

April 14, 1964

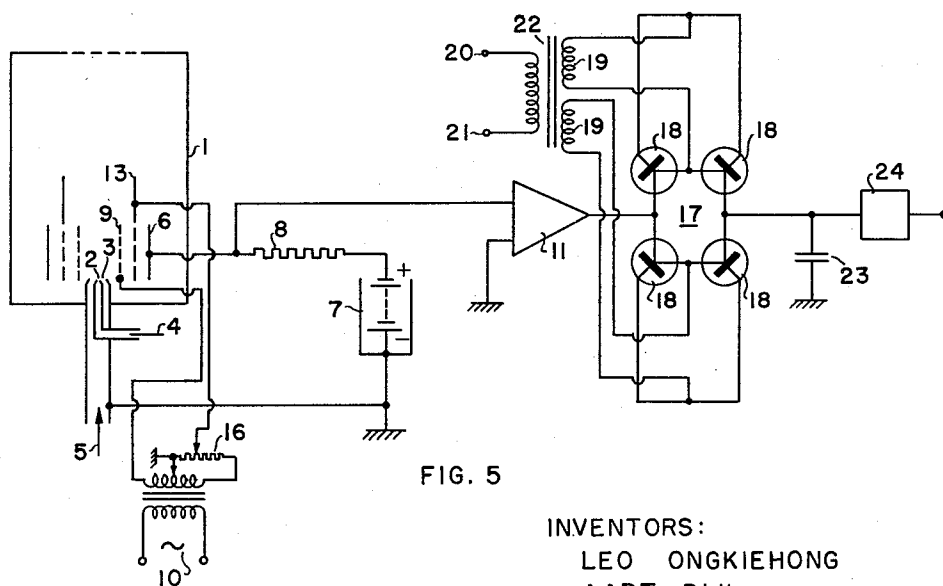
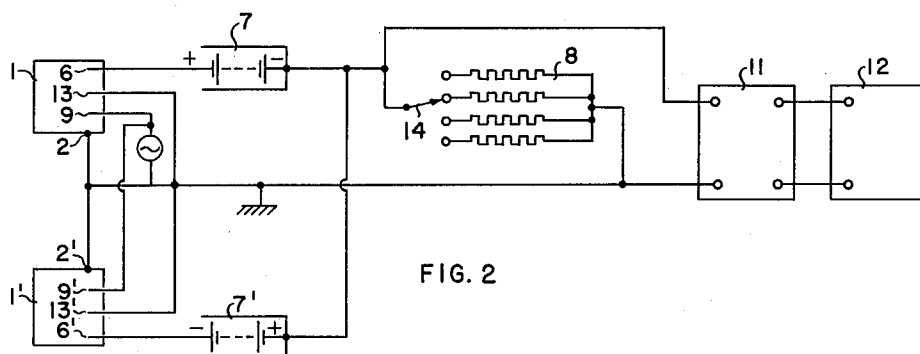
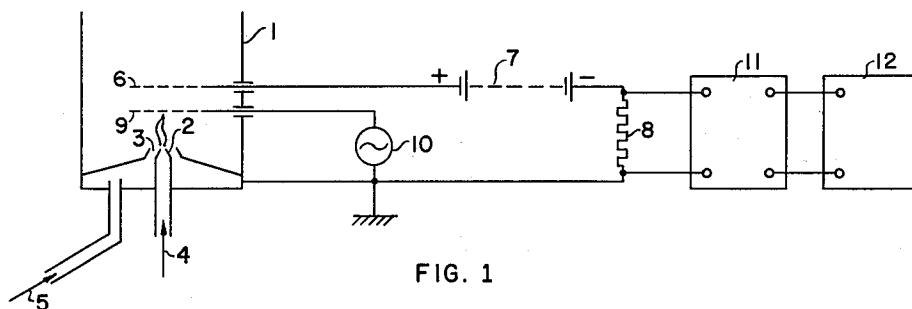
L. ONGKIEHONG ETAL

3,129,062

FLAME IONIZATION DETECTOR

Filed May 2, 1961

2 Sheets-Sheet 1



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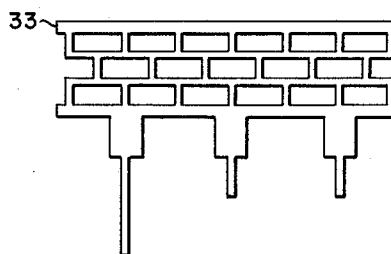
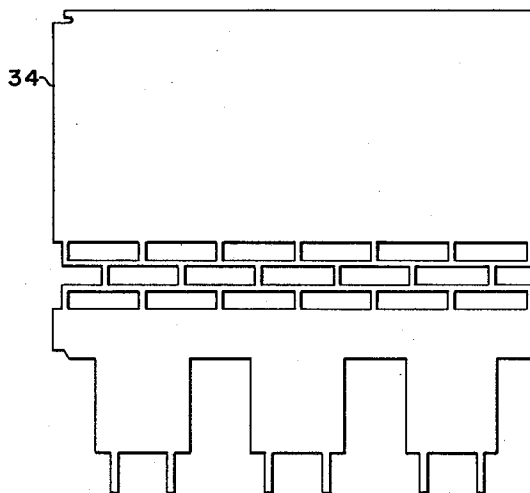
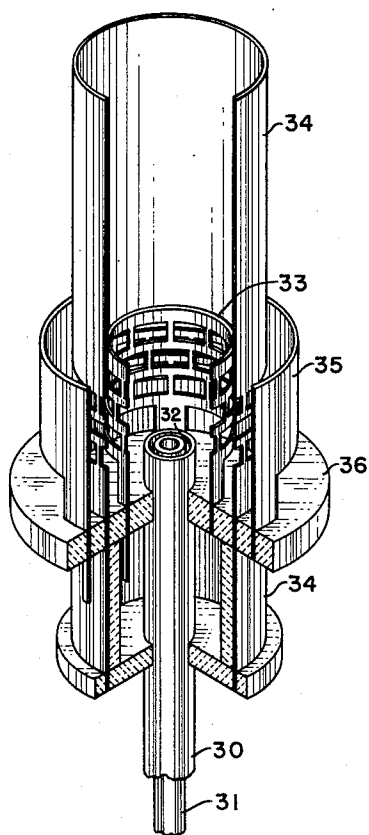
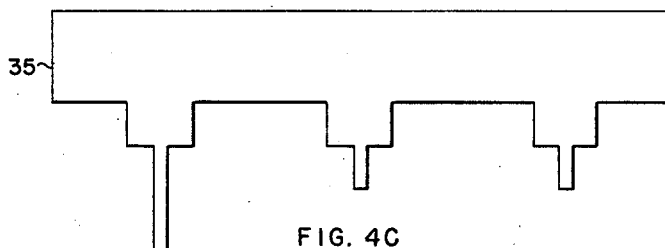
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2 Sheets-Sheet 2



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3,129,062

FLAME IONIZATION DETECTOR

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7 Claims. (Cl. 23-255)

The invention relates to a circuit including a flame ionization detector for the examination or analysis of gases, particularly gases obtained by a chromatographic separation.

It is known to investigate or analyze gases by means of a flame ionization detector, particularly to use a detector of this kind in the technique of chromatographic separation.

In a flame ionization detector use is made of a burning gas, usually pure hydrogen or a mixture of gases of which hydrogen is an integral part, in the form of a small flame whose electrical conductivity is measured by means of two electrodes disposed in the plasma of the flame. The gas to be examined or analyzed is supplied to the flame.

Of the electrodes inserted in the plasma of the flame one is usually formed by the burner (which in this case is made of metal) and the other by a gauze or wire of platinum or bronze positioned about 10 mm. above the burner. In principle, however, the electrodes may also be arranged transversely to the flame. The flame itself is usually not greater than a few millimeters.

The conductivity of the hydrogen flame is very low on the order of magnitude of 10^{-12} to 10^{-13} mhos. Even the addition of small amounts of organic material is, however, sufficient to greatly increase the conductivity of the flame; depending on the concentration of organic components in the flame the conductivity may be 10^5 to 10^6 as great. The changes in the conductivity can be measured and if necessary recorded; the result of the measurement is an index of the presence or concentration of organic material in the gases supplied to the flame.

If the flame ionization detector is used as a detector behind a gas chromatography column in which hydrogen is used as the carrier gas, the gas from the column can be directly burnt in the detector; if another gas such as nitrogen is used as the carrier gas the gas in the column is first mixed with hydrogen and then supplied to the detector.

The conductivity is usually measured by connecting a direct voltage source and a resistance in series with the electrodes and measuring the voltage over the measuring resistance. Since the absolute value of the resistance of the flame is very high the measuring resistance will also have to have a high value in order to obtain measurable signals. The measuring resistance should, however, not be too high compared to the flame resistance to ensure that the magnitude of the current in the series connection is determined by the detector; in this case variations in the flame resistance give substantially proportionate variations of voltage over the measuring resistance.

The signal over the measuring resistance may also be recorded and/or indicated and thus is usually amplified to provide sufficient signal to drive a chart recorder. Owing to the high impedance level at which the signal becomes available it is, however, impossible to supply the signal directly to a recording or indicating device. The signal is therefore first amplified by means of a direct voltage amplifier. To obviate as far as possible the trouble caused by the drift to which all direct voltage amplifiers are subject, the input signal of the direct voltage amplifier, notwithstanding the amplification em-

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ployed, should, however, be as large as possible, so that the measuring resistance should have the highest possible value. In practice, these difficulties have been solved by using an electrometer amplifier in combination with a measuring resistance of 10^8 to 10^{10} ohms, depending on the concentration range of the gases to be examined in the flame of the detector.

Electrometer amplifiers are, however, expensive, fragile and costly to maintain. Moreover, there is the drawback that their response velocity is small, thus the reproducibility of relatively rapid variations occurring in the gas being examined is difficult.

Accordingly, the principle object of this invention is to provide a novel detecting system for a gas chromatograph unit using an alternating voltage amplifier.

A further object of this invention is to provide a unique flame ionization detecting unit for a gas chromatograph that permits the use of an alternating voltage amplifier.

A further object of this invention is to provide a novel flame ionization detecting unit having a third or control electrode, with the control electrode being coupled to an alternating voltage source.

A still further object of this invention is to provide a flame ionization detecting unit utilizing a control electrode coupled to an alternating voltage source with the signal from the detecting unit being supplied to a rectifying circuit that passes only the positive peaks of the signal.

This invention provides a circuit using a flame ionization detector by means of which a simple, low cost, alternating voltage amplifier may be used. The circuit also shows a much faster response and, consequently, detects rapid variations in the composition of the gas to be examined or analyzed, this being particularly advantageous when the flame ionization detector is used as a detector in chromatography technique and in gas chromatography in particular.

According to the invention, a third electrode (control electrode) is placed in the field between the electrodes of the detector. The control electrode is coupled to a varying voltage, preferably a periodically varying voltage that temporarily interrupts the current between the two electrodes, or at least partly suppresses the said current. An output signal is derived from the output of the detector, preferably via an alternating voltage amplifier. The magnitude of this output signal constitutes the result of the measurement and may be recorded and/or indicated either directly or after rectification.

The control electrode need not, as regards its spatial arrangement, be positioned exactly between the two other electrodes, since it is sufficient to place the control electrode in such a way that its potential influences the current between the other electrodes in the manner indicated. In practice, the control electrode temporarily completely suppresses the current of one of the other electrodes.

In addition, an auxiliary electrode for screening is preferably arranged in the field between the control electrode and one of the other electrodes, the said auxiliary electrode being incorporated in the circuit in such a way that direct capacitive currents from the control electrode to the detector output are reduced or eliminated.

The above objects and advantages of this invention will be more easily understood from the following detailed description of specific embodiments when taken in conjunction with the attached drawings in which:

FIGURE 1 is a block diagram of one embodiment of this invention using a flame ionization detector having only a control electrode;

FIGURE 2 is a block diagram of a second embodiment of this invention showing the use of two detectors having both control and screen electrodes in order that

the difference between the two detector signals may be measured and recorded;

FIGURE 3 shows the detailed construction of a flame ionization detector in accordance with this invention;

FIGURE 4 shows the detailed construction of the electrodes of the detector shown in FIGURE 3; and,

FIGURE 5 is a schematic diagram showing a third embodiment of this invention.

The flame ionization detector system is shown diagrammatically in FIGURE 1 in which the detector consists of a housing 1, burner 2, and an air supply aperture for the flame 3. The housing 1 is electrically connected to ground while the mixture of hydrogen gas and the gas to be examined is supplied at 4 with the combustion air being supplied at 5. The metal burner acts as one electrode (burner electrode), while above the burner is placed a platinum gauze 6 forming the other electrode (collector electrode) that is electrically insulated from the housing 1. The collector electrode is connected to earth via a source of direct voltage 7 and a measuring resistance 8.

According to the invention a third electrode 9 is also arranged in the detector in the field between the burner electrode 2 and the collector electrode 6, with the third electrode, being electrically insulated from the housing 1. The electrode 9 is connected to the burner electrode 2 via a source 10 which supplies a varying electric voltage. The purpose of this voltage is the repeated temporary suppression (complete or partial) of the ionization current in the circuit 2-6-7-8. The magnitude of the voltage 10 is preferably such that the current is completely interrupted. The voltage 10 need not be a sinusoidal alternating voltage but may, for example, be of a pulsating voltage of a rectangular nature. A direct voltage may also be coupled to the electrode 9.

Whenever the amplitude of the voltage 10 exceeds a certain value the ionization current in the collector circuit is interrupted. This occurs both when the voltage of electrode 9 is positive and when it is negative with respect to the electrode 2. The value of the positive voltage required to suppress the current in the collector circuit may vary from the value of the negative voltage required to suppress the current. To avoid the asymmetry in the interruption a rectified, a non-filtered alternating voltage may be used for the source 10 of varying voltage.

The result of the interruptions is that an alternating voltage is established across the resistance 8 which is a measure of the conductivity of the flame. This alternating voltage can be amplified in a simple manner by an alternating voltage amplifier 11 and indicated and/or recorded by an indicator and/or recording instrument 12.

The great advantage of the present circuit is the possibility which it affords of employing an alternating voltage amplifier instead of a direct voltage amplifier. Such an amplifier is much cheaper and is capable of stable operation at a much lower input voltage than a direct voltage amplifier. Consequently, the value of the measuring resistance 8 may be relatively low (about 100 times smaller than with the corresponding use of the known circuit with a very good direct voltage amplifier), as a result a much more rapid response (100 times more rapid) of the instrument is obtained and hence it is possible to indicate more rapid variations in the conductivity of the flame.

A second embodiment of this invention is shown in FIGURE 2 which, however, differs in two respects from the embodiment of FIGURE 1. The circuit is of a double design: the detector 1 has the same function as the detector 1 in FIGURE 1, and the other detector 1' is fed with the hydrogen gas without the gas to be examined. The difference in the two ionization currents sets up a current over the measuring resistance 8. To this end the direct voltage sources 7 and 7' are connected in th opposite directions to the detectors 1 and 1'.

In addition, extra screening electrodes 13 and 13' are connected between the electrodes 9 and 9' and electrodes

6 and 6'. The screening electrodes in turn are connected to the electrode 2 and 2'. The use of screening electrodes 13 and 13' ensure that capacitive currents from the control electrodes 9 and 9' to the detector output resistance 8 are substantially blocked, thus benefiting the accuracy and sensitivity of the measurement.

In order to give the measuring instrument a number of measuring ranges the magnitude of the measuring resistance 8 may be modified by means of a switch 14.

The direct voltage sources 7 and 7' are provided with a shield so that leakage currents from the batteries 7 and 7' are not reflected over the measuring resistance.

The above-mentioned circuits are particularly suitable for use as a detector circuit behind a column for gas chromatography. The gases derived from the column may be supplied to the hydrogen stream introduced through pipe 4; if hydrogen is already used as a carrier gas in the column, the gas stream from the column may be directly connected to 4, in which case a special hydrogen stream is usually unnecessary.

In another use the detector circuit according to the invention may be employed for measuring the concentration of hydrocarbons in the atmosphere. In this case the air to be examined may be mixed continuously or batchwise with the hydrogen stream introduced at 4. In principle, it is also possible to supply this air at 5 in the form of combustion air, although this method is less sensitive.

The combustion air normally supplied at 5 is usually passed through a filter which prevents solid particles from entering the flame with pure air or pure oxygen preferably being used. The hydrogen supplied at 4 may be pure hydrogen, although it may also contain an amount of other gases such as nitrogen, argon, helium or the like. Use is frequently made of a mixture comprising 50% hydrogen and 50% nitrogen.

The frequency of the periodically varying voltage may be ordinary 60-cycle-per-second voltage, but under certain circumstances it may also be lower or higher and even considerably higher. A frequency higher than about 1000 cycles per second is usually, however, less suitable owing to the capacity which is present parallel to the measuring resistance 8. The direct voltage source 7 may have a value of, for example, 90 volts, while the peak value of the auxiliary voltage 10 may be 50 to 60 volts, for example. The distance of the electrodes 2 to 6 is usually about 10 mm.

It is, of course, not strictly necessary to connect the burner electrode to ground and one of the other electrodes, for example the collector electrode, may be grounded if it is desired.

The electrodes may also be arranged transversely to the flame. In this case electrodes are then preferably arranged concentrically around the flame in order that they envelope the flame. In this way a very compact construction may be obtained.

A construction of this type is shown in FIGURE 3, in which the burner consists of two concentric pipes 30 and 31. The combustible gas is generally passed through the inner pipe 31 and the combustion air through the annular space 32 between the two pipes, although this procedure may also be reversed. The two streams may even be previously mixed and then burnt, although the effect is slightly less favorable with this method.

The control electrode 33, the screening electrode 34 and the collector electrode 35 are cylindrical and arranged concentrically around the burner. They may be fabricated by various means, preferably etching from 0.2 mm. thick stainless steel. FIGURES 4a, 4b and 4c show developed views of these electrodes. The various electrodes are secured to a disc 36 made of insulating material for example ceramic material. In addition, the system is surrounded by a shield (not shown) which ensures that it is electrostatically screened and also prevents false air currents from reaching the flame. The

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system shown in FIGURE 3 has a diameter of approximate 45 mm., although it is quite possible to build a smaller system, for instance one-half this size.

The interruption of the ionization current by a voltage 10 having a frequency of 60 cycles per second sets up an alternating voltage of 120 cycles per second over the measuring resistance which after amplification constitutes the output signal. With the use of an alternating voltage of 25 volts on the control electrode and a direct voltage of +400 volts on the collector electrode a sensitivity of 10^{-12} amp. is obtained for 1 p.p.m. of n-butane in a gas stream consisting of 50 percent hydrogen and 50 percent nitrogen with the gas stream being adjusted to a constant value of 1.5 cc./sec. The screening electrode minimized cross-talk from the control electrode to the collector electrode caused by the second harmonic of the voltage 10 to a value of 3.10^{-14} amperes.

It was, however, found that the above circuit could only be used if the concentration of the gas to be examined or analyzed in the hydrogen flame was less than that corresponding to about 200 p.p.m. of n-butane. If this limit was exceeded the linearity of the output signal decreased since the sensitivity of the detector decreases with higher concentrations of the gas in the hydrogen flame. This results from space charge effects between the electrodes. After an interruption by the positive half of the voltage 10 the subsequent ionization current peak through the measuring resistance is in fact found to be a true measure of the concentration in the flame of the gas to be measured; but after an interruption by the negative half of the voltage 10 the ionization current peak is not saturated, and depends on both this concentration and on the space charges still present in the field at that moment. In other words, the first peak is a saturated current of which the peak value merely depends on the charge carriers produced by the flame, but the second peak is not saturated on account of diffusion and recombination effects and hence does not solely depend on the charge carriers produced by the flame at that moment.

In order to obtain an output signal with optimum linear dependency on the said concentration it is advisable to ensure that only the first-mentioned current peaks contribute to the output signal. The output signal is preferably solely determined by the maximum values of these peaks (top detection). This may be achieved by coupling alternating current amplifier to a circuit which in the frequency of the voltage 10 passes only the desired series of peaks and which blocks the other series. If, moreover, the pass-through phase is restricted to the moments at which the peaks have reached their maximum values, the desired top detection is obtained. Smoothing of the peaks and suppression of the frequency of the voltage 10 then results in an output signal which is, in fact a measure of the concentration of the gases in the flame. In this way an output signal could be produced for concentrations up to a 1000 p.p.m. of normal butane which is still entirely linear, the sensitivity being 10^{-11} amp. for a concentration of 1 p.p.m. of normal butane.

If the above-described method is employed it is highly desirable to ensure the complete absence of cross-talk from the control electrode to the collector electrode, since in the above case of top detection the collector current peaks have the same frequency as the voltage 10. Hence a low voltage which may be a controllable voltage derived from the voltage source 10 is preferably supplied to the screening electrode 13 of FIGURE 2.

FIGURE 5 shows a complete circuit as used when peak detection is employed. The circuit essentially corresponds to the one shown in FIGURE 1 with the addition of a screen electrode 13.

The voltage source 10 may be ordinary 120-volt 60-cycle power which is coupled to the control electrode 9 by a transformer and in opposite phase to the screening electrode 13. The secondary winding of the transformer

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includes a center tap which is grounded. The secondary of the transformer is coupled to the screening electrode via an adjustable resistance 16. Suitable adjustment of the magnitude of the compensating voltage by means of the resistance 16 substantially prevents cross-talk from the control electrode to the collector electrode.

A circuit 17 consisting of a bridge circuit formed of four transistors 18 is coupled to the alternating current amplifier 11. The conduction of these transistors is determined by the voltage 19 between the base and collector of each of these transistors. A pulsating voltage derived from a monostable multivibrator (not shown in the drawing) is connected between the terminals 20 and 21 of a transformer 22. This voltage is passed to the primary winding of a transformer 22 with two secondary windings supplying the voltage 19. The frequency of the multivibrator voltage is the same as that of the alternating voltage 10. The voltage preferably consists of sharp rectangular pulses having a width of approximately 1 msec.

During the period of the pulse of voltage 19 the circuit 17 is conductive (resistance in the order of magnitude of 10 ohms) and during the remainder of the period the circuit 17 is not conductive (resistance in the order of magnitude of a few thousand ohms). The moment at which a pulse arrives may be so selected as to coincide with the appearance of the top of the desired current peak. In this way the top of the current peak is allowed to pass through while other signals are blocked. The peaks are smoothed by means of a condenser 23 and the resultant varying direct current is then passed through a filter 24 cutting off the fundamental frequency. The filter is usually so selected that only the variations in the direct current which are lower than 5 to 10 cycles per second are transmitted.

A circuit, such as a mechanical or electronic interrupter controlled in the desired manner could, of course, be used instead of the circuit 17. Moreover, the upper (or lower) half of the circuit 17 shown is sufficient and in this case the resistance in the pass-through period and the blocking resistance in the blocking period would be doubled.

The sensitivity of the equipment may be controlled, for example by controlling the measuring resistance 8. The full scale deflection of the indication may, for example, correspond to 20 p.p.m. of n-butane (1% noise), but may also be adjusted to a lower value (1 p.p.m. of n-butane) or a much higher value. If a high sensitivity is desirable the flame ionization detector will generally be given the smallest possible dimensions.

We claim as our invention:

1. A flame ionization type of detector system for analysis of gases obtained by a chromatographic separation comprising: a detector having a first electrode; a burner assembly, said burner assembly forming a second electrode a control electrode disposed between said first and second electrode; a source of alternating voltage coupled to said control electrode and said second electrode; a source of direct voltage coupled to said first and second electrodes and an alternating voltage amplifier coupled to said first and second electrodes to detect the signal appearing across said first and second electrodes.

2. The system of claim 1 in which a screen electrode is disposed between the control electrode and one of the spaced electrodes, said screen electrode being coupled to the other of said spaced electrodes.

3. The system of claim 1 in which the output side of the amplifier is coupled to a rectifying circuit that passes signals appearing on said spaced electrodes as a result of the positive phases of said alternating voltage source and blocks all other signals.

4. The system of claim 3 in which the rectifying circuit includes a gating circuit having the same frequency as said alternating voltage, said gating circuit being adjusted to pass only the peak value of the signal.

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5. The system of claim 3 in which the rectifying circuit consists of a transistor bridge circuit and a source of pulsating voltage having a square wave form coupled to said transistor bridge to bias said transistors at the same frequency as the alternating voltage coupled to the control electrode.

6. The system of claim 2 in which the detector consists of three cylindrical electrodes arranged concentrically around a burner, said burner being arranged to burn the gas discharged from a chromatograph, said burner in addition forming the fourth electrode.

7. A flame ionization detector comprising: a central burner arranged to burn the gas discharged from a chromatograph unit said burner forming one electrode; a

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cylindrical collector electrode disposed concentrically around the burner; a cylindrical control electrode disposed concentrically around said burner between the burner and the collector electrode; and a cylindrical screen electrode disposed concentrically around said burner between said collector and control electrodes.

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