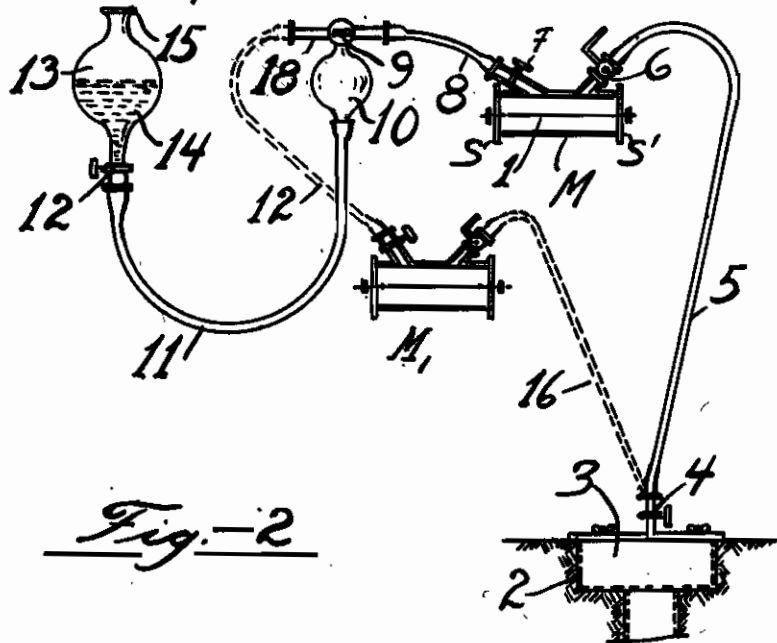
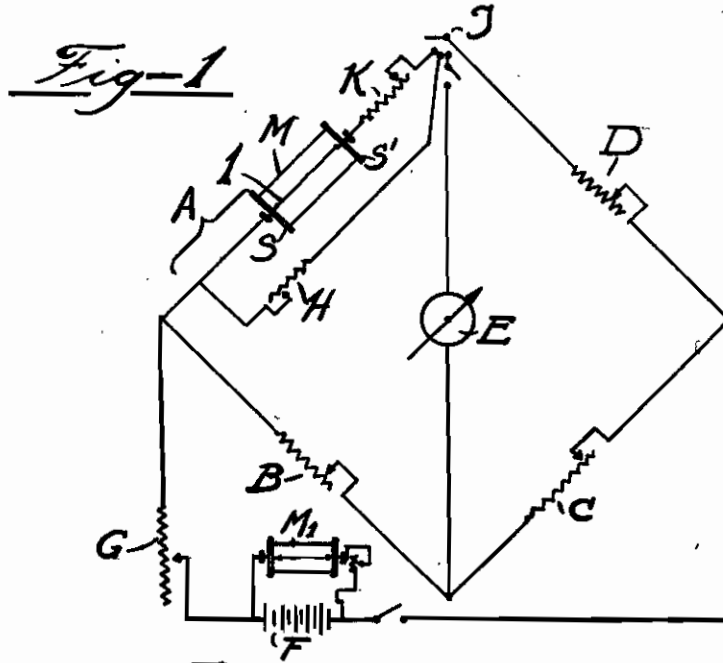


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## METHODS AND APPARATUS FOR DETERMINING COMBUSTIBLE GASES IN GAS MIXTURES

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This invention relates to a process and apparatus for the quantitative determination of combustible gas in gas mixtures, more particularly in soil gas for exploration of deposits containing hydrocarbons according to German Patent Specification No. 567,698.

As stated in German Patent Specification No. 573,579, the process consists in burning any hydrocarbons or combustible gases present by means of an electrically heated catalytic wire in combination with a galvanometer in the electric circuit of the heated wire, to measure the variations in the resistance of the wire caused by the combustion. Whilst it has already been suggested to employ a ballistic galvanometer in such methods, according to the present process an ordinary highly sensitive galvanometer is employed.

In the method described in German Patent Specification No. 573,759 the soil gas is introduced in a quiescent condition into the reaction chamber containing the catalytic wire. In this procedure, certain disadvantages are encountered, therefore, according to the present invention the soil gas is caused to flow past the catalytic wire whereby any hydrocarbons or other combustible substances present are burned. Of course, the same electrical measuring devices can also be used with gas mixtures in a quiescent condition.

In German Patent Specification No. 573,759 it has been shown possible to use a bridge system. This invention utilizes this known idea in that the catalytic wire forms one arm of a Wheatstone Bridge system.

In contradistinction to the known methods, according to the present invention the soil gas is measured by catalytic combustion by means of the catalytic wire twice, firstly in that it is caused to flow past the catalytic wire in the unaltered state, and secondly, it is caused to flow past the catalytic wire after the hydrocarbons or other combustible gases are removed from the mixture, the resistance of the wire being measured in each case, and the difference in the resistance of the catalytic wire during both measurements, serves as a measure of the amount of hydrocarbons or other combustible substances present in the soil gas.

By this means, in addition to a particularly simple and convenient construction of the device, an absolute comparison of the presence of hydrocarbons or the like is possible.

This feature is particularly important as comparison measurements are always necessary in catalytic methods for the determination of hydrocarbons.

In the case of measurements of soil gas, atmospheric air cannot be used for comparison as the soil gas usually has a different composition to atmospheric air and would, therefore, give different value to the resistance of the catalytic wire, which would give rise to wrong measurements. Also, variations caused by different moisture and carbon monoxide contents of the soil gas at different points are not taken into account.

The process, which completely obviates all these errors, is preferably carried out by aspirating the soil gas before measurement in the unaltered state through the reaction chamber, without switching in the catalytic wire into a receiver, from which after switching in the catalytic wire it is fed through the reaction chamber, whilst in the second case the soil gas is passed over the fully heated catalytic wire in the first passage whereby any hydrocarbons present are burned, so that during the second passage of this air from the container through the reaction chamber, the gas freed from hydrocarbons is measured.

When switched in, the catalytic wire is preferably heated so that its temperature is about 1000°C. so that all hydrocarbons or other combustible substances present in the soil gas are actually burned. It is also preferable that the aspiration and respiration of the soil gas into and out of the receiver is effected by raising and lowering a separate vessel filled with mercury.

The invention also relates to a suitable construction of a device for carrying out the process.

In the drawing one constructional form of a device according to the invention is illustrated in diagrammatic form,

Fig. 1 shows the electrical system.

Fig. 2 shows the apparatus for receiving and measuring the soil gas.

In Figs. 1 and 2, the reaction chamber is indicated at M. It consists of a tubular casing with two sealed covers S and S' between which the catalytic wire *l* is held in a cartridge-like container (not shown in the diagrammatic illustration).

The catalytic wire may be composed of platinum or other suitable substance which can be stretched out lengthwise or arranged in any other suitable position, for example, as a coil in a correspondingly shaped and arranged cartridge.

The catalytic wire *l* forms one branch A of the Wheatstone Bridge system, whilst the other branches B, C, and D consist of variable resistances which are preferably divided up into small units in order to enable better regulation of the balance of the bridge, and to produce good

ventilation to enable a temperature balance to be obtained rapidly. E indicates the galvanometer of the bridge system, F is the heating battery, and G the heating resistance. In parallel with the catalytic wire I in branch A of the bridge, is arranged a substitute resistance H. A switch J enables either the catalytic wire or this substitute resistance H to be switched on the bridge circuit. In series with the catalytic wire is a heat regulator K which allows the catalytic wire to be switched in or out in a gradual manner in order to spare it and prolong its life as much as possible.

A second reaction chamber M' similar to the reaction chamber M can be arranged in parallel with the heating battery F.

According to Fig. 2, a collecting device 2 which can be constructed as described in German Patent Specification No. 567,689, is inserted in a bore-hole 2. From the bore-hole 2 through a cock 4 and a pipe 3, soil gas is supplied to the reaction chamber through the three-way cock 6. From the reaction chamber the soil gas passes through a cock 7, pipe 8 and three-way cock 9 into the receiver 10 which is connected by a flexible pipe 11 and a cock 12 to a vessel 13, partly filled with mercury 14, and capable of being closed at the top by a cover 15. When the second reaction chamber M' is used, this is connected by pipe 16 to cock 4 and through a second pipe 17 to an otherwise free connection 18 to the receiver 10.

With the device described the following measurements are made, and as previously mentioned preferably in a current of gas.

The bridge is first connected to the catalytic wire in the reaction chamber and the galvanometer adjusted to a zero position by altering the resistances in the branches B, C, and D of the bridge. The vessel 13 filled with mercury is then raised and after opening the cock 12 the air is forced out of the receiver 10. For this purpose the three way cock 9 is so adjusted that the air can escape outwardly through the connection 18. After closing the three-way cock 9 the mercury vessel 13 is lowered and after the remaining cocks are opened or adjusted correctly, soil gas is aspirated through the reaction chamber M into the receiver 10 under the action of the sinking mercury. It is preferable to arrange the mercury vessel 13 in such a form that the surface of the mercury is as large as possible. By this means a high initial or final velocity of the gas current is avoided.

It is also preferable, apart from the absolute uniformity of motion during the lift of the vessel 13, to arrange fully automatic valve devices at the cocks, junctions, and the like, to ensure absolute uniformity of the current of gas. In order to drive the soil gas out from the receiver 10, after setting the cock 6, the mercury vessel 13 is raised and the gas is forced through the reaction chamber M in the reverse direction and escapes into the open air.

The soil gas is measured by catalytic combustion by means of the catalytic wire twice. The difference between the measured values obtained by these two measurements forms a direct absolute measurement of the hydrocarbon content of the soil gas.

The one measurement consists in that the soil gas is aspirated through the reaction chamber and into the receiver 10 without the catalytic wire being heated. In this case the substitute resistance H is switched in. The soil gas thus remains unaltered, that is, any hydrocarbons contained

therein are not burned. During the forcing of the soil gas out through the reaction chamber 9, the catalytic wire is switched in so that any hydrocarbons present can be burned, and the alteration set up in the temperature and resistance causes the galvanometer to vary from the zero position. The measurement is carried out several times until a uniform value is obtained, and an average value can be calculated for normal soil gas.

In the second measurement the catalytic wire is switched in during the first passage of the soil gas through the reaction chamber. Any hydrocarbons which may be present in the soil gas are thus burned during the passage into the receiver, and the receiver therefore, receives and contains purified gas. When this is passed back through the reaction chamber into the open air, the catalytic wire is switched in, the throw of the galvanometer is again measured, but it will be different from the throw during the first measurement depending on the presence of hydrocarbons or other combustible substances in the soil gas. This difference as stated is a direct measure of a function of the hydrocarbon content.

In the second measurement the gas is burned during the aspiration through the reaction chamber into the receiver 10, and can thus be described as 'pre-burned', whilst in the first measurement it may be designated 'unburned' gas. If hydrocarbons or other combustible substances are present in the soil gas, the measurement for the unburned gas is more or less different from that of the preburned gas whilst they may well have the same value when no hydrocarbons or other combustible substances are present.

The velocity of the gas during the passage through the reaction chamber must have a definite value. It must not be too great or too small. Above all turbulence must be avoided in the reaction chamber. For this purpose the inlet and outlet openings of the cocks 6 and 7 to the chamber must have definite proportions.

The catalytic wire and its cartridge like casing are arranged to be rotatable, so that the gas can be arranged to flow over it in the best position for the measurement, and the galvanometer throw can be adjusted. For this purpose a cover S or S' is rotatably arranged with a scale and indicator and can be fixed in a definite position by calibrating the wire.

The catalytic wire can also be arranged in the reaction chamber as shown in the drawing, i. e. suspended. It can also be stretched by suitable devices, e. g. a spring, or by its own weight or by stretching in the incandescent state.

The method can also be carried out by collecting from the bore-hole at one time and in one large container, all the gas required to make the individual measurements, which have to be made at the bore-hole. This may be accomplished by air displacement or by first emptying the container of air. The container can then be taken to any desired place, e. g. the laboratory, where only the quantity of air required for each individual measurement can be taken out. In this manner the measurements can be made independently of the weather conditions prevailing at the bore-hole.

In practice it has been shown that the production and handling of usable catalytic wires, in particular when as proposed in German Patent Specification No. 573,759, a compensating treatment is carried out, is extremely difficult. Therefore it is a great advantage of the invention that only

one catalytic wire is used in the bridge, as a calibration of a number of wires is almost impossible, as their properties often alter during measurements.

With the use of this one wire the bridge can be calibrated to it without difficulty. Further, this wire which can be inserted in a cartridge can be replaced easily and quickly.

In order to avoid the residue of both kinds of gases passed through the reaction chamber remaining in dangerous spaces in the tube 8 and cock 9, so that it can only be removed by repeated rinsing, the following method is adopted.

A second chamber M' which can only be used as a combustion chamber, is employed. This is similar to the reaction chamber I, and also contains a catalytic wire, which can be switched in and out at will.

The soil gas is first fed from the tap 4, through the tube 16 into the combustion chamber M' and from here, after preburning or non-burning of the air current, is passed through the tube 17 into the receiver 10. Tube 5 is not used in this method. From the container 10 the air is passed through the actual reaction chamber M and there measured. This form of the process has the advantage that the catalytic wire I in the reaction

chamber M is actually used for measurement only, and the gas is passed over it in one direction only, so that no alterations occur in the wire. As the wire arranged in the second chamber M' which only serves as a combustion chamber, is only used for burning any hydrocarbons or other combustible material present in the soil gas, it is not necessary that it should have exactly the same properties as the wire I in the reaction chamber M.

It is thus possible to make the auxiliary resistance H as a catalytic acting wire and to effect the combustion of the hydrocarbons or the like so that in this case the actual catalytic wire I is preserved.

Should it be required, under certain circumstances, to measure a quiescent mixture, then the auxiliary resistance H can be reduced down to the equivalent of the wire resistance used.

The method of measurement is then as follows: once preburned and once unburned soil gas are fed through the chamber M' into the chamber M and there enclosed, and after closing the switch J which is specially provided therefor, and the galvanometer throw is determined in both cases.

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