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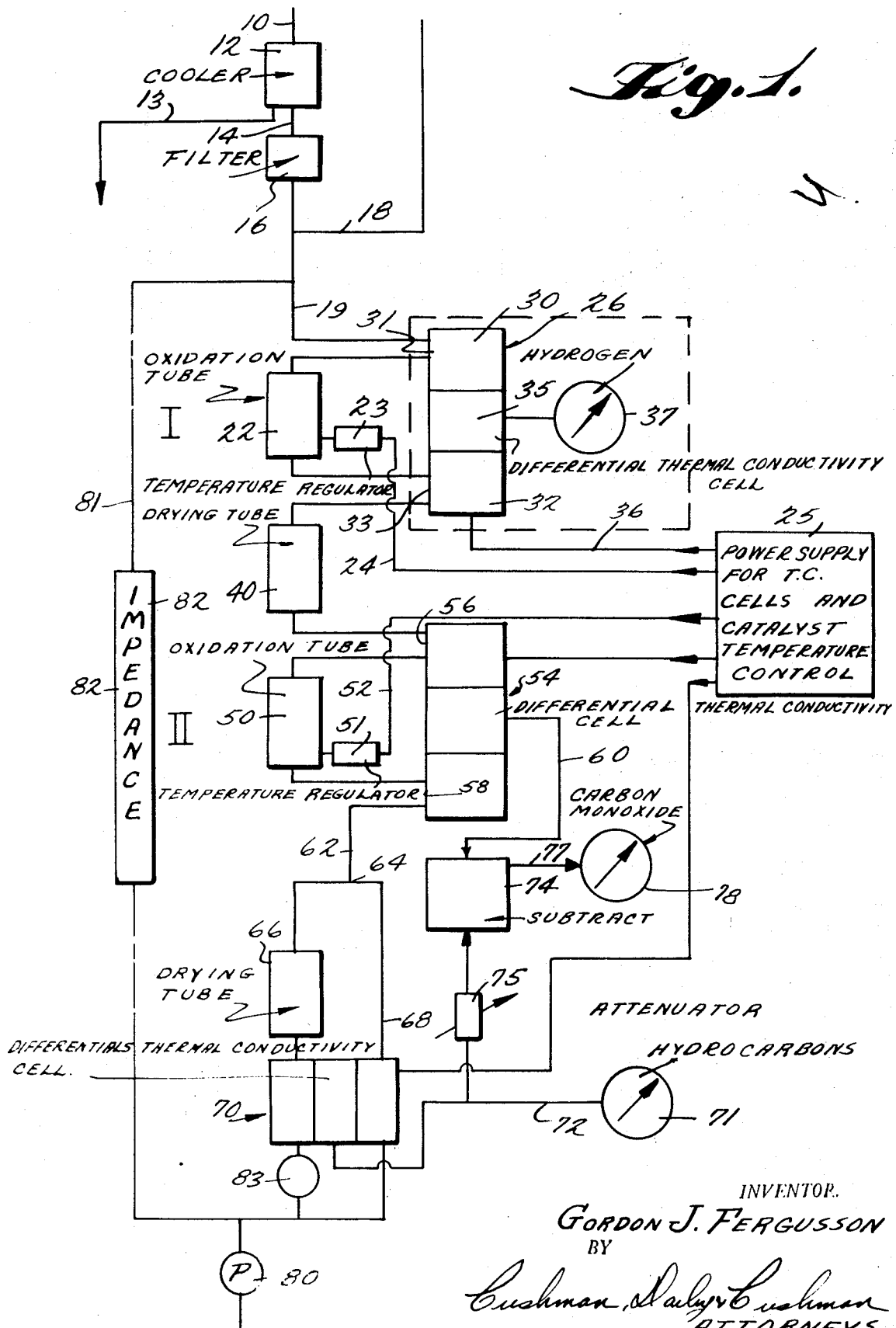
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METHOD AND ANALYZER FOR HYDROGEN, CARBON MONOXIDE
AND HYDROCARBONS IN EXHAUST GASES

Filed Dec. 5, 1967

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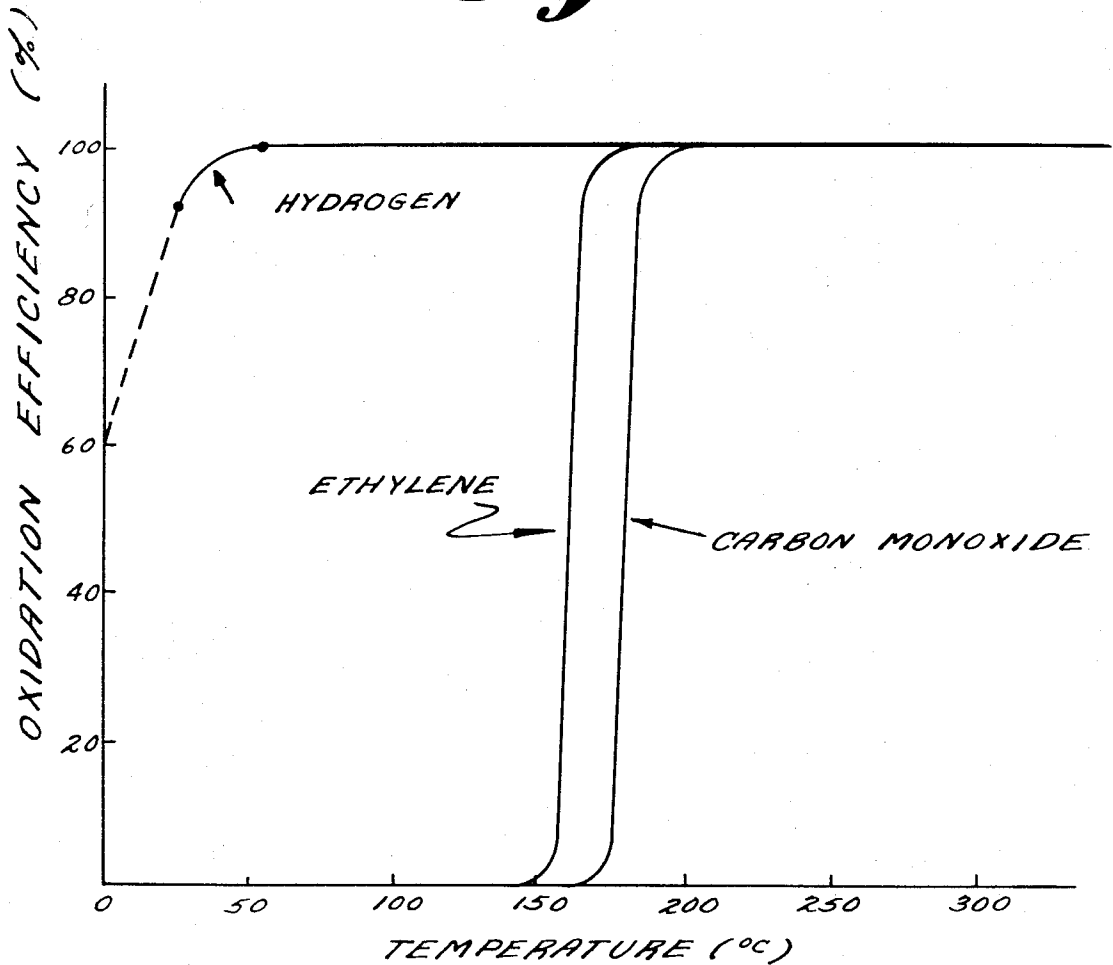
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Fig. 2.



OXIDATION EFFICIENCY OF CATALYST

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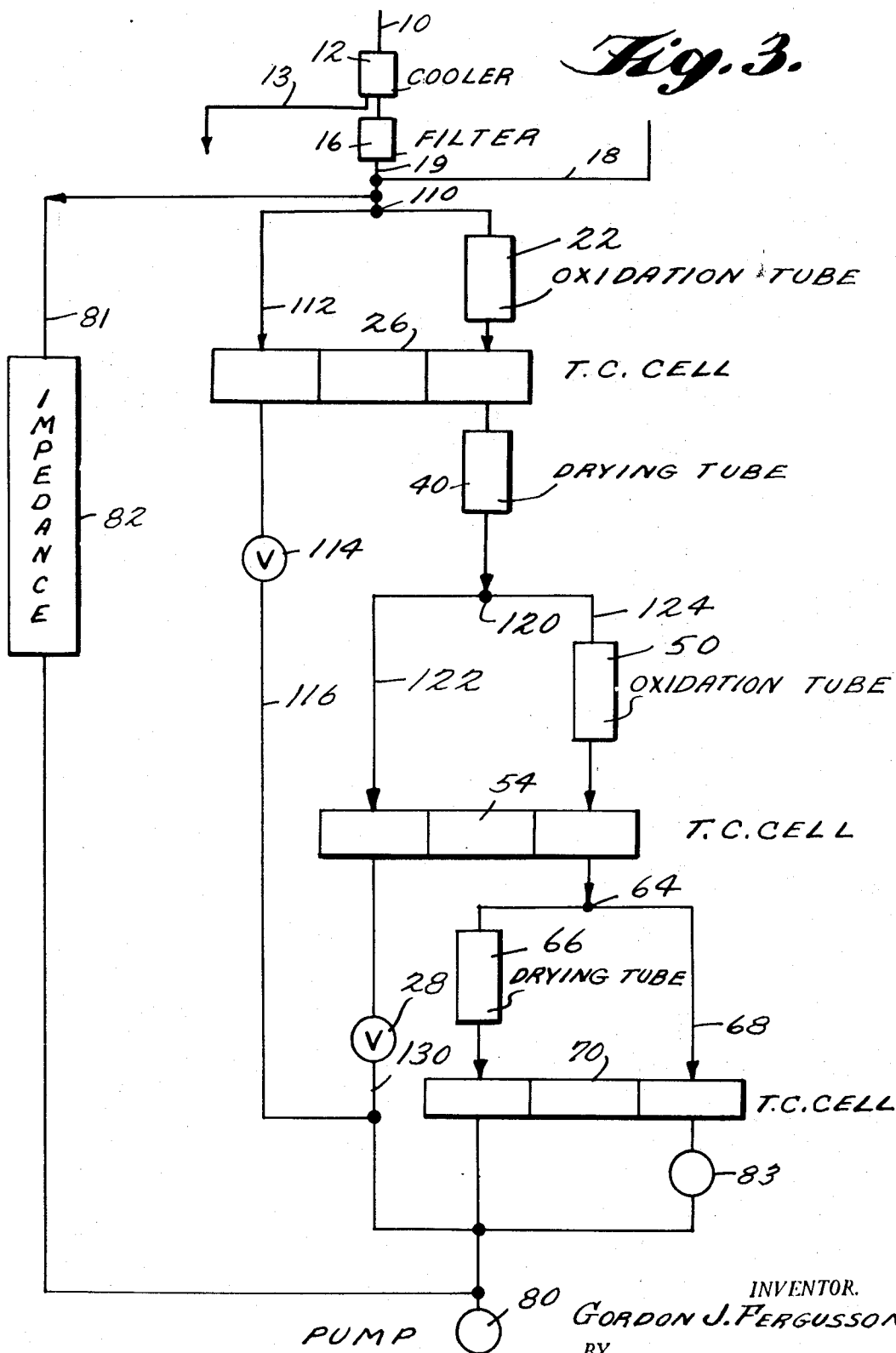
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3 Sheets-Sheet 3



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METHOD AND ANALYZER FOR HYDROGEN CARBON MONOXIDE AND HYDROCARBONS IN EXHAUST GASES

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25 Claims

ABSTRACT OF THE DISCLOSURE

The following specification discloses method and apparatus for determining hydrocarbon and carbon monoxide concentrations in the gases produced by the combustion of hydrocarbon fuels. A sample of gas is passed through a first stage wherein the free hydrogen present is selectively oxidized in a catalytic oxidation tube without oxidizing any of the hydrocarbons or carbon monoxide present therein. The sample is then passed through a drying tube wherein any water present is substantially completely removed. The dried gas is then passed through a second oxidation tube wherein the hydrocarbons and carbon monoxide are oxidized to water and carbon dioxide. The thermal conductivity change caused by the oxidation of the hydrocarbons and carbon monoxide is measured and a first signal proportional thereto is produced. The water concentration is also measured and a signal produced which is indicative of the hydrocarbon concentration. A portion of this hydrocarbon signal is subtracted from the first signal in order to generate an output indicative of the carbon monoxide content.

The present invention relates to method and apparatus for gas analysis. More particularly, the present invention concerns method and apparatus for the quantitative determination of carbon monoxide and hydrocarbon concentration as well as the hydrogen concentration of exhaust gases produced by the imperfect combustion of hydrocarbon fuels.

The gaseous products of combustion of hydrocarbon fuels which are invariably discharged to the atmosphere are causing severe air pollution problems in many parts of the world. The pollutants produced by imperfect combustion of hydrocarbon fuels, i.e., carbon monoxide and hydrocarbons, have already become a public nuisance in many cities in the United States as well as in other parts of the world. One of the main contributors to this problem is the exhaust gas from vehicles burning hydrocarbon fuels, such as automobiles and busses.

The severity of this pollution problems can be judged from the large scale effort being put forth by the United States Federal Government as well as various state governments and the automobile industry to reduce and control the amount of carbon monoxide and hydrocarbons that are discharged.

Maximum permissible concentrations of carbon monoxide and hydrocarbons in the exhaust gas of vehicles have already been set by law in several states of the United States. The enforcement of these maximum concentrations, however, is being severely hampered by the present lack of a simple, relatively inexpensive analyzer for carbon monoxide and hydrocarbons in the exhaust gases.

The present invention provides a method and apparatus which is both simple and relatively inexpensive and in addition, requires little time to effect the desired analysis and may be operated by individuals having limited or no experience with testing apparatus of this type.

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The exhaust gases from internal combustion engines burning hydrocarbon fuels and air, for example, is a mixture of the following gases (omitting some trace constituents that are not important in the analysis problem considered here):

	Percent
Nitrogen	70-80
Oxygen	0-10
Carbon dioxide	0-15
Carbon monoxide	0-30
Water	0-7
Hydrogen	0-5
Hydrocarbons	0-1
Sulphur dioxide	0-0.3

In accordance with the present invention, a method and apparatus are provided so that the concentration of carbon monoxide and of the hydrocarbons in such an exhaust gas can be determined without interference from these varying concentrations of oxygen, carbon dioxide, hydrogen, water, sulphur dioxide and nitrogen.

Briefly and in accordance with the present invention, a sample of exhaust gas is first cooled to ambient temperature. A portion of the water vapor present in the sample is condensed by this cooling and removed. The sample is then filtered to remove any particulate matter. The thus filtered and cooled gas, containing hydrocarbons and carbon monoxide, hydrogen and carbon dioxide as well as sulphur dioxide and nitrogen, which are essentially non-combustible, is combined with a quantity of oxygen at least stoichiometrically equivalent to the hydrogen, carbon monoxide and hydrocarbons present in the sample, and then fed to a first stage wherein the free hydrogen is selectively oxidized, i.e., the hydrogen is oxidized to H_2O , under circumstances wherein the carbon monoxide and hydrocarbons present are unaffected. The water produced by the selective oxidation of the free hydrogen, as well as any water vapor remaining in the sample, is then removed and the dry, hydrogen free exhaust gas containing the carbon dioxide, carbon monoxide and hydrocarbons is fed to a second stage wherein the hydrocarbons and carbon monoxide are completely oxidized to carbon dioxide, and water.

Apparatus is provided to sense the change in thermal conductivity produced by oxidation of the carbon monoxide and hydrocarbons and to generate a signal indicative of this quantity. The water produced by the oxidation of the hydrocarbons is also monitored and a signal generated which is indicative of the water concentration. The water concentration is proportional to the hydrocarbon content of the exhaust gas sample and suitable indicating means is provided to register the concentration of the hydrocarbons in a meaningful manner. The signal indicative of the change in thermal conductivity caused by the second oxidation stage is combined with a predetermined portion of the signal from the water responsive apparatus in a subtraction circuit whereby a portion of the signal indicative of the hydrocarbon content is subtracted from the signal proportional to the change in thermal conductivity caused by the second combustion stage, the resulting difference being proportional to the carbon monoxide content of the exhaust gas sample. Suitable output indicating means, such as meters and the like, appropriately calibrated, can be used to provide an easily readable indication of the carbon monoxide content.

The present invention may be better understood by referring to the following detailed description in conjunction with the accompanying drawings in which:

FIG. 1 is a schematic block diagram of a gas analyzer constructed in accordance with the teachings of the present invention;

FIG. 2 illustrates the relationship between oxidation

efficiency and temperature for hydrogen on the one hand and carbon monoxide and ethylene on the other hand; and

FIG. 3 is a block diagram of the parallel mode embodiment of the present invention.

In FIG. 1, the exhaust gas sample containing the various constituents hereinbefore mentioned, is fed via input conduit 10 to a cooling apparatus 12 of any suitable and well known construction wherein the hot exhaust gases are cooled to ambient temperature and wherein a portion of the water vapor present in the exhaust gases is condensed and removed via conduit 13. The cooled exhaust sample is then passed through conduit 14 to a particulate filter 16 wherein any particulate matter present in the exhaust sample is removed. The particulate filter and the cooling apparatus are not necessary elements in the analysis of the gas, however, it is helpful to prevent malfunction due to clogging and other deleterious effects attributable to such matter.

The filtered, partially dried gas is combined with a quantity of oxygen supplied through intake tube 18 and then fed via conduit 19 through a hydrogen removal stage I wherein the hydrogen is selectively oxidized to water and then completely dried. The hydrogen free and dried sample is finally fed to a stage II wherein the carbon monoxide and hydrocarbons are completely oxidized and their respective concentrations determined. The quantity of oxygen added must be at least stoichiometrically equivalent to the hydrogen, carbon monoxide and hydrocarbons present in the sample in order to completely oxidize the hydrogen in stage I and the hydrocarbons and carbon monoxide in stage II. The oxygen may be supplied in any desired manner as by supplying pure oxygen through tube 18 or by supplying a sufficient quantity of air through tube 18. This latter method is preferred in view of the simplicity of apparatus required therefore and the inherent economic savings. In practice it has been found that 40 to 50% air is usually satisfactory, however, as much as 100% can be used.

The oxidation tube 22 contains a catalyst which must meet the requirement that it oxidize the hydrogen with virtually 100% efficiency at a temperature which does not oxidize carbon monoxide or any of the hydrocarbons present. The group of catalysts consisting of platinum, palladium and copper oxide have been found to comply with this requirement at the particular flow rates employed in the present invention, however, it is to be understood that any catalyst meeting these requirements may be employed.

Platinum has been found to be the preferred catalyst and more specifically, platinum disposed on a base of asbestos (platinized asbestos). With reference to FIG. 2, it can be seen that there is a substantial range of temperatures between that required for 100% oxidation efficiency for hydrogen and 100% oxidation efficiency for carbon monoxide and the hydrocarbons when platinized asbestos is used as the catalyst in both oxidation tubes. By maintaining the oxidation tube 22 at a temperature between 50°C. and 150°C. the selective oxidation or combustion of hydrogen can be effected. In FIG. 1, temperature regulating means 23 is located in the line 24 which supplies electrical energy to the oxidation tube 22 from the power supply 25, and is effective to regulate the current delivered to the oxidation tube and consequently the temperature.

Stage I of this apparatus may optionally include means for determining the amount of hydrogen removed during the selective oxidation in the oxidation tube 22 in order to determine the hydrogen concentration of the gas sample. This is an optional feature since hydrogen is not a pollutant but its concentration is of interest, for example, in evaluating the operation of internal combustion engines. This may be effected in any well known manner such as, for example, measuring the difference in thermal conductivity of the gas before and after combustion. This

method is preferred, and as shown in FIG. 1, a differential thermal conductivity cell 26 is provided for this purpose. The thermal conductivity cell is well known to those skilled in the art and is shown here in block diagram form only. It is to be understood, however, that the cell contains a first thermal conductivity cell 30 for determining the thermal conductivity of the gas at input 31 and a second cell 32 for determining the thermal conductivity at the other input 33. The differential thermal conductivity cell 26 also includes the required electrical circuitry 35 which is supplied from power source 25 via lead 36 to compare the signals from the thermal conductivity cells and to generate an output proportional to the difference therebetween which is in turn, proportional to the amount of hydrogen removed in the oxidation tube 22. This signal is fed to a suitable indicator 37 which may be in the form of an ammeter or voltmeter, for example, calibrated to read in terms of percent hydrogen or any other suitable units desired.

After stage I, the gas sample is passed through a drying tube 40 in which the water produced by the oxidation of the hydrogen in oxidation tube 22 is removed. Any suitable drying agent may be employed in the drying tube 40 which is effective to reduce the water content to less than 20 p.p.m., while not affecting the carbon monoxide or hydrocarbon content. Anhydrous calcium sulfate has been successfully used for this purpose.

After drying, the gas stream is passed through another catalytic oxidation tube 50 which is maintained, by temperature regulating means 51 located in the lead 52 from the power supply 25, at a temperature sufficient to burn all of the carbon monoxide and at least 95% of the hydrocarbons.

A wide range of catalysts could be used in oxidation tube 50 including any of the platinum group metals (Pt, Pd, Ru, Rh, Os, Ir) or oxides of metals of period IV of the Periodic Table or mixtures of the above oxides. Of these catalysts, platinum or palladium are preferred because they will oxidize carbon monoxide and hydrocarbons at a low temperature, approximately 200° C., whereas temperatures in excess of 500° C. are required for most of the other catalysts mentioned. Platinum and palladium on a base of asbestos to give a large effective surface area are readily available commercially. It is also well known that platinum catalysts possess good resistance to "poisoning" and subsequent loss of catalytic activity upon exposure to certain impurities. It is preferred therefore to use platinized asbestos maintained at a temperature of about 300° C., which as shown in FIG. 3, lies well above that required for 100% oxidation of ethylene. It should be pointed out that it is not necessary to have the temperature high enough to burn methane completely for methane is only a minor constituent of the mixture of hydrocarbons present in the exhaust gases.

A differential thermal conductivity cell 54 is provided in stage II, which is substantially identical to the cell 26 in stage I, and is operative to determine the change in thermal conductivity produced by the oxidation of the carbon monoxide and hydrocarbons in oxidation tube 50. Cell 54 accomplishes this determination by first measuring the thermal conductivity of the gas stream before oxidation which enters input 56 of the cell and then by measuring the thermal conductivity in the gas stream after oxidation, which enters the input 58 of the cell 54. Due to the fact that the change of carbon monoxide to carbon dioxide affects the thermal conductivity of the gas stream much more than the change of the hydrocarbons to carbon dioxide and water, the output of the differential thermal conductivity cell 54 at lead 60 is approximately proportional to the difference in carbon dioxide content of the gas entering inputs 56 and 58 of the cell and is therefore also proportional to the carbon dioxide produced in the oxidation tube 50 from the oxidation of carbon monoxide plus a small signal from the oxidation of the hydrocarbons.

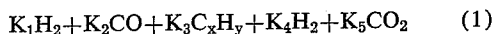
The hydrocarbon content of the sample is determined by measuring the H_2O produced by the oxidation in tube 50. The H_2O can be determined by any one of a plurality of analysis procedures including dew point by means of thermoelectric cooler, hygroscopic chemicals and materials, phosphorus pentoxide electrolytic cells, thermal conductivity, etc.

In the preferred embodiment shown in FIG. 1, thermal conductivity measurements are made to determine the H_2O produced by the oxidation of the hydrocarbons. The hydrocarbon content of the gas stream is determined by passing the exhaust gas sample from the thermal conductivity cell 54 through conduit 62 to the flow splitter junction 64 and thence through a drying tube 66 on the one hand, and through an unimpeded tube section 68 on the other. The drying tube 66 is similar to drying tube 50 and is effective to remove all of the water resulting from the combustion of the hydrocarbons in the tube 50. The thermal conductivity cell 70 which is identical to the cells 26 and 54, hereinbefore described, is therefore effective to determine the water concentration produced in the oxidation tube 50 by measuring the thermal conductivity of the dry gas and comparing it with the thermal conductivity of the undried gas, and generating a signal which is proportional to this difference. This is proportional to the water content and consequently the hydrocarbon content of the exhaust gas sample under inspection. Suitable indicating means 71, such as indicator 37 hereinbefore described, may be connected to the output lead 72 to indicate the hydrocarbon concentration.

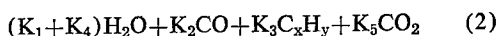
The signal on lead 72 is also connected to a subtraction circuit 74 through a variable attenuator 75 which may be, for example, a rheostat or potentiometer or any other circuit component effective to connect a controlled or predetermined portion of the signal on lead 74 to the subtraction circuit. The output from thermal conductivity cell 54 is also connected to this subtraction circuit via lead 60. This subtraction circuit is effective (as will be explained hereinafter) to generate an output signal on lead 77 proportional to the carbon dioxide produced in the tube 50 by the oxidation of carbon monoxide. From the foregoing explanation, it can be seen that the signal on lead 77 is directly proportional to the carbon monoxide concentration of the exhaust gas sample. Again a suitable meter 78 may be provided to indicate the carbon monoxide concentration.

The flow through the various elements of Stage I and II is regulated by the pump 80 and the shunt flow circuit 81 and impedance 82 as well as the flow balance controller 83 located in line 84. The flow balance controller 83 is effective to balance the flow through thermal conductivity cell 70 from the flow splitter junction 64. The shunt flow circuit 81 and impedance 82 are not required for the successful operation of the present invention but are beneficial in increasing the flow rate through the cooler 12 and filter 16.

By way of explanation of the function of the subtraction circuit 74, the operation of the apparatus of the present invention will now be described in terms of the chemical steps involved in the analysis procedure hereinbefore discussed. At the input to Stage I of the analysis apparatus, shown in FIG. 1, the content of the five gaseous components of interest in this invention may be expressed by the following:



wherein $K_{1,2,3,4}$ and 5 represent the respective concentrations of the elements of the exhaust gas sample and the terms x and y represent the general formula for the hydrocarbon content. After Stage I, i.e., the oxidation of hydrogen to water, the gas sample contains the following elements:

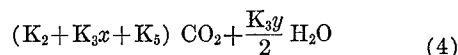


The water is then removed in the drying tube 40 and

therefore the gas entering Stage II at the input 56 of thermal conductivity cell 50 is:



The gas sample now is completely oxidized in tube 50 so the make-up of the gas passing through input 58 of thermal conductivity cell 54 is:



The exhaust gases from imperfect combustion of hydrocarbon fuels contain a large number of different hydrocarbon gases. The three dominant groups are olefins (C_nH_{2n}), diolefins (C_nH_{2n-2}) and paraffins (C_nH_{2n+2}), with olefins usually being the largest of these three groups. Thus C_xH_{2x} is an excellent approximation for the average of this complex mixture. Therefore, in the general formula C_xH_y used in expressions 3 and 4, above, y may be replaced by $2x$. Since the output on lead 60 is the difference between the thermal conductivity of the gas before and after oxidation tube 50, it is proportional to the quantity:

$$K_2(CO_2' - CO') + K_3(xCO_2' + xH_2O' - C_xH_{2x}') \quad (5)$$

where the quantities CO_2' , CO' , H_2O' and C_xH_{2x}' represent the thermal conductivities of these gases. Values of 2, 3, 4 for x cover the major portion of the hydrocarbons in exhaust gases. Expression 4 above is, therefore, closely proportional to: $K_2 + K_3K_6$, where K_6 is substantially constant and is the thermal conductivity ratio:

$$\frac{1/x(xCO_2' + xH_2O' - C_xH_{2x}')}{CO_2' - CO'}$$

Although the conductivity ratio K_6 varies slightly depending on the particular hydrocarbons, it has been found that an average value is applicable to typical exhaust gases. Once the value of K_6 is determined, the attenuator 75 is set to attenuate the signal on lead 72 by the fraction K_6 so that the signal fed to the subtraction circuit is proportional to K_3K_6 . This is evident since the signal on lead 72 is indicative of the hydrocarbon concentration or K_3 .

Thus, it can be seen that by subtracting the quantity K_3K_6 from the signal on lead 60, i.e., $K_2 - K_3K_6$, the result is a signal proportional to K_2 , the carbon monoxide concentration.

In practice, the calculation of K_6 is not actually performed, but instead a quantity of pure hydrocarbons, preferably representing the average properties of the expected sample hydrocarbons, is passed through the apparatus and the attenuator is adjusted so that the output from the subtraction circuit is zero. Ethylene, propane or butene is adequate for calibrating the instrument for use in analyzing automobile exhausts.

The signal on lead 72 as previously indicated is proportional to xK_3 and, therefore, the indicator 71 may be appropriately calibrated to indicate hydrocarbon concentration. For the purpose of most state regulations, the hydrocarbon concentration limit is expressed in terms of n-hexane which contains 6 carbon atoms per molecule and, therefore, the signal on lead 72 would be equal to $6K_3$. In order for the indicator to read accurately, it would, therefore have to be scaled by a factor of 6.

The differential thermal conductivity cells 26 and 54 and the oxidation tubes 22 and 50 in FIG. 1 are arranged in series mode, i.e., all of the gas sample in conduit 19 after the junction of by-pass circuit 81, flows through each of these elements. The differential thermal conductivity cell 70, drying tube 66 and conduit 68, on the other hand, are arranged in "parallel" mode, i.e., half of the sample is passed through drying tube 66 and one side of the cell 70 and the other half is passed through conduit 68 and the other side of the cell 70.

In FIG. 3, there is shown another embodiment of the present invention wherein the differential thermal conduc-

tivity cells 26 and 54 and their associated oxidation tubes are arranged in parallel mode. The electrical circuitry has been eliminated from FIG. 3 for the purpose of clarity.

As can be seen in FIG. 3, the gas sample introduced at conduit 10 passes through the cooler 12 and the particulate filter 16 in the same manner as in FIG. 1. The air is supplied also in the same manner through conduit 18. A flow regulator (not shown) may be placed in line 18 in the apparatus shown in FIGS. 1 and 3 in order to control the rate of air flow into the sample.

The sample then passes through conduit 19 to a flow splitter 110 whereat the sample is caused to flow through conduit 112, one side of cell 26 and flow balance regulator 114 on the one hand and through oxidation tube 22 and the other side of cell 26 on the other hand. In this manner, the left side of cell 26 measures the thermal conductivity of the sample containing free hydrogen and the right side of the cell 26 measures the thermal conductivity of the sample after the free hydrogen is removed by the oxidation tube 22. The output from cell 26 is therefore proportional to the hydrogen concentration of the sample in the manner discussed with regard to FIG. 1.

The conduit 116 delivers the portion of the sample still containing free hydrogen to the pump 80. The hydrogen free sample leaving the right side of the cell 26 is dried in tube 40 and fed to a second flow splitter 120. Flow splitter 120 again divides the flow into two conduits 122 and 124. The portion of the sample in conduit 122 contains hydrocarbons and carbon monoxide and flows through the left side of cell 54, which is thereby effective to measure the thermal conductivity of the sample containing the pollutants. The sample in conduit 124 is passed through oxidizing tube 50 wherein the carbon monoxide and hydrocarbons are completely oxidized and then through the right side of cell 54. The output of cell 54 is therefore proportional to the difference in thermal conductivity caused by the oxidation of the hydrocarbons and carbon monoxide.

The sample leaving the left side of cell 54 flows through flow balance regulator 128 and conduit 130 to the pump 80 and thence out of the system. The portion of the sample leaving the right side of cell 54, contains the water which was produced by the oxidation of the hydrocarbons in tube 50 and is passed to the cell 70 in the same manner as in FIG. 1.

The signals from cells 54 and 70 are then combined in the manner disclosed in FIG. 1 to derive an indication of the hydrocarbon and carbon monoxide concentrations in the sample.

In actual practice of the invention in the series mode as shown in FIG. 1 and using platinized asbestos catalysts in the oxidation tubes, the following flow rates were found to be satisfactory:

	Ml./min.
Sample in input conduit 10	1,000
Air in conduit 18	500
Sample plus admixed air through combustion tubes 22 and 50	200
Sample plus admixed air through each side of thermal conductivity cell 70	100

These flow rates, of course, are only an example and many other and different flow rates may be used. In the parallel flow mode for example, the flow rate would, of course, have to be increased to maintain sufficient sample in each thermal conductivity cell.

From the foregoing, it can be seen that the present invention provides very simple, yet accurate apparatus which is capable of rapid determination of the carbon dioxide and hydrocarbon concentration in exhaust and flue gases.

It is to be understood, however, that the particular apparatus disclosed herein is only the preferred embodiment of the instant invention, and it is not to be limited thereto

since the invention is susceptible to various changes and modifications within the scope thereof and which would be readily apparent to those of ordinary skill in the art.

What is claimed is:

1. Apparatus for determining the carbon monoxide and hydrocarbon concentration of gaseous products of the imperfect combustion of hydrocarbon fuels, comprising: means for passing a sample of said gaseous products through a first stage including, first oxidizing means for selectively oxidizing all of the free hydrogen in said sample to water and means for drying said gas sample after the free hydrogen has been oxidized, means for passing the hydrogen free and dried sample through a second stage including a second oxidizing means for substantially completely oxidizing the carbon monoxide and hydrocarbons present in said sample, first sensor means for measuring the change in thermal conductivity of said sample caused by the oxidation of said hydrocarbons and carbon monoxide, and for generating a first signal indicative of said change in thermal conductivity, said sensor means for measuring the water concentration in said sample produced by the combustion of said hydrocarbons and for generating a second signal indicative of the hydrocarbon concentration of said sample; and means responsive to the difference between said first signal and a preset fraction of said second signal determined by calibration with known gases for generating a third signal indicative of the carbon monoxide concentration of said sample.
2. The apparatus of claim 1 wherein said first oxidation means comprises a catalytic oxidation tube for selectively oxidizing, in the presence of more than a stoichiometrically equivalent amount of oxygen, the free hydrogen present in said sample.
3. The apparatus of claim 2 further comprising means for maintaining the temperature of said catalyst at a level sufficient to oxidize said free hydrogen but not the carbon monoxide and hydrocarbons.
4. The apparatus of claim 3 wherein the catalyst employed in said catalytic oxidation tube is selected from the group consisting of platinum, palladium and copper oxide.
5. The apparatus of claim 4 wherein the catalyst is platinum disposed on a base of asbestos.
6. The apparatus of claim 5 further comprising means for maintaining the temperature of said catalyst at a temperature within the range of 50 to 150° C.
7. The apparatus of claim 1 wherein said second oxidation means comprises a catalytic oxidation tube, the catalyst employed being selected from the group consisting of Pt, Pd, Rh, Os, Ir, Ru and the oxides of the metals of period IV of the Periodic Table.
8. The apparatus of claim 7 wherein the catalyst is Pt disposed on a base of asbestos.
9. The apparatus of claim 8 further comprising means for maintaining the temperature of said platinum above 200° C.
10. The apparatus of claim 1 wherein a first differential thermal conductivity cell comprises said first sensor, said first differential thermal conductivity cell comprising a first input where at the thermal conductivity of said hydrogen free sample is determined prior to passing through said first oxidation means, and a second input where at the thermal conductivity of said sample is determined after passing through said first oxidation means and means for comparing the thermal conductivities as measured at said first and second inputs and for generating said first signal.
11. The apparatus of claim 1 wherein second sensor means comprises flow splitter means for separating the output from said second oxidation means into a first and second stream, means for removing the water from said first stream, and a second differential thermal conductivity cell for measuring the difference in thermal conductivity

ity of said second stream and said first stream and for generating said second signal indicative of the hydrocarbon concentration of said sample.

12. The apparatus of claim 1 further comprising a third differential thermal conductivity cell for determining the difference in thermal conductivity of said sample before and after the free hydrogen has been removed in said first oxidation means as a measure of the hydrogen concentration of said sample.

13. The apparatus of claim 1 wherein said last mentioned means comprises a subtraction circuit having first and second inputs and an output, means for connecting said first signal to said first input and attenuator means for connecting said preset fraction to said second terminal, the signal appearing at said output of said subtraction thereby constituting said third signal.

14. The apparatus of claim 1 further comprising means for injecting a quantity of oxygen into said gas sample prior to said first stage, which is at least stoichiometrically equivalent to the hydrogen, carbon monoxide and hydrocarbon content of said sample.

15. The apparatus of claim 1 further comprising cooling means for cooling said sample to ambient temperature, means for removing water condensed in said cooling means and filter means for removing any particulate matter present in sample prior to said first stage.

16. The apparatus of claim 1 wherein said first sensor means comprises flow splitter means for separating the hydrogen free and dried sample into a first and second stream, means for passing said first stream through said second oxidizing means, and a differential thermal conductivity cell for generating said first signal proportional to the difference in thermal conductivity of said second stream and said first stream after passage through said second oxidizing means.

17. The apparatus of claim 1 further comprises first and second indicator means respectively responsive to said second and third signals for respectively indicating the hydrocarbon and carbon monoxide concentration of said sample.

18. The method for determining the carbon monoxide and hydrocarbon concentration of a gas sample produced by the combustion of hydrocarbon fuels, comprising the steps of:

- (a) selectively oxidizing the free hydrogen present in said sample to water;
- (b) drying the sample after the free hydrogen has been oxidized;
- (c) substantially completely oxidizing the carbon monoxide and hydrocarbons present in said hydrogen free and dried sample to water and carbon dioxide;

(d) generating a first signal proportional to the change in thermal conductivity of said sample caused by the oxidation of said carbon monoxide and hydrocarbons;

(e) generating a second signal proportional to the water concentration produced by the oxidation of said hydrocarbons as a measure of the hydrocarbon concentration in said sample; and

(f) generating a third signal proportional to the difference between said first and a preset fraction determined by calibration with known gases of said second signal as an indication of the carbon monoxide in said sample.

19. The method of claim 18 wherein the step of oxidizing the hydrogen comprises selectively oxidizing the free hydrogen in the presence of a catalyst and more than a stoichiometrically equivalent amount of oxygen.

20. The method of claim 19 wherein said catalyst is maintained at a temperature sufficient to combust the hydrogen but not the carbon monoxide and hydrocarbons.

21. The method of claim 20 wherein said catalyst is platinized asbestos.

22. The method of claim 21 wherein said temperature is between 50 and 150° C.

23. The method of claim 18 further including the step of measuring the amount of hydrogen oxidized.

24. The method of claim 18 comprising the further step of adding to said gas sample prior to the oxidation of said free hydrogen a quantity of oxygen at least stoichiometrically equivalent to the hydrogen, hydrocarbon and carbon monoxide concentrations of said gas sample.

25. The method of claim 24 wherein said quantity of oxygen is in the form of air, the quantity of air being between 40-50% by volume of the quantity of said sample.

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