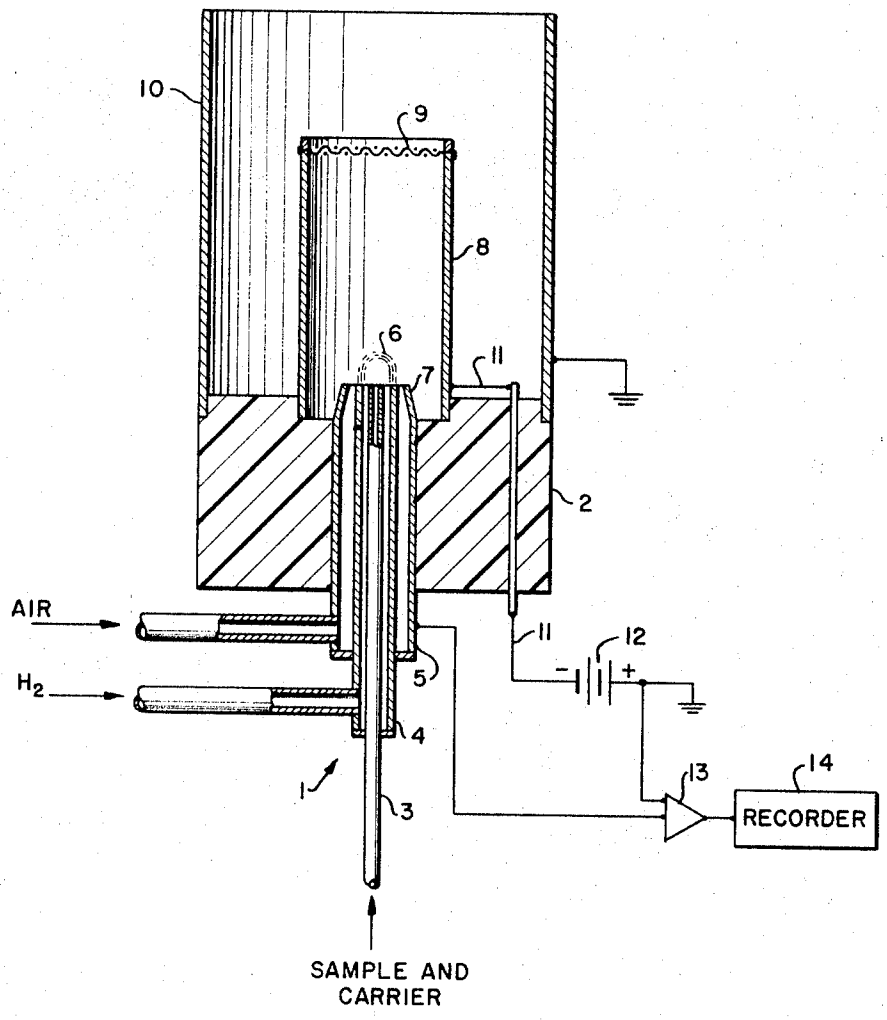
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FLAME IONIZATION DETECTOR

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INVENTORS:
B. O. PRESCOTT
H. L. WISE
D. A. CHESNUT
BY:
THEIR ATTORNEY

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FLAME IONIZATION DETECTOR

Basil O. Prescott and Harold L. Wise, Houston, and Dwayne A. Chesnut, Bellaire, Tex., assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A flame ionization detector wherein the sensitivity is improved by generating an electric field about the flame and burner jet by means of an electrode located out of the path of the flame and hot combustion gases and to which is connected a source of DC voltage, and utilizing the burner jet of an electrode located thereat as the collector electrode.

This invention relates to an improved flame ionization detector to detect and measure the concentration of organic components of gases.

The use of flame ionization detectors to investigate or analyze gases for their organic components, and in particular automobile exhaust gases for air pollution studies and gases wherein the components have been separated by gas chromatography, is an old and well-known art. In such a flame ionization detector the variation in current developed by the flame and measured between two electrodes, one at the flame and the other some distance away, is a measure of the concentration of the organic material introduced into the flame. The current developed by the hydrogen flame is very low, and even the addition of very small quantities of organic material to the flame is sufficient to produce a greatly increased current. Accordingly, the measurement of the changes of current are directly related to the concentrations of organic material contained in the sample gases introduced into the flame.

In order to measure the current developed by the flame, an electric circuit connected across the aforementioned electrodes is provided. Although various shapes and geometrical arrangements for the two electrodes have been tried, in the usual flame ionization detector one of the electrodes is formed by the metal burner tip or jet, while the second electrode is a cylinder, cone or plane made of metal gauge, wire or sheet, suspended approximately one centimeter from the flame. To collect and measure the charges created by the flame, a relatively large DC voltage, usually negative to lessen the noise caused by thermoemission of the heated suspended (collector) electrode, is applied to the burner electrode, and a suitable current measuring device, such as an electrometer amplifier, is connected to the collector electrode. The voltage applied to the burner tip or electrode is a matter of geometry and is usually from 60 to 2000 volts DC. The flame ionization detectors operating in the manner described above are shown, for example, in U.S. Patent 3,039,586, issued June 19, 1962, to I. G. McWilliams, and U.S. Patent 3,129,062, issued Apr. 14, 1964, to L. Ongkiehong et al.

Since flame ionization detectors are extremely sensitive instruments, they are primarily used for detecting very low concentrations of organic material, for example, in

the parts per million range, as is found, for example, in air or water pollution studies or as contaminants in chemical process streams. As the requirements for the detection of smaller and smaller quantities or lower concentrations of hydrocarbons becomes necessary, attempts are continually made to improve the sensitivity of the flame ionization detectors, and thereby enable the detection of lower concentrations with the conventional detecting apparatus. Additionally, because of the small signals which are detected, the problem of accurately detecting the useful signal in the presence of the electrical noise in the measuring circuit becomes greater. Although some of this noise may be the result of hydrocarbons of organic material in the gases used for the flame, and consequently may be substantially eliminated by using purer gases or compensated for during the measurement, a significant quantity of the noise is due to the thermal effect of the heat generated by the flame on the collector electrode. While it is possible by various means to reduce the electrical noise due to the thermal effects on the collector electrode, such noise cannot be totally eliminated. Accordingly, attempts are continually made to arrive at a flame ionization detector arrangement which tends to improve the signal-to-noise ratio in the flame ionization detector output signal in order to arrive at a greater usable signal for indication of the organic constituent in the sample stream.

This invention provides an improved flame ionization detector whereby, through a relatively simple modification of the conventional flame ionization detector, the sensitivity of the detector is improved by a factor of about 2.5 to 3 times and the signal-to-noise ratio is increased from about 50 to 100 times. This results in a detector which has a usable sensitivity of about 200 times greater than that obtainable with the conventional flame ionization detector. Briefly, the improved sensitivity of the flame ionization detector is achieved by generating an electric field about the flame and the burner jet by means of an electrode located out of the path of the flame and the hot combustion gases therefrom and to which is connected the source of DC voltage, and utilizing the burner jet or an electrical conductor located at the burner jet but out of the flame as the collector electrode, i.e., the current measuring device is connected to the jet electrode. With this arrangement the field set up around the flame and burner by the electrode and the voltage supply connected thereto forces the electrons and/or negative ions back onto the burner electrode for detection. Since the flame is only about 1 or 2 millimeters in height, the total travel distance of the electrons and/or negative ions is only about 1 or 2 millimeters, as opposed to the travel distance of about 1 centimeter for the usual flame ionization detector configuration. This reduces the recombination of the electrons with the positive ions before detection, thereby resulting in an increased signal and hence increased sensitivity for the detector. Moreover, since both of the electrodes are out of the path of the flame, the heating thereof is decreased and hence the thermoemission noise is reduced.

The jet collector flame ionization detector according to the invention and the advantages thereof will be more clearly understood from the following detailed description taken in conjunction with the attached figure which shows the preferred embodiment of the flame ionization detector according to the invention.

Referring now to the figure, there is shown a burner assembly **1** of conventional design and dimensions which is mounted in a base **2** formed from a very high resistance insulating material such as Kel-F (a monochlorotrifluoropolyethylene resin). The burner assembly **1** consists essentially of three concentric pipes or conduits **3**, **4** and **5** having suitable input connections thereto through which, respectively, the carrier gas with sample, the hydrogen, and the air may be introduced to the burner assembly. Although not shown, it is understood that suitable pressure and flow regulators for the various input streams to the burner assembly are provided as is common in the art. Preferably, the entire burner assembly or at least the outer conduit **5** of the burner assembly is constructed of corrosion resistant metal such as stainless steel so that the outer shell of the burner assembly may function as one of the electrodes for the electrical detecting circuit. It should be noted, however, that it is possible to construct the burner assembly from other materials than metal, for example, glass; but in such cases the instrument becomes more fragile and the problem of extraneous ions released into the flame **6** by the glass becomes a problem. However, if such a construction, i.e., glass burner, is utilized, then according to the invention at least the tip or jet **7** of the burner assembly should be constructed of metal or, alternatively, an electrical conductor, such as a coating on the outer conduit **5** or a conductive ring, should be positioned adjacent the outlet jet or tip of the burner assembly adjacent the flame. Such a conductor, however, should be positioned so that it is not in the flame or in the path of the combustion gases for the flame and is relatively close to the flame, for example, about one millimeter away, or approximately the distance between the flame and the outer conduit **5** of the burner assembly.

Also secured to the base **2** in a manner whereby it is electrically insulated from the burner assembly **1** is a metal electrode **8** which surrounds the flame **6** and at least the tip or jet **7** of the burner assembly **1**, i.e., the electrode **8** extends below the level of the flame. The electrode **8** has a large surface area relative to the size of the flame and the electrode formed by the burner jet and preferably has a cylindrical or barrel shape. As shown in the figure, the electrode **8** is arranged concentrically about the flame and the burner jet and is horizontally displaced therefrom, for example, by a distance of 5 or more millimeters, and consequently is not in the combustion zone formed by the flame or in the path of the combustion gases therefrom. In order to prevent solid material from coming into contact with the burner jet and hence possibly clogging the jet, while at the same time allowing the combustion gases from the flame to leave the detector, wire mesh **9**, for example, of Chromel, may be provided across the opening at the upper end of the electrode **8** and fastened thereto in any desired manner. Also mounted on the support **2** is a grounded electrical shield **10**, which electrostatically screens the detector and which also prevents false air currents from reaching the flame.

Connected to the electrode **8** by means of a conductor **11** extending through the base **2** is the high side of a source of DC potential such as battery **12**, the low side of battery **12** being connected to a point of reference potential, for example, ground. As shown in the drawing, the battery **12** preferably applies a negative potential to the electrode **8**. However, it is to be understood that the detector will operate satisfactorily if a positive potential is applied to the electrode **8**. The use of a positive potential on the barrel **8**, however, usually results in more noise in the signal than that which is obtained with a negative potential on the barrel.

As opposed to the prior art devices, the current detecting device, i.e., the electrometer **13**, is connected between hte jet collector electrode formed by the conduit **5** and the low side of the source of reference potential **12**, i.e., ground. A recorder **14** or other suitable current indicating device is connected to the output of the electrometer **13** to record the detected current.

The application of the voltage electrode **8** causes an electrostatic field to be generated which, because of the particular geometrical relationships between the electrode **8** and the flame and burner assembly **1**, surrounds the flame and the burner jet and extends from above the flame, i.e., from outside the combustion zone, to the burner jet. This resulting field forces the electrons and/or negative ions resulting from the burning of the hydrogen and the gaseous sample back onto the jet collector electrode formed by the conduit **5** for detection by the electrometer amplifier **13**. Since, with this configuration, the resulting ions need only travel from the flame or combustion zone to the jet collector electrode, i.e., the conductor formed by the conduit **5**, the travel distance of the electrons and ions is only about 1 to 2 millimeters. This is opposed to the conventional flame ionization detector using a collector electrode above or around the flame wherein the electrons and/or negative ions must travel a distance of about 1 centimeter. This decreased travel distance results in less recombination between the electrons and the positive ions and produces a greater sensitivity for the detector. Tests using this detector have shown that as indicated above the average sensitivity is 2½ to 3 times greater than that exhibited by previously used flame ionization detector systems, even systems using collector electrodes similar to the voltage electrode **8** of the instant application, for example, see the above-mentioned patent to Ongkiehong et al. Additionally, and more significantly, with the above-described geometrical configuration, wherein none of the electrodes are in the path of the flame, and with the electrical connections shown, the signal-to-noise ratio is increased from about 50 to 100 times over the prior art flame ionization detectors. Thus, the overall increase in usable sensitivity of the instrument is greater than 200 times that of the previously used flame ionization detectors.

It should be noted that in the present system an optimum of sensitivity and accuracy results when a relatively high voltage of approximately 90 volts is supplied to the barrel electrode **8** even though tests of the responses of the present system with voltages ranging from 0 to 1000 volts have indicated that there is substantially no variation in the sensitivity of the detector within the range of from about 4½ to 1000 volts. The relatively high potential, i.e., at least 90 volts, is preferably applied to the electrode **8** in order that the detector maintain a linear response with respect to relatively high concentrations of hydrocarbons in the flame. It is to be understood, however, that obviously the particular value of voltage applied to the electrode **8** will vary to some extent in accordance with the geometrical dimensions of the flame ionization detector.

In order to further illustrate the improved sensitivity obtainable with a jet collector flame ionization detector as disclosed above, comparative data from tests comparing the performance of a flame ionization detector according to the invention with a high quality commercially available flame ionization detector are presented below. For the tests, the jet collector hydrogen flame ionization detector used was substantially as shown in the figure with a negative D.C. potential of 90 volts applied to the barrel electrode **8**, while the commercially available flame ionization detector, as is conventional in the art, had the current detecting means, i.e., the electrometer amplifier, connected to a barrel electrode similar to the electrode **8** and a negative D.C. potential of 300 volts connected to the second electrode adjacent the flame. The voltages applied to the electrodes of the respective flame ionization detectors as well as the other operating conditions for the detectors, e.g., the flow rates of the various gases, were those suggested as optimum by the respective manufacturers, and the same column for the introduction of the sample, the same amplifier and the same recorder were used for all detectors tested. The respective flow rates for the gases

to the detectors and the results of the tests, which consisted of injecting the same volume of a solution of wax in carbon disulfide into the instrument and comparing the signals from the two types of detectors, were as follows:

	Jet collector detector	Prior art detector	
		No. 1	No. 2
Flow rates, ml./min.:			
Hydrogen	70	25	25
Air	400	250	250
Helium	70	25	25
Integrated signal, counts:			
Run No. 1	82,212	32,889	31,404
Run No. 2	85,152	24,815	25,263
Run No. 3	85,198	26,815	34,111
Average count	84,187	28,173	30,259
Relative response	1.00	0.33	0.35

It should be noted that three determinations or measurements were made with each detector tested in order to compensate for any experimental variations, e.g., sample size, and that two of the commercially available detectors, one of which was newly purchased, were tested to insure a fair comparison.

As is clearly shown from the results of the tests, the signal amplitude response and hence the sensitivity of the detector according to the invention is approximately three times that of the high quality commercially available detector, i.e., the relative responses of the detectors is 1:0.33 or 1:0.35. In order to illustrate that the difference in response of the two types of detectors is not due to the different flow rates of the input gases and in particular the carrier gas, i.e., the helium, the integrated values of the detected signals are also shown. From the integrated signal values, a relationship of approximately three to one is again evident, indicating that the improved sensitivity is in fact due to the improved hydrogen flame ionization detector configuration according to the invention, i.e., the jet collector flame ionization detector.

We claim as our invention:

1. A flame ionization type of detector system for the analysis of gases comprising:

a burner assembly;

inlet means for introducing a sample of the gas to be analyzed, hydrogen and a combustion supporting gas to said burner assembly to sustain a flame at the outlet jet of said burner assembly;

an electrical conductor located at said jet and out of the flame at said jet;

a metal electrode surrounding said flame and horizontally spaced therefrom whereby said electrode is out of the path of said flame and the combustion products therefrom, said metal electrode extending below said flame and surrounding said electrical conductor;

a DC voltage source connected between said electrode and a point of reference potential; and

an ionization current detecting means connected between said burner assembly and said point of reference potential whereby said burner assembly functions as the collector electrode of the flame ionization detector.

2. The apparatus of claim 1 wherein at least the outer surface of said burner assembly is constructed of metal and wherein said electrical conductor comprises the outer surface of said burner jet.

3. The apparatus of claim 1 wherein said voltage source is a source of negative voltage.

4. The apparatus of claim 3 wherein said voltage source is a source of relatively high voltage.

5. The apparatus of claim 4 wherein said voltage source is at least 90 volts.

6. The apparatus of claim 1 wherein said metal electrode is cylindrical and is concentrically arranged with respect to said burner assembly.

7. The apparatus of claim 1 wherein said metal electrode has a large surface area relative to the flame and the surface area of said electrical conductor.

8. The apparatus of claim 1, wherein the distance between said flame and said electrical conductor is small relative to the distance between said flame and said electrode.

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MORRIS O. WOLK, *Primary Examiner.*

R. E. SERWIN, *Assistant Examiner.*

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