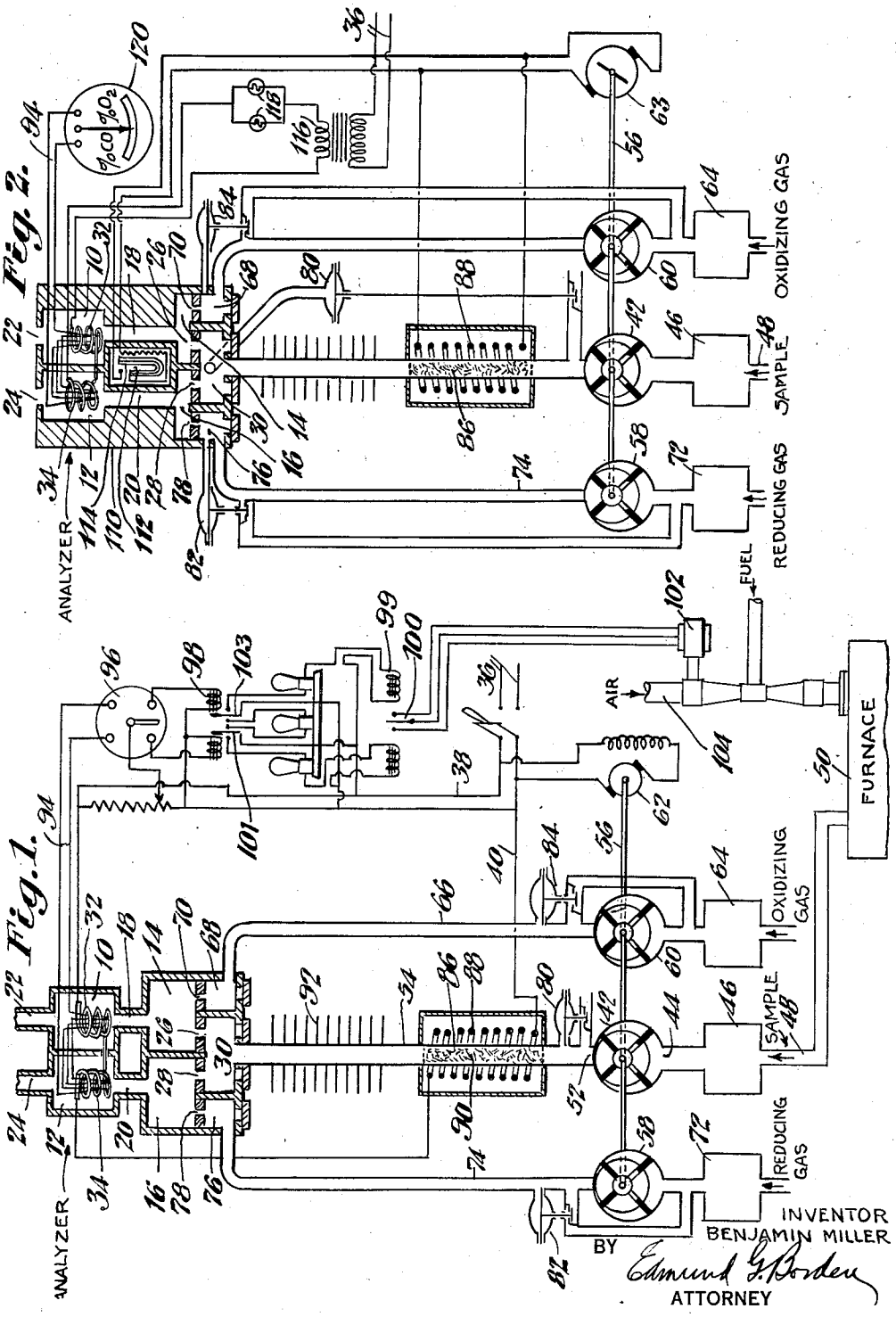
June 8, 1937. B. MILLER 2,083,521

ANALYSIS OF FLUID MIXTURES

Filed March 9, 1934 2 Sheets-Sheet 1



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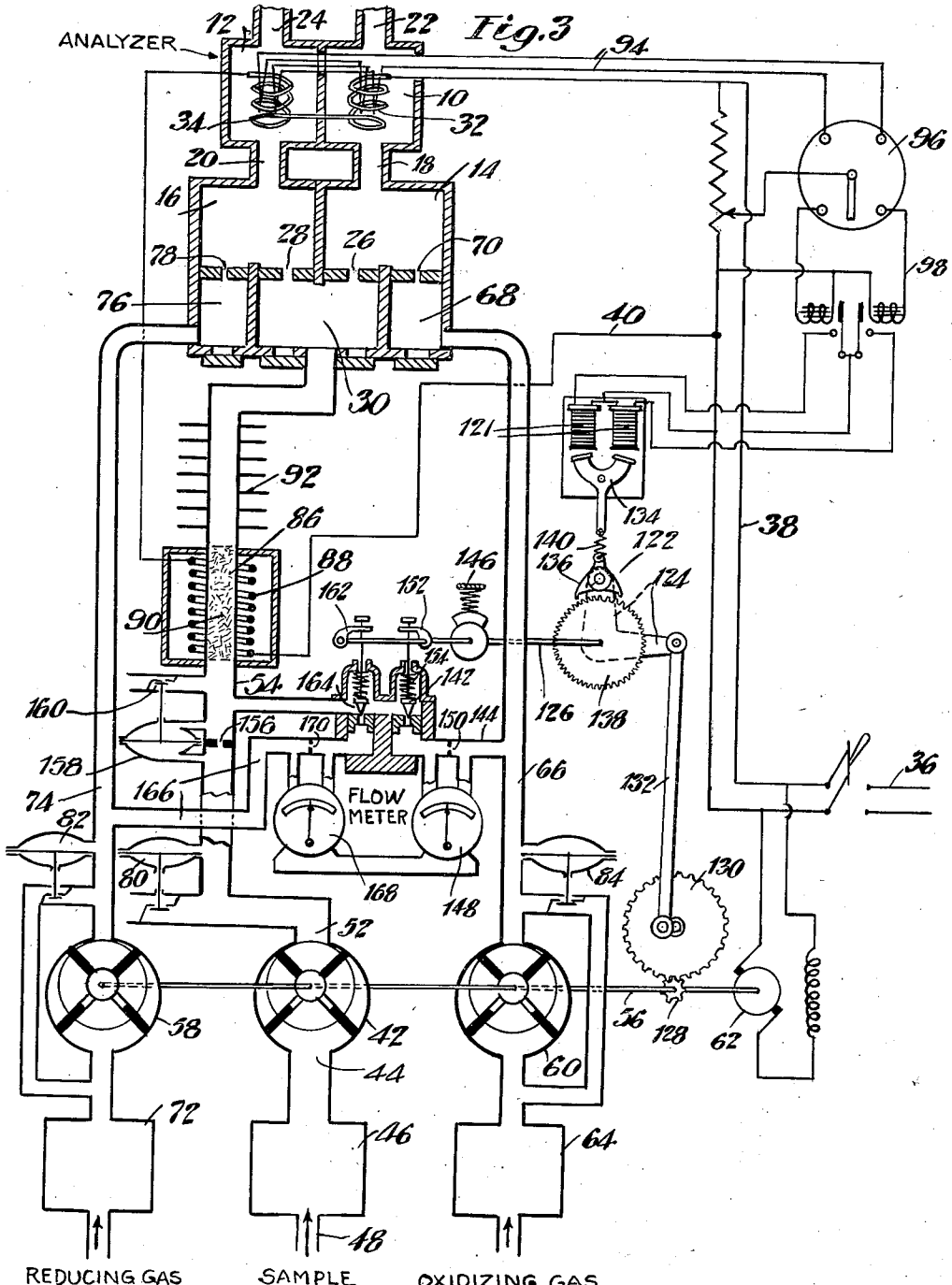
ANALYSIS OF FLUID MIXTURES

Filed March 9, 1934 2 Sheets-Sheet 2

Fig. 3



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ANALYSIS OF FLUID MIXTURES

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12 Claims. (Cl. 23—255)

This invention relates to the analysis of fluid mixtures and more particularly to the quantitative measurement of combustion components of gaseous mixtures of the type of flue gases which are produced in combustion operations.

It has been heretofore proposed to analyze qualitatively the gaseous products of a furnace combustion operation for the purpose of ascertaining the presence therein of an element of combustion, by withdrawing a current of flue gas from the furnace, dividing the current into two branches or streams, adding a combustion-supporting reagent such as oxygen or air to one branch and a combustible reagent to the other, inducing flow of the branch streams over wires electrically heated to the ignition temperature of any combustible mixture in either stream, and utilizing the change in electrical resistance set up in the respective wires by the differential heats of combustion of said streams to unbalance a Wheatstone bridge and to actuate mechanism for automatically controlling the supply of an element of combustion to the furnace.

A primary object of the present invention is to provide improvements in methods and apparatus heretofore proposed for analyzing fluid mixtures whereby to adapt same to a quantitative measurement of the excess of one of two mutually reactive components of the mixture.

Methods of the type above referred to for qualitatively analyzing gaseous products of combustion, have not made adequate provision for adjusting all of the variable and mutually related factors affecting the analysis so as to insure that any change in the temperature of the wires forming the active legs of the Wheatstone bridge which is not due to the presence of an element of combustion in the flue gas, must not unbalance the bridge. The temperature of each of the wires changes with a change in the temperature of the surroundings, or in the voltage of the source of electrical energy, or with the thermal conductivity of the gas bathing the wires, or with the heat capacity of the gas bathing the wires, or with the rate of flow of the gas over the wires. Moreover, the air or other combustion-supporting agent which is added to one branch stream has a thermal conductivity different than that of the flue gas and also different than that of the combustible reagent, such as hydrogen, which may be added to the other branch stream. The cooling effect of hydrogen is greater than the cooling effect of air at any particular temperature, and such cooling effect varies with the temperature. Thus hydrogen has a thermal conductivity which is 7.35 times that of air at zero degree C., but only six times that of air at 100° C., and the heat capacity also changes with the temperature. Therefore when the amounts of combustible and combustion supporting reagents which are added to the respective gas streams are proportioned in accordance with their respective thermal conductivities and heat capacities so as to insure a balancing of the bridge at a given temperature of say 800° C., current will nevertheless flow through the galvanometer element of the bridge if the average temperature of the wire changes for any reason, and the amount of current flow will be greater the greater the change of average temperature in the wire. However, a definite minimum current is required to make the galvanometer needle move over to the contact through which the combustion control mechanism is actuated. Therefore there will always be a definite temperature range in which the compensation between the thermal properties of the added combustible and combustion-supporting constituents, though not perfect, will be close enough to keep the control mechanism from functioning.

An important feature of the present invention resides in passing sample streams of flue gas or other fluid mixture to be analyzed for combustion elements, respectively over identical wires connected in series and similarly disposed in identical surroundings or combustion cells, and in adding small substantially thermally balanced increments of combustible and air or oxygen to the respective streams on the up-stream side of the cells. The smaller the volumes of the added increments of combustible and oxygen relative to the flow rate of the flue gases, the greater the temperature range through which their respective cooling effects are practically balanced. The amount of added combustible or oxygen is preferably limited to that required to get an indication with the smallest amount of combustion element in the flue gas which it is desired will operate the instrument. Since methane causes the smallest galvanometer deflection per unit of heat content of the combustion elements which are commonly present in flue gas, it is usually satisfactory to adjust the flow rate of the added air or other combustion-supporting element relative to the flow rate of flue gas sample so as to cause the instrument to indicate when the flue gas contains the maximum permissible percentage of methane, at the same time adjusting the flow rate of the added hydrogen or other combustible to balance the cooling effect of the added

air at the most probable operating temperatures. If the method is designed to respond to small percentages of methane, i. e. hundredths of a per cent, it is advantageous to use oxygen and carbon monoxide respectively, as the combustion supporting and combustible reagents.

By using identical combustion cells (including wires) and adding small quantities of combustible and air or oxygen to the respective streams of flue gas on the up-stream side of the cells, the present invention is rendered independent of changes in average wire temperature, so long as the normal operating temperature is maintained somewhat higher than the ignition temperature of combustion components in the flue gas sample, but not so high as to approach the temperature which causes rapid volatilization of the wire. The galvanometer needle will remain in a neutral position between the two contacts so long as the flue gas sample contains neither combustible gas nor oxygen. When combustible gas appears in the sample, it reacts with the added oxygen on the surface of one of the wires. This causes the temperature of that wire to increase, thus increasing the total resistance in the circuit. The current in the circuit then decreases, which decreases the temperature of the other wire. Thus the wire on which combustion takes place becomes hotter, while the other wire becomes colder. If the difference in temperature is greater than a certain minimum value depending on the operating temperature and the instrument constants, sufficient current will flow through the galvanometer to cause the needle to make the appropriate contact, which will set the combustion control actuating mechanism into operation. The sample of flue gas may contain a large proportion of air or a large proportion of combustible without causing an excessive temperature rise in the wire, since when the proportion of combustible in the sample exceeds a certain value, the temperature rise is limited by the rate of addition of oxygen, which being small is safely below the danger point at which rapid volatilization of the wire takes place. Because of this protection against excessive temperature rise which results from using no more reagent than is required to indicate the maximum permissible departure of the flue gas from inertness, it is possible to operate in the temperature range of 1600° F. to 2000° F., in which range the sensitivity to methane is highest.

Methods heretofore proposed for determining the presence of a combustion element in gaseous combustion products are not reliable when applied to combustion products containing both combustible and oxygen or air. Thus, if the flue gas contains high percentages of both oxygen and combustible by reason of an inefficient combustion operation, the rise of temperature which occurs in the wires of the Wheatstone bridge analyzer may be sufficient to destroy the wires. If both combustible and oxygen are present in the flue gas, but one is present in large excess, the galvanometer may function to show the excess. But if the excess is small, the galvanometer may show the excess, may show nothing, or may give the wrong indication. For example, the instrument may be adjusted so as to operate when the sample contains 0.1% methane, the balance being inert. But if the sample contains 2% oxygen and 1.1% methane, which is a 0.1% excess of methane, and if the reagent added is hydrogen, the galvanometer may indicate an excess of oxygen, since the wire is much more sensitive to a hydrogen-oxygen mixture then to a methane-oxygen mixture of the same total potential combustion energy content.

A more particular object of the present invention is to provide methods and means for making reliable qualitative analyses of gas mixtures of the type of flue gas containing variable quantities of either or both combustible and combustion-supporting constituents.

Another important object of the invention is to provide method and means adapted for making reliable quantitative analyses of gas mixtures of the type of flue gas containing variable quantities of either or both combustible and combustion-supporting constituents.

Other more specific objects of the invention are: To provide in connection with analyses of the combustible constituents of gas mixtures, for making accurate analyses independently of the rate of flow of the gases over an igniting element; to provide a combustion type gas analyzer which will have a substantially permanent calibration throughout its period of use; to provide a combustion gas analyzer employing a heating element in an electric circuit in connection with which the need for current balancing means has been eliminated; to provide for maintaining the accuracy of a combustion gas analyzer independently of the presence of unburned hydrocarbon vapors or water vapor in the gases being analyzed; to provide in novel manner for prolonging the effective life of a catalytic element associated with a gas analyzer operating under combustion principles; and to provide a novel combustion gas analyzer apparatus which is completely reliable and operative over a relatively wide temperature range.

With the above and other objects and features in view, the invention consists in the improvements in fluid mixture analysis which are hereinafter described and particularly defined in the claims. In its broadest aspect, the invention contemplates both the qualitative and quantitative analysis of a fluid mixture such as flue gas which may contain both combustible and oxygen. Although in the following description the gas mixture undergoing analysis is described as comprising flue gases from a furnace, it will be understood that the invention is broadly applicable to the analysis of fluid mixtures generally, and contemplates analysis of engine exhaust gases. In the practice of the invention as applied to qualitative analysis, a measured sample of the flue gas to be analyzed is passed through a combustion zone which is maintained at a temperature at which reaction will take place between combustible and oxygen components of the flue gas. The said flue gas sample is then cooled and divided into two streams which preferably are equal in mass or at least maintained in the same relative proportions. To one of the said portions there is added a relatively small regulated amount of a combustible such as hydrogen, and to the other portion there is added a relatively small proportion of a combustion-supporting fluid such as air. These two portions of the gas are then simultaneously passed into contact respectively with separate highly heated wires similarly disposed in separate identical combustion cells. The added portions of hydrogen and air should substantially balance each other with respect to their cooling effect on the wires. Combustion of any combustion element present in excess in the flue gas sample takes place in one of the cells, generating heat unequally in the cells. Visual evidence

of the heat unbalance of the cells may be indicated by a galvanometer disposed in circuit with thermocouples mounted in the cells.

Quantitative analysis of the flue gas is preferably effected by adding to the flue gas sample before it enters the first named combustion zone a measured amount of a reagent which is reactive with a combustion component of the flue gas known to be present in excess, to bring the temperatures produced in the respective analyzer cells in balance. The amount of the reagent thus required to secure a heat balance between the analyzer cells is then measured by a flow meter in terms of the amount of excess combustible or combustion-supporting components in the flue gas under test, as will hereinafter be more fully described.

The invention will be hereinafter described more particularly by reference to the accompanying drawings, in which:

Fig. 1 illustrates diagrammatically apparatus designed for use in determining the presence of an excess of a combustion element in a gas mixture by a qualitative analysis;

Fig. 2 illustrates diagrammatically apparatus designed for use in measuring the excess of a combustion element in a gas mixture by a quantitative analysis; and

Fig. 3 illustrates diagrammatically, a preferred embodiment of the invention designed for use in measuring the excess of a combustion element in a gas mixture by a quantitative analysis carried out under my titration principle.

Referring more particularly to Fig. 1, numerals 10 and 12 designate identical tubular combustion cells having their lower ends connected respectively with mixing chambers 14 and 16 by conduits 18 and 20. The cells 10 and 12 have gas outlets 22 and 24 on their respective upper ends. Mixing chamber 14 has a gas inlet in the form of a fixed orifice 26 in one wall thereof, and mixing chamber 16 has a gas inlet in the form of a fixed orifice 28 in one wall thereof. The orifices 26 and 28 are constructed so that gas flows therethrough from a supply chamber 30 at an equal or uniformly proportioned flow rate at all times. Secured within cells 10 and 12, respectively, in identical relation with the cell walls, are identical resistance heating elements 32 and 34 in the form of coil filaments of refractory metal which may have catalytic properties or may be catalytically inert. It is preferred to use platinum or rhodium, or platinum-rhodium alloys, in the construction of coils 32 and 34. In the form shown in Fig. 1, coils 32 and 34 are connected in series with a source 36 of house current, by means of lead wires 38 and 40.

Cells 10 and 12 are combustion cells of a gas analyzer which is particularly designed for making qualitative analyses of flue gas for the purpose of ascertaining whether such gas contains an excess of oxygen or an excess of incompletely burned combustible such as CO. In order to feed a sample stream of flue gas to each of the cells 10 and 12 through the supply chamber 30, a pump 42 is provided having its suction inlet 44 connected through a filter chamber 46 and through a conduit 48 with the exhaust gas flue of a furnace 50. Discharge outlet 52 of pump 42 is connected by a conduit 54 with supply chamber 30. Pump 42 is shown as embodying an eccentrically mounted slotted rotor with freely slidable blades cooperatively engaging the inner surface of the pump wall, the rotor being keyed to a drive shaft 56. Two other similar pumps 58 and 60 are shown in Fig. 1 as also keyed to shaft 56; shaft 56 being powered from an electric motor 62 which in turn receives its energy from source 36. Pump 60 is connected to draw air or other suitable combustion-supporting reactant from a source of supply through a filter 64 and to force air thus drawn through a conduit 66 into a chamber 68 from which a regulated small portion of air discharges into mixing chamber 14 through a fixed orifice 70. Similarly, pump 58 is connected to draw a combustible reactant such as hydrogen or CO from a suitable source of supply through a filter 72, and to force such combustible reactant through a conduit 74 into a chamber 76, from which a regulated increment thereof discharges through a fixed orifice 78 into mixing chamber 16.

Filters 46, 64 and 72 contain cotton or other suitable filtering material adapted to separate solid or liquid impurities from the gases passed therethrough. Each of pumps 42, 58 and 60 is provided on its discharge side with a back pressure regulator and relief valve designated respectively 80, 82, and 84, whereby the gas pressure on the down-stream side of each pump is maintained approximately constant, and any excess gas handled by pump 42 is vented to atmosphere, or in the case of the gas handled by pumps 58 and 60, the excess is returned to the suction side of the pump. Mounted in conduit 54 on the down-stream side of pressure regulator 80 and on the up-stream side of chamber 30, is a heat insulated combustion chamber 86. This chamber is lined with quartz or other high temperature refractory material, and is provided with an electric heating coil 88 connected in the aforementioned heating circuit 40. The interior of chamber 86 is preferably filled with a combustion catalyst 90 such as platinized silica or platinum gauze. Between the downstream end of combustion chamber 86 and the analyzer supply chamber 30, conduit 54 is provided with a plurality of heat radiating fins 92 or equivalent cooling devices for reducing the temperature of the gas leaving chamber 86 to a point where it will not endanger the resistance heating elements employed in cells 10 and 12.

In the practice of the invention as thus far described, a clean sample stream of flue gas is forced by pumps 42 at a substantially constant rate through the electrically heated combustion chamber 86 and thence, after division into equal or constantly proportional portions, into mixing chambers 14 and 16. As the flue gas passes through chamber 86 a combustion reaction takes place between any combustible and combustion-supporting components of the gas thereby insuring that the ratio of excess is great between the combustible and combustion-supporting components. Thus a flue gas sample entering chamber 86 may have therein 2% oxygen and 0.2% methane. After passing through chamber 86, the methane content of the gas should be reduced to substantially zero, and the oxygen content to approximately 1.6%, but the excess ratio of oxygen to methane has been greatly increased. From chamber 86 the thus treated gas sample passes through a cooling zone 92 into supply chamber 30, and thence in equal portions to the mixing chambers 14 and 16. Simultaneously air is forced into chamber 14 in a regulated small increment by pump 60, and a combustible gas such as hydrogen is forced into chamber 16 in regulated small increment by pump 58. The quantities of air and hydrogen added to the respective portions of the

flue gas sample in chambers 14 and 16 are relatively small, and may for example be from 0.5% to 5% by volume of the flue gas portions introduced into these chambers respectively through orifices 26 and 28. The quantity of added hydrogen should be adjusted to substantially balance the cooling effect of the added air. This balance can be secured by calibrating the air and hydrogen flows when passing through the analyzer a flue gas which contains neither combustible nor combustion-supporting components. The gas mixtures then flow through the respective cells 10 and 12, where they come in contact with the highly heated resistance elements 32 and 34. The elements 32 and 34 are heated to a temperature well above the ignition temperature of any combustion elements in the gas mixtures flowing through the cells, thereby insuring combustion whenever combustion elements are present. Thus the wires are heated to a temperature which will hold wires 32 and 34 in the operating range of 1400° to 2000° F. under calibrating conditions when air alone is flowing therethrough. Any difference in energy developed in cells 10 and 12 is measured by a thermocouple circuit 94 having hot and cold junctions mounted respectively in opposed E. M. F. relation within cells 10 and 12. Any difference in temperature developed in cells 10 and 12 will set up flow of current in circuit 94 through a galvanometer 96, thus causing the galvanometer needle to swing to the left or right. If the galvanometer needle swings to the right it will indicate for example, the presence of an excess of combustible in the flue gas sample under test; and when the swing is substantial the needle may close the circuit of a power relay 98 which in turn actuates through another relay 99 a switch 100 closing the circuit of a motor valve 102, whereby the valve is opened and additional air supplied to furnace 50 through an air supply line 104. When the supply of air to the furnace has thus been increased, the amount of excess combustible in the flue gas sample correspondingly drops; at which time the galvanometer needle may swing to the left and break contact with power relay circuit 98, whereupon the combustion control mechanism will cease to function until a sufficient excess of either air or combustible again develops in the flue gas sample to again close the power relay circuit and actuate the combustion control mechanism. For the purpose of notifying an operator of the general qualitative characteristics of the flue gas under test, small light circuits may be connected as shown for closure by means of the relay switches 101 and 103, to apprize the operator when the gas is neutral and when it contains an excess of oxygen or an excess of combustible.

One of the outstanding advantages of the qualitative combustion analyzer hereinbefore described and illustrated in Fig. 1, is the wide temperature range within which it will operate. While it is preferred to have the temperature of the heating wires 32 and 34 in the range of 1800° F. to 2000° F., particularly in cases where small concentrations of methane are to be detected, nevertheless the analyzer will operate satisfactorily anywhere within a temperature range between 1400° F. and 2400° F. The arrangement of the qualitative analyzer of Fig. 1 can be modified as illustrated in Fig. 2, to adapt it for quantitative analysis, by substituting a calibrated galvanometer in place of the galvanometer 96 of Fig. 1, and by including mechanism for maintaining constant temperatures in, and rates of gas flow through, the analyzer device. One big advantage of the qualitative analyzer of Fig. 1 resides in the fact that it operates independently of changes in current flow through the heating coils 32, and 34, and independently of changes in rate of flow and inlet temperature of gases entering the analyzer cells 10 and 12. The control of the rate of gas flow which is afforded by the flow regulators 82 and 84 of Fig. 1 is qualitative only, to insure that the sample flow rate be large as compared to the flow rate of the added air and combustible gas reagents. So long as this relative flow relation is maintained between the flue gas samples and the added reagents, relatively large fluctuations in the flow rates of the individual gases through the analyzer cell will not affect the reliability of the analyzer readings. In other words, the regulators 80, 82 and 84 need maintain only approximately constant back pressures, and any fluctuations in flow rate which are caused by changes in the speed of motor 62 or by changes in flow resistance through the catalyst bed 90 will not adversely affect the readings of the analyzer any more than will changes in temperature of the gases delivered to the analyzer. It is convenient, however, to have the three back pressure regulators 80, 82, and 84 set to deliver gas at the same pressure in order that there may be no back flow of any of the gases into the supply line of one of the other gases.

Referring now more particularly to the quantitative continuous analyzer which is illustrated in Fig. 2, it will be noted that the cells 10 and 12 and the orifices 26, 28, 70 and 78, together with the mixing chambers 14 and 16 and the connecting conduits 18 and 20, are all mounted in a thermostat 110 provided with an electric heater 112 having an automatic thermostat switch 114, by means of which the temperatures of the gas entering each of the analyzer cells are kept constant at a temperature higher than that of the surrounding atmosphere. In order to maintain the rates of flow of each of the gases entering mixing chambers 14 and 16 constant, quantitative pressure regulators 80, 82 and 84 are in each case directly connected with the chambers 30, 68 and 76 on the upstream side of orifices 26, 28, 70 and 78. The pressure regulators 80, 82, and 84 must be more accurate and precise in operation than those used in the corresponding analyzer of Fig. 1, and in addition the speed of motor 63 of Fig. 2 must be very nearly constant, for which reason a synchronous motor is preferred. Electric current is preferably supplied to coils 32 and 34 of Fig. 2 from a source 36 through a step-down transformer 116 having constant current characteristics, and through ballast resistances 118. As previously indicated, the quantitative analyzer of Fig. 2 employs a calibrated galvanometer 120 in the thermocouple circuit 94.

The operating temperature range of the calibrated quantitative analyzer of Fig. 2 is necessarily very narrow. The qualitative analyzer of Fig. 1 operates over a wide temperature range for the reason that the amount of combustible reagent which is added to the gas entering one combustion cell, and the amount of air or oxygen added to the gas entering the other cell, is relatively small as compared to the volume of the gas; and the amounts of added combustible reagent and oxygen should substantially balance with respect to cooling effect over a wide temperature range. When the method is adapted to quantitative analysis, the amounts of added reagent cannot be very small, since the amount of added

oxygen must be equivalent to the highest concentration of excess fuel which will be at any time present in the flue gas sample, or otherwise the galvanometer would not deflect proportionally with an increase in fuel content of the sample. Likewise sufficient combustible must be added to the sample to react with the highest concentration of excess oxygen which may be present in the sample. Moreover, the galvanometer needle should remain at its zero position when the sample contains neither excess oxygen nor excess combustible. Therefore the cooling effect of the added air or oxygen must balance the cooling effect of the added combustible. This limits the operating temperature of the instrument within a narrow range, since the cooling effect of each of the added reagents changes with the operating temperature, and the changes are not proportional. Moreover, the operating temperature range is further limited by the fact that the sensitivity of the instrument, as well as its calibration, changes with the temperature. Thus the instrument might be calibrated to give a scale reading of 100 for 1% CO in the flue gas sample at 500° C. If for any reason the wire temperature should increase from 500° C. to 600° C., the scale reading would drop to about 76 for 1% CO. Conversely, if the temperature should drop to 400° C., the scale reading would rise to about 138. Therefore the quantitative analyzer of Fig. 2 can be depended upon for measuring the concentration of excess combustible or excess oxygen only when operating in a limited temperature range. The nature of the combustible must not change and the nature of the inert gases must not change. For satisfactory operation, it is necessary to maintain substantially constant the supply of current to the analyzer heating elements, the rate of flow of the sample, the rate of flow of the added combustible reagents, the rate of flow of the added combustion-supporting reagent, and the operating temperature of the combustion cell.

The apparatus illustrated in Fig. 3 represents a quantitative analyzer which is a practical improvement over the analyzer shown in Fig. 2. The quantitative analyzer of Fig. 3 is designed for operation on the titration principle of continuous quantitative gas analysis, which underlies the invention described in my copending application Serial No. 650,133, filed January 4th, 1933. The method of analysis for which the apparatus of Fig. 3 is adapted, is entirely independent of changes in current supply to the analyzer heating element, and is also independent of changes in operating temperature of the analyzer cells and of changes in rate of flow of gas sample and of combustible and combustion-supporting reagents through the instrument. In principle, the method of analysis which is practiced in the apparatus of Fig. 3 consists broadly of adding to a flue gas sample the quantity of air required to exactly combine with any excess combustible in the sample, or the quantity of combustible required to exactly combine with excess oxygen in the sample. This titration is carried out automatically and the percentage of excess oxygen in the sample is determined by measuring the amount of hydrogen, for example, which must be added to a unit quantity of the sample, in order to neutralize the sample. The method and apparatus of the qualitative analyzer illustrated in Fig. 1 affords a reliable determination as to whether the flue gas sample is neutral or contains excess oxygen or excess combustible. This determination is then used as a basis for a titration determination of the amount of such excess. The titration method of analysis for which the apparatus of Fig. 3 is adapted is of particular utility for analyzing a gas such as the ordinary furnace flue gas, the composition of which is likely to change frequently from having an excess of oxygen to having an excess of combustible.

In the operation of the apparatus of Fig. 3, a sample of flue gas is drawn from the furnace through conduit **48**, filter **46**, pump **42**, and thence is forced through combustion chamber **86** into a supply chamber **30**, from which equal portions pass through orifices **26** and **28** into mixing chambers **14** and **16**, and thence through identical analyzer cells **10** and **12**. Simultaneously, air is forced by pump **60** through orifice **70** into mixing chamber **14** from whence it passes in admixture with one portion of the flue gas sample through cell **10**. At the same time a combustible gas reagent such as hydrogen is forced by pump **58** through orifice **78** into mixing chamber **16**, and thence in admixture with the other portion of flue gas sample through combustion chamber **12**. If the temperature developed in cell **10** is greater than the temperature developed in cell **12**, the flue gas sample contains excess combustible, and the needle of galvanometer **96** will indicate the presence of such excess by swinging to the right. The contact made by the galvanometer will close the circuit of power relay **98**, and will thereby energize one of the solenoids **121** of a reversing mechanism **122**. In addition to the solenoids **121** which are energized by power relay **98**, the reversing mechanism **122** embodies as elements a rocker crank **124** which is journaled on a shaft **126** and which is powered from shaft **56** of pump motor **62** through a pinion **128**, meshing with a gear crank **130**, from which a reciprocating motion is imparted to crank **124** through connecting rod **132**. When the proper solenoid **121** of reversing mechanism **122** is energized by the needle of galvanometer **96** swinging to the right, an armature member **134** which is pivotally mounted on the solenoid frame is rotated in a counter-clockwise direction about its pivotal support by the attraction of the electric field of the solenoid. A pawl **136** is rotated clockwise on its pivotal support on rocker arm **124** and thereby brought first into and then out of engagement with the teeth of ratchet gear **138**, each time crank arm **124** reciprocates. A coil spring **140** normally holds armature **134** and pawl **136** in the disengaging position illustrated, except when the solenoids of mechanism **122** are energized through power relay **98**.

When the galvanometer needle swings to the right as previously described in response to the presence of an excess of combustible in the flue gas sample, mechanism **122** operates through ratchet gear **138** to slowly rotate shaft **126** in a clockwise direction, thereby opening a valve **142** in a cross connection **144** between air supply pipe **66** and gas sample supply pipe **54** on the upstream side of catalyst combustion chamber **86**. This results in the addition of air to the gas sample entering the combustion chamber **86**, and the air thus added combines with excess combustible in the sample during the passage of the sample through catalyst chamber **86**, so that when the thus modified sample reaches cell **10** there has been a decrease in the amount of combustible in the sample equivalent to the amount of air added by the opening of valve **142**. When the amount of air added to the gas sample by

the opening of valve 142 is just sufficient to burn out any excess combustible in the sample, the thus modified sample entering mixing chambers 14 and 16 will be neutral, and this neutrality will act through galvanometer 96 and the power relay 98 to disengage pawl 136 from ratchet 138, thereby arresting further opening of valve 142. It will be noted that the adjustment of valve 142 is a step by step adjustment effected by the intermittent motion imparted to shaft 126 and ratchet 138 by the mechanism 122. A spring brake 146 operatively connected with shaft 126 serves to prevent rotation of the shaft except when actuated through ratchet 138. The slow intermittent step-by-step motion imparted to the shaft 126 and valve 142 is preferred in order to avoid over-control and hunting.

The quantitative analysis of the flue gas sample is made by a titration principle previously referred to. According to this method, the volume of air which valve 142 must pass in order to neutralize the excess combustible content of the gas flowing into combustion zone 86 is metered by a differential flow meter 148 connected across orifice 150 in the air conduit 144 on the up-stream side of valve 142. The opening of valve 142 is effected through the medium of a cam 152 which on clockwise rotation of shaft 126 raises the stem of valve 142. Counter-clockwise rotation of the cam 152 allows a valve spring 154 to close valve 142. Flow meter 148 measures the amount of air or oxygen required to neutralize excess combustible in the flue gas sample, the meter being preferably calibrated in terms of ratio of flow of air passed by orifice 150 to ratio of flow of gas sample passed by orifice 156 in the gas sample supply line. Thus, if the rate of flow of the sample past orifice 156 is 10 cubic feet per hour, and if the equilibrium rate of flow of air past orifice 150 is one cubic foot per hour, the air demand of the flue gas sample to bring it to neutrality is 10%. This is an air demand of a flue gas sample containing 4% carbon monoxide or 4% hydrogen, or 1% methane.

The flow rate of the gas sample through the crifice 156 is maintained constant by maintaining a constant pressure ahead of the orifice 156 in the discharge line of pump 42 by means of pressure regulator 80, and by maintaining a constant pressure drop across the orifice by means of a pressure regulator 158 actuating a relief valve 160 on the downstream side of the orifice. The pressure regulator 84 acts to maintain a constant air pressure on the upstream side of air supply orifice 150. All that is necessary in the operation of this apparatus is to maintain a relatively constant ratio between the flow rate of flue gas sample and the flow rate of the added reagent. In this respect the apparatus of Fig. 3 differs from that of Fig. 2, in which an absolute constant ratio must be maintained between the flow rates of the flue gas sample and the flow rate of the added air or combustible. No temperature control is required other than that of keeping the temperature of the flue gas sample and that of the reagent the same at the respective orifices 150 and 156. This is automatically accomplished for the reason that the gases at this point are both substantially at atmospheric temperature.

When the flue gas sample carries excess oxygen rather than excess combustible, the needle of galvanometer 96 will swing in the opposite direction thereby actuating through power relay 98 the other solenoid 121 of reversing mechanism 122, thereby rotating shaft 126 step-by-step in a counter-clockwise direction. The counter-clockwise rotation of shaft 126 acts through cam 152 to first close valve 142, and then through a cam 162 to open a valve 164 in a pipe connection 166 between combustible reagent supply pipe 74 and flue gas conduit 54. The amount of combustible gas such as hydrogen which it is necessary that valve 164 shall pass in order to neutralize excess oxygen contained in the flue gas sample, is then measured by a differential flow meter 168 connected across an orifice 170 in pipe 166. The valves which control the supply of air and fuel to the furnace from which the flue gas sample is taken, may be automatically controlled by means such for example as the reversing mechanism 122 acting through an extension of shaft 126 (not shown). In other words the reversing mechanism may be made the connecting link whereby combustion in the furnace is automatically controlled in accordance with the analysis of the flue gas which is made by analyzer cells 10 and 12.

The speed reduction ratio between shaft 56 and rocker arm 124 is preferably so adjusted (as by varying the speed ratios of pinion 128 and gear 130) that the rocker arm reciprocates once during the period consumed in passing a unit volume of the gas or other fluid sample under test from orifice 156 through the analyzer, and in completing the analysis. Thus if after analysis has shown that a sample of the flue gas contains 4% excess CO the composition of the flue gas should change so that the CO content drops to 3%, the analyzer would almost immediately indicate the presence of an excess of oxygen in the gas stream leaving combustion chamber 86 resulting from the addition to the gas stream through valve 142 of more air than that necessary to combine with the CO now present in the sample. The higher temperatures developed in cell 12 would now cause the galvanometer needle to swing to the left and thereby actuate the reversing mechanism 122 to rotate shaft 126 counterclockwise. The rotation of the shaft would be so slow as to arrest the closing of valve 142 at the point where the air passed thereby will substantially balance the reduced CO content in the flue gas delivered to combustion chamber 86 through orifice 156. It will be understood that cam 162 does not operate to open valve 164 until valve 142 has been entirely closed by rotation of shaft 126 acting through cam 152.

In place of the two differential meters or pressure gauges 148 and 168, a single differential pressure gauge may be substituted having two pressure taps, one connected to the up-stream side of valve 142 and the other to the up-stream side of valve 164.

By subjecting the gas sample to temperatures favoring combustion in combustion chamber 86, the intensities of any reactions which may later take place in cells 10 and 12 may be more accurately measured without the possibility of injury to the heating elements or thermocouples by development of excessively high temperatures.

The invention as described is also adapted for the measurement of reactive components of fluid mixtures by the addition thereto of fluid reactants which produce endothermic instead of exothermic reactions.

It is not essential that wire heating elements be employed within the cells 10 and 12, nor is it essential that catalytic material be employed in combustion chamber 86. All that is necessary is that conditions favoring combustion be main-

tained by some means in chamber 86 and in cells 10 and 12.

It will also be understood that only a part of the gas passed through combustion chamber 86 need go to the analyzer cells 10 and 12; and that the flow meters 148 and 168 of the apparatus of Fig. 3 are the only elements thereof which need be calibrated, and this calibration need not be a made in place if the proper type of differential meter is used. The titration method of analysis underlying the apparatus of Fig. 3 not only operates independently of fluctuations in all operating factors except the composition of the fluid mixture being measured, but it is also advantageous in that there is no great time lag between the operation of the combustion analyzer and the moment that the indicating mechanism is actuated to record the composition of the fluid mixture under examination by the analyzer.

The invention having been thus described, what is claimed as new is:

1. The method of determining which one of two mutually reactive components is present in excess in a gaseous mixture, which comprises subjecting a continuously flowing sample of said mixture to conditions under which reaction takes place between said components so as to increase the ratio of the excess component to the deficient component, dividing the resulting reaction mixture into two uniformly proportional streams, adding a small increment of a gas reactive with one of said components to one stream, adding a small increment of a second gas reactive with the other component to the other stream, employing a sufficient volume of the increment gas which reacts with the excess component of the gas mixture to give an indication of the presence of said excess component, proportioning the volumes of said added increments with relation to each other so as to balance said increments with respect to their thermal capacities and heat conductivities, passing the thus modified streams through identical reaction zones while subjecting the streams to uniform conditions under which reaction takes place between the components and the gases reactive therewith, and indicating any difference in the intensities of the resultant reactions in the respective gaseous streams.

2. The method of determining the amount of excess of one active component in a continuously flowing measured stream of a gaseous mixture which may contain two mutually reactive components which comprises, adding to said mixture a reagent reactive with said one active component, reacting said reagent and said component, dividing the reaction mixture into two uniformly proportional portions, adding to one portion a small increment of said reagent, and simultaneously adding to the other portion a small increment of a second reagent which is reactive with the first reagent adjusting the volumes of said added increments so as to balance their thermal capacities and heat conductivities, concurrently subjecting the thus modified portions of the reaction mixture to conditions under which reaction takes place between the reactive components and the added reagents, measuring the difference in the intensities of the resulting reactions in the respective gaseous portions, adjusting the amount of first-named reagent added to the original gaseous mixture so as to balance the intensities of the last named reactions, and measuring the amount of said first named reagent thus required.

3. The method of determining the amount of excess of one combustion element in exit gases from a combustion operation which may contain another combustion element reactive with the former, which comprises adding a measured amount of a fluid reactive with said first named combustion element to a continuously flowing measured sample stream of said exit gases, heating said stream to a temperature favoring reaction between said fluid and said element, cooling the reaction mixture and dividing it into two uniformly proportional portions, adding to one portion a small increment of combustible and simultaneously adding to the other portion a small increment of a combustion supporting gas, the volumes of said added combustible and combustion supporting gas increments being substantially balanced with respect to their thermal capacities and heat conductivities within the reaction temperature range, concurrently subjecting the thus modified portions to temperatures favoring combustion reactions, measuring the difference in the intensities of the resultant reactions in the respective gas portions, adjusting the amount of reactive fluid added to the original gas sample so as to balance the intensities of the final reactions, and measuring the amount of fluid reactant thus added in terms of the amount of said combustion element with which it reacts.

4. The method of measuring the amount of a reactant in a fluid mixture which comprises adding to a continuously flowing measured stream of the mixture a second reactant, subjecting the resultant mixture to conditions under which said reactants become mutually reactive, dividing the resultant reaction mixture into two uniformly proportional portions, adding a small fixed increment of a fluid reactive with one of said reactants to one of the said portions, adding to the other portion a small fixed increment of a fluid reactive with the other reactant, proportioning the volumes of said added increments so as to balance said increments with respect to their thermal capacities and heat conductivities, concurrently reacting the respective portions in separate reaction zones thereby producing heat of unequal intensity in the respective zones, adjusting the amount of the second reactant added to the fluid mixture so as to balance the temperatures developed within the said reaction zones, and measuring the amount of second reactant thus required.

5. The method of measuring the extent of an incomplete chemical reaction which comprises, mixing a continuously flowing measured stream of a fluid product of the reaction with a regulated amount of a second fluid reactive with a component of the fluid product, reacting the fluid mixture under conditions substantially to reduce the amount of one of the reactive components and form a residual reaction mixture, dividing the residual reaction mixture into two uniformly proportional portions, adding to one of the said portions a small increment of said second reactive fluid, adding to the other portion a small increment of a fluid reactive with said second reactive fluid, proportioning the volumes of said added increments so as to balance said increments with respect to their thermal capacities and heat conductivities, thereafter concurrently subjecting the said fluid portions to conditions producing reactions therein, measuring the intensities of the last-named reactions in the respective fluid portions, adjusting the amount of the second reactive fluid added to the

chemical reaction product so as to balance the intensities of the last-named reactions, and measuring the amount of second reactive fluid thus required.

6. The method which comprises mixing a continuously flowing measured stream of a fluid with a regulated amount of a second fluid reactive with the former, reacting the fluid mixture thus formed under conditions substantially to reduce the amount of one of the reactive fluids and to form a residual reaction mixture, dividing the said reaction mixture into two uniformly proportional portions, adding to each of said portions a small fixed increment of one of two mutually reactive fluids, each of which is reactive with one of said first-named fluids, thereafter concurrently subjecting the said fluid portions to similar conditions producing reaction therein, developing opposed electromotive forces varying respectively in response to variations in the intensity of reaction in the respective portions, noting the direction of the resultant electromotive force, adjusting the amount of the second reactive fluid so as to balance the intensities of said reactions, and measuring the amount of the second fluid thus required.

7. Apparatus adapted for analyzing a continuously flowing sample stream of a fluid which may contain two mutually reactive components for the purpose of measuring the amount of excess of one of said components which comprises, means for mixing with said first-named fluid a second fluid reactive with the component which is present in excess, a reaction chamber in which said mixture is subjected to temperatures favoring reaction between said second fluid and said component, means for dividing the resultant reaction mixture into two uniformly proportional portions, a device for modifying one of the said portions by introducing thereto a small fixed increment of a fluid reactive with one of said active components, a device for similarly modifying the other portion by introducing thereto a small fixed increment of a fluid adapted to react with the other active component of said mixture, two reaction cells, means for directing one of said modified portions into one cell, means for directing the other modified portion into the other cell, means for indicating any difference in temperature developed in the two cells, and calibrated means for regulating and measuring the amount of second reactive fluid which is added to the first-named fluid stream in order to balance the temperature developed in the cells.

8. In combination, means for continuously forming a regulated mixture of waste combustion gases and a gaseous element of combustion, a combustion chamber and means for subjecting said gas mixture to temperatures favoring combustion reactions therein, means adapted to divide combustion gases leaving said combustion chamber into two uniformly proportional portions, a device for mixing with one of said portions a small fixed increment of a combustion-supporting gas, a second device for mixing with the other portion a small fixed increment of a combustible gas, two combustion cells, means for separately conducting the respective portions to corresponding cells, means adapted to measure any temperature differential between the respective cells, and calibrated means for measuring the volume of combustion element added to the waste gases in order to balance the temperatures developed in the cells.

9. The method of determining whether the gaseous products of a combustion operation contain an excess of a combustible gas or an excess of oxygen, which comprises subjecting a continuously flowing stream of said products to a temperature under which combustion reaction takes place between said combustible gas and said oxygen so as to increase the ratio of the excess constituent to the deficient constituent, dividing the resultant products of reaction into two uniformly proportional streams, adding a small increment of an oxidizing gas such as air to one stream, adding a small increment of a combustible gas such as hydrogen to the other stream, proportioning the volumes of said added increments so as to balance said increments with respect to their thermal capacities and heat conductivities, passing the thus-modified streams through identical combustion zones while subjecting the streams to uniform conditions of temperature under which combustion reaction takes place, and indicating any difference in the intensities of the resultant reactions in the respective streams.

10. The method of determining the amount of excess of oxygen in the gaseous products of a combustion operation which may also contain combustible gas, which comprises adding a measured amount of a combustible gas to a continuously flowing sample stream of said combustion products, heating said stream to a temperature at which combustion reaction takes place between said oxygen and said combustible gas, cooling the stream of products of said combustion reaction and dividing the stream into two uniformly proportional portions, adding a small fixed increment of an oxidizing gas to one of said portions, adding to the other portion a small fixed increment of combustible gas, proportioning the volumes of said added increments so as to balance said increments with respect to their thermal capacities and heat conductivities, concurrently subjecting the respective portions to conditions supporting combustion in separate identical combustion zones, thereby producing heat of unequal intensity in the respective zones, adjusting the amount of combustible gas added to the original gaseous products so as to balance the temperatures developed within the said combustion zones, and measuring the amount of combustible gas thus required in terms of the amount of oxygen with which it reacts.

11. The method of determining the amount of excess of a combustible gas in the gaseous products of a combustion operation which may also contain oxygen reactive with the combustible gas, which comprises adding a measured amount of oxygen to a continuously flowing sample stream of said combustion products, heating said stream to a temperature at which combustion reaction takes place between said oxygen and said combustible gas, cooling the stream of products of said combustion reaction and dividing the stream into two uniformly proportional portions, adding a small fixed increment of a combustible gas to one of said portions, adding to the other portion a small fixed increment of oxygen, proportioning the volumes of said added increments so as to balance said increments with respect to their thermal capacities and heat conductivities, concurrently subjecting the respective portions to conditions supporting combustion in separate reaction zones thereby producing heat of unequal intensity in the respective zones, adjusting the amount of oxygen added to the gaseous products of combustion so as to balance the temperatures

developed within the said reaction zones, and measuring the amount of oxygen thus required.

12. In apparatus for analyzing waste combustion gases for unburned combustible, a combustion chamber and associated heating elements for maintaining temperatures forming combustion reactions therein, means for continuously forming a regulated mixture of waste combustion gases and a combustion supporting gas and introducing said mixture to said chamber, means adapted to withdraw a stream of products of combustion from said chamber and to cool the same, means adapted to divide said stream of products into two uniformly proportional portions, a device for modifying one of the said portions by adding thereto a small fixed increment of a combustion supporting gas, a second device for modifying the other portion by introducing thereto a small fixed increment of a combustible gas, said device being arranged to balance the volumes of added increment of combustion supporting gas and combustible gas with respect to their heat capacities and heat conductivities, means for adjusting and measuring the relative proportions of the waste combustion gases and combustion supporting gas flowing to the first named mixing means, two combustion cells, means for directing one of the said modified portions through each cell, and means for indicating any difference in temperature developed in the two cells.

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