at least one thermistor, which contacts the gas being analyzed.

In the known gas analyzers, a thermistor heated by a current passed therethrough experiences a heat loss and, consequently, a temperature variation depending upon the thermal conductivity of a sample gas, the potential across the bridge diagonal being a gas analyzer output signal, which is proportional to the thermal conductivity of the sample gas.

The known gas analyzers are suitable for analyzing only simple binary gas mixtures, since the thermal conductivity of a complex mixture depends upon the thermal conductivities of all mixture components.

Further disadvantages of the known gas analyzers are a relatively high power consumption and the fact that the output signal (a low-level direct-current voltage) is inconvenient as a digital computer input signal.

Accordingly, it is an object of the present invention to provide a gas analysis method, in particular a method for moisture concentration measurements, which will be noted for a marked selectivity in analyzing a complex mixture of gases for a given component.

It is a further object of the present invention to provide a gas analyzer for carrying out gas analyses by the method of the invention which will make it possible, despite its relatively simple design, to determine various components of gas mixtures and whose output signal will be suitable as a digital computer input signal.

It is the principal object of the invention to provide a method of gas analysis, particularly a method for determining the content of moisture, which lends itself to realization by means of a gas analyzer having a unified standard design and a set of sensitive elements, wherein successive incorporation of said elements into the measuring circuit will make it possible to enhance the sensitivity of gas mixture component analyses.

This object is accomplished by the provision of a method of gas analysis, particularly a method of moisture content analysis, which comprises absorbing the gas being analyzed by sorbents, followed by desorbing the gas in question wherein, according to the invention, gas desorption is effected by heating at least one sorbent to pre-set thermal state characterizing the amount of the desorbed gas, e.g. to a temperature that corresponds to maximum desorption, the concentration of the absorbed gas mixture component being evaluated by measuring, in the course of sorbent heating, the time required to attain the aforesaid thermal state.

To realize said gas analysis method, in the gas analyzer, which incorporates at least one measuring bridge, whose arms consist of resistors and of at least one thermistor placed in the gas being analyzed, provision is made, according to the invention, for coating the thermistor with a sorbent that absorbs the sought-for gas mixture component and for incorporating into the measuring diagonal of the bridge a balance detector that sends a signal once the thermistor attains the pre-set temperature, while the other diagonal of the bridge incorporates a key intended to switch on power supply to the bridge and to a circuit that controls thermistor heating commencement.

The key may be made in the form of a balance detector-controlled control element of the thermistor temperature stabilizer, provision being made for means of thermistor temperature setting.

It is further preferable that the key be furnished with a delayed self-actuating means.

It is further preferable that the means of thermistor temperature setting be made in the form of an auxiliary thermistor, which serves to warm up the sample gas surrounding the sorbent-coated thermistor and should be switched into the measuring bridge in place of the said sorbent-coated thermistor for a period of time that precedes the commencement of sample gas analysis.

It is also advantageous to provide in the circuit that controls the commencement of thermistor heating at least one key in order to obtain a signal whose duration equals that of the thermistor heating period.

The abovementioned design features make the present gas analyzer simple in design, diminish power requirements, and provide for an output signal which can be readily digitalized, while the method of gas analysis realized by the present gas analyzer makes for an enhanced selectivity of gas mixture analyses.

The present invention is illustrated hereinbelow by the description of specific embodiments thereof with reference to the accompanying drawings.

FIG. 1 represents the electrical circuit of the gas analyzer suggested herein;

FIG. 2 represents the electrical circuit of the second modification of the same gas analyzer incorporating two measuring bridges;

FIG. 3 represents the electrical circuit of the third modification of the gas analyzer described herein with a sorbent-coated thermistor temperature stabilizer.

FIG. 4 represents the electrical circuit of the fourth modification of the same gas analyzer with an auxiliary thermistor;

FIG. 5 represents the electrical circuit of the fifth modification of the gas analyzer described herein, including two measuring bridges and an auxiliary thermistor; and

FIG. 6 represents the temperature variations versus time of a sorbent-coated thermistor of the gas analyzer described herein according to FIG. 3.

The gas analyzer for gas mixture analyses, according to the present invention, includes power source **1** (FIG. 1), which energizes a measuring bridge, whose arms are formed by resistors **2–4** and thermistor **5**, which is contained in sample gas cell **6** and coated with sorbent **7**, said sorbent being capable of absorbing a gas mixture component being analyzed. Resistor **4** may be replaced with a thermistor selected so that current passage therethrough causes practically no heating thereof.

Incorporated in the measuring diagonal of the bridge is balance detector **8**, which sends a signal once thermistor **5** reaches a pre-set temperature.

The other diagonal of the bridge incorporates key **10** actuated by external control signal circuit **11** so that key **10** in the "on" positions provides for power supply from power source **1** to the measuring bridge. The interval meter **9** of any type is connected to the output of balance detector **8** and the power source of the measuring bridge.

Where the thermal conductivity of the gas being analyzed varies within a wide range and said gas contains a component whose absorption by the sorbent introduces a significant error, use is made of a second modification of the gas analyzer, according to the invention, wherein, in contrast to the first modification, provision is made for two measuring bridges. In the second bridge, thermistor **12** (FIG. 2) and resistors **13**, **3** and **4** are the bridge arms. Thermistor **12** is coated with sorbent **14**, which is characterized by properties different from those of sorbent **7**, and placed in the gas being analyzed.

The measuring diagonal of the second bridge incorporates balance detector **15**, which transmits an appropriate signal once thermistor **14** attains the pre-set temperature. Time interval meter **9** is connected to the outputs of balance detectors **8** and **15** and to the power source of the measuring bridges.

When the temperature of the gas being analyzed varies within a wide range, or where it is desired to determine the content of a plurality of components in the gas mixture under test, said components being essentially different from one another as to desorption temperatures, or else in case the gas analyzer is to be readjusted for operation in different control ranges, in a third modification of the gas analyzer, according to the invention (FIG. 3), key **10** comprises a control element of the temperature stabilizer of thermistor **5**, said key being controlled by balance detector **8**, while said temperature stabilizer serves as a sensor of said control element. In the temperature stabilizer of thermistor **5**, provision is made for a means of setting the requisite temperature of thermistor **5**.

The measuring bridge arms consist of thermistor **5** and resistors **2**, **4** and **16–18**, provision being made in key **10** for a delayed self-actuating means **19**, e.g. a single steady-state trigger.

In the gas analyzer modification under consideration, a means of setting the temperature of thermistor **5** consists of resistors **17** and **18**, which are shunted by means of keys **20** and **21**.

The supply circuit of the measuring bridge is connected to the inputs of two time interval meters, **9** and **22**, through keys **23** and **24**. The other inputs of time interval meters **9** are connected to the output of balance detector **8**.

Keys **21** and **23** are incorporated in external control signal circuit **25**, while keys **20** and **24** are the components of external control signal circuit **26** (the circuits in question are denoted in the drawing by reference numerals **25** and **26**).

Coupled to the measuring bridge is integrating unit **27**, which comprises resistor **28** and capacitor **29**, the output signal of said integrating unit over the intervals between measurements (in the absence of signals in circuits **25** and **26**) being proportional to the temperature difference between thermistor **5** and the gas being analyzed.

The incorporation of integrating unit **27** into the gas analyzer circuit provides the possibility of controlling continuously whether the analyzer circuit is intact, as well as of obtaining additional data on the temperature of the gas being analyzed.

A fourth modification of the gas analyzer, according to the invention, differs from the third modification in that a means of setting the temperature of thermistor **5** should, preferably, be made in the form of auxiliary thermistor **30** (FIG. 4), which effects warming up the sample gas in the vicinity of thermistor **5**. Thermistor **30** consists of a winding disposed around cell **6** which is coupled to the measuring bridge in place of thermistor **5** for a period of time preceding the actual analysis of the sample gas, said winding being connected together with thermistor **5** to key **31**. Key **31** is coupled to the measuring bridge and is a component of external control signal circuit **32** (designated in the drawing by reference numeral **32**), another component of said circuit being key **23**, which is included, as pointed out hereinbefore, in the circuit of time interval meter **9**.

A fifth modification of the present gas analyzer, which may be regarded as a combination of the second and fourth modifications described earlier, should preferably be used in instances where it is desired to attain a shorter response time of the gas analyzer, or where the temperature and thermal conductivity of the gas being analyzed vary within a wide range.

The essential distinctive feature of this gas analyzer modification (FIG. 5) consists in that use is made of two measuring bridges whose arms are formed by thermistor **5** and resistors **2**, **3** and **4**, and thermistor **12** and resistors **13**, **3** and **4**, respectively. Thermistor **12** is coated with sorbent **14**, whose properties are distinct from the properties of sorbent **7**, said thermistor being placed in the sample gas.

A means of setting the temperature of thermistor **5** in the fifth modification of the present gas analyzer consists of auxiliary thermistor **30**, whose functions and location were described in detail earlier.

The first modification of the present gas analyzer (FIG. 1) operates on the following principle.

In intervals between measurements, key **10** is in the "off" position, so that the measuring bridge is deenergized. Sorbent **7** that coats thermistor **5** contacts the gas being analyzed and absorbs therefrom a component of interest, e.g. moisture, in an amount that is proportional to the partial pressure of said component.

To determine the concentration of the component, external control circuit **11** sends a control signal, which sets key **10** in the "on" position, thereby energizing the measuring bridge from power source **1**, so that there commences the heating of thermistor **5** and associated description of the gas mixture component previously absorbed by sorbent **7**. In so far as gas component desorp-

tion consumes heat, the process of heating of thermistor **5** slows down.

Once the thermistor **5** attains the pre-set temperature, which depends upon the ratio of resistance offered by thermistor **5** and resistors **2, 3** and **4**, the potential across the measuring diagonal of the bridge drops to a value, at which balance detector **8** is actuated. Key **10**, which switches on the power supply circuit, simultaneously sends a signal that there commences the heating of thermistor **5**, while balance detector **8** sends a signal when the heating of thermistor **5** has been terminated. The time interval between said signals is measured by meter **9** to evaluate the concentration of the gas component that has been absorbed by sorbent **7**.

The gas analyzer, therefore, embodies the gas analysis method, according to the invention, which comprises heating sorbent **7** until there is attained a pre-set thermal state consistent with the amount of the desorbed gas, and measuring the time interval required for attaining said thermal state, the temperature at which balance detector **8** is actuated being the thermal state in question. The temperature is selected so that, once it is attained, the desorption of the previously absorbed gas component will be at a maximum.

The second modification of the gas analyzer (FIG. 2) functions similarly to the first gas analyzer modification, except for the fact that in the interval between two measurements there occurs the sorption of two components from the gas mixture being analyzed or of combinations of gas mixture components by sorbents **7** and **14** applied onto two thermistors **5** and **12**. Once key **10** is set in the "on" position, there commences the heating of thermistor **12** simultaneously with thermistor **5**, and on reaching the pre-set temperature by thermistor **12**, said temperature being governed by the ratio of the bridge arms constituted by resistors **3, 4** and **13**, and thermistor **12**, balance detector **15** will be actuated by using time interval meter **9** both the duration of each thermistor, **5** and **12**, heating and the difference of these durations can be measured. In the latter instance, the sensitivity of the method is essentially enhanced and the effect of variations in the thermal conductivity of the gas is compensated.

The third modification of the present gas analyzer (FIG. 3) functions as follows. In intervals between measurements, keys **20, 21, 23**, and **24** are in the "off" position, the ratio of the resistances of the measuring bridge arms formed by resistors **2, 16–18**, and **4** and thermistor **5** being such as to balance the bridge when the temperature of thermistor **5** corresponds to the selected stabilization temperature which is somewhat higher than the temperature of the gas being analyzed. The operating mode of the gas analyzer is set by the two-step temperature stabilizer of thermistor **5**. When there occurs the heating of thermistor **5**, which serves as the sensitive element of thermistor **5**, and heating proceeds until the stabilization temperature is attained, balance detector **8** will be actuated and will send a signal to switch off key **10**, said key being the control element of the temperature stabilizer. This action deenergizes thermistor **5**, and there commences thermistor cooling. After a certain delay governed by self-actuating means **19**, key **10** will again close the circuit. This sequence of operations is repeated continuously until the measuring period is commenced at a moment of feeding an external control signal via circuit **25** to keys **21** and **23**.

Key **21** serves to switch resistor **18** in or out of the measuring bridge circuit, which action alters the ratio of bridge arm resistances. Next there starts the transition period of heating thermistor **5** from the stabilization temperature to another temperature, whose magnitude depends upon the ratio of resistances of the measuring bridge arms formed by thermistor **5** and resistors **2, 4, 16** and **17**.

The process of heating is accompanied by the desorption of the previously absorbed gas mixture component, the time interval from the moment of switching on key **23** to the moment of switching off key **10** is controlled by meter **9**. This sequence of gas analyzer operation having been terminated, an external control signal fed to circuit **26** actuates keys **20** and **24**, and this action switches resistor **17** out of or in the measuring bridge, so that there occurs a transition process of after-heating thermistor **5** to another temperature and an appropriate signal is fed via key **24** to time interval meter **22**, said transition process being analogous to that described earlier.

In said gas analyzer modification, the operating mode can be illustrated by a "temperature (T) vs. time (t)" graph for thermistor **5** coated with sorbent **7** (FIG. 6). In the graph, T_0 denotes the stabilization temperature of thermistor **5**; T_1 and T_2 are the temperatures to which is heated thermistor in the course of two successive measuring steps; t_1 and t_2 are the time intervals measured by meters **9** and **22**, whcih make possible the estimation of the concentration of gas components that undergo desorption in appropriate temperature intervals.

In time intervals between measurements, a pulsating voltage normally fed to the measuring bridge is supplied to integrating unit **27**, which generates a direct curent output signal proportional to difference between the stabilization temperature of thermistor **5** and the sample gas temperature. Said output signal makes it possible to evaluate the temperature of the gas being analyzed and to check whether the electric circuits of the gas analyzers are intact.

The fourth modification of the gas analyzer (FIG. 4) operates in a manner similar to that of the third gas analyzer modification described herein before, except for the fact that during time intervals that precede measurements the measuring bridge arm incorporates auxiliary thermistor **30** in place of thermistor **5**, the resistance of thermistor **30** being selected so as to balance the bridge at a pre-set stabilization temperature. Thermistor **30** serves to heat thermistor **5** and the surrounding sample gas to said stabilization temperature. To carry out measurements, an external control signal is fed to circuit **32**, thereby setting key **23** in the "on" position, while key **31** disconnects thermistor **30** from the measuring bridge arm and incorporates thereinto thermistor **5** in place of thermistor **30**. The resistance of thermistor **5** is selected so that at a new pre-set temperature the measuring bridge will be balanced, the duration of heating thermistor **5** in order to attain said temperature providing an output signal measured by time interval meter **9**.

The fifth modification of the present gas analyzer (FIG. 5) functions similarly to the fourth modification of the gas analyzer, except for the fact that feeding an external control signal to circuit **32**, apart from substituting thermistor **5** for auxiliary thermistor **12** in the measuring bridge arm, results simultaneously in connecting to the power supply circuit second thermistor **13** and resistor **13**, which, in conjunction with resistors **3** and **4**, constitute the second measuring bridge.

As pointed out earlier in the second modification, thermistors **5** and **12** are coated with different sorbents **7** and **14**, respectively, and undergo heating during unequal time intervals. By using time interval meter **9** both the duration of each thermistor, **5** and **12**, heating and the difference of these durations can be measured.

The implementation of the technique suggested herein in the gas analyzers enables to obtain gas analyzers of simple design, small dimensions and power consumption, and to adjust the gas analyzer for measurements of various components by mere switching of the thermistor.

Moreover, the gas analyzers, according to the invention, provide the possibility of measuring the temperature of the gas being analyzed and of checking continuously the circuitry.

What is claimed is:

1. A method of gas analysis, particularly of measuring the concentration of moisture, which comprises absorbing the gas being analyzed by means of sorbents, followed by heating at least one sorbent until it attains a pre-set thermal state, which state characterizes the amount of the gas thus desorbed, e.g. to a temperature at which desorption is at a maximum, and measuring, during the process of heating, the period of time required for the sorbent to attain said thermal state, said period of time being indicative of the concentration of the absorbed gas component.

2. A gas analyzer for carrying out gas analyses, which comprises at least one measuring bridge, a power source for energizing said measuring bridge; resistors, which form some of the arms of said measuring bridge; at least one thermistor placed in the gas being analyzed and constituting, in conjunction with said resistors, all the arms of said measuring bridge; a sorbent that coats said thermistor and absorbs a gas mixture component to be analyzed; time interval meter; a balance detector incorporated into the measuring diagonal of said measuring bridge and intended to generate a signal which is fed to the input of said time interval meter once said thermistor attains a pre-set temperature; a key incorporated into the other diagonal of said measuring bridge and intended to switch on power supply from said power source to said measuring bridge; to send the signal of said thermistor heating start to the input of said time interval meter.

3. A gas analyzer according to claim 2, wherein

said key comprises a balance detector-controlled control element of the temperature stabilizer of said thermistor, provision being made for means of thermistor temperature setting.

4. A gas analyzer according to claim 3, wherein in said key provision is made for a delayed self-actuating means.

5. A gas analyzer according to claim 3, wherein said means of temperature setting of said thermistor comprises one of said resistors, which form, in conjunction with said thermistor, said measuring bridge.

6. A gas analyzer according to claim 3, wherein said means of temperature setting of said thermistor comprises an auxiliary thermistor, which warms up the sample gas in the vicinity of said thermistor, coated with said sorbent, said auxiliary thermistor being switched into the measuring bridge in place of said thermistor for a period of time preceding the moment of determining the composition of the sample gas.

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U.S. Cl. X.R.

73—23