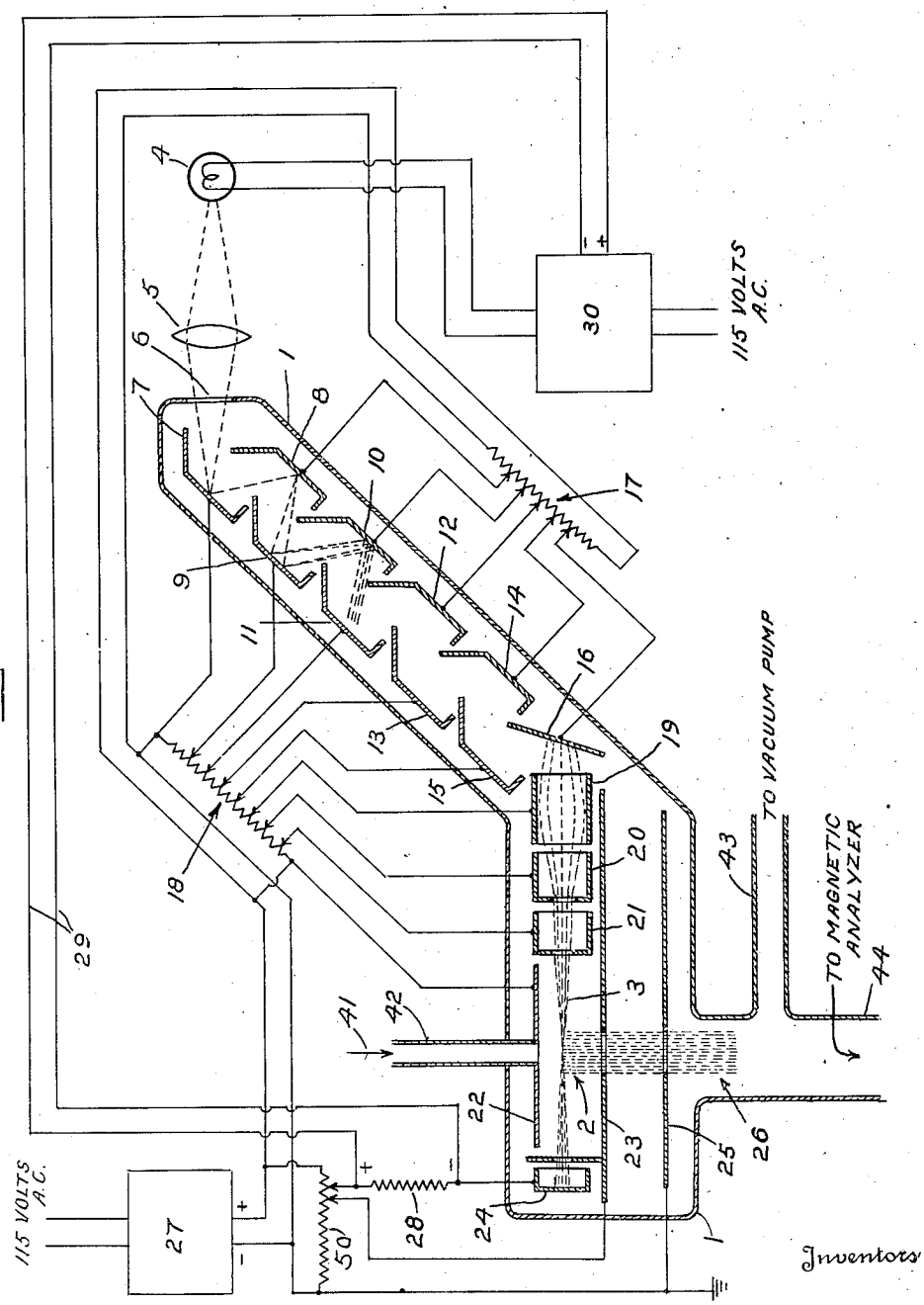
Dec. 28, 1948. N. D. COGGESHALL ET AL 2,457,530

ELECTRON GUN FOR MASS SPECTROMETERS

Filed Aug. 6, 1946 2 Sheets-Sheet 1

Fig. 1.



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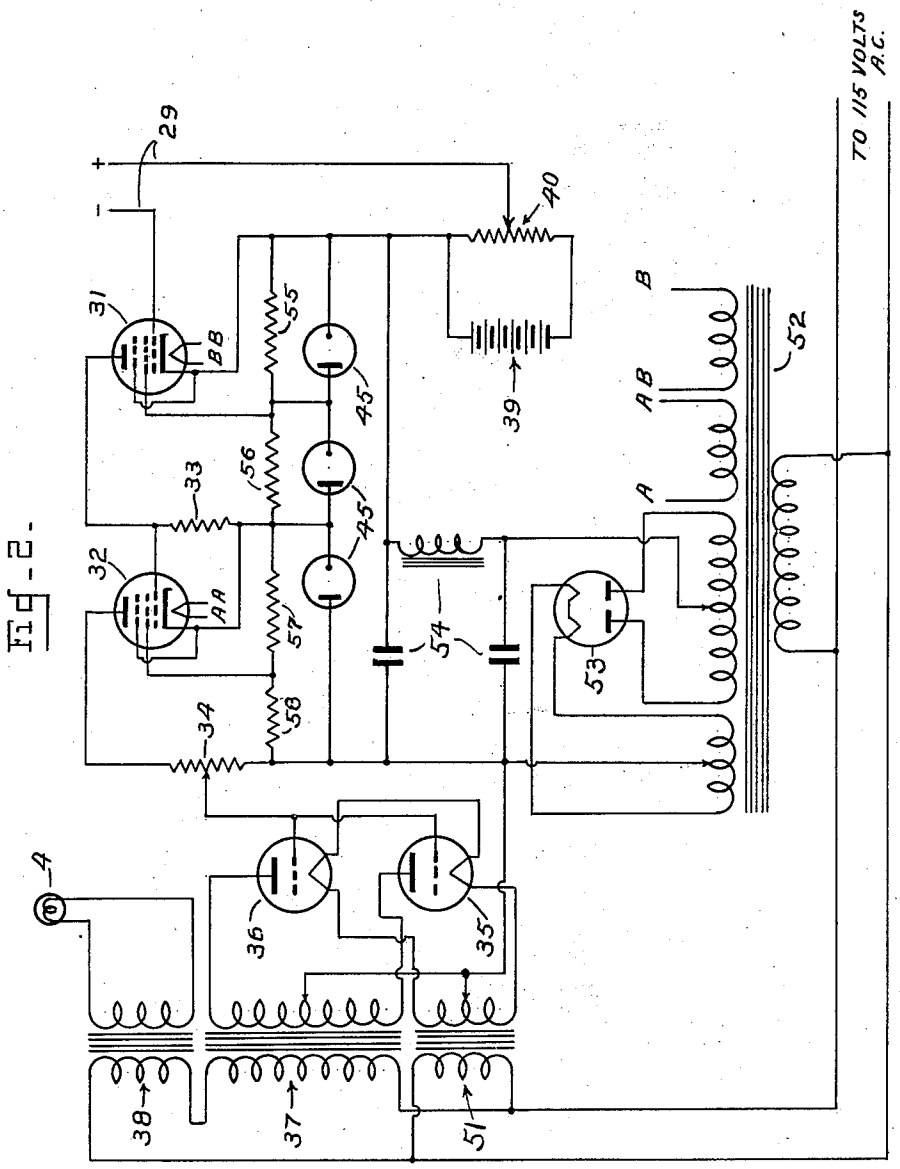


Fig-2-

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Patented Dec. 28, 1948

2,457,530

UNITED STATES PATENT OFFICE

2,457,530

ELECTRON GUN FOR MASS SPECTROMETERS

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Application August 6, 1946, Serial No. 688,736

5 Claims. (Cl. 250—41.9)

1

This invention relates to devices for furnishing a plurality of electrons in motion and for employing the said electrons.

The mass spectrometer is today an analytical and research instrument of great economic importance. It is used for routine analysis of gas and liquid samples, hydrocarbon analyses adjunct to refinery control, for following isotopic tracers, for studying molecular energy levels, and for other purposes. In the mass spectrometers in use today the ion beam is formed by that component of the aparatus known as the ion source. Basically, this consists of an arrangement of electrodes across which there are impressed direct current voltages. In the free space between the electrodes an electron beam is made to pass. In traversing this region the electrons create positive ions from the gas molecules or atoms present. These ions are drawn in one direction by the impressed voltages, and by means of two slit apertures a beam of ions is defined. The electron beam has heretofore been formed by a filament and electrode arrangement known as an electron gun. It may consist merely of a filament which emits electrons and one or more electrodes with apertures which are at a positive potential relative to the filament. This results in electrons being drawn towards the electrodes and passing through the apertures to form a beam. A relatively weak magnetic field in the direction of electron travel may be employed to aid in the forming and maintaining of a beam.

The filament used by the electron gun may be tungsten, thoriated tungsten or the source of electrons may be an indirectly heated oxide coated cathode. In any case, the electron beam originates from a source of thermionic emission. A thermionic emission source of electrons, although practically the only type heretofore usable in mass spectrometers, has several very serious disadvantages. These disadvantages, which will be explained below, result in considerable expenditure of time and money to keep the instrument in operating order.

The enumeration and description of the disadvantages of the thermionic emission type of cathode may be limited to a discussion of ordinary tungsten filaments, inasmuch as they are easier to use than oxide coated cathodes or thoriated tungsten filaments. The latter two are very susceptible to "poisoning" of the emitting surfaces by improper vacuum conditions and are not considered practical to use in a routine instrument. Furthermore, most of the disadvantages named for the tungsten filament will be common to these other two types of sources.

2

In the application of the mass spectrometer to the problem of quantitative analysis of multicomponent mixtures of hydrocarbons the cracking patterns of the individual components are used. When a single compound is examined in the instrument it is found that in the ion beam there are ions of many different masses. That is, there may be the molecule ionized by losing an electron, but it may also dissociate by electron impact to form neutral and ionized fragments. For example, n-butane will give rise to ions of masses 58, 56, 43, 42, and so forth. Iso-butane will give rise to ions of the same masses but their relative intensities will be considerably different. The pattern of ionic masses and their relative intensities for any compound is referred to as its "cracking" pattern and it is the differences in these patterns that make the analysis of multicomponent mixtures possible. The instrument is calibrated for any particular mixture by examining in a pure form each of the components contained in the mixture. This data, that is, the relative intensities of the various ions formed, must be known accurately in order to perform accurate quantitative analyses. Furthermore, the instrument must be so designed and operated as to render the cracking patterns as independent as possible of such parameters within the ion source as may change with time. This condition is very important for if not satisfied it may be necessary to recalibrate the instrument quite often, perhaps once a week or every few days, and this is an expensive and time consuming operation. As will be explained, the filament type of electron source is very troublesome in causing changes in the cracking patterns.

Although the major part of the ions coming from the ion source are due directly to electron impact on the gas molecules there are a substantial number that owe their origin partly or wholly to the filament. One reason for this is that the filament which operates in the neighborhood of 2000° Kelvin causes the dissociation of some of the molecules that impinge on it. The neutral fragments may then by diffusion enter the ionization region where they may be converted into ions. Also the process may take place wherein some of the parent molecules or their fragments may be ionized on the surface of the filament and subsequently diffuse into the ion beam. The two above effects, although not responsible for the major number of ions in the ion beam, can contribute a substantial number. Furthermore,

the contribution from these two effects depends greatly upon the filament temperature and surface condition which change with time and mode of operation. This causes the cracking patterns of the pure compounds to change with time and mode of operation, a highly undesirable situation.

Attempts have been made to remedy the above effects by placing a separate vacuum pumping connection on the filament assembly so that there is a pressure differential across the apertures through which the electrons pass from the filament into the ionization region. This is not very successful, due to the high mobility of the molecules and ions at the tempertures encountered and due to long mean free paths at the pressures used.

Another disadvantage somewhat akin to the ones explained above comes about from the heat output from the filament. As the filament is surrounded on all sides by electrodes or shielding, and as the gas pressure surrounding it is low, being of the order of 10^{-4} mm. of mercury, most of its heat output is absorbed as radiant energy by the metal parts of the electron gun and ion source. This results in a temperature of these parts higher than the ambient one. Molecules impinging on the walls of the ion source will assume a nearly equivalent temperature and this affects their mobility or average velocity. This latter quantity is an important one in controlling the speed of pumping of the gas through the ion source. This means then that the temperature of the ion source affects the molecular density within it and this in turn affects the intensity of the ion beam which it is desirable to maintain very constant. If the temperature of the ion source could be maintained very constant, the above effect would not be very important. However, due to the relatively poor vacuum in which the filament must operate and to the variety of compounds with which it has contact, the surface conditions on it change in such a manner that it operates at different temperatures at different times. This gives rise to the effects just explained and it constitutes a serious disadvantage in using this type of electron source. For example, we have experimentally found that the sensitivity of the mass spectrometer may vary as much as 0.3 per cent per degree Centigrade change of ion source temperature. Sensitivity as here used means the ion intensities per unit pressure of admitted gas.

As we have seen above, there are strong disadvantages of a filament or heated cathode type of electron source when it is desired to operate a mass spectrometer under very constant conditions. There are in addition certain other disadvantages due to the frequent maintenance this type of electron source requires. Since the gas atmosphere in a mass spectrometer is of the order of 10^{-4} mm. of mercury, which is a much higher pressure than in a sealed vacuum tube, the filament is subjected to the emission inhibiting effects of the different gases. As a result the operating temperature must be raised above that for a filament in a vacuum tube of the conventional type, in order to get sufficient emission. At this temperature, an appreciable amount of tungsten evaporates, weakening the filament and eventually necessitating a change of filaments, a costly job and one which puts the instrument out of operation for at least several hours.

Often, the gas being examined by a mass spectrometer has oxygen as one of its constituents. It

is well known that oxygen can poison certain electron emitting surfaces and that it can cause oxidation of tungsten filaments, thus shortening their lives. Another disadvantage of the tungsten filament is its fragility. For example, a filament that has been operated for some time becomes very brittle and a slight disturbance will break it. This means that practically each time the filament assembly is removed from the ion source for inspection or repair, the filament must be replaced before re-assembly. This is very undesirable, as it increases the time during which the instrument is out of operation.

It is an object of this invention to provide an electron gun for mass spectrometers, cathode ray oscillographs, television equipment, electron microscopes and other devices, that does not have the disadvantages named above which are attendant to a thermionic emission type of electron source.

It is a further object of this invention to provide an electron gun for the above named instruments which has certain positive advantages, as will be apparent from the following explanation, over conventional types of electron guns which employ thermionic emission as the source of electrons.

It is another object of this invention to provide apparatus and several alternative means for the close and accurate control of an electron stream emerging from the new type of electron gun described below.

A further object of this invention is to provide means of using the ion accelerating voltage supply of a mass spectrometer to operate our new type electron gun, when it is used on a mass spectrometer, thus eliminating the need of extra equipment.

Still another object of this invention is to provide a mass spectrometer having an external light source casting light through a window in an envelope containing a photocathode, electron multiplier and electron lens for forming a stream of electrons for ionizing gaseous and gaslike matter in said envelope.

Other objects and advantages, together with certain details of construction and mode of operation, will be apparent from the following description of a preferred embodiment of the invention as illustrated in the accompanying drawings, and in which,

Figure 1 is a diagram illustrating the application of our invention as a source of electrons in a mass spectrometer, and

Figure 2 shows one type of control circuit that may be used to regulate the current output from the electron gun.

In Figure 1, the vacuum tight envelope housing the ion source and electron gun is represented by 1. Inside the envelope, numeral 2 represents the region of ionization through which passes the stream of electrons 3. In one mode of practicing this invention there is a light source 4 which may be a tungsten filament incandescent lamp. Light from 4 is focussed by the lens 5 onto a photosensitive cathode 7, passing into the evacuated envelope through the transparent window 6. Electrodes 8, 9, 10, 11, 12, 13, 14, 15, 16 are arranged inside the evacuated envelope in juxtaposition somewhat as shown and maintained at successively increasing positive potentials in the known manner of electron multipliers. Light from the lamp 4 falling on the cathode 7 causes photoelectrons to be emitted from the cathode 7. These photoelectrons are drawn towards electrode

8 by the potential difference between the cathode 7 and the electrode 8. These electrons strike electrode 8 with considerable velocity and cause secondary electrons to be emitted. The secondary electrons are emitted with a small initial energy, of the order of a few volts, and as a result are drawn to electrode 9 by the potential difference between electrodes 8 and 9. At the surface of electrode 9, these electrons in turn cause the emission of more secondary electrons. As the surfaces chosen for the electrodes 8, 9, and so on, are such that the secondary electron emission coefficient is greater than unity, being preferably from 4 to 8, there is a multiplication at each successive electrode. As a result the electron emission from electrode 16 is very much larger than that from electrode 7. There are a number of factors that control the final current from electrode 16 and they will be discussed below when automatic controlling methods of the unit are described.

The operating voltages for the electrodes of the electron multiplier are obtained by tapping off suitable fractions of the resistances 17 and 18. The tapping off contacts are made so that each successive electrode is at a higher potential, that is, 8 is higher that 7, 9 is higher than 8, and so forth. These voltages may alternatively be obtained by suitably tapping off from a single resistor.

Electrons leaving the last secondary emission electrode 16 are focussed by means of an electron lens. One way in which this may be done is to accelerate them towards the cylindrical electrode 19 and towards the electrodes 20 and 21. The three electrodes 19, 20 and 21 may be so arranged and have such potential distribution as to form a beam of electrons from those originating from electrode 16. This illustrates only one of several types of electrostatic and/or magnetostatic electron lenses which may be employed.

The beam of electrons is made to pass between electrodes 22 and 23 and through an aperture in 23, to the electron collector electrode 24. A potential is maintained between electrodes 23 and 24 so that 24 functions essentially as a trap and secondary electrons from electrode 24 are drawn back to it. The voltages for the focussing electrodes 19, 20 and 21 may be obtained by taps from the resistor 18 and the potential between electrodes 23 and 24 may be obtained from taps on resistor 50.

In operation, the electron beam traversing the region between electrodes 22 and 23 creates ions by impact of the individual electrons on the gas molecules or atoms present. These ions, which are mainly positive, are drawn by the existing potential differences towards electrode 23. A slit in electrode 23 allows some of the ions to emerge into the region between electrodes 23 and 25. A large potential difference, of the order of a thousand volts is maintained between electrodes 23 and 25. The ions are thereby further accelerated and as a result pass through a slit in electrode 25 in a spatially well defined beam of ions 26 having the form of a ribbon. This beam of ions 26 goes to the magnetic analyzer through tube 44 and is separated into individual beams of different mass characteristics in the usual manner of a mass spectrometer. The gas to be analyzed enters the envelope 1 along the path indicated by arrow 41 through inlet tube 42 which is normally small in cross section, a vacuum pump being connected to tube 43.

As seen in Figure 1, all the voltages required to operate the ion source and the associated electron multiplier electron gun are obtained from one voltage supply shown as 27. It is of great advantage to be able to use the same high voltage supply for both the acceleration of the ions and also for operation of the electron gun.

In one mode of operation, the different ion masses to be found in the ion beam 26 are successively brought to the mass spectrometer collector by varying the magnetic field of the magnetic analyzer in a manner well known in mass spectrometry. Another mode of operation is to bring the different ion masses to the collector by varying the total ion accelerating voltage. The former mode is to be preferred, however, as it lends itself to overall simpler operation.

It is very important to keep the electron gun current quite constant as the intensity of the ion beams will depend upon it. As mentioned above, there are a number of ways in which the current output of the electron gun may be controlled and in Figure 1 is to be seen one preferred manner. In this case, the electron collector 24 collects a certain fraction of the total electron emission from electrode 16. The electron current collected by 24 is that which traverses the entire length of the ionization region. Current collected by electrode 24 returns to electrode 16 after passing through the high resistance 28. Variations in the current from electrode 24 will cause voltage variations across resistance 28 and these variations are conducted by lead wires 29 to the low voltage power supply 30.

The power supply 30, which is shown in more detail in Figure 2, responds to voltage variations in leads 29 in such a way as to maintain constant the electron current that passes through the ionization region and which is collected by electrode 24. The control is through the temperature of the filament of lamp 4, that is, an increase of voltage across resistor 28, due to an increase in electron current, will cause a drop in the filament temperature and conversely a decrease in voltage across resistor 28 will cause an increase in filament temperature of lamp 4. These temperature changes may be made in the direction to maintain a constant electron flow, since the number of photoelectrons initially leaving electrode 7 depends upon the light output of lamp 4.

Figure 2 shows the controlling circuit which utilizes and amplifies the signal on leads 29 in such manner as to control the heating current in lamp 4. Here 31 represents a first amplifier tube and 32 a second. When the electron current falling on collector 24 (Figure 1) exceeds its normal value it causes an increase of potential drop in resistance 28 (Figure 1) which causes an increase of negative grid bias in tube 31 of Figure 2. Grid bias battery 39 and potentiometer 40 provide grid voltage and adjustment thereof in tube 31 in conjunction with resistor 28 of Figure 1. The change in control grid bias of tube 31, due to the increase of potential drop in resistor 28 decreases the plate current of tube 31, with the result that the potential drop across resistor 33 is decreased. As this drop controls the bias of the control grid of tube 32, the result of the above changes is an effective positive increase of the control grid bias in tube 32 with a consequent increase in its plate current. This increase of plate current will cause an increased potential drop across resistance 34. Resistance 34 controls the bias of the grids in both tubes 35 and 36, the net result being a decrease in the plate currents of both. The triodes 35 and 36, together with the secondary windings of trans-

formers 37 and 51, which supply the plate and heater voltages, form a dissipative circuit controlled only by the grid voltage which is the voltage drop across resistor 34.

It is to be noticed that the transformer 37 which supplies the plate voltage for tubes 35 and 36 has its primary in series with the primary of transformer 38 which supplies the current for lamp 4. Thus, if the current flow through tubes 35 and 36 is reduced, it is equivalent to increasing the impedance of the secondary of transformer 37. This in turn increases the impedance of the primary of transformer 37, with the result that the primary current of both 37 and 38 is reduced. A reduction of primary current of transformer 38 reduces the secondary current with the result that the light intensity of lamp 4 is reduced. This is the desired end effect, as it will reduce the number of photoelectrons emitted by electrode 7 of Figure 1.

If one assumes the opposite condition, that is, a decrease of electron current reaching electrode 24 and follows out the resulting changes of operation of the components of Figure 2, one finds that the end result is an increase of light from lamp 4 which would cause more initial photoelectrons to be emitted. Thus, we have the conditions satisfied for self regulation, that is, the electron current or stream of electrons creates a signal which is utilized to maintain the current constant. In Figure 2, power is supplied to tubes 31 and 32 through power transformer 52 with rectifier 53 and filter components 54 in conventional manner. Screen voltages are obtained through resistors 55, 56, 57, 58 whose voltages are regulated by regulator tubes 45.

The above circuit represents one method of achieving self control but it is not by any means to be construed to be the only method by which the result may be achieved, since it is intended to represent only one operable method of many. Other well known types of regulating circuits may be used, and it is intended that their use fall within the scope of this invention.

Although we have shown the control signal coming from the current to the collector electrode 24 of Figure 1, there are other means of obtaining a control signal and it is intended that they all fall within the scope of this invention. For example, that portion of the electron current which is collected by electrode 21, Figure 1, may be used for a control signal and similarly for the currents collected by electrodes 23, 20 or 19. Furthermore, the final means of control, which is the temperature of the filament of the lamp 4 in the mode of operation explained above, can be any of several possibilities each of which falls within the intended scope of this invention. For example, the control signal may be utilized to control a power supply so that a decrease of electron current would cause an increase of voltage between the electrodes of the electron multiplier and, conversely, an increase would cause a decrease of voltage. The circuit for such a control would be familiar to those versed in the art.

Although we has illustrated our invention with one arrangement of electrodes, it is not to be limited to this arrangement but rather applies to all such configurations as admit multiplication of an electron current by secondary electron emission. Also, we have shown our new type electron gun as applied to a mass spectrometer; however, it is not to be construed that this places a limitation on its use, as other applications, as in electron microscopes, cathode ray oscillographs, television equipment and other uses, are intended.

Our illustration also shows an electron multiplier, the initial electrons of which are those due to photo-emission. It is not intended that this invention be limited to electron multipliers of this type but should embrace all types including those where the initial electrons are due to thermionic emission, electrons from radioactive transformations, and so forth.

Some positive advantages of our new type of electron gun may be mentioned. Our improved new electron gun has unlimited lifetime and does not need to be periodically replaced as does a tungstem or other type of filament. Our new type of electron gun may run cold, thus eliminating two undesirable features of the filament type gun, namely, the change of cracking pattern due to pyrolysis on the filament surface and the overall rise of temperature of the ion source which affects instrument sensitivity. Our new type of electron gun is sturdier. If it is desired to remove it for alteration of the instrument, it contains no sensitive, brittle filament that is easily broken. Our new type of electron gun can be put into operation immediately after applying the light signal and the necessary voltages; it requires no warm-up time for proper emission, as do some thermionic emitters; also, it does not necessitate a lengthy wait for overall temperature equilibrium, as do some thermionic emitters.

In our Figure 1, we have shown an electron gun as applied to a mass spectrometer. While we have shown no separate vacuum pumping line direct to the electron gun, it may, under certain conditions, be advisable and it is intended that our invention cover such modification. Also, it is intended that the scope of this invention encompass the situation wherein the electrodes of the new type electron run hot, that is, at whatever elevated temperature is desired. Often it is desired to operate a mass spectrometer with the ion source hot and in such a case the electron gun must be at the same temperature. The heating in this instance could be attained either using suitable insulated internal heaters or by using an external heater of high resistance wire suitably applied to the vacuum jacket.

Although we have described a preferred embodiment of our invention in specific terms, it is to be understood that various changes may be made in the size, shape, materials and arrangement without departing from from the spirit and scope of the invention as claimed.

What we claim as our invention is:

1. A mass spectrometer comprising an envelope having a light permeable window, a photosensitive cathode in said envelope for receiving light entering through said window, a plurality of multiplying electrodes in said envelope, means comprising at least one electron lens element for focusing electrons from said multiplying electrodes into an electron stream, a collector electrode disposed in the path of said stream for collecting electrons therefrom, means for admitting molecules into said envelope into the path of said electron stream for ionizing said molecules, and analyzer means including a magnet for analyzing said molecules.

2. A mass spectrometer comprising an envelope, light permeable means for permitting light to enter said envelope, a photocathode disposed in said envelope in the path of said entering light, a plurality of electron multiplying electrodes in said envelope in cooperative relationship to said photocathode, means comprising at least one electron

lens element for focusing electrons from said multiplying electrodes into an electron stream, a collector electrode disposed in said envelope for collecting electrons from said stream, means for admitting gaseous and gas-like matter into said envelope, means for moving said matter through said electron stream whereby at least a portion of said matter becomes ionized, analyzing means operating upon at least a portion of said ionized matter for analyzing said matter, and self regulating means constructed and arranged for maintaining the magnitude of said electron stream at a predetermined level by regulating the light entering said envelope.

3. In a mass spectrometer, the improvement which comprises an external light source, a light permeable window in the envelope of the mass spectrometer, a photocathode within said envelope for receiving light from said external source, electrodes for forming an electron stream, self regulating means constructed and arranged for maintaining the magnitude of said electron stream at a predetermined level by automatically regulating the light entering said envelope.

4. A mass spectrometer comprising an envelope, means for admitting molecules to be ionized into said envelope, means for producing and forming an electron stream in said envelope for ionizing said molecules, said means including a photocathode actuated responsive to light entering said envelope from an external source, an electron collecting electrode upon which said electron stream impinges self regulating means actuated responsive to the current from said collecting electrode and constructed and arranged for maintaining the flow of electrons in said stream at a predetermined level by regulating the said light that enters the envelope, means including a magnet for analytically operating upon said ionized molecules, and means for moving at least a portion of said ionized molecules into cooperative relationship with said last named means.

5. A mass spectrometer comprising an envelope, means for admitting molecules to be ionized into said envelope, an external source of light, means for producing and forming an electron stream in said envelope for ionizing said molecules, said means including a photocathode actuated responsive to light entering said envelope from said external source, a plurality of electron multiplier electrodes in the path of electrons emitted by said photocathode, electron lens means cooperating with said multiplier electrodes for forming a fast moving, relatively concentrated electron stream in the path of said molecules being admitted whereby ions are produced, an electron collecting electrode upon which said electron stream impinges, means including a magnet for operating upon and analyzing at least a portion of said ions, and regulating means actuated responsive to the current from said collecting electrode for maintaining the magnitude of said electron stream at a predetermined level by regulating the intensity of said external light source.

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