May 27, 1958 W. M. HICKAM ET AL 2,836,790

IONIZATION TUBE

Filed May 25, 1953

Fig. 1.

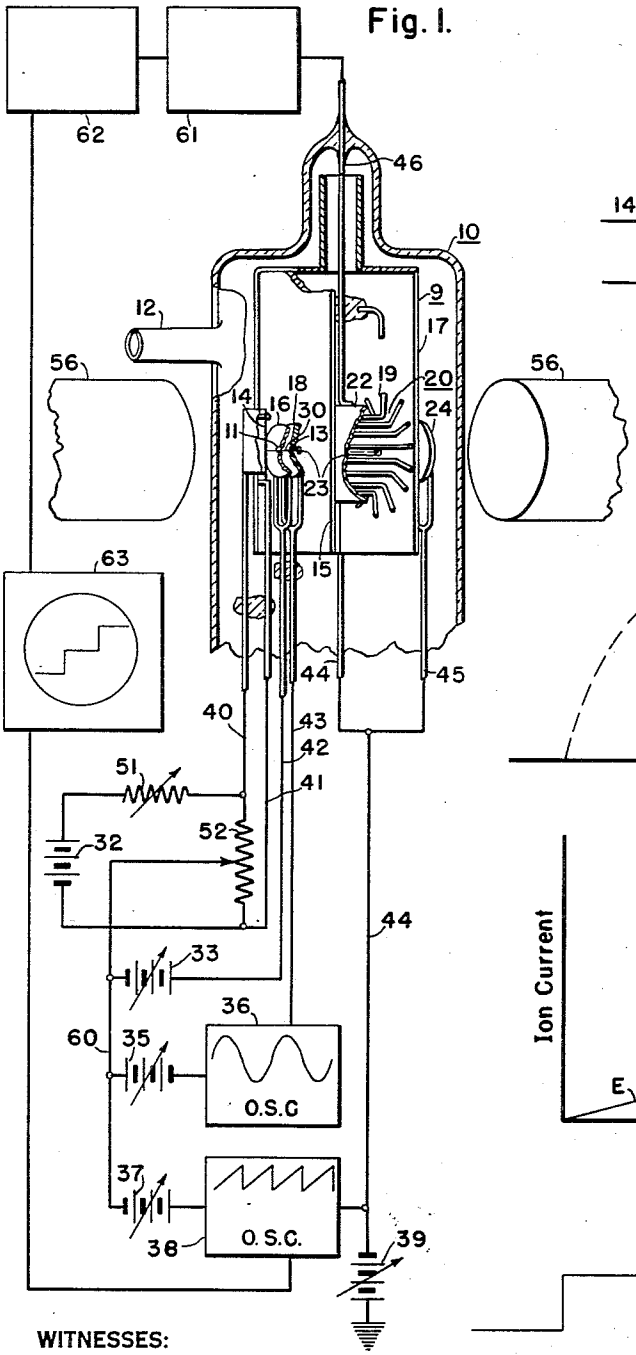


Fig. 2.

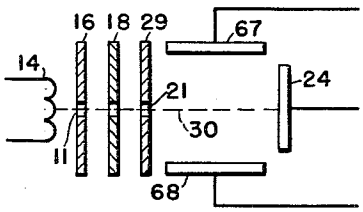


Fig. 3.

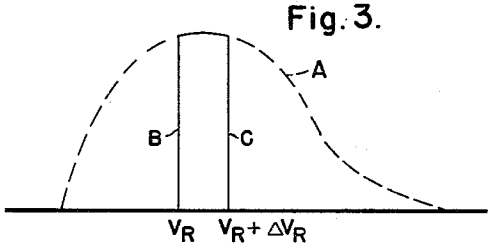


Fig. 4.

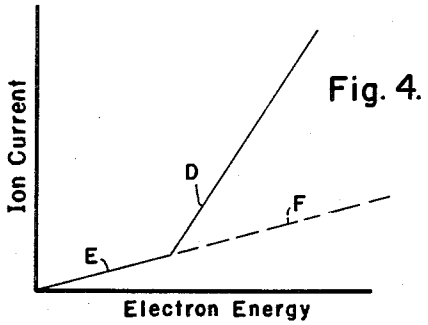
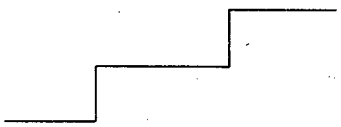


Fig. 5.



WITNESSES:

John E. Hanley

C. F. Renz

INVENTORS
William M. Hickam &
Russell E. Fox

BY
F. E. Browder
ATTORNEY

United States Patent Office

2,836,790

Patented May 27, 1958

2,836,790

IONIZATION TUBE

William M. Hickam and Russell E. Fox, Pittsburgh, Pa., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Application May 25, 1953, Serial No. 356,936

11 Claims. (Cl. 324—33)

Our invention relates to a tube, and more particularly to a tube for the measurement and identification of the constituents in a gaseous mixture.

It is an object of our invention to provide a tube to measure, by obtaining the ionization probability curve of a gaseous mixture, the partial pressures of the gases in the gaseous mixture.

Another object is to provide a tube to identify, by obtaining the ionization potentials of a gas, the components of a gaseous mixture.

It is another object to provide an ionization tube having a varying ion current the difference of which is proportional to an ion current that would be obtained from bombarding a gas with an electron beam having nearly mono-energetic electrons of known energy.

Another object is to provide a system to permit the observation of the detailed structure in the ionization probability curve of a gas where a measurable portion of the ion current is nearly equal to that obtained from bombarding the gas with an electron beam containing mono-energetic electrons of known energy.

Another object is to provide a tube for the identification of gases, which form ions, by determining the precise electron energy required to produce ionization.

Still another object of our invention is to provide a tube for the identification of gas by determining the kinetic energy of the ions formed near the ionization potential of the gas.

These and other objects are effected by this invention as will be apparent from the following description and claims taken in accordance with the accompanying drawing throughout which like reference characters indicate like parts, and in which:

Figure 1 is a perspective view, with a partial section, of a preferred embodiment of our invention;

Fig. 2 is a sectional view showing a modification of the electrode structure of our invention;

Fig. 3 is a curve representing a possible electron energy distribution of an electron emitter;

Fig. 4 is an ionization probability curve for a gaseous mixture of CO and N_2 obtained by our invention; and

Fig. 5 shows the trace obtained on an oscilloscope by taking the first derivative of the ionization probability curve shown in Fig. 4.

Referring in detail to Fig. 1, we have shown an ionization tube which comprises an envelope 10 of glass or other suitable material which is impervious to gas. The envelope 10 is provided with an opening 12 leading to a vessel or other container (not shown) containing the gas to be measured and identified. The opening 12 is also utilized for exhausting the envelope 10. Within the envelope 10 there is provided a plurality of electrodes including a cathode 14, a focusing electrode 16, a retarding electrode 18, an ion chamber 20, an ion collector 22, and an electron collector 24. Suitable lead-in connections and supports are connected from the electrodes to the base (not shown) and the top of the envelope 10.

Within the envelope 10 there is provided means for developing an electron beam 30. Such means may include any known type of "electron gun" and that illustrated in Fig. 1 constitutes only one example of many possible constructions. In the arrangement shown, the electron source comprises the thermionic cathode 14 of a filamentary cathode type. The cathode 14 having two lead in connections 40 and 41 is energized by means of a suitable energy source, such as a battery 32. The battery 32 has its positive terminal connected through a variable resistor 51 to the lead in connections 40, and its negative terminal connected to the lead in connection 41. The variable resistor 51 permits the adjustment of the intensity of electron emission from the cathode 14. A large resistance 52 is connected between the lead in connections 40 and 41.

Somewhat spaced from the cathode 14 is the focusing electrode 16 in the form of a circular disc or diaphragm provided with an aperture 11 for focusing the electron emission from the cathode 14. The focusing electrode 16 is also used to control the intensity of the electron beam. The focusing electrode 16 is, in the normal case, maintained at a positive potential with respect to the cathode 14 of the order of 5 volts and is effective by the aperture 11 in collimating electrons emitted from the cathode 14 into the electron beam 30. The focusing electrode 16 is energized by means of a suitable energy source, such as a battery 33, having its positive terminal connected to the focusing electrode 16 through a lead-in connection 42 with the negative terminal of the battery 33 connected by a conductor 60 to the center tap of the resistor 52.

Adjacent to and somewhat spaced on the side of the focusing electrode 16, remote from the cathode 14, is the retarding electrode 18 of similar construction to that of the focusing electrode 16. The retarding electrode 18 is transverse to the electron beam 30 and is provided with an aperture 13 to permit passage of the electron beam 30. The retarding electrode 18 is in the normal case maintained at a negative potential with respect to the focusing electrode of the order of .5 volt. The retarding electrode 18 is energized by means of a suitable direct-current potential supplied by battery 35 and an alternating current potential supplied by a generator 36 of the order of .1 volt and of the frequency of 10 kilocycles per second connected in series with the retarding electrode 18 through lead-in connection 43. The positive terminal of the battery 35 is connected by means of the conductor 60 to the center tap of the resistor 52.

Somewhat spaced from and on the side of the retarding electrode 18, remote from the cathode 14, is the ion chamber 20. It should be noted here that it is advisable to place adequate shielding around the ion collector 22 and its lead-in connection 46 to eliminate the effects of stray electric fields. This is accomplished by shielding chamber 9 which encloses the ion collector 22 and lead-in connector 46. The side walls 15 and 17 of the shielding chamber are transverse to the electron beam 30 and also serve as the end plates for the ion chamber 20. The ion chamber 20 is comprised of a tubular gridlike member 19 concentric to the electron beam 30 and a portion of the walls 15 and 17 of the shielding chamber 9 which closes off the ends of the tubular grid-like member 19. The ion chamber 20, thus defined, is transversed by the electron beam 30 which may enter through an opening 23 in the end plate 15 and leave through a corresponding opening 23 in the end plate 17. The openings 23 are positioned so as to permit the electron beam 30 to pass through the ion chamber 20. The ion chamber 20 in the normal case is varied in range of the order of 10 to 20 volts positive with respect to the retarding elec-

trode 18. The ion chamber 20 is energized by means of a suitable direct-current potential supplied by a battery 37 and a varying current potential supplied by a generator or oscillator 38. The voltage supply from the generator 38 is in the normal case of the order of 10 volts in magnitude, of sawtooth wave form, and of a frequency of 100 cycles per second. The generator 38 and battery 37 in series are connected to the ion chamber 20 through the lead-in connection 44. The negative terminal of the battery 37 is connected by the conductor 60 to the center tap of the resistor 52.

The ion collector 22 is a tubular member positioned concentric to the grid member 19 of the ion chamber 20. The ion collector 22 is in the normal case maintained at a negative potential of the order of one volt with respect to the ion chamber 20. The ion collector 22 is usually connected into the circuit so as to be near ground potential. The ion collector 22 is connected to an amplifier 61 of suitable design by means of the lead-in connection 46 through the top of the envelope 10. The amplifier 61 is connected to a differential amplifying circuit 62 which in turn is connected to an oscilloscope 63. The oscilloscope 63 is connected to the sawtooth generator 38 so as to obtain a voltage to trigger the oscilloscope 63 and thereby synchronize the oscilloscope 63 with the sawtooth generator 38.

The electron collector 24, in the form of a circular disc or plate, is positioned adjacent to and exterior to the ion chamber 20 so as to collect the electrons from the electron beam 30 as they leave the ion chamber 20 by means of the aperture 23 of the end plate 17. The electron collector 24 is connected by means of the lead-in connection 45 to the lead-in connection 44 so as to be at the same potential as the ion chamber 20. The lead-in connection 44 is also connected to ground through a battery 39.

A magnetic field is impressed by a pair of pole pieces 56 coincident with the electron beam 30 so as to collimate the electrons. The magnetic field may be produced by a permanent magnet or an electromagnet.

A modification of the electrode structure in Fig. 1 is shown in Fig. 2 in which the ion chamber 20 and the ion collector are replaced by an accelerating grid 29 and a set of parallel plates 67 and 68. The accelerating grid 29 is of a similar construction to that of the focusing electrode 16 and retarding electrode 18 and is adjacent to the retarding electrode 18. The accelerating grid 29 is positioned transverse to the electron beam 30 and has an aperture 28 to permit the electron beam 30 to pass. A similar direct-current potential and alternating current potential would be applied to the accelerating grid 29 as was applied to the ion chamber 20 in Fig. 1. The ion collector in Fig. 2 is in the form of parallel plates 67 and 68 which are positioned on opposite sides of the electron beam 30. It is necessary to apply an electric field between the plates 67 and 68 so that the ions produced by the electron beam 30 may be collected on one of the plates 67 or 68. It is possible to pulse the electric field across the plates 67 and 68 in synchronism with the alternating current potential applied to the retarding electrode 18 so as to have a field free space between the parallel plates when a pulse of electrons from the electron beam 30 arrives between the parallel plates 67 and 68. It is again advisable to place adequate shielding around the ion collector and its leads to eliminate the effect of stray electric fields.

In the operation of the device, a gas sample to be analyzed is introduced into the envelope 10 through the opening 12. As illustrated in Fig. 1, the electrons emitted from the cathode 14 are directed in an electron beam 30 through the aperture 11 of the focusing electrode 16 having a positive potential with respect to the cathode 14. The electron energy of distribution of the electron beam 30 may be represented by curve A in Fig. 3.

For purposes of explanation, if we assume the retarding electrode 18 is operated at a negative direct-current potential V_R with respect to the cathode 14, only those electrons with sufficient kinetic energy to overcome this negative potential barrier can pass beyond the retarding electrode 18. This results in a sharp low energy cut off as shown by the line B in Fig. 3. It is to be noted that the lowest energy electrons in the electron beam 30 in this new distribution have near zero velocity at the retarding electrode 18 and hence their kinetic energy in the ionization chamber 20 will be determined by the difference in the potential between the retarding electrode 18 and the positive potential or accelerating potential on the ion chamber 20. The electron beam 30 entering the ion chamber 20 will cause the ionization of the gas sample if of sufficient energy.

When the electrons in the electron beam 30 bombard the molecules in the gas sample in the ionization chamber 20, positively charged ions are formed in amounts characteristic of the structure of the molecules and in amounts proportional to the electron beam 30 intensity and velocity. The positively charged ions pass through the grid-like structure 19 to the more negative biased ion collector 22, causing an ion current to flow through the ion collector circuit, which current may be measured by suitable means.

If the direct potential voltage V_R applied to the retarding electrode 18, for purpose of an explanation, is now changed to $V_R+\Delta V_R$ a new energy distribution of electrons in the electron beam 30 will be obtained and the low energy cut off is shown by the line C in Fig. 3. The ion yield from the electrons in this distribution is then measured and the difference in the ion yield from these two energy distributions V_R and $V_R+\Delta V_R$ is equal to the ion yield from the electrons mono-energetic within the area defined by ΔV_R. The electrons within this area ΔV_R are substantially of zero velocity at the retarding electrode 18 and the energy of the electrons in the ion chamber 20 is determined by the accelerating voltage of the ion chamber 20.

By applying an alternating voltage of magnitude ΔV_R to the retarding electrode 18, a difference current for a fixed value of ion chamber 20 voltage yields a single point on the ionization probability curve by utilizing a narrow band current amplifier 61 in the ion collector circuit. The ΔV_R voltage applied to the retarding electrode 18 is obtained from the alternating current potential generator 36.

It should be noted that in the use of the described method the contact potential between the cathode 14 and the electrodes 16, 18 and 20 does not enter into the determination of the electron energy of the electrons within ΔR. The contact potential between the retarding electrode 18 and the ionization chamber 20 has the sole effect on the electron energy of the electrons within the beam 30. The electrodes 16, 18 and 20 are made of similar metals to reduce the contact potential effect with respect to the filament. It should also be noted that the difference in the varying ion yields due to alternating voltage on the retarding electrode 18 as measured in the ion collector circuit results from a nearly mono-energetic electrons of known energy. It is this feature of our invention which permits obtaining a true ionization probability curve that can be used for quantitative gas analysis.

The identification of the gas constituents is made by the measurement of the ionization potentials. In Fig. 1, the described voltages applied to the elements are for measuring the formation of positive ions of the gas. It is obvious to those skilled in the art that it would be possible with the electrode structure as shown in Fig. 1 to apply a positive voltage to the ion collector and with sufficient electron energy in the electron beam 30 for measuring the formation of negative ions of a gas for the purpose of identification of certain gases. It is also possible to identify certain gases by observing the kinetic energy of the ions formed. This measurement would require a re-

tarding potential between the ionization chamber 20 and the ion collector 22 such that only ions formed with a certain kinetic energy would reach the ion collector 22.

The ionization tube is designed to operate at sufficiently low pressures (below 10^{-3}) that the ion yield is a linear function of pressure for constant electron current. We have found that the ion yield is a linear function when mono-energetic electrons are used. In Fig. 4 we have plotted typical ionization probability curves for a blend of CO and N_2. Curve E is the ionization produced by CO while D is the ionization for CO and N_2. By taking the extrapolated curve F and subtracting it from curve D, one can obtain ionization due to N_2 alone.

Using the described system it is possible to make a quantitative analysis of a gas mixture. If the selected electron band is introduced and removed by applying the voltage ΔV_R to the retarding electrode with the oscillator 36, the use of a narrow band pass amplifier 61 in the ion collector circuit permits direct measurement of ions formed by mono-energetic electrons of known energy. The electron energy as determined by the potential between the retarding electrode 18 and ion chamber 20 is varied periodically in a linear fashion by the oscillator 38 having a sawtooth wave form.

If the oscilloscope 63 is connected in the ion collector circuit with the amplifier 61 and the scope is triggered by the sawtooth generator, the scope will display a pattern whose envelope will be that shown in Fig. 4.

Furthermore, by the insertion of a differential amplifier 62 in the ion collector circuit, it is possible to observe directly on the scope the first or second derivative of the ionization probability curve. A typical trace is shown in Fig. 5 where the first derivative of the ionization curve shown in Fig. 4 was taken. This curve can be correlated with the concentration of the individual gases in the mixture and thus can be used for a quantitative analysis of the gases or for monitoring to maintain the concentration constant in control processes.

It is obvious that the generators 36 and 38 may be removed from the circuit shown in Fig. 1 and vary the voltages by use of batteries 35 and 37. A direct current amplifier and meter would be connected in the ion circuit and readings taken directly and the difference in readings for two voltages on the retarding grid 18 at one value of accelerating voltage could be plotted. By plotting a number of these points, using the same voltages on the retarding electrode 18 and varying the acceleration voltage, the ionization probability curve could be obtained.

While we have shown our invention in several forms, it will be obvious to those skilled in the art that it is not so limited, but is susceptible of various other changes and modifications without departing from the spirit and scope thereof.

We claim as our invention:

1. A tube comprising an envelope having an orifice to provide admittance of a gas, an electron gun for bombarding the gas with electrons to produce ions, means for applying a field to modify the energy distribution of said electrons, a target electrode on which the electrons impinge, and a collector electrode for collecting ions formed.

2. An electrical discharge device for use in analyzing a gas by establishing ionization currents therein comprising an envelope having an opening through which a sample of gas to be examined is introduced, an electron gun within said envelope for developing an electron beam for bombarding the gas in said envelope to produce ions of substances present in the gas, said gun including a first electrode for emitting electrons having a given electron energy distribution, a second electrode, means for applying a varying potential to said second electrode to alter said electron energy distribution, a target for said electron beam, and an ion collector electrode positioned between said electron gun and said target for collecting ions formed.

3. An electrical discharge device for use in analyzing a gas by establishing ionization currents therein comprising an envelope having an opening through which a sample of gas to be examined is introduced, means within said envelope for developing an electron beam for bombarding the gas in said envelope to produce ions of substances present in the gas, said means including a first electrode for emitting an electron beam having a wide electron energy distribution and a second electrode having a varying potential applied thereto for varying said energy distribution of the electrons within said electron beam, a target for said electron beam and an ion collector electrode positioned between said means and said target for collecting the ions formed.

4. An electrical discharge device for use in analyzing a gas by establishing ionization currents therein comprising an envelope having an opening through which a sample of gas to be examined is introduced, means within said envelope for developing an electron beam for bombarding the gas sample to produce ions of substances present in the gas, said means including a retarding electrode, means for applying a potential to said retarding electrode for varying the normally wide energy distribution band of electrons from the emitting source of said electron beam in a uniform manner, a target for said electron beam, an ion collector electrode positioned between said electron gun and said target for collecting the ions formed, and means for measuring the difference in ion current due to the varying effect of said retarding electrode.

5. An electrical apparatus for use in determining the property of a gas comprising an envelope having an opening through which a sample of gas is introduced, means within said envelope for producing an electron beam for bombarding the gas in said envelope to produce ionization of molecules of the gas, said means including a retarding electrode and an electron emitting source, means of applying an alternating current potential to said retarding electrode so as to vary the kinetic energy distribution of the electrons from said source in a uniform manner, a target for said electron beam, an ion collector positioned between said electron producing means and said target for collecting the ions formed, and means for measuring the difference in varying ion current due to the alternating current potential applied to said retarding electrode of said electron producing means.

6. An electrical discharge device for use in analyzing a gas by establishing ionization currents therein comprising an envelope having an orifice through which a sample of a gas to be examined in introduced, means for producing an electron beam within said envelope including an electron emissive source and means for varying the energy distribution of the electrons from said source, means for collecting the electrons from said electron beam, and means for collecting the ions due to the ionization of the molecules of the gas introduced into said envelope.

7. An ionization tube comprising an envelope provided with an opening for the introduction of molecules of a gas into said envelope, a first electrode structure for developing an electron beam within said envelope having a wide band of electron energy distribution, a second electrode structure with a potential applied for varying the energy distribution of the electrons within said electron beam, an anode for collecting the electrons from said electron beam, an accelerating electrode positioned between said anode and said second electrode structure, an ion collector disposed between said accelerating electrode and said anode and an ion circuit connected to said ion collector for registering the ion current due to varying the voltage on said second electrode structure.

8. An electrical discharge device for use in analyzing a gas by establishing ionization currents therein comprising an envelope having an orifice through which a sample

of gas to be examined is introduced, a plurality of electrodes in said envelope including an electron-emitting element, a focusing electrode cooperating with said electron-emitting element for developing an electron beam, an anode disposed in the path of said electron beam for collecting electrons, a retarding electrode disposed transversely to the electron beam between the anode and focusing electrodes means of applying a varying potential to said retarding electrode, an accelerating electrode positioned between said anode and said retarding electrode and an ion collector disposed between said anode and said accelerating electrode.

9. A device comprising an envelope provided with an opening for the introduction of molecules of a gas into said envelope, an electron-emitting element positioned within said envelope, an anode for collecting the electrons from said electron-emitting element, a focusing electrode disposed between said electron-emitting element and said anode and cooperating with said electron-emitting element for developing an electron beam, a magnetic field coincident with said electron beam for collimating the electrons within said electron beam, a retarding electrode transverse to said electron beam and positioned between said focusing electrode and said anode, means for applying a varying voltage to said retarding electrode so as to vary the energy distributions of the electrons within said electron beam, an ion chamber disposed between said anode and said retarding electrode comprising a tubular grid-like member concentric with said electron beam, and an ion collector adjacent to said tubular grid-like member.

10. A device comprising an envelope provided with an opening for the introduction of molecules of a gas into said envelope, a first electrode structure for developing an electron beam, a second electrode structure disposed in the path of said electron beam for collecting the electrons emitted from said first electrode structure, means for developing a magnetic field coincident with the electron beam, a third electrode structure positioned between said first and second electrode structure, means for applying a varying potential to said third electrode for varying the energy distribution of the electrons within said electron beam, a fourth electrode structure positioned between said third electrode structure and said second electrode structure for accelerating the electrons within said electron beam and forming a field-free region between said second electrode structure and said third electrode structure, a fifth electrode structure disposed near to said fourth electrode structure for collecting the ions formed as a result of the ionization of the molecules of gas by the electron beam within the field-free region.

11. An electron discharge device comprising an electron gun for generating an electron beam, said gun including an electron emissive element for generating electrons having a wide band of energy distribution, a retarding electrode and means for applying a varying potential to said retarding electrode for altering the energy distribution of said electrons so as to obtain a sharp, low energy cutoff distribution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,507,652	Smith	May 16, 1950
2,516,704	Kohl	July 25, 1950
2,639,397	Clark et al.	May 19, 1953
2,648,818	Cohen	Aug. 11, 1953