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DEVICE FOR THE ANALYSIS OF A FLUID MATERIAL
BY BOMBARDING THE SAME WITH PHOTOELECTRONS

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DEVICE FOR THE ANALYSIS OF A FLUENT MATERIAL BY BOMBARDING THE SAME WITH PHOTOELECTRONS


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This invention relates to detectors for use in the analysis of gas samples and the like to detectors that are particularly suited for use in gas chromatography.

It is an object of the present invention to provide a new and improved detector and methods of detection which may utilize the various characteristic properties of a wide range of constituents that may be found in samples. A further object is to provide such an instrument which may be operated in various modes to provide maximum sensitivity and selectivity, depending upon the particular constituents being analyzed for. These modes include electron multiplication and ionization detection, electron capture detection, breakdown voltage detection, electron mobility detection, and electron energy spectrum detection.

It is a particular object of the invention to provide a new and improved detector incorporating a photoelectric source of low energy electrons with the electrons being released directly into the detection zone between the cathode and anode. Another object is to provide a detector including a cathode for releasing photoelectrons into the detection zone with the cathode being illuminated via a light path which does not pass through the sample gas. A specific object is to provide such a detector including an apertured cathode illuminated from a source outside the detection zone via the cathode apertures to release the photoelectrons within the zone.

It is an object of the invention to provide a new and improved detector which in one form may comprise a sample cell and in another form may utilize a dual cell design with a light intensity control system for maintaining the sample cell current substantially constant.

It is an object of the invention to provide a detector and new and novel circuitry for operation therewith. A particular object is to provide a detector incorporating a reference source and a light intensity control system for maintaining the sample cell current substantially constant.

It is an object of the invention to provide a detector for a gas chromatograph or the like including means defining a chamber having an anode and an apertured cathode, means for directing a light onto said cathode and releasing photoelectrons in the chamber, means for connecting the cathode and anode in circuit with the voltage source and an amplifier, and means for flowing a gas stream through the chamber in the zone between the cathode and anode.

It is an object of the invention to provide a detector for a gas chromatograph or the like including means defining a first chamber, means defining a second chamber and including a first anode, means defining a third chamber and including a second anode, a first apertured cathode positioned between the first and second chambers, a second apertured cathode positioned between the first and third chambers, a light source in the first chamber for directing light onto the cathodes and releasing photoelectrons in the second and third chambers, means for deflecting a stream of sample gas through the second chamber, and means for flowing a stream of reference gas through the third chamber.

It is an object of the invention to provide a method of operating a cell to detect the presence of selected constituents of a flowing gas stream, the method including the steps of flowing the gas stream through the zone between the cathode and an anode, exciting the cathode from a location remote from the zone to release photoelectrons in the zone, applying a potential of predetermined characteristic across the cathode and anode, and measuring the change in anode-cathode current or voltage as a measure of the particular constituents in the gas stream.

The invention also comprises novel details of construction and novel combinations and arrangements of parts, which will more fully appear in the course of the following description. The drawings merely show and the description merely describes preferred embodiments of the present invention which are given by way of illustration or example.

In the drawings:

FIG. 1 is a sectional view of a single cell embodiment of the invention;

FIG. 2 is a sectional view of a dual cell embodiment of the invention;

FIG. 3 is a sectional view of an alternative form of a dual cell detector;

FIGS. 4, 5, 6 and 7 are diagrams illustrating the electrical connections of the detectors; and

FIG. 8 is a graph illustrating the current-voltage characteristics of a gas in a cell.

The detector of FIG. 1 includes a housing 10 having a chamber 11 and a housing 12 having a chamber 13, the housings being clamped together by appropriate screws and nuts. A light source in the form of an ultraviolet lamp 14 is mounted in a socket 15 carried on the housing 10, with the lamp disposed in the chamber 11 for directing light toward the chamber 13.

An apertured cathode 18, here shown as a fine mesh screen, is clamped between the housings 10, 12 and defines the boundary between the chambers 11, 13. An electrical connection may be made to the cathode 18 via a terminal 19 carried in the housing 10 and a wire 20. Two anodes 21, 22 are mounted in the housing 12, the anode 21 being a needle or rod which projects into the chamber 13 and the anode 22 being a plate or screen usually positioned at one end of the chamber 13. The choice of the particular form of anode for a particular application normally is based upon the mode of operation for the detector, as will be discussed in detail hereinafter.

Lines 23, 24 provide for flowing a stream of sample gas through the chamber 13. Another line 25 may be mounted in the housing 10 for flowing a stream of reference or carrier gas through the chamber 11 and past the cathode 18 into the chamber 13. It is preferred to maintain a flow of carrier gas over the cathode to prevent contamination thereof by constituents of the sample gas stream.

A typical circuit for operation of the detector of FIG. 1 is shown in FIG. 4. A voltage source 30 and a load resistor 31 are connected between circuit ground and the cathode 18. The anode 22 is connected to an electrometer amplifier 32, with the anode 21 being removed from the housing and the opening plugged. The amplifier develops an output voltage across resistor 33 which output voltage is recorded at a suitable recording device 34.

Light from the lamp 14 falls on the cathode 18 generating photoelectrons in the chamber 13. The cathode preferably is made of or plated with a metal of low work function such as silver, gold or copper to facilitate the production of electrons. The anodes preferably are made of or plated with a metal of high work function such as platinum or stainless steel to minimize emission of electrons therefrom. In an alternative form, the cathode may be made of a solid material such as quartz with the surface facing the chamber 13 partially covered with a metal film such as a silver grid, thus permitting the light to produce the photoelectrons within the chamber. In another alter-
native form the metal film may be uniform but of a density such that a portion of the incident light is transmitted therethrough to release the photoelectrons within the chamber. Such a structure is included within the expression aerated cathode.

The housings 10, 12 preferably are made of a suitable insulating material such as Teflon. Of course, the housings themselves could be made of metal with two portions appropriately insulated to serve as the electrodes. However, the electrode arrangements illustrated herein are preferred in that more uniform fields are achieved.

The detector as described in FIGS. 1 and 4 may be operated in several modes, depending upon the nature of the voltage source. The mode of operation is selected to provide the best sensitivity and selectivity for the particular sample being analyzed. A curve illustrating the voltage-current characteristic of a typical gas in the detector is shown in FIG. 8. In the region indicated at A (ordinarily from zero up to 25 to 100 volts) the variation in current is due to capture of low energy electrons by a constituent of the sample. Hence the variation in current for a particular operating potential can be directly related to the quantity of a particular electron capturing constituent present in the sample. This mode of operation may be referred to as electron capture detection. Referring to the circuit of FIG. 4, the source 30 is normally made variable between 0 and 100 volts and is set to a particular voltage depending upon the particular constituent being analyzed for. This mode of operation is particularly suitable in the analysis of halogenated compounds, certain pesticides and herbicides such as lindane, aldrin and DDT, and other materials which show affinity for low voltage electrons. Nitrogen is usually used as a carrier gas in these analyses.

When operating in the region B of the curve of FIG. 8, the low energy photoelectrons are accelerated by the high potential field to generate additional electrons by collision and to ionize certain constituents of the sample. For this mode of operation, the voltage source 30 is relatively high (usually in the range of 400 to 3,000 volts) and is selected to provide sufficient electron energy to ionize the constituents of interest but not to ionize the carrier gas. Ionization detection may be used in the analysis of various hydrocarbons and other organic compounds using argon as a carrier.

In the region C of FIG. 8, electron multiplication has increased to the point at which current through the detector tends to become infinitely high. This is known as the breakdown region and this characteristic may be utilized to an extent. The electron beam voltage detection of constituents. The detector is operated at a high voltage with a current limiting resistor in series with the electrodes to maintain operation in the region C and prevent an excess current from damaging the equipment. With this arrangement, the electrometer amplifier 32 is connected as a voltmeter as shown in FIG. 5 and provides an output which varies as a function of the voltage across the electrodes at which breakdown occurs. When the composition of the gas in the detector changes, the voltage at which breakdown occurs will change and this change in breakdown voltage is quantitatively related to the change in composition of the gas. This mode of operation has been found particularly suited to the measurement of H₂, O₂, N₂, and CO in helium carrier gas. In utilizing the detector of FIG. 1 in breakdown voltage detection, it is preferred to employ the anode 21 about which a stable corona discharge readily occurs. The anode 22 may be connected in parallel with the anode 21.

In another mode of operation, the detector may be used as an electron mobility or drift velocity detector with the source 30 providing an A.C. voltage across the electrodes of a potential to provide operation between regions A and B. Certain sample constituents will lower the random energy of electrons and increase their drift velocity. The collection rate of electrons at the anode is a function of the drift velocity and of the frequency. Hence operation of the detector at a particular frequency provides discrimination between constituents and a quantitative measure of the presence or absence of constituents. Typically the instrument may be operated with half-wave rectified sine wave pulses in the range of 200 to 500 kilocycles per second for detecting diatomic and polyatomic gases, such as nitrogen and propane, in argon and helium carriers.

In another mode of operation, the electron energy spectrum of a sample may be measured to provide a qualitative identification of constituents of a sample. The detector is operated at a reduced pressure, typically in the range of 10⁻¹ to 1 mm. of mercury, at which the current-voltage characteristic curve of the gas exhibits discrete peaks and discontinuities. The more frequent collisions occurring at normal operating pressures smooth out these effects of discrete energies and produce the curve of FIG. 8.

The voltage across the electrodes is cyclically varied over the electron capture range, typically from zero to 25 volts or higher, with the cyclical voltage sweep being rapid enough to complete a cycle during the presence of a particular constituent in the chamber.

An alternative form of the detector is shown in FIG. 2, utilizing identical sample and reference chambers. A lamp 40 is mounted in a housing 41. A cathode 42 and an anode 43 are clamped between housing units 44, 45 to provide a sample space between the housing and anode and the anode 48 are clamped between housing units 49, 50 to provide a reference chamber 51. The sample gas is directed into the chamber 46 via line 52 and may flow out through line 55. Similarly, the reference gas is directed into the chamber 51 through a line 53 and may flow out through line 56. Another stream of reference or carrier gas may be directed into the chamber 54 via line 57 for flow into the chambers 46, 51 past the cathodes 42, 47. Some of this gas may also exit around the lamp base for purging the chamber 54.

In an alternative mode of operation, a stream of reference gas may be directed into the chamber 54 via line 57 for flow outward past the cathodes 42, 47 into the chambers 46, 51, with the line 53 closed and with the sample gas flowing in through line 52 and out line 55. In another mode of operation, the reference gas stream may be directed into the reference chamber 51 (via line 53 or 56 with the other closed), out past the cathode 47 and lamp 40 into the sample chamber 46 past the cathode 42. The line 57 can be closed in this mode with both streams exiting via line 55. These modes of operation provide for a flow of clean gas over the cathode to maintain a constant electron capture rate by constituents of the sample gas stream. The particular arrangement of flow paths in the detector cells is not critical although it is preferred to keep the sample gas stream from impinging on the cathode and it is preferred to have the sample gas stream flow from the anode toward the cathode to provide maximum exposure of the sample to the electrons moving from cathode to anode. The various flow paths illustrated and described may be used with the various physical embodiments shown.

A circuit for operation of the detector of FIG. 2 is shown in FIG. 6. A voltage source 60 is connected between circuit ground and the anode 48 and a similar voltage source 61 is connected between circuit ground and the cathode 42. The cathode 47 and anode 43 are connected together as the input to the electrometer amplifier 32. With identical gases in both reference chambers 46, 51, the currents through the cells will be equal and opposite, providing zero input to the amplifier. The change in composition in the sample resulting in a change of current in the sample cell will produce an unbalance and input to the amplifier. This arrangement substantially compensates for variation in lamp output and amplifier operation. The system may be balanced by making one or both of the voltages 60,
The detectors have been described herein utilizing a conventional ultraviolet lamp as the light source for releasing the photoelectrons from the cathodes. However, it should be noted that any source which will release photoelectrons from a cathode may be used, including mercury lamps, hydrogen lamps, xenon lamps and other D.C., A.C., and R.F. discharge lamps.

Although exemplary embodiments of the invention have been disclosed and discussed, it will be understood that other applications of the invention are possible and that the embodiments disclosed may be subjected to various changes, modifications and substitutions without necessarily departing from the spirit of the invention.

We claim as our invention:

1. In a detector useful in a gas chromatograph, the combination of:
   - means defining a first chamber;
   - means defining a second chamber and including an anode;
   - an apertured cathode positioned between said chambers;
   - a light source in said first chamber for directing light onto said cathode and releasing photoelectrons from said cathode in said second chamber;
   - means for connecting said cathode and anode in series circuit with a voltage source; means for connecting a measuring circuit including an amplifier to said series circuit; and
   - means for flowing a sample through said second chamber for interaction with said photoelectrons to modify the collection at said anode and cathode.

2. In a detector useful in a gas chromatograph, the combination of:
   - means defining a first chamber;
   - means defining a second chamber and including an anode;
   - an apertured cathode positioned between said chambers;
   - a light source in said first chamber for directing light onto said cathode and releasing photoelectrons from said cathode in said second chamber;
   - means for connecting said cathode and anode in series circuit with a voltage source; means for connecting a measuring circuit including an amplifier to said series circuit;
   - means for flowing a stream of gas from said first chamber to said second chamber past said cathode to prevent contamination of said cathode; and
   - means for flowing a stream of sample gas through said second chamber for interaction with said photoelectrons to modify the collection at said anode and cathode.

3. In a detector useful in a gas chromatograph, the combination of:
   - means defining a first chamber;
   - means defining a second chamber and including an anapured anode;
   - an apertured cathode positioned between said chambers;
   - a light source in said first chamber for directing light onto said cathode and releasing photoelectrons from said cathode in said second chamber;
   - means for connecting said cathode and anode in series circuit with a voltage source; means for connecting a measuring circuit including an amplifier to said series circuit;
   - means for flowing a stream of gas from said first chamber to said second chamber past said cathode to prevent contamination of said cathode; and
   - means for flowing a stream of sample gas into said second chamber past said anode for interaction with said photoelectrons to modify the collection at said anode and cathode; and
   - means for flowing both of said streams out of said second chamber.
4. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber;
means defining a second chamber and including a first anode;
means defining a third chamber and including a second anode;
a first apertured cathode positioned between said first and second chambers to provide a sample cell;
a second apertured cathode positioned between said first and third chambers to provide a reference cell;
a light source in said first chamber for directing light onto said cathodes and releasing photoelectrons from said cathodes in said second and third chambers;
means for flowing a stream of sample gas through said second chamber for interaction with said photoelectrons to modify the collection at said first anode and cathode;
means for flowing a stream of reference gas through said third chamber to establish a reference current between said second anode and cathode and to prevent contamination of said cathodes and said first anode;
means for connecting said cathodes and anodes in circuit with a voltage source, an amplifier and a measuring circuit, said measuring circuit being adapted to compare the signals from the sample and reference cells.

5. In a detector useful in a gas chromatograph, the combination of:
means defining a chamber including an anode and an apertured cathode;
means for directing a light onto said cathode and releasing photoelectrons from said cathode in said chamber;
means for connecting said cathode and anode in series circuit with a voltage source; means for connecting a measuring circuit including an amplifier to said series circuit; and
means for flowing a sample gas through said chamber in the zone between said cathode and anode for interaction with said photoelectrons to modify the collection at said anode and cathode.

6. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber;
means defining a second chamber and including a first anode;
means defining a third chamber and including a second anode;
a first apertured cathode positioned between said first and second chambers to provide a sample cell;
a second apertured cathode positioned between said first and third chambers to provide a reference cell;
a light source in said first chamber for directing light onto said cathodes and releasing photoelectrons from said cathodes in said second and third chambers;
means for flowing a stream of sample gas through said second chamber for interaction with said photoelectrons to modify the collection at said first anode and cathode;
means for flowing a stream of reference gas through said first chamber and past said first and second cathodes and second and third chambers to establish a reference current between said second anode and cathode and to prevent contamination of said cathodes; and,
means for connecting said cathodes and anodes in circuit with a voltage source, an amplifier and a measuring circuit, said measuring circuit being adapted to compare the signals from the sample and reference cells.

7. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber;
means defining a second chamber and including a first anode;
means defining a third chamber and including a second anode;
a first apertured cathode positioned between said first and second chambers to provide a sample cell;
a second apertured cathode positioned between said first and third chambers to provide a reference cell;
a light source in said first chamber for directing light onto said cathodes and releasing photoelectrons from said cathodes in said second and third chambers;
means for flowing a stream of sample gas through said second chamber for interaction with said photoelectrons to modify the collection at said first anode and cathode;
means for flowing a stream of reference gas through said third chamber to establish a reference current between said second anode and cathode; and
means for connecting said cathodes and anodes in circuit with a voltage source, an amplifier and a measuring circuit, said measuring circuit being adapted to compare the signals from the sample and reference cells.

8. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber;
means defining a second chamber and including a first anode;
means defining a third chamber and including a second anode;
a first apertured cathode positioned between said first and second chambers to provide a sample cell;
a second apertured cathode positioned between said first and third chambers to provide a reference cell;
a light source in said first chamber for directing light onto said cathodes and releasing photoelectrons from said cathodes in said second and third chambers;
means for flowing a stream of sample gas into said second chamber past said first anode and out of said second chamber between said first cathode and anode for interaction with said photoelectrons to modify the collection at said first anode and cathode;
means for flowing a stream of reference gas through said third chamber past said second anode and cathode, and through said first chamber into said second chamber past said first cathode to establish a reference current between said second anode and cathode and to prevent contamination of said cathodes; and,
means for connecting said cathodes and anodes in circuit with a voltage source, an amplifier and a measuring circuit, said measuring circuit being adapted to compare the signals from the sample and reference cells.

9. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber;
means defining a second chamber and including a first anode;
means defining a third chamber and including a second anode;
a first apertured cathode positioned between said first and second chambers to provide a sample cell;
a second apertured cathode positioned between said first and third chambers to provide a reference cell; and
means for connecting said cathodes and anodes in circuit with a voltage source, an amplifier and a measuring circuit, said measuring circuit being adapted to compare the signals from the sample and reference cells.
means for connecting said first cathode and anode in parallel and current cancelling relation with said second cathode and anode and in circuit with an amplifier, voltage source and recorder;
means for flowing a stream of sample gas through said second chamber for interaction with said photoelectrons to modify the collection at said first anode and cathode; and
means for flowing a stream of reference gas through said third chamber to establish a reference current between said second anode and cathode and to prevent contamination of said cathodes.

10. In a detector useful in a gas chromatograph, the combination of:
means defining a chamber having an anode and an apertured cathode;
means for directing a light onto said cathode and releasing photoelectrons from said cathode in said chamber;
a voltage source;
an electrometer amplifier;
means for connecting said source, amplifier, anode and cathode in a series circuit;
means for recording the output of said amplifier; and
means for flowing a stream of sample gas through said chamber for interaction with said photoelectrons to modify the collection at said anode and cathode.

11. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber having a first anode and a first apertured cathode;
means defining a second chamber having a second anode and a second apertured cathode;
means for directing a light onto said cathodes and releasing photoelectrons from said cathodes in said first and second chambers;
a first voltage source connected to said first cathode and to a first junction point;
a second voltage source connected to said second anode and said first junction point, with said second cathode and first anode connected at a second junction point to form a parallel unit;
an electrometer amplifier;
means for connecting the output of said parallel unit to said amplifier;
means for recording the output of said amplifier;
means for flowing a stream of sample gas through one of said chambers for interaction with said photoelectrons to modify the collection at said anode and cathode in said one chamber; and
means for flowing a stream of reference gas through the other of said chambers to establish a reference current between said anode and cathode in said other chamber and to prevent contamination of said cathodes.

12. In a detector useful in a gas chromatograph, the combination of:
means defining a first chamber having a first anode and a first apertured cathode to form a sample cell;
means defining a second chamber having a second anode and a second apertured cathode to form a reference cell;
means for directing a light onto said cathodes and releasing photoelectrons from said cathodes in each of said chambers;
a first voltage source connected in series with said sample cell;
a second voltage source connected in series with said reference cell;
a reference signal source;
control means for varying the intensity of the light at said cathode to maintain the sample cell output substantially constant and including a comparison circuit having said reference signal source and the sample cell output as inputs;
an electrometer amplifier having the reference cell output as an input;
means for recording the output of said amplifier;
means for flowing a stream of sample gas through said first chamber for interaction with said photoelectrons to modify the collection at said first anode and cathode; and
means for flowing a stream of reference gas through said second chamber to establish a reference current between said second anode and cathode and to prevent contamination of said cathodes.

13. In a detector useful in a gas chromatograph, the combination of:
means defining a chamber including an anode and an apertured cathode;
means for directing a light onto said cathode through the apertures thereof and releasing photoelectrons from said cathode in said chamber;
means for connecting said cathode and anode in series circuit with a voltage source; means for connecting a measuring circuit including an amplifier to said series circuit;
means for flowing a gas stream into said chamber through the apertures of said cathode to prevent contamination of said cathode; and
means for flowing a sample gas stream through said chamber in the zone between said cathode and anode for interaction with said photoelectrons to modify the collection at said anode and cathode.

14. A method of operating a cell to detect quantitatively the presence of selected constituents in a flowing gas stream, including the steps of:
flowing the gas stream through the zone between a cathode and an anode;
exciting the cathode from a location remote from the zone to release photoelectrons from said cathode in the zone;
applying a potential across the cathode and anode of a magnitude to raise the energy of the electrons to a level to produce by collision additional electrons and ionization of the selected constituents; and
measuring the change in anode-cathode current resulting from such ionization.

15. A method of operating a cell to detect quantitatively the presence of selected constituents in a flowing gas stream, including the steps of:
flowing the gas stream through the zone between a cathode and an anode;
exciting the cathode from a location remote from the zone to release photoelectrons from said cathode in the zone;
applying a potential across the cathode and anode of a relatively low magnitude such that electrons are collected at the anode but that electron multiplication by collision does not occur, permitting the selected constituents in the sample to capture a portion of the low energy electrons; and
measuring the change in anode-cathode current resulting from such electron capture.

16. A method of operating a cell to detect quantitatively the presence of selected constituents in a flowing gas stream, including the steps of:
flowing the gas stream through the zone between a cathode and an anode;
exciting the cathode from a location remote from the zone to release photoelectrons from said cathode in the zone;
applying a potential across the cathode and anode in series with a current limiting resistor, with the potential of a magnitude to raise the energy of the electrons to a level to produce by collision additional electrons and breakdown current in the cell, with the voltage across the cell at breakdown varying with the composition of the sample gas; and
11 measuring the change in voltage across the cell to provide a measure of the change in composition of the sample gas.

17. A method of operating a cell to detect quantitatively the presence of selected constituents in a flowing gas stream, including the steps of:
flowing the gas stream through the zone between a cathode and an anode;
exciting the cathode from a location remote from the zone to release photoelectrons from said cathode in the zone;
applying an A.C. potential across the cathode and anode of selected frequency and of a relatively low magnitude such that electrons are collected at the anode but that electron multiplication by collision does not occur; and
measuring the change in anode-cathode current resulting from capture of the electrons by constituents of the sample gas stream.

18. A method of operating a cell to determine changes in electron energy spectrum in the presence of selected constituents in a flowing gas stream, including the steps of:
flowing the gas stream through the zone between the cathode and an anode;
exciting the cathode from a location remote from the zone to release photoelectrons from said cathode in the zone;
maintaining a reduced pressure of selected magnitude in the zone;
applying a potential across the cathode and anode with the magnitude of the potential cyclically varying over the electron capture range; and
measuring the change in anode-cathode current during such cyclical potential variations.

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