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Hofmann

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[54] **FLAME IONIZATION DETECTION**

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **G01n 31/12**

[58] **Field of Search** ..... 23/254 EF, 232

[56] **References Cited**

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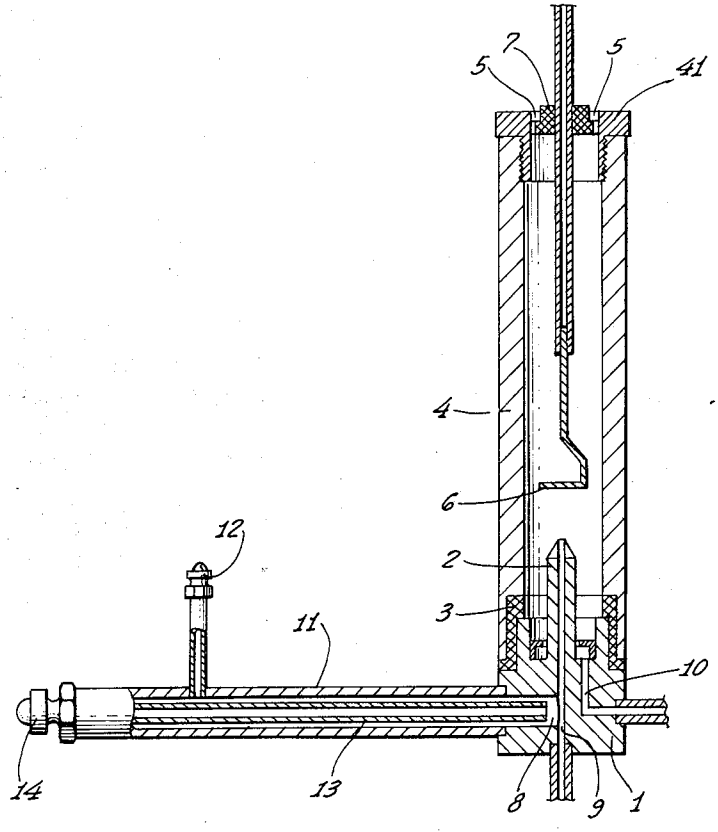
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[57] **ABSTRACT**

In a method for gas analysis, particularly for detecting hydrocarbons, using flame ionization detection for the sample gas to be analyzed and a burner for developing the flame upon receiving fuel gas; a gas, for example air, for compensating the detrimental effect oxygen in the sample gas may have on the measurement, is fed to the burner in addition to the gas to be analyzed and the fuel gas, and mixed with fuel and sample gases prior to reaching the flame developing burner nozzle tip, and independently from the air supply to the burner for sustaining combustion.

3 Claims, 3 Drawing Figures

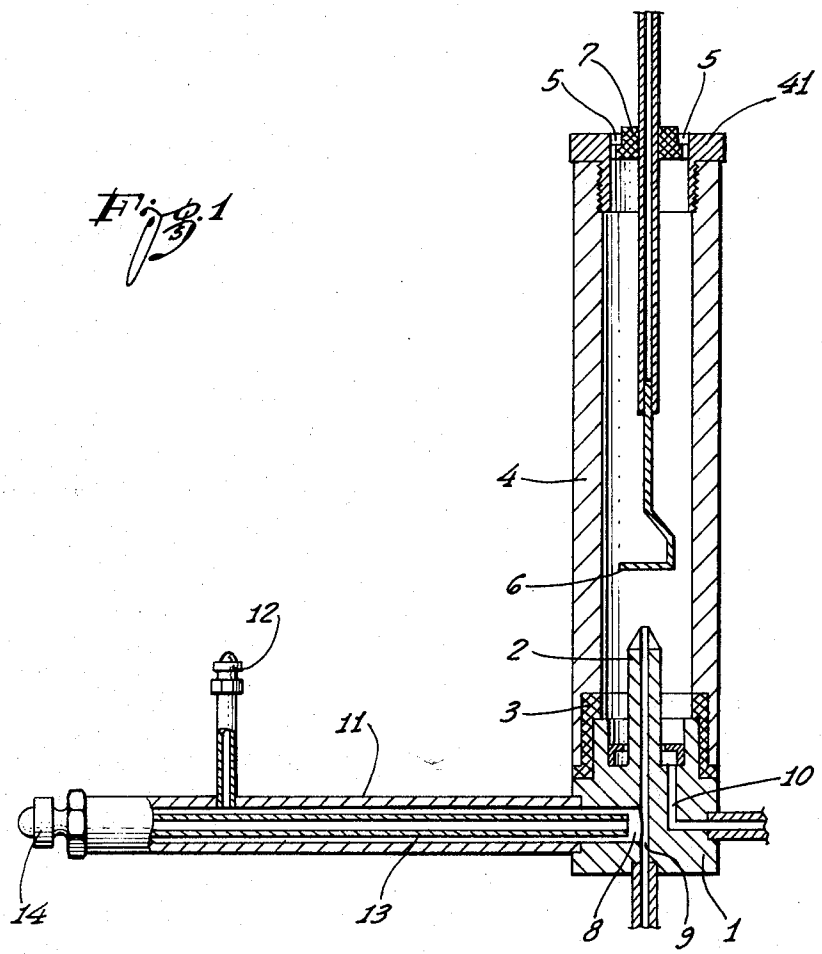


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SHEET 1 OF 2

Fig. 1



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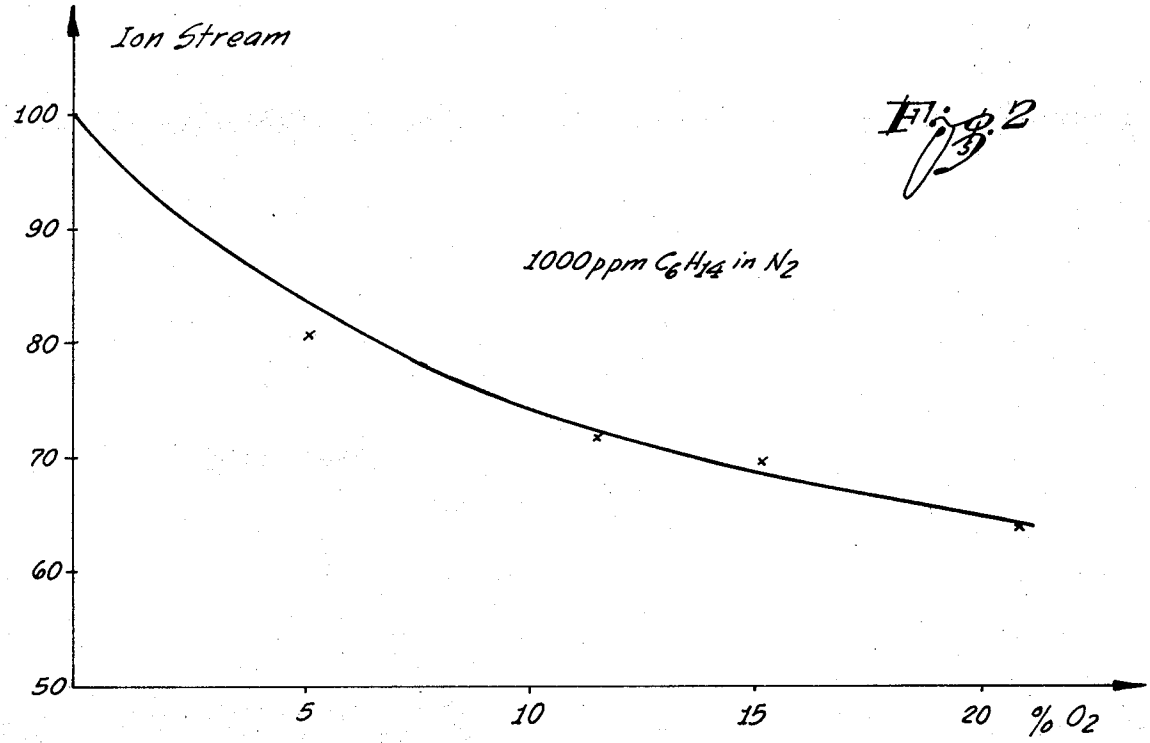


Fig. 2

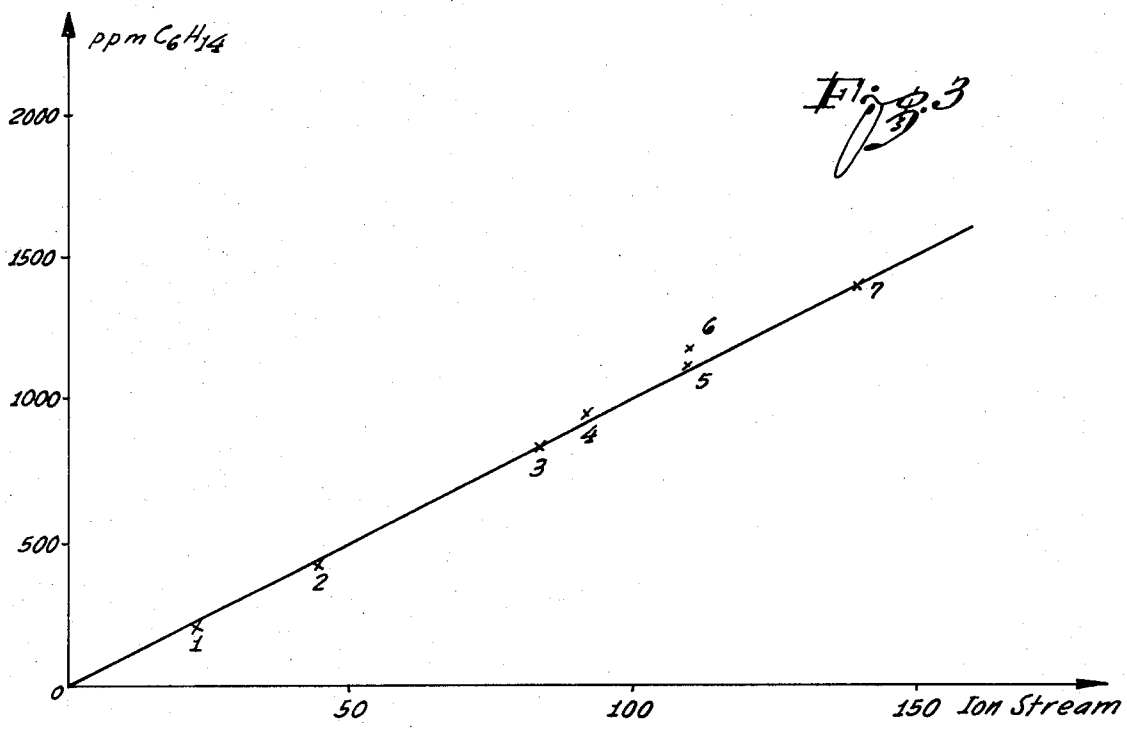


Fig. 3

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FLAME IONIZATION DETECTION

The present invention relates to a method for improving the detection of particular gas components by means of flame ionization detectors, whereby a stream of ions is produced that is to represent, for example, the hydrocarbon content in the sample gas to be analyzed. The ion stream is to be independent, or at least substantially independent, from the oxygen content in the sample gas. A flame ionization detector improved in accordance with the present invention is particularly adapted and provided for determining the content of hydrocarbons in the exhaust gas of an internal combustion engine.

Flame ionization detectors of known construction, as they are used for detecting and measuring the content of hydrocarbons, are to a considerable extent subject to errors, due to oxygen in the sample gas that contains the hydrocarbons. The measuring result reflects that uncertainty accordingly. For example, in a sample gas mixture of 1,000 ppm hexane in nitrogen, it was found that an oxygen content in excess of 10 percent reduces the ion stream developed in the detector by about 25 percent. Such reduction in sensitivity represents directly an indicating error. Determining the hydrocarbon content in the exhaust gas of an internal combustion engine by means of a flame ionization detector is, therefor, uncertain and incorrect to the extent that the oxygen content varies. As the oxygen content varies, it is impossible to provide error compensation in the measuring system without determination of that variation in the oxygen content.

It is an object of the present invention to operate a flame ionization detector in such a manner that the ion stream no longer varies (or only insignificantly) upon variations in the oxygen content in the sample gas to be anlayzed, e.g., as to its content in hydrocarbons. In accordance with the present invention, it is suggested for the burner in the flame ionization detector to receive a constant flow of oxygen which mixes well, i.e., intimately upon contact, with the combustion gas. In accordance with the preferred embodiment of the invention, the burner will receive a mixture of oxygen and of an inert gas such as nitrogen. Thus, the invention can be practiced by using regular air as additive to the burner. The added gas will in the following be called a compensating gas.

Adding the compensating gas to the sample gas does not require a particular path, except that the compensating gas must be added before the mixed fuel and sample gases reach the nozzle tip of the burner. Basically then, the compensation gas can be added either to the sample gas to be analyzed or to the fuel of combustion gas. It is, however, decisive that the compensating gas mixes well with the combustion or fuel gas, that the amount of compensating gas that is added is accurately predetermined, and that a constant flow rate be maintained. It could be assumed erroneously that the invention operates on basis of suppressing the effect of the oxygen content in the sample gas by adding so much oxygen as part of the compensating gas so as to "drown out" the effect of the small initial oxygen content in the sample gas. This, however, is not the case. First of all, increasing excessively the oxygen content will actually reduce the sensitivity of the flame ionization detector to a completely unsatisfactory level. Therefore, the oxygen content in the compensating gas

may be of comparable magnitude to the content of oxygen in the sample gas. The suprising result of the invention is that the oxygen content in the compensating gas amounts to only about 5 percent of the total amount of gas involved, including fuel gas for combustion, sample gas and compensating gas, while the oxygen content in the sample gas may even be as high as the oxygen content in air, and there still is complete compensation.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention, it is believed that the invention, the objects and features of the invention and further objects, features and advantages thereof will be better understood from the following description taken in connection with the accompanying drawings in which:

FIG. 1 is a cross-sectional view, somewhat schematic, of a flame ionization detector improved in accordance with the preferred embodiment of the present invention;

FIG. 2 is a graph in which ion stream is plotted against oxygen content of a sample gas as it may occur in an unimproved ionization detector; and

FIG. 3 illustrates an ion stream characteristic as resulting from using the method in accordance with the present invention, and showing control measurements of ion stream as representing differing hexane contents of otherwise also differing sample gases.

Proceeding now to the detailed descriptin of the drawing, in FIG. 1 thereof is illustrated a flame ionization detector having a base part **1**, and a burner nozzle **2** extends from the base in up direction. A tubular housing or sleeve **4** extends from base **1**, also in up direction and receives the nozzle **2**. Combustion gases flow in up direction within the tube **4** and are discharged through the openings **5** in a cover **41**. The cover closes the interior tube **4** from above, except for the exhaust openings **5**. An insulation layer **3** is interposed between tube **4** and base **1**.

An electrode **6** is supported by a holder and disposed inside of tube **4**. The electrode **6** faces nozzle **2** and its holder traverses an insulative carrier **7**, which actually is an insert in annular cover plate **41**, and together therewith closes off tube **4**; the openings **5** are defined particularly between plate **41** and insert **7**.

The base member **1** is provided with bores **8, 9** and **10** through which respectively flow the combustion or fuel gases, the sample gas to be analyzed and air as required to obtain combustion and development of a flame. For example, hydrogen can be used as fuel gas and is assumed to flow through bore **8**; prior to entering the burner nozzle **2**, the hydrogen mixed with a sample gas that enters base member **1** through bottom bore **9**. Air is charged to the burner, i.e. flows particularly into the interior of tube **4** via the bore **10** and flows around nozzle **2** and up.

A pipe **11** extends laterally from base member **1** and communicates with bore **8** to serve in effect as an extension thereof. A connecting sleeve **12** extends laterally from pipe **11** and communicates with the interior thereof. Connection **12** is provided for connection to a supply of fuel gas.

A capillary tube **13** with connecting end piece **14** traverses and passes through pipe **11** and reaches into bore **8**. Compensating gas is fed through pipe **13** to render the ion stream in the flame of the burner independent from any oxygen content of the sample gas. Bore

8 meets bore 9 in the interior of base member 1, and that region may also be called a mixing chamber. Significantly now, capillary tube 13 extends right to that mixing chamber. Thus, fuel gas, compensating gas, and sample gas are mixed in the interior of base 1 and the mixture flows into nozzle 2. Hydrogen as fuel gas mixes readily with oxygen containing compensating gas.

In accordance with the invention, and as was mentioned above, the compensating gas may be or includes oxygen; preferably it is a mixture of oxygen and of an inert gas. For example, the compensating gas may be so-called synthetic air, which is a nitrogen-oxygen mixture corresponding to the ratio of oxygen to nitrogen in regular air, but very clean. However, it was found that even uncleaned air could be used in cases as compensating gas, provided the air does not contain ion forming components that may disturb the measuring process; but even if the air used as compensating gas has a low but constant content of hydrocarbons, the resulting ion stream attributable to that content can be compensated in the process that evaluates the measurement. It is a source for a constant error and can be eliminated, for example, electrically through bias in the measuring circuit as connected to electrode 6. However, if the hydrocarbon content in air, or any other ion forming impurities therein, are not constant, it is of advantage, or even necessary, to clean the compensating gas from these disturbing components prior to feeding the gas to the flame ionization detector.

Proper metering of the compensating gas will be carried out individually in each detector by calibrating procedure, prior to use, and wherein, for example, a reference gas sample of known consistence is analyzed by ion stream detection and quantitative analysis. The flow of compensating gas is controlled to be maintained at a constant rate by means of known pneumatic equipment as is commonly used for the control of gas flow through conduits generally, and for the control of fuel and sample gas flow for flame ionization detectors in particular. As that control is known, it does not have to be described in detail.

During experimental measurements, it was found that the adding of pure oxygen as a compensating gas still causes some reduction in the ion stream, and the sensitivity of the instrument is thereby reduced. On the other hand, if a gas mixture as mentioned above (oxygen-nitrogen as in air) is added as compensating gas, the sensitivity of measurement is not detrimentally influenced. This observation can be explained in that the adding of oxygen increases the flame temperature and that, in turn, causes combustion of a higher proportion of hydrocarbons in the sample gas so that a lesser amount of these hydrocarbons is available for the formation of ions. On the other hand, if the compensating gas includes an inert component, that component has a cooling effect so that the flame temperature is only insignificantly changed, and the ion yield is, therefore, maintained and attributable essentially to the concentration of the component to be detected.

The advantage of the invention and the improvement in obtaining representation of hydrocarbon content by flame ionization detection is readily derivable from FIGS. 2 and 3. In both cases, the hydrocarbon concentration in exhaust gases of internal combustion engines was to be measured. For example, FIG. 2 assumes a sample gas mixture that contains 1,000 ppm hexane in nitrogen, and the figure particularly depicts the ion stream produced in a conventional flame ionization detector, wherein a variable amount of oxygen, up to 22 percent, had been added to the sample gas. The oxygen content is plotted along the abscissa, the ordinate shows ionization stream on an arbitrary scale, with a value 100 assumed for zero oxygen content in the sample gas. It can readily be seen that with increasing oxygen content, up to a value equivalent to the relative oxygen content in air, the sensivity of the flame detector drops by about 35 percent.

Now compare FIG. 3, which shows the measuring results with a flame ionization detector improved in accordance with the invention. The burner was operated as follows. Hydrogen (H_2) was used as fuel gas at a flow rate of about 30 cm^3 per minute. Sample gas of different consistencies was used (see table below) but at a flow rate of about 5 cm^3/min. in all cases. Air was used as compensating gas at a flow rate of 10 cm^3/min. Air for sustaining combustion was flowing into the tube 4 at a rate of about 300 cm^3/min. The control measurement points 1 thorugh 7 as plotted in FIG. 3 have been arrived at as follows:

Measuring point	C_6H_{14} (in ppm)	Host gas of sample
No. 1	207	N_2
No. 2	427	N_2
No. 3	840	Air
No. 4	955	N_2 + 15% O_2
No. 5	1120	N_2 + 5% O_2
No. 6	1140	N_2 + 12% O_2
No. 7	1400	N_2

Wherein FIG. 3 illustrates very clearly that the ion flow is no longer dependent upon the oxygen content of the sample gas, but represents the hexane content. The ion flow characteristic is linear, whereby small deviations from a true straight line can readily be explained as likely variations in the true content of sample gases, as far as hexane, nitrogen and oxygen are concerned. In other words, the content of the sample gases used for obtaining this calibrating and test charactertistics hat not been learned otherwise to a degree of accuracy that, in fact, a true straight line could be expected. Most significantly, the significant oxygen content in the sample gas as per points 4 and 6 causes practically no deviation from the linear relationship as established by the measuring points where there was no oxygen in the sample gas.

The invention is not limited to the embodiments described above but all changes and modifications thereof not constituting departures from the spirit and scope of the invention are intended to be included.

I claim:

1. In a flame ionization detector having a base, a burner with a burner nozzle extending from the base and ending in a nozzle tip, a first bore in the base for receiving a sample gas to be analyzed, a second bore in the base for receiving fuel gas, there being pipes connected to the bores respectively for feeding sample gas and fuel gas thereto, the fuel gas mixing with the sample gas and flowing therewith through the nozzle to the tip thereof, there being additonal means at the base for feeding air to the burner, external to the nozzle, the air flowing around the nozzle to sustain combustion with the fuel gas as flowing from the nozzle tip, the improvement comprising:

an additional pipe extending into the base through one of said bores for feeding oxygen as compensating gas to the burner nozzle, upstream from the

nozzle tip, so that the nozzle receives a mixture of fuel gas, sample gas and oxygen, the oxygen of the compensating gas being insufficient to sustain combustion with the fuel gas, the fuel gas being capable of intimately mixing with the compensating gas.

2. In a detector as in claim 1, the additional pipe being a capillary inside of the fuel gas pipe.

3. In a detector as in claim 2, there being a chamber in the burner where the fuel gas is injected into the flow of sample gas, the capillary extending to said chamber.

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