

Fig. 1.

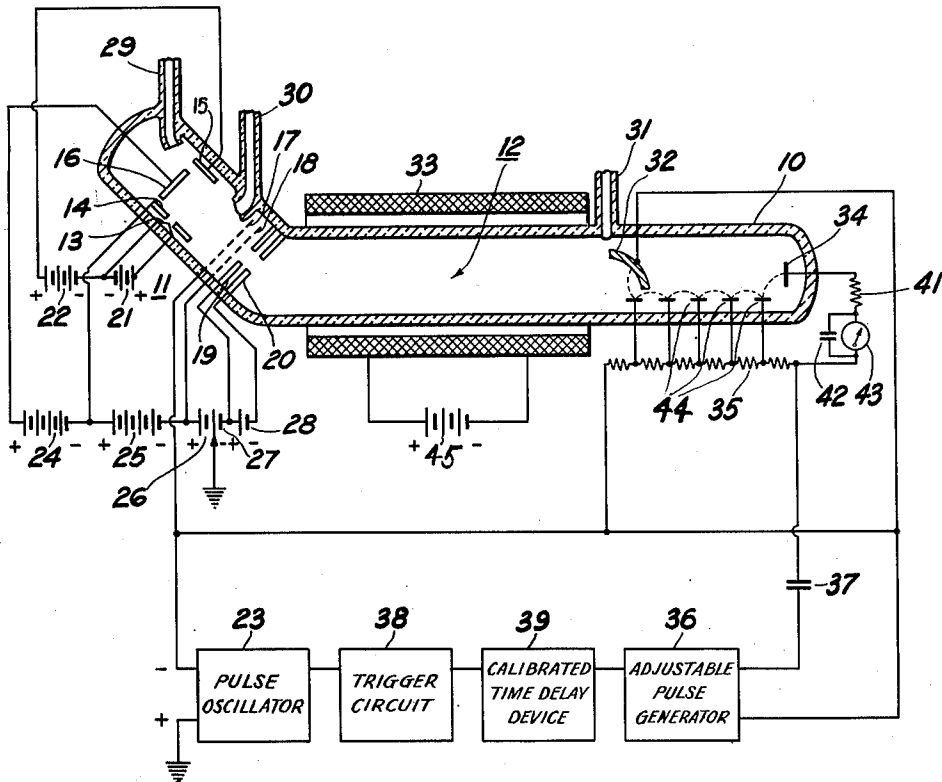
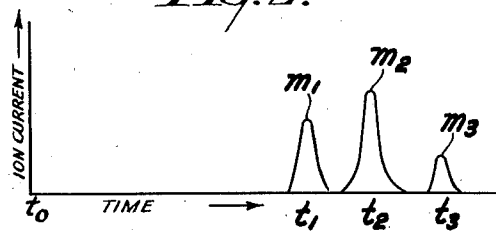


Fig. 2.



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MASS SPECTROMETER

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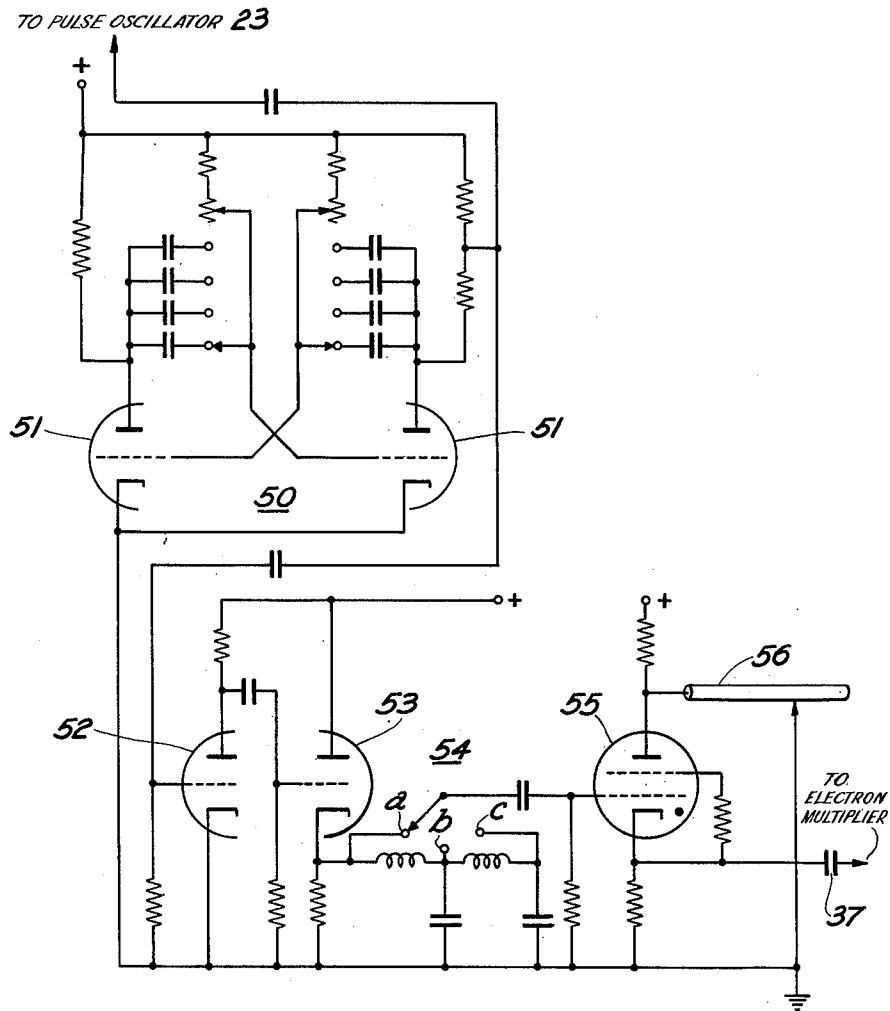


Fig. 3.

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2,798,162

MASS SPECTROMETER

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10 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometers of the type wherein a composition of matter is analyzed by means of a mass-velocity electron discharge system, and more particularly to improved detection and measuring apparatus for such mass spectrometers.

In one known "time of flight" mass spectrometer, positive ions of a gas to be analyzed are subjected to an accelerating and a magnetic field, whereby the constituent ions are separated into spaced groups whose relative positions are determined by the respective mass-velocity constants of the ions. The spaced groups of the positive ions are caused to impinge on a collector electrode, and the relative spacing of the groups as well as the quantity of ions in each group are indicated by suitable visual metering or recording instruments. Inasmuch as weak positive ion currents of relatively small energy content must be detected and measured, it has heretofore been proposed to constitute the collector electrode as a secondary emitter, which emitter is followed by a plurality of secondary electron multiplier sections. By reason of the electron multiplier's high gain and low residual currents, an effective detector is provided for most purposes.

Since the electron multiplier is positioned within the same vacuum system in which the ions are produced, the normal vacuum conditions for the ion producing system constitute a serious drawback with respect to the multiplier section. Multiplier characteristics such as gain and amount of dark current are highly sensitive to the degree of vacuum to which the multiplier elements are exposed. Gas-generated noise will arise in the electron multiplier when the multiplier electrodes are operated in a conventional manner with constant direct-voltages thereon, and this effect is particularly troublesome in the low vacuum conditions ordinarily encountered in the ion producing chamber.

Accordingly, it is the principal object of the invention to provide improved apparatus for the detection and measurement of ion currents including means for converting the ion currents into electron currents.

More particularly, it is an object of the invention to provide a mass spectrometer including an electron multiplier ion detector responsive to relatively weak ion currents.

It is a further object of the invention to provide an improved electron multiplier circuit for a mass spectrometer wherein the multiplier electrodes are operated at many times their normal direct operating potential without producing gas-generated noise therein.

For a better understanding of the invention, as well as further objects and features thereof, reference is had to the following detailed description thereof to be read in conjunction with the accompanying drawing, wherein:

Fig. 1 is a schematic circuit diagram of a mass spectrometer arrangement in accordance with the invention;

Fig. 2 is a graph obtained by means of the apparatus shown in Fig. 1; and

Fig. 3 is a schematic diagram showing one form of a

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pulse generator and control system suitable for the purposes of the invention.

Referring to Fig. 1, the mass spectrometer shown comprises an envelope 10, which may be of almost any configuration but which, preferably, is of tubular form, bent near one end to form an ion gun portion 11 and an ion trajectory portion 12.

The ion gun portion 11 comprises a filament 13, a beam forming apertured electrode 14, and an anode 15, which elements produce a narrow beam of electrons traversing the tube normally with respect to the axis of said gun portion of the envelope. An impeller electrode 16 is mounted in a plane parallel to the electron beam and normal to the axis of the envelope. On the opposite side of the electron beam and in succession along said axis there are provided grid electrodes 17 and 18 and accelerating electrodes 19 and 20. Accelerating electrodes 19 and 20 have centrally located apertures by means of which, in conjunction with the impeller 16, a narrow beam of ions is injected into the ion trajectory portion 12 at an angle to the axis of said trajectory portion.

The filament 13 is heated by means of a battery 21 and the anode 15 is positively charged by means of battery 22. Grid 17 is coupled to a pulse wave oscillator 23, as later to be more fully explained, and biased by means of the potential appearing across battery 26. The electrodes 14, 16, 18, 19 and 20 are given suitable operating potentials as shown by the batteries 24, 25, 26, 27 and 28. The gas to be analyzed is circulated through the gun portion 11, through an inlet passage 29 and an exhaust passage 30. An additional exhaust port 31 is preferably placed at the end of trajectory portion 12 to evacuate this portion.

At the end of the trajectory portion 12 remote from the gun portion 11, there is provided a collector electrode 32. The portion 12 is enclosed in a solenoid 33 energized by battery 34 to provide an axial magnetic field through the said portion.

The collector 32 is preferably made of a material having the property of high secondary emissivity to positive ion bombardment, such as beryllium copper alloys, and it is preferably curved in order to focus the stream of secondary electrons leaving its surface. The collector 32 acts as the cathode element in an electron multiplier further including a plurality of dynodes 44 and an anode 34. The collector 32 is connected to one end of a voltage divider 34, and the dynodes 44 are connected to progressively spaced taps thereon.

A pulse generator 36, producing operating pulses for the electron multiplier is connected via coupling capacitor 37 to the other end of voltage divider 35. The pulse generator 36 is preferably provided with means for controlling the pulse amplitude and pulse width. A suitable circuit for this purpose as well as a more detailed description of a multiplier electrode structure is disclosed in my copending application, entitled "Light Detectors," Serial No. 399,870, filed December 23, 1953. Such a circuit is shown in Fig. 3 and comprises a variable frequency astable multivibrator 50 corresponding to the trigger circuit 38 of Fig. 1, and having a twin-triode tube 51 which supplies a triggering voltage to the pulse oscillator 23 and the calibrated time delay 39 which in turn actuates the adjustable pulse generator 36. With more specific reference to Fig. 3, it is seen that the triggering voltage from the multivibrator 50 is applied to the control grid of the amplifier tube section 52. The amplified triggering voltage is then applied to the control grid of a cathode-follower amplifier tube section 53 which provides a low impedance trigger through the step delay line 54 to the thyratron 55. The step delay line 54 may have a plurality of step positions, e. g., three step positions, as shown in Fig. 3. Position *a* may represent no delay; position *b*

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one microsecond delay; and position *c* two microseconds delay. The length of coaxial cable 56 determines the width of the output pulse from thyatron 55 in a manner which is well known in the art. The positive pulse produced across the cathode resistor of the thyatron 55 is then applied to the electron multiplier system through the capacitor 37.

The operation of generator 36 is controlled by a trigger circuit 38 which generates periodic synchronizing impulses, said impulses being applied to generator 36 via a calibrated time delay device 39, and also to the pulse oscillator 23. The output circuit of the multiplier is constituted by a resistor 41 in series with an indicating device 43 connected between anode 34 and said other end of voltage divider 35. The indicating device 43 may take the form of an electronic micro-ammeter or a recording potentiometer whenever a permanent record of output signal is desired. Connected across device 43 is a condenser 42 whose value in conjunction with the internal impedance of device 43 provides integration of the anode pulse currents. Obviously, other forms of integration networks may be used for this purpose.

The operation of the invention is as follows:

A sample of the matter to be analyzed is introduced in the form of a gas into the gun portion 11 through the inlet 29 and ionized by the electron beam from the cathode 13. The resulting positive ions are propelled by the positively charged impeller 16 toward the ion gate formed by the grids 17 and 18. By means of a varying voltage, preferably a pulse voltage, in the order of one microsecond duration, derived from the pulse wave oscillator 23, the positive ions are propelled into the portion 12 in the form of intermittent blocks of ions. Since the ions have equal kinetic energy and different velocities depending on their respective masses, different ions of each block will separate into a plurality of spaced groups, the relative spacings of which at any given point in the trajectory of the ion beam are determined by the velocities of the ions. The longitudinal magnetic field produced by coil 33 is given such a value that the ions which enter at an angle to the axis of the magnetic field assume a multiturn helical path and impinge on the collector 32. The helical path thus provided is many times longer than the distance between the electrodes 20 and 32.

Since the magnetic field exerts its influence only at right angles to the axis of the field which is coincident with the axis of the portion 12, it is evident that minor variations of field strength will not affect the transit time of the ions along the axis of the portion 12.

In accordance with one form of the invention, the desired mass-velocity separation of the ions into individual spaced groups is realized by means of a tube 10 in which the portion 12 is 30 cm. long, the incident ion beam makes an angle of 20° with the axis of the magnetic field and the field has a strength of the order of 1000 gauss.

The ion beam impinges on collector-cathode 32 to excite secondary emission therefrom and the resultant electrons are multiplied by applying a voltage pulse having an amplitude well in excess of the normal D.-C. operating level to the dynodes 44 to direct the flow of electrons from collector-cathode 32 to anode 34 via dynodes 44. These voltage pulses which are derived from generator 36 may have a short duration in the order of one hundredth of a micro-second, but the duration may not be shorter than the transit time of the electron from cathode to anode of the multiplier.

Inasmuch as triggering pulses from circuit 38 activate the pulse oscillator 23 as well as the pulse generator 36, the variable time delay device 39 may be shifted in time or phase to supply an output pulse to trigger on the multiplier at any predetermined instant subsequent to an initiation of ion groups at the source end thereof. The output of the electron multiplier is detected as an integrated current on the meter or recorder 43.

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As the multiplier operating voltage pulse is shifted in time to scan the interval following the initiation of ion groups, the quantities and distributions of the ions constituting the substance may be analyzed. By displacing the pulsing of the multiplier in time relative to the pulsing of oscillator 23 and recording the ion current amplitudes throughout the time interval following the initiation of ion groups, a graph such as shown in Fig. 2 may be developed wherein peaks m_1 , m_2 and m_3 correspond to different ions and wherein t_1 , t_2 and t_3 correspond to respective transit times and hence the velocity of the ions. The area of the peaks m_1 , m_2 and m_3 are a measure of the quantity of ions in each group.

It is also to be understood that the invention is not limited to a mass spectrometer providing a helical ion path or trajectory, as disclosed herein, but may make use of a curved path as shown in the patent to J. A. Hipple, Jr., 2,331,189, a linear path as shown elsewhere in the literature, or with a "Bennett" R.-F. type mass spectrometer.

The chief advantages and further refinements of the present invention are as follows:

1. Higher pulse multiplier voltages can be used than D. C. voltages and, therefore, greater amplification of the signal is obtained;

2. Pulse voltages may be short (less than one microsecond) and therefore amplified gas noise is not obtained. Consequently vacuum requirements are not as stringent as in D. C. operation;

3. High resolution of the collected pulses may be obtained by keeping the multiplier voltage pulse duration a small fraction of the ion pulse duration;

4. A permanent record can be made of the whole spectrum by recording the output current;

5. The integration of the anode currents proportional to ion groups makes it possible to detect ion groups of extremely low level. Moreover, where a group occurs intermittently by reason of its very low abundance in a particular sample so that only one ion is collected for several initiations, the integration technique reveals the presence of the ion as well as its relative abundance; and

6. The signals are of a high level D. C. character, therefore, readily adaptable for either monitor or isotope ratio (or peak height ratio) work. For ratio work the pulse delay times corresponding to the two or more isotopes (or masses) can be alternately or successively used and the output gated to two or more different measuring channels. This may be accomplished by conventional electronic switching or distributor means to introduce different time delay networks in the pulse generator circuit. The ratio of the currents in the two channels represents the ratio of the mass intensities. An alternate method for this ratio work would be to mix the delay times in such a fashion that the ratio of the average repetition rates is the same value as the corresponding ratio of the mass intensities. This occurs when the currents in the two output channels are identical. This system may be used to advantage in a quality control arrangement preset for given ratio conditions and operative to adjust the process under control when the given ratio departs from the preset value.

While I have disclosed what is believed to be a preferred embodiment of the invention, it is to be understood that many changes and modification will be readily apparent to those skilled in the art without departing from the spirit and the scope of the invention as defined in the appended claims.

What I claim is:

1. Apparatus for analyzing a composition of matter in gaseous form comprising means to form a block of the ions of the gas and to accelerate said ions to velocity values dependent upon their individual masses, means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups hav-

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ing a time spacing proportional to the masses of the individual ions of the gas, means to collect said spaced groups of ions in succession to produce an ion current, and measuring means including an electron multiplier responsive to said ion current and having a plurality of dynodes and means to apply an operating pulse to said dynodes for a period shorter than the time in which gas-generated noise is developed in said multiplier.

2. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of the gas, electrical means to accelerate said ions to velocity values dependent upon their individual masses, means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups having a time spacing proportional to the masses of the individual ions of the gas, means to collect said spaced groups of ions in succession to produce an ion current, and means to measure the spacing of said spaced groups, said measuring means including an electron multiplier responsive to said ion current and having a plurality of dynodes and circuit means therefor, and means to apply an operating pulse to said dynodes subsequent to the initiation of said ion block and for a period shorter than the time in which gas-generated noise is developed in said multiplier.

3. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of the gas, electrical means to accelerate said ions to velocity values dependent upon their individual masses, means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups having a time spacing proportional to the masses of the individual ions of the gas, means to collect said spaced groups of ions in succession to produce an ion current and means to measure the spacing of said spaced groups, said measuring means including an electron multiplier responsive to said ion current and having a plurality of dynodes, and means to apply an operating pulse to said dynodes subsequent to the initiation of said ion block and for a period shorter than the time in which gas-generated noise is developed in said tube, said multiplier and said ionization means being contained in a common evacuated envelope.

4. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of the gas, electrical means to accelerate said ions to velocity values dependent upon their individual masses, means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups having a time spacing proportional to the masses of the individual ions of the gas, a collector for collecting said spaced groups of ions in succession to produce an ion current, said collector having a high degree of secondary emissivity to constitute a cathode, a plurality of dynodes and an anode in operative relation with respect to said cathode to form an electron multiplier, and means to apply direct-voltage operating pulses to the elements of said multiplier in synchronism with the arrival of said ion groups at said collector.

5. Apparatus, as set forth in claim 4, further including means coupled to said anode to integrate the electron current flow therethrough, and means to indicate the integrated current.

6. Apparatus, as set forth in claim 5, wherein said indicating means is a micro-ammeter connected in the anode circuit of said multiplier and said integrating means includes a condenser connected across said micro-ammeter.

7. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of the gas, electrical means

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to accelerate said ions to velocity values dependent upon their individual masses, means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups having a time spacing proportional to the masses of the individual ions of the gas, a collector for collecting said spaced groups of ions in succession to produce an ion current, said collector having a high degree of secondary emissivity to constitute a cathode, a plurality of dynodes and an anode in operative relation with respect to said cathode to form an electron multiplier, and means to apply direct-voltage operating pulses to the elements of said multiplier subsequent to the initiation of said ion block and for a period shorter than the time in which gas-generated noise is developed in said multiplier.

8. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of the gas including an accelerating electrode and a periodic pulse source connected thereto to initiate said block, said accelerating electrode imparting to said ions velocity values dependent upon their individual masses, electrical means to traject said block of ions along a given course thereby to separate said block of ions during the transit thereof through said course into a plurality of ion groups having a time spacing proportional to the masses of the individual ions of the gas, means to collect said spaced groups of ions in succession to produce an ion current and means to measure the spacing of said spaced groups, said measuring means including an electron multiplier responsive to said ion current and having a plurality of dynodes and circuit means therefor, and means including a pulse generator to apply an operating pulse to said dynodes subsequent to the initiation of said block and for a period shorter than the time in which gas-generated noise is developed in said multiplier.

9. Apparatus for analyzing a composition of matter in gaseous form comprising means to ionize the gas, means to form a block of the ions of said gas including an accelerating electrode for the ions and a source of pulsatory potential coupled to said electrode to initiate said block, means to traject said block of ions in a given direction, means to produce a magnetic field having lines of force at an acute angle to said direction to thereby impart a helical path to said blocks of ions, means to impart an equal electrostatic force to the ions of all masses to separate the block of ions into a plurality of ion groups having time spacing relative to each other proportional to the masses of the individual ions of the gas, a collector to collect said spaced group of ions in succession, said collector having a high degree of secondary-emissivity to constitute a cathode, a plurality of dynodes and an anode to form with said cathode an electron-multiplier, means including a pulse generator to apply direct-voltage operating pulses to the elements of said multiplier, and adjustable means to synchronize said generator with said pulsatory source to trigger off said generator at a given instant after the initiation of a block.

10. Apparatus, as set forth in claim 9, wherein said adjustable means includes a variable time delay device, and a trigger circuit coupled to said source and via said device to said generator.

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