

Aug. 22, 1939.

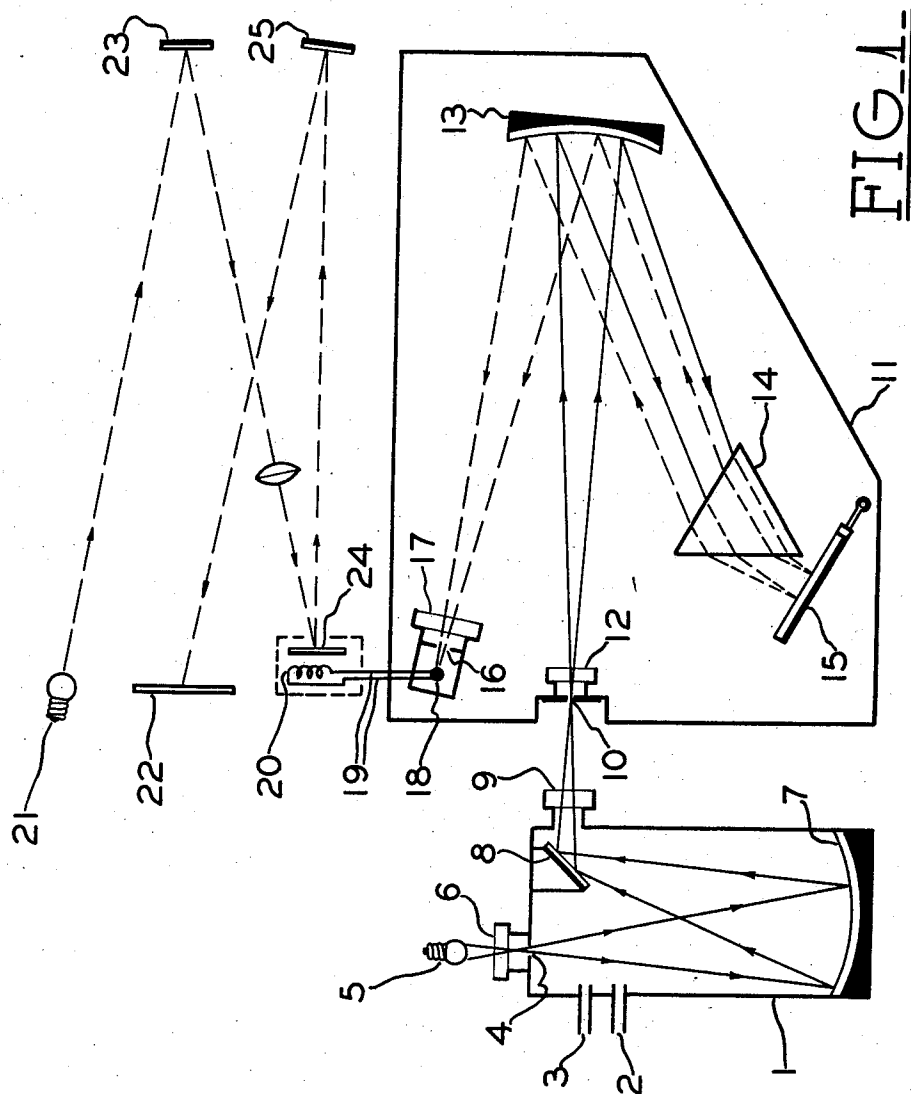
W. J. SWEENEY

2,170,435

GAS ANALYSIS APPARATUS

Filed Dec. 14, 1937

2 Sheets-Sheet 1



William J. Sweeney INVENTOR.
BY J. H. Small ATTORNEY.

Aug. 22, 1939.

W. J. SWEENEY
GAS ANALYSIS APPARATUS

2,170,435

Filed Dec. 14, 1937

2 Sheets-Sheet 2

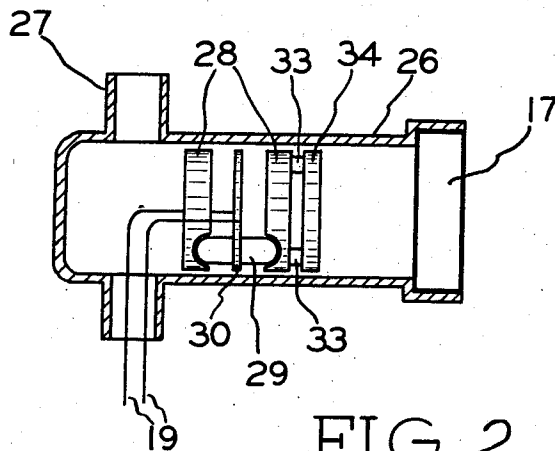


FIG. 2.

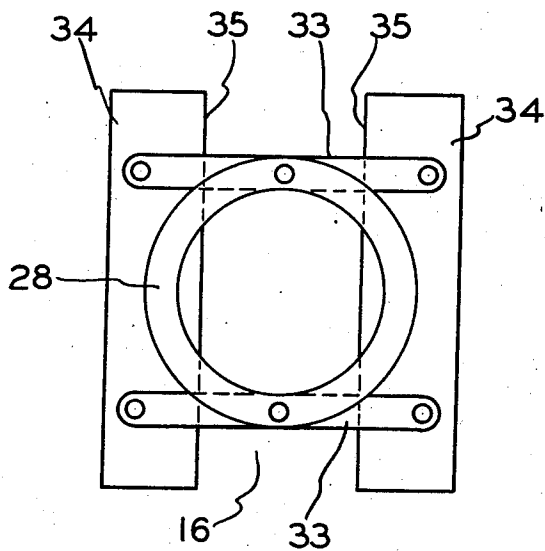


FIG. 3.

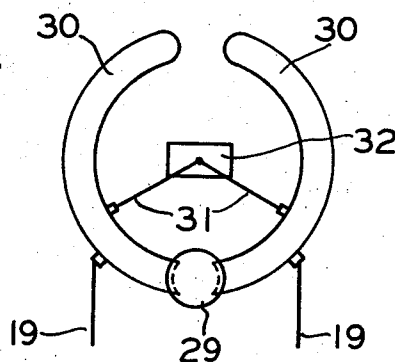


FIG. 4.

William J. Sweeney INVENTOR.
BY *J. M. Small* ATTORNEY.

UNITED STATES PATENT OFFICE

2,170,435

GAS ANALYSIS APPARATUS

William J. Sweeney, Westfield, N. J., assignor to
Standard Oil Development Company, a corporation
of Delaware

Application December 14, 1937, Serial No. 179,677

6 Claims. (Cl. 73—51)

The present invention is directed to a method for detecting and measuring minute concentrations of normally gaseous hydrocarbons in gas mixtures. It is especially useful in detecting these hydrocarbons in soil gases in which their presence is indicative of valuable subterranean deposits.

It has long been recognized that these hydrocarbons have the power of absorbing energy from infrared rays of various wave lengths. This property was ascertained by placing a sample of substantially pure hydrocarbon in the absorption cell of a spectroscope, such as a Littrow spectroscope, passing bands of the infrared spectrum through the hydrocarbon in a path of a predetermined length, resolving the spectrum after its passage through the hydrocarbon into its various wave lengths and focusing selected wave lengths on a thermocouple connected to a galvanometer. To ascertain the absorptive power of the hydrocarbon undergoing examination for any given wave length, the current set up in the thermocouple by the wave length, after passage through the hydrocarbon, is compared with the current set up after passage of the wave length through a blank gas; that is, a gas known to have no absorptive power.

It is the object of the present invention to provide a method for detecting the presence of and measuring these hydrocarbons in gas mixtures in which they are present in amounts as small as one part in a million. Generally, the gas mixtures examined for the purpose of the present invention will contain ethane and higher hydrocarbons in an amount of at least ten parts in a million and this concentration has significance in establishing the presence of petroleum deposits beneath the surface at which the gas sample is connected.

One of the difficulties which is encountered in utilizing the energy absorptive properties of these hydrocarbons lies in the fact that there is an overlapping of the bands in which the respective hydrocarbons have the most pronounced absorptive power; for example, ethane absorbs in the band between 6μ and 7.6μ , while methane absorbs in the band between 6.5μ and 8.5μ . On the other hand, the effect of ethane is most pronounced at 6.8μ while the greatest effect of methane is at 7.7μ .

It might appear that the obvious thing to do is to examine the effect of the gas containing the hydrocarbon only at that band at which the hydrocarbon being sought has the strongest absorptive effect. The difficulty is that in that portion of the spectrum above 6μ , the amount

of energy transmitted by the infrared rays is relatively small, whereby, in order to transmit sufficient energy to get an appreciable deflection of the galvanometer employed to measure the transmitted energy it is necessary to transmit a fairly wide band. This deficiency of the higher wave lengths in energy is not due to the wave length but to the source of infrared rays. The sources of infrared rays at present known give off most of their energy in wave lengths ranging between 1μ and 3μ .

It has now been found that the difficulty in determining the presence of extremely small quantities of ethane and higher hydrocarbons in gas mixtures by observing the energy absorptive power of these mixtures in that portion of the spectrum in which these hydrocarbons have exhibited strong absorptive power, but in which the present sources of infrared rays give off only relatively small amounts of energy, can be relieved in a large measure by converting the hydrocarbons in the gas mixture into carbon dioxide and water by combustion and measuring the absorptive power of the combustion products in that portion of the spectrum in which the present sources of infrared rays transmit the greatest amount of energy, and in which carbon dioxide and water exhibit strong absorptive power. This procedure makes it possible to work with larger energy values not only because it places the working range in that portion of the spectrum in which the maximum amount of energy is transmitted but because it increases the volume of absorptive ingredients since for every volume of ethane two volumes of carbon dioxide and three volumes of water are formed, for every volume of propane three volumes of carbon dioxide and four volumes of water are formed, and for every volume of butane four volumes of carbon dioxide and five volumes of water are formed.

According to the present invention the sample of gas to be examined is first carefully decarbonated by being passed through lime water, a solution of barium chloride, or caustic or any other suitable reagent, and then carefully dehydrated by the action of phosphorus pentoxide, calcium chloride or other suitable reagent, and is then subjected to combustion, either with the oxygen which is contained in the sample itself or by the addition of oxygen or air carefully freed from water and carbon dioxide, and is then placed in the absorption cell of a spectroscope. The spectroscope is so operated that only wave lengths of 4μ to 4.7μ are focused on the thermocouple. The energy transmitted in this wave length by

any known source of infrared rays is a multiple of that transmitted in wave lengths of the order of 6.7μ in which ethane exhibits its strongest absorptive power.

For a more pronounced effect upon the galvanometer of the spectroscope it is preferred to first remove the water of combustion from the sample and operate the spectroscope so as to focus on the thermocouple only wave lengths between 2.5μ and 2.8μ . In this range of wave lengths the energy transmitted is at its maximum. For this reason it is possible to focus on the thermocouple single wave lengths, such as 2.6μ or 2.8μ , because there is sufficient energy transmitted by this single wave length to cause a considerable deflection of the galvanometer.

According to one embodiment of the present invention two observations are made on the same sample, including both carbon dioxide and water, the one observation being made in the band including wave lengths between 4 and 4.7μ , and the second observation being made in the band ranging from 2.5 to 2.8μ . The latter observation gives the combined effect of carbon dioxide and water while the first observation gives the effect of carbon dioxide alone. With these two observations it is possible to calculate the relative proportions of carbon dioxide and water in the sample and to thereby determine the carbon-hydrogen ratio of the hydrocarbons contained in the sample before combustion. These two observations may be made simultaneously by using two thermocouples, each operating on its own slit and on its own galvanometer.

Alternatively, both observations may be made at the band ranging from 2.5 to 2.8μ , the one observation being made on the sample containing both carbon dioxide and water and the other observation being made on the sample from which water has been removed. When this procedure is followed, two spectroscopes can be employed, each with a separate thermocouple and with provision made for connecting the two thermocouples to the same galvanometer in opposition to each other. In carrying out the method with this arrangement the absorption due to carbon dioxide can be observed on the galvanometer first and then the two thermocouples hooked up to the galvanometer which will then record the difference between the two samples or the absorption due to water.

According to one modification of the above described procedure it is possible to attain greater sensitivity by the use of a galvanometer so calibrated as to have a greater deflection for a unit of current set up by the thermocouple. In order that such a galvanometer may be utilized two absorption cells, two beam paths and two thermocouples are employed, the two thermocouples being connected in opposition to each other to the same galvanometer. A blank gas, or a gas of known composition, is placed in one cell. The gas to be tested is placed in the other. The galvanometer records merely the difference in energy absorption in the two cells. With this arrangement it is possible to utilize bands of narrower width since a galvanometer with a greatly magnified deflection can be employed.

In examining soil gas, according to the present invention, the primary interest is in identifying ethane and higher hydrocarbons, and it is not necessary for the realization of the utility of this embodiment of the present invention that the quantity of ethane and higher hydrocarbons be measured accurately. It is sufficient that their

presence in substantial quantities be detected. For this purpose a certain standard gas mixture may be selected, such as one containing five parts of ethane or higher hydrocarbons per million, and all samples compared with it. The standard selected, of course, is one which will have the minimum content of these hydrocarbons to be expected in a soil gas collected over a subterranean petroleum deposit.

When prospecting for oil by a method of the present invention, the samples of soil gas may be procured by any one of a number of methods. One of these methods is to suck the gas from a hole in the ground sealed from the atmosphere. Another method is to place an absorbent material, such as active carbon, in a borehole sealed from the atmosphere, leave it there for a sufficient time for it to become saturated with the hydrocarbons in the soil gas and then withdraw it and recover the adsorbed hydrocarbons by evacuation or by treatment with steam or inert gas.

For the purpose of the present invention it is preferable to secure the sample of soil gas by removal of adsorbed gases from the soil itself. This removal can be accomplished by any of the known methods referred to above. The samples of gas so obtained are much richer in hydrocarbons than samples obtained by mere suction from a borehole, since the latter are contaminated with large quantities of air. A novel procedure for obtaining an excellent sample is to place a sample of soil in a suitable container, evacuate the container to draw off water and adsorbed gases, pass the recovered gases through a train of adsorbing media for the removal therefrom of water vapor and carbon dioxide and compressing the purified sample, after combustion, into a previously evacuated absorption cell which is then directly examined in the spectroscope. It is advantageous in some cases to heat the soil sample during evacuation.

Another method for procuring a sample contemplated by the present invention is to place a sample of soil in a suitable container chilled to the temperature of liquid methane and subject it to evacuation. This operation will remove any adsorbed methane from the soil. When no more gas is recovered by evacuation at this temperature the temperature of the container can be raised to that of ethane and the evacuation repeated. If desired, this procedure can be repeated for the recovery of propane and butane. The procedure can be simplified to suit the purpose of locating oil by following the methane removal step with an evacuation at the temperature of boiling propane or butane as desired. In the latter case, ethane, propane and butane will be recovered. The sample recovered at this temperature must be subjected to dehydration before being examined in the spectroscope.

Some of the diluent effect of the methane can be avoided without resorting to refrigeration by collecting the soil sample at a depth adjacent to the uppermost watertable. This will usually be at least twenty feet below the surface of the ground and may be as deep as sixty feet. In this zone there is a tendency for the soil to adsorb higher hydrocarbons such as propane and butane to the exclusion of methane. With such a sample it may be possible to identify propane and/or butane by simply heating the sample and collecting and condensing the evolved vapors. Any condensable quantity of propane or higher hydrocarbon contained in such a sample is direct

evidence of the existence of an oil deposit at a lower level.

Other methods for obtaining a sample of soil gas include the evacuation or steaming of cores of soil obtained while drilling, boiling large bodies of stagnant water, boiling samples of subsurface water obtained in the area to be explored, and boiling or steaming samples of drilling mud used in the drilling of a well in the neighborhood under investigation. Still another method is to bore a hole in the ground, seal the top of the hole from the atmosphere, run a pipe through the seal to the bottom of the hole, feed in carbon dioxide, steam or other absorbable gas through this pipe and draw out gas from the hole through another pipe in the seal. The gases so recovered are passed through absorbing agents for carbon dioxide and water and the remaining permanent gases are utilized for examination according to the method of the present invention.

In carrying out a spectrum analysis according to the present invention, an apparatus well known for this purpose is employed. It consists essentially of a source of light such as a Nernst lamp, an absorption cell, a Littrow spectroscope, a thermocouple and a galvanometer operatively associated therewith. For the sake of clarity, a suitable apparatus is illustrated in the accompanying drawings in which,

Fig. 1 is a plan view showing the path of the beam of light;

Fig. 2 is a side elevation of the tube containing the thermocouple;

Fig. 3 is a detail view showing the adjustability of the slit; and

Fig. 4 is a detail view of the thermocouple.

Referring to Fig. 1 specifically, numeral 1 is an absorption cell having an inlet 2 and an outlet 3 for the sample of gas to be tested. Inlet 2 is in practice connected to a combustion chamber, now shown, in which the sample containing hydrocarbons is subjected to combustion. At one end of 1 is a slit 4, through which pass infrared rays from a source 5 which will usually be a Nernst lamp. This slit is covered with a halite window 6. In the opposite end of cell 1 is a gold sputtered spherical mirror 7. This mirror receives the rays from lamp 5 and reflects them back to a mirror 8, which deflects the rays through a halite window 9 in the side of the cell 1.

The rays then pass through an adjustable slit 10 in the wall 11 of the spectrograph. Slit 10 is covered by a halite window 12. From the slit 10 the rays are directed onto a second gold sputtered mirror 13 parabolized off its axis, which in turn reflects them to a triangular resolving prism 14 through which they are refracted to a pivoted mirror 15, which in turn reflects them back to the prism which refracts them back to mirror 13 which reflects them through an adjustable slit 16, covered by halite window 17, to thermocouple 18. This thermocouple is connected by leads 19 to a galvanometer 20.

The galvanometer illustrated is the reflected beam type in which a source of light 21 is mounted over a scale 22 and casts a beam of light to a mirror 23, which reflects it to a mirror 24 in the galvanometer which in turn reflects it to a third mirror 25 from which it is reflected to the scale 22. This arrangement imparts a high sensitivity to the galvanometer which is ordinarily calibrated in terms of the content of carbon dioxide and water in the sample of gas undergoing examination in the absorption cell 1. The sensitivity of the device can be increased by increasing

the length of the cell 1, or by increasing the length of the path of the rays in cell 1 by a system of mirrors, thereby giving the carbon dioxide and water in the gas sample a longer time in which to absorb heat from the infrared rays.

In Fig. 2 the tube containing the thermocouple is shown in greater detail. It consists of an enclosed chamber 26 adapted to be evacuated by a pump connected thereto by pipe 27. The galvanometer leads 19, are shown issuing from one side wall of chamber 26. Mounted at the end of chamber 26 are two metal rings 28 separated by an insulating bead of glass 29. Carried by the bead 29 are a pair of thin copper plates 30 in the form of crescents or half circles. Each one of these disks carries one of the leads 19 to the galvanometer and a wire 31 of the thermocouple, these wires being joined on a thin sheet of nickel 32. The face of sheet 32 facing the slit is coated with bismuth or zinc-black.

The hot junction is composed of chromel X which is iron alloyed with 0.8% of chromium, 0.8% of manganese, 0.8% of molybdenum and 0.3% of carbon or copal P, which is an alloy of 55% of copper and 45% of nickel. The cold junction can be copper.

Pivoted at the top of the outer ring 28 is a bar 33. A similar bar is pivoted at the bottom of said ring. Each bar has a pivot point at each of its outer ends and is attached at each of these pivot points to one end of a thin metal plate 34 having a straight edge 35. By swinging the bars 33 the distance between the straight edges is varied. The space between these straight edges constitutes the slit 16.

In carrying out the process of the present invention the width of slit 16 is adjusted, as hereinbefore stated, to pass that part of the infrared spectrum between 4 and 4.7μ , when carbon dioxide is being detected in the presence of water, or between 2.5 and 2.8μ when carbon dioxide is being detected in the absence of water or when both carbon dioxide and water are being detected. In practice it is desirable to correspondingly regulate the width of slit 10.

The method of the present invention is advantageously employed in conjunction with any chemical method for determining the carbon content of the initial gas sample. For example, the initial gas sample is subjected to combustion and a portion of it is passed through any solution capable of absorbing carbon dioxide, whereby the carbon content of the sample can be determined. A second gas sample is then made up having the determined carbon content present as methane and this sample is subjected to combustion. The combustion products of the samples are then placed in separate absorption cells connected to separate spectrographs and thermocouples, both thermocouples being connected to the same galvanometer. The slits are adjusted so as to focus a band containing wave lengths between 2.5 and 2.8μ on the thermocouples. In this band energy is absorbed from the infrared rays by both water and carbon dioxide. Since more water will be produced by the combustion of ethane and higher hydrocarbons than is produced by the combustion of the same amount of carbon, as methane, any difference in energy absorption by the two samples, observed by opposing the thermocouples to each other, will indicate the presence of ethane and higher hydrocarbons in the sample under investigation.

The nature and objects of the present invention having been thus described and illustrated, 75

what is claimed as new and useful and is desired to be secured by Letters Patent is:

5 1. A process for detecting minute amounts of ethane and higher hydrocarbons in soil gases which comprises subjecting the hydrocarbons in the soil gas to combustion, passing infrared rays through the combustion products and observing the amount of energy absorbed from a band of rays from which carbon dioxide has the power to absorb energy.

10 2. A process for detecting a minute amount of ethane in a gas mixture containing it in association with methane which comprises dehydrating and decarbonating the mixture, subjecting the mixture to complete combustion, passing the infrared rays through the combustion product and observing the amount of energy absorbed from a band of the rays from which carbon dioxide has the power to absorb energy.

15 3. A process for detecting a minute amount of ethane in a gas mixture containing it in association with methane which comprises dehydrating and decarbonating the gas mixture, subjecting the mixture to complete combustion, passing infrared rays through the combustion product and observing the amount of energy absorbed from a band of rays including a wave length between 4 and 4.7 μ .

20 4. A process for detecting a minute amount of ethane in a gas mixture containing it in association with methane which comprises dehydrating and decarbonating the mixture, subjecting the mixture to complete combustion, dehydrating the combustion product, passing infrared rays through the remainder of the product, and observing the amount of energy absorbed from a band of rays including wave lengths between 2.5 and 2.8 μ .

35 5. A method for detecting the presence of

higher hydrocarbons in a gas mixture containing them in association with methane which comprises dehydrating and decarbonating the mixture, subjecting the mixture to complete combustion, passing infrared rays through a given volume of the combustion product, observing the amount of energy absorbed from a band of rays composed of wave lengths between 4 and 4.7 μ , passing infrared rays through a second equal volume of the product, observing the amount of energy absorbed from a band of rays composed of wave lengths between 2.5 and 2.8 μ , and determining the carbon-hydrogen ratio of the hydrocarbons contained in the original sample by comparison of the quantities of energy absorbed from the separate bands of rays.

6. A method for detecting the presence of higher hydrocarbons in gas mixtures containing them in association with methane which comprises dehydrating and decarbonating the mixture, determining the carbon content of the mixture, preparing a blank gas having the determined carbon content present as methane, subjecting the dehydrated and decarbonated gas mixture to combustion, passing infrared rays through the combustion product, focusing a band of said rays, after passage through said combustion product, composed of wave lengths between 2.5 and 2.8 μ on a thermocouple whereby an electromotive force is set up in the latter, subjecting the blank sample to combustion, passing infrared rays through the combustion product, focusing a band of said rays, after passage through said combustion product, composed of wave lengths between 2.5 and 2.8 μ on a thermocouple, whereby an electromotive force is set up in the latter, and comparing the generated electromotive forces.

WILLIAM J. SWEENEY.