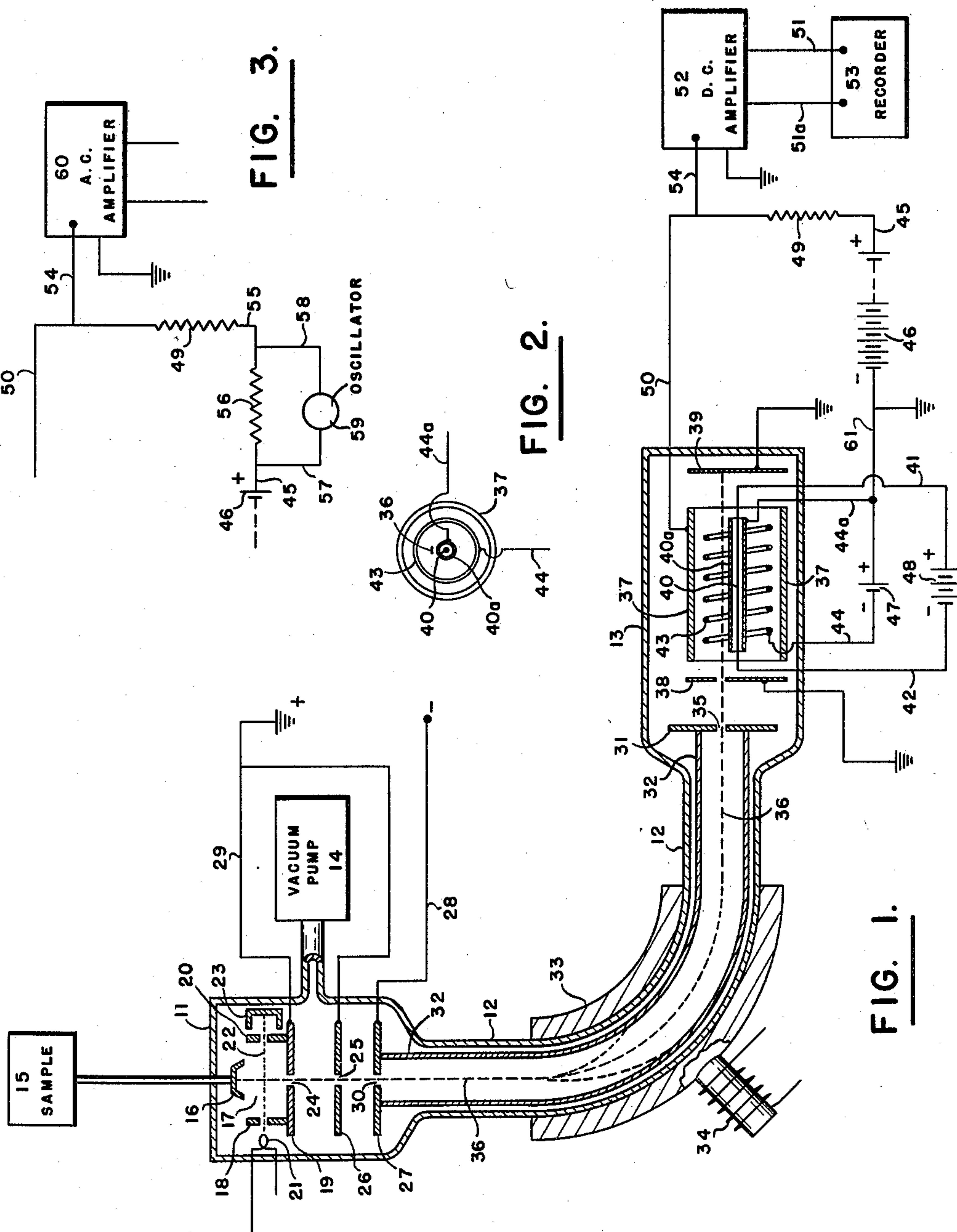


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SYSTEM AND METHOD FOR ANALYZING
SUBSTANCE BY MASS SPECTROMETRY
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SYSTEM AND METHOD FOR ANALYZING
SUBSTANCE BY MASS SPECTROMETRY

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The present invention relates to the field of mass spectrometry. More particularly, the present invention is directed to a method of analysis wherein ions obtained from a substance to be analyzed are formed into a beam which is employed to modulate directly a novel detection system from which an amplified signal is obtained.

This application is a continuation-in-part of my copending application Serial No. 761,787, filed July 18, 1947, now abandoned.

The art of analyzing gaseous mixtures in a mass spectrometer is well known. The analysis is usually carried out by admitting a gas under reduced pressure into an ion source contained in a high vacuum spectrometer tube. The molecules of the gas are bombarded with low energy electrons emitted from a hot filament such that a small portion of the molecules are converted into parent ions and fragments of many different masses. Each ion usually possesses a unit of positive electricity. The charged ions pass from the ion source into an ion accelerating field where they are accelerated to high velocities. The ions are caused to pass from the ion source into the accelerating field by imposition of an auxiliary electrostatic field. The ions in the accelerating field acquire equal kinetic energies and thus their velocities are inversely proportional to the square roots of their masses. The accelerated ions then pass through an entrance slit into an analyzing portion of the mass spectrometer which comprises a curved conduit within an external magnetic field.

The ions moving at a high velocity constitute an electric current and a magnetic field is produced simultaneously by the moving ions. The magnetic field caused by the moving ions is acted upon by the external, crossed magnetic field which causes a deflection of the ions in the curved conduit. The magnitude of the magnetic field and the accelerating voltage creating the accelerating field may be controlled precisely such that ions representing only one mass may navigate the curved conduit of the analyzer. This is because ions of different masses are deflected by different amounts. Consequently, ions of any one mass will follow a path having a radius of curvature of magnitude different from the radii of curvature of paths of ions having any other mass. A number of ions of any given mass are thus caused to focus on an exit slit of the analyzer and from the exit slit they enter a Faraday cage or other collecting means which is grounded through a resistance. The neutralization of the charge car-

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ried by the ions causes a current to flow through the resistance setting up a potential drop. This potential drop may then be amplified in a D. C. amplifier and measured by means of a sensitive galvanometer or a recorder. The current set up by neutralization of the ions impinging on the collector plate is proportional to the number of ions of a particular mass striking the plate per unit of time. By manipulation of the external magnetic field and/or the accelerating electric field strength, ions representing components of different molecular weights or masses can be caused to pass through the analyzer exit slit in sequence. Therefore, the voltage across the aforementioned resistance changes with time depending on the quantity per unit of time of the different ionized masses passing through the exit slit, and a record or mass spectrum representing the composition of the gases may be obtained. If a chart recorder is employed, a mass spectrum will be obtained having peaks corresponding to ions of any particular mass and will show the relative abundance of these particular ions.

In the conventional type of mass spectrometer, positive ions produced at the ion source are usually measured. Because a small positive potential gradient is maintained in the ion source, the positive ions are caused to pass into the ion accelerating field and are eventually passed through the analyzer portion of the mass spectrometer, whereas negative ions formed at the ion source are repelled. Thus, the ions passing through the analyzer form a direct or steady positive ion beam which eventually impinges on the collector plate, as mentioned above, and are neutralized by a flow of electrons from ground. The electron flow is directly equivalent to the positive ion charge flow onto the collector plate and thus, the I (current) $\times R$ (resistance) $= E$ (voltage) difference across the ends of the grounded resistor is directly related to the current through the resistor. As previously mentioned, this current is related to the number of ions collected per unit time. Hence, the variations of the number of ions collected per unit time are converted into signals represented by voltage changes which are impressed on an electronic tube designed to amplify the magnitude of the original current to a magnitude more amenable to standard measuring devices or recorders.

It is thus seen that direct currents set up by the neutralization of the positive ion beam on the collector plate are amplified and measured in a conventional system. It is also readily seen that the conventional procedure for amplifying

the signal resulting from the ion beam involves a detection system in which losses result as the signal from the neutralized ion beam is transferred to an electrical network before the signal is amplified. It would be very desirable to minimize the losses which invariably occur when the signal is transferred from the detector system of the mass spectrometer to the conventional type of amplification equipment. Another disadvantage encountered in the conventional use of mass spectrometers is that of direct current amplification of the voltage charge occurring when the ion beam is neutralized. It is well known that A. C. amplifiers are inherently more stable than D. C. amplifiers. Direct current amplifiers also are subject to what is known as "zero drift" resulting from the fact that aging of filament, minute changes of potentials within the electronic tubes, and similar disturbances upset the balance of conditions previously established causing a new set of operating parameters to exist. These new parameters obviously produce a shift of the apparent balance which is interpreted as a "zero drift." Alternating current amplifiers respond only to signals of periodic character and have no output for no input signal; hence, in the quiescent period no output is obtained which means that no shift of balance can appear. Direct current amplifiers are also known to have less usable sensitivity and to respond more slowly to voltage fluctuations than do A. C. amplifiers. It would, therefore, be extremely desirable to use A. C. amplification of the ion beam currents in order to eliminate the aforementioned difficulties.

It is, therefore, an object of the present invention to provide a means for improving the operation of a mass spectrometer.

Another object of my invention is to provide a method of detecting and amplifying the signal resulting from an ion beam formed in a mass spectrometer such that losses occurring from transferring the ion beam signal to an amplifier are minimized.

It is a further object of the present invention to improve the stability and sensitivity of a mass spectrometer with respect to the amplification and recording of ion beam currents used therein.

The above mentioned objects of the present invention are accomplished as follows: The mass spectrometer tube, which is maintained under high vacuum, is provided with a suitable amplifying-collecting means comprising an anode such as a right circular cylinder or cage made of conducting material. The cylinder or cage contains an electron emissive cathode or a filament heated by a suitable electrically controlled means such that electrons are emitted therefrom. The anode is given a positive potential such that an electron current flows thereto from the cathode after a space charge has been built up around the heated cathode. An ion beam comprising ions of any one mass is then passed through the cage in the vicinity of the space charge near the heated filament. The electrostatic disturbance caused by the ion beam passing in the vicinity of the space charge region varies the electron current to the cage in accordance with the ion beam intensity which causes an amplified response to the ion beam intensity which causes an amplified response to the ion beam signal to appear in an output electrical network of the cage. The signal, which is many times stronger than the original ion beam current, allows greater sensitivity and speed of response without sacrificing stability.

The amplified response occurring on the anode may then be further amplified in a suitable D. C. amplifier. If desired, the positive voltage applied to the anode or cage may be periodic in character such that an A. C. signal of constant frequency is produced which is amenable to amplification in an A. C. amplifier.

The application of an ion collector means of the type described above to a mass spectrometer is made possible because the mass spectrometer tube itself is under extremely high vacuum, and a flow of electrons from the filament to the walls of the cage or anode will occur. In effect, the filament and cage comprises a diode, familiar in the electronic art. By the insertion of a grid electrode near the filament, one obtains a triode by means of which the magnitude of the current to the cage is more easily controlled. The insertion of the grid, of course, produces a triode in which a small energy input controls a very large energy output and, at the same time, retains the original character of the controlling energy. Therefore, high amplification of the small energy input is obtained. Other types of multi-electrode detecting means may be employed.

One embodiment of the device of the present invention will now be described in detail in conjunction with the accompanying drawings in which

Fig. 1 is an elevation, partly in section, showing a mass spectrometer tube into which has been incorporated the collector-amplifier detector of the present invention;

Fig. 2 shows diagrammatically the end view of the collector-amplifier system illustrated in Fig. 1; and

Fig. 3 shows diagrammatically a preferred means of employing the collector-amplifier system to produce pulsating signals amenable to A. C. amplification.

In Fig. 1, the numeral 11 designates the ionization chamber, numeral 12 designates the analyzing portion and number 13 designates the collecting portion of the mass spectrometer tube. It is noted that the analyzer portion forms a 90° angle which is one type of analyzer that is frequently employed in conventional mass spectrometers. My invention is not limited to any special type of mass spectrometer tube but is applicable to analyses in the horizontal, 60°, 180°, or other types of mass spectrometer tubes. The entire tube may be constructed conveniently of glass and is maintained under an extremely low pressure, such as from 10^{-3} to 10^{-6} mm. of mercury absolute pressure by the gas evacuation system designated by numeral 14.

A small amount of substance which will be in a gasiform state under the reduced pressure is passed from sample system 15 through draw-out electrode 16 into the ionization region designated by numeral 17. The ionization region 17 is defined by electrodes 18, 19 and 20. Electrons emitted from heated filament 21, which is controlled by an electronic power system, not shown, flow through small apertures in electrodes 18 and 20 as a beam designated by the numeral 22. The electron beam flows in a direction perpendicular to the flow of gas emitted downwardly through drawout electrode 16. Beam 22 is maintained in a horizontal flat ribbon through ionization region 17 by means of an externally applied magnetic field, not shown, such that electrons impinge on electron collector 23.

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A portion of the electrons in beam 22 bombard molecules of gas in region 17 causing ionization of a fraction of the molecules. If positively charged ions are to be analyzed, the ions formed in region 17 are slowly moved toward accelerating entrance slit 24 in electrode 19 by means of a small positive electrical potential applied to electrode 16 as compared to the potential applied to the accelerating electrodes to be described hereinafter. The ions then pass through slit 25 in focusing electrode 26 before reaching the strong accelerating field existing between electrodes 26 and 27. The accelerating field is produced by applying a voltage through lead 28 to electrode 27 while maintaining electrodes 19 and 26 grounded through lead 29. This method of operation is conveniently termed "ion source grounded" since electrodes 19 and 26 may be referred to as the ion source and since only the useful portions of the ions pass through the slits in these electrodes.

The ions passing through the accelerating field enter slit 30 in electrode 27, this slit being the analyzer entrance slit. The analyzer portion of the mass spectrometer comprises two electrodes 27 and 31 at opposite ends of curved conduit 12. The electrodes are connected through an internal non-magnetic shield designated by the numeral 32. An external, transverse or crossed magnetic field 33, controlled by electromagnet 34, is employed to deflect ions entering the analyzer. By controlling the magnitude of magnetic field 33 and/or the magnitude of the potential applied to electrode 27, ions of a given mass may be focused on exit slit 35 in electrode 31. Ions of either less or greater mass than those focused on the aforementioned exit slit are discharged by striking the non-magnetic shield and are pumped out of the tube by evacuating system 14. The ions focused on exit slit 35 may conveniently be designated as beam 36.

The collecting portion of the mass spectrometer designated by numeral 13 contains a supported cage electrode 37, conveniently in the form of a right circular cylinder. The cylinder may be made of an electrically conducting non-magnetic material such as copper, brass, nickel-chromium alloy, gold, platinum, and the like, or a suitable non-conducting material plated with such materials or alloys. The ends of cage 37 are electrostatically closed by grounded grid network 38 and grounded plate 39. Grid network 38 contains a suitable small aperture through which ion beam 36 may pass. In the center portion of cage 37 and suitably insulated therefrom is positioned a heater or filament 40 electrically connected through leads 41 and 42 to a source of potential 48. Surrounding heater 40 is a suitable metal tube 40a acting as a cathode capable of emitting electrons when heated. Cathode 40a is electrically connected through lead 44a to lead 61. Cathode 40a is preferably placed coaxially within the cage 37 and the cage is preferably positioned such that ion beam 36 passes adjacent and parallel to the longitudinal axis of cathode 40a intermediate the inner surface of cage 37 and the outer surface of cathode 40a. It will be understood that, when filament 40 is itself capable of being heated to produce a sufficient abundance of electrons, cathode element 40a may be omitted and filament 40 may be employed as an electron emissive cathode. A control grid 43 may be positioned concentrically around the inner surface of cage 37 and

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spaced intermediate the wall of the cage and the path of ion beam 36. Control grid 43, when used, is electrically connected through lead 44 to the negative side of a source of potential 47 which is also connected to lead 44a and grounded lead 61.

Cage 37 is electrically connected by means of lead 50 to a resistance 49 and may be connected by lead 54 to electrometer tubes, not shown, in D. C. amplifier 52. Amplifier 52 is connected to a recorder 53 by means of leads 51 and 51a. Resistance 49 is connected through lead 45 to the positive terminal of a source of anode potential 46. The negative terminal of source of potential 46 is connected through grounded lead 61 to cathode 40a and potential 47.

It may be seen that cage 37, cathode 40a and helical grid 43 comprises a triode. When heater 40 is heated to incandescence and maintained at ground or other low potential and when cage or anode 37 is made positive with respect to cathode 40a, there is an electron flow from cathode 40a to the inner surface of anode 37. The magnitude of the electron flow will generally be limited either by space charge limiting or temperature limiting. In this particular case, only the space charge limiting condition is applicable since it exists if the voltage applied to anode 37 is low for a sufficiently high filament temperature, in which case an excess of electrons are available. The excess electrons boiling off of heated cathode 40a concentrate a short distance from the cathode and form a negative cloud or space charge. A potential is soon formed which is so high as to prevent other electrons from being boiled off of the cathode. Actually, an equilibrium exists between the number of electrons returning to the cathode from the space charge and the number leaving the cathode to the space charge. By inserting grid 43 having applied to it -2 volts for example, a means is provided for easily controlling the magnitude of the current to anode 37. A small energy input into grid 43 thus controls a large energy output from anode 37 while retaining at the same time the character of the controlling energy. This makes it possible to obtain a very high amplification for a very small energy input. When a collimated beam of positive ions from slit 35 passes parallel to the axis of the triode, a disturbing electrostatic field occurs in the vicinity of the space charge around cathode 40a which causes great changes to occur in the current flowing between the cathode and anode 37. This is due to the fact that a beam of positive ions neutralizes a portion of the space charge in direct proportion to the abundance of the positive ions in the beam and thereby upsets the equilibrium conditions existing between the space charge and cathode 40a. When the temperature of heater 40 and the potential difference between grid 43 and cathode 40a are maintained constant, the electron current to anode 37 is changed by such magnitude as to set up an appreciable electrical signal which is a direct function of the abundance of ions in the positive ion beam.

Therefore, the electrons passing from cathode 40a to cage or anode 37 are varied in quantity in proportion to the ion beam 36 causing an amplified response of the ion beam to occur on cage 37. Subsequently, the electrons striking cage 37 then cause a flow of current in resistance 49 which produces a signal which is passed to D. C. amplifier 52. The advantage of the amplifier-collector system comprising the triode is

that the ion beam is directly amplified inside the mass spectrometer tube into a signal of a magnitude many times stronger than the original ion beam. This results in greater sensitivity and speed of response than possible heretofore without sacrificing stability. Since the signal passing to D. C. amplifier 52 is much stronger than those signals obtained in conventional mass spectrometers, it is not necessary to employ amplification means as sensitive as those conventionally employed.

The amplified signal passing through D. C. amplifier 52 then reaches recorder 53 wherein the signal is suitably recorded on an oscillograph, a galvanometer type or a pen type recorder.

The end view of anode 37 and its related parts is shown in Fig. 2 in which the numbering of the anode, cathode, grid, heater and the ion beam corresponds to that used in Fig. 1.

Turning now to Fig. 3, a preferred modification of the apparatus that may be used in the present invention is illustrated. In this modification, one end of resistor 49 is connected through lead 55 to one end of resistor 56. The other end of resistor 56 is connected through lead 45 to source of potential 46 as shown. The ends of resistor 56 are electrically connected through leads 57 and 58 to a source of alternating current and voltage 59 which may suitably be an oscillator or multivibrator circuit. Oscillator 59 supplies periodically varying current and voltage having any desired wave form to resistor 56. The magnitude of resistor 56 will obviously depend upon the operating parameter desired. When no alternating voltage is applied through leads 57 and 58 from oscillator 59, there will be no alternating current flow through resistor 56, and, consequently, anode 37 will be substantially at the reference or bias potential set up by source 46. When a pulsating voltage from oscillator 59 is applied to resistor 56, the positive half cycle of the alternating voltage charge reaches anode 37 and attracts electrons boiled off of cathode 40a whereas the negative half cycle of the alternating voltage will offer no attracting or repelling influence on the electrons. In effect, a pulsating signal results from the electrons reaching cage 37 during the positive half cycle. The pulsing flow of electrons causes a flow of current in grounded resistance 49 setting up a pulsating signal amenable to amplification in A. C. amplifier 60. A. C. amplifier 60 may be of the type conventional to the art such as a "peaked response" A. C. amplifier which is tuned to the interruption frequency imposed on cylinder 37. Therefore, by employing this mode of operation, the triode effectively amplifies and collects the ion beam as a signal which is pulsating in character and which is easily amplified in an A. C. amplifier. This results in the benefits previously described when using A. C. instead of D. C. amplification. The amplified signal leaving amplifier 60 may suitably be rectified and recorded in means well known to the art.

It is obvious that other modifications of the amplifier-controller system than those heretofore described may be employed. For example, the electrode system need not necessarily be triode in character, as shown in Fig. 1, but may be a diode comprising only cage 37 and filament 40 without the control grid 43 as such. The insertion of a grid electrode between plate 37 and filament 40 is usually desirable for control purposes but, in some cases, very close control of the electron current may not be needed. The system

could also be multi-electrode either with or without control grid 43. For example, greater amplification and improved stability of the amplifier-collector system can be obtained by employing a system equivalent to a pentode or beam tetrode which usually produces greater amplification than a triode. Such modifications will be obvious to those skilled in the art. It will also become obvious in the case of diode, tetrode and pentode systems that a periodic voltage may be applied to cage 37 as described in connection with Fig. 3 such that the steady no signal output will be A. C. of constant frequency. That is, by passing an ion beam through cage 37, the impedance of the system will be altered as hereinbefore described and the output signal will be varied in accordance with the signal changes due to the ion beam entering the amplifier-controller system. If desired, the periodically varying voltage from oscillator 59 may be applied across resistances inserted in either lead 44 or lead 44a in the triode system shown in Fig. 1, thus applying periodically varying potentials to grid 43 or cathode 40a. Periodically varying voltages may be applied to one or more of the grids in tetrode or pentode systems if desired.

The amplifying-detecting means of the present invention is particularly suitable in mass spectrometers wherein positive ions are analyzed. This mode of operation is due to the fact that positive ions destroy electronic space charges. Hence, by placing a hot tungsten filament emitting electrons along the axis of a positively charged cylinder, the electron current to the cylinder is limited by the negative space charge surrounding the filament at a sufficiently high filament temperature and a given cylinder voltage. The passage of a beam of positive ions near the filament permits a portion of the positive ions to neutralize the negative space charge which in turn permits the cylinder current to increase. The current increase to the cylinder is many times stronger than the original ion beam current; therefore, one obtains a signal which is not only a function of a characteristic of the ion beam but also the signal is greatly amplified, as compared to the original ion beam, within the mass spectrometer tube itself. All this occurs without resorting to conventional amplifiers exterior to the mass spectrometer. Auxiliary amplifiers may, of course, be employed to advantage in the present invention under some circumstances.

Prior art workers have passed molecular beams (neutral atoms and molecules) parallel to the axis of a diode wherein partial ionization of the neutral particles by electrons occurred which resulted in forming positive ions. The positive ions then partially neutralized the negative space charge and affected the electron current to the plate. It has also been known to amplify fluctuating input voltages of electronic tubes by passing a current of positive ions of constant intensity in the vicinity of the cathode at the place where the space charge accumulates. The practice of the present invention is advantageous in that a beam of ions rather than a beam of neutral particles is passed parallel to the axis of the diode, triode or other arrangement, and, hence, none of the electron beam is used in ionizing the particles. The present invention involves first ionizing a substance, forming beams of ions having selected masses, varying abundances and, accordingly, varying intensities, and employing the ion beams of varying intensities to modify a constant

input voltage by passing the ion beam in the vicinity of or in close proximity to the space charge resulting from an electron current such that the extent to which the electron current is altered is an amplified function of a characteristic of the particular ion beam. The passage of an ion beam comprising ions of another mass in the vicinity of the space charge produces still another effect which is characteristic of the particular mass and number per unit of ions passed near the space charge.

Actually, it may be said that the present invention involves in part ionizing a volatile substance in order to segregate positive ions of a desired or selected mass, and deionizing the ions of one mass to obtain an amplified signal which may be used to determine the relative abundance of the ions of the particular mass deionized.

The present invention is not limited to the collection and amplification of positive ions but may satisfactorily be employed in cases where negative ions are to be analyzed. The analysis of negative ions requires that proper polarity changes be made throughout the entire mass spectrometer tube such that negative ions rather than positive ions are pushed into the ion accelerating field, separated into ions of particular masses in the analyzer portion of the mass spectrometer, and the beam of negative ions passed through the amplifier-controller system as previously described. An electrostatic disturbance likewise occurs in the vicinity of the space charge around cathode 40a which results in variation of the electron current. It is to be understood that the mass spectrometer may be operated with the analyzer electrodes 27 and 31 at ground potential while ion source electrodes 19 and 26 are at high potential with respect to ground.

Although other modifications of the present invention will become obvious to one skilled in the art, it is emphasized that the principal advantage to be derived from the practice of my invention is the fact that direct amplification occurs in the detector system within the mass spectrometer evacuated tube rather than outside of the tube as is the case in conventional systems. Although I have described the amplification of the signal from the ion beam both in the mass spectrometer tube and in auxiliary amplification means outside of the mass spectrometer tube, under some conditions, particularly when employing a multi-electrode amplifying means within the mass spectrometer tube, it is possible to obtain sufficient amplification of the signal resulting from an ion beam to eliminate or minimize the extent to which the signal must be amplified outside of the mass spectrometer tube. It will usually be preferred, however, to employ auxiliary amplification, with D. C. or A. C. amplifiers as the case may be, outside of the mass spectrometer in order to obtain optimum results.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. In a mass spectrometer having a means for producing a beam of ions, a means for amplifying and collecting said ion beam which includes, in combination, an electron emissive cathode, a charged anode coaxially surrounding said cath-

ode and spaced therefrom, said cathode being positioned whereby a beam of ions may be passed in close proximity thereto, and means for collecting a signal produced on said anode.

2. In a mass spectrometer having means for producing ions and means for focusing a beam of ions of a particular mass along a definite ion path, an improved means for collecting said ions and producing a signal therefrom which comprises, in combination, an elongated electron emissive cathode arranged adjacent to and with its longitudinal axis parallel to said ion path, an anode of electrically conducting material spaced from and arranged concentrically around said cathode in a manner to include said ion path therebetween, means for heating said cathode and causing it to emit electrons, a resistance electrically connected between said anode and said cathode, and means electrically connected in series with said resistance for applying a potential difference between said anode and cathode and capable of causing an electron current to flow therebetween and produce a saturated space charge.

3. An improved ion collector and signal producing means in accordance with claim 2 which includes at least one electron-control grid electrode arranged concentrically within said anode in a manner to include said ion path between said electrode and said cathode.

4. An improved ion collector and signal producing means in accordance with claim 2 in which said means for applying a potential difference is a source of unidirectional voltage.

5. An improved ion collector and signal producing means in accordance with claim 2 in which said means for applying a potential difference includes a source of unidirectional biasing potential and a means for superimposing a periodically varying bi-directional potential thereon.

6. A mass spectrometer comprising, in combination, means for producing ions of various masses, means for focusing ions of a selected mass along a selected ion path, means for producing an electron space charge adjacent said selected ion path whereby the focused ions vary said space charge, and means for indicating variations in said space charge.

7. A mass spectrometer for testing a vaporizable substance comprising, in combination, means for forming at least a portion of said substance into a beam of ions, means for passing ions of a selected mass along a selected ion path, means for producing an electron space charge in close proximity to said selected ion path whereby ions of said selected mass vary said space charge, means for producing from variations in said space charge an amplified signal which is a function of a characteristic of said beam of ions, and means for displaying said signal.

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