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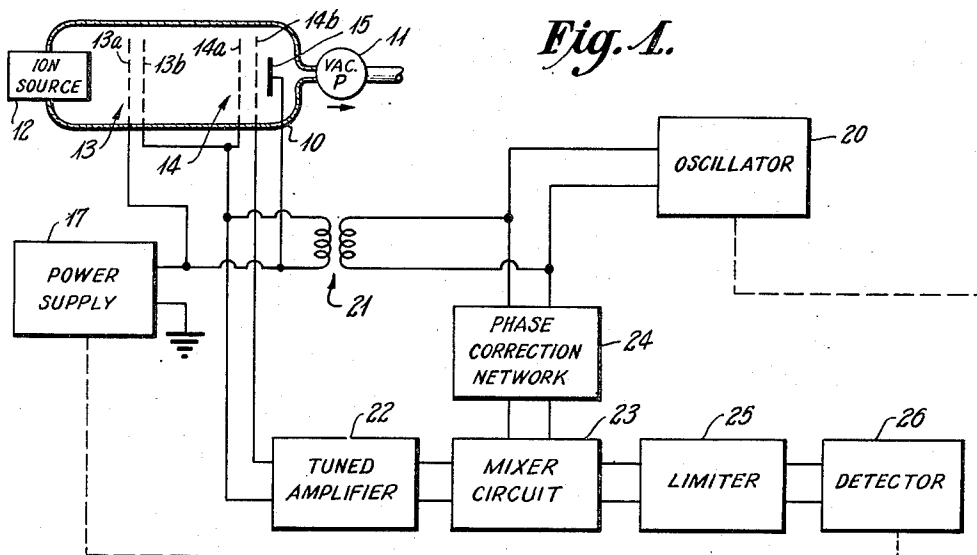
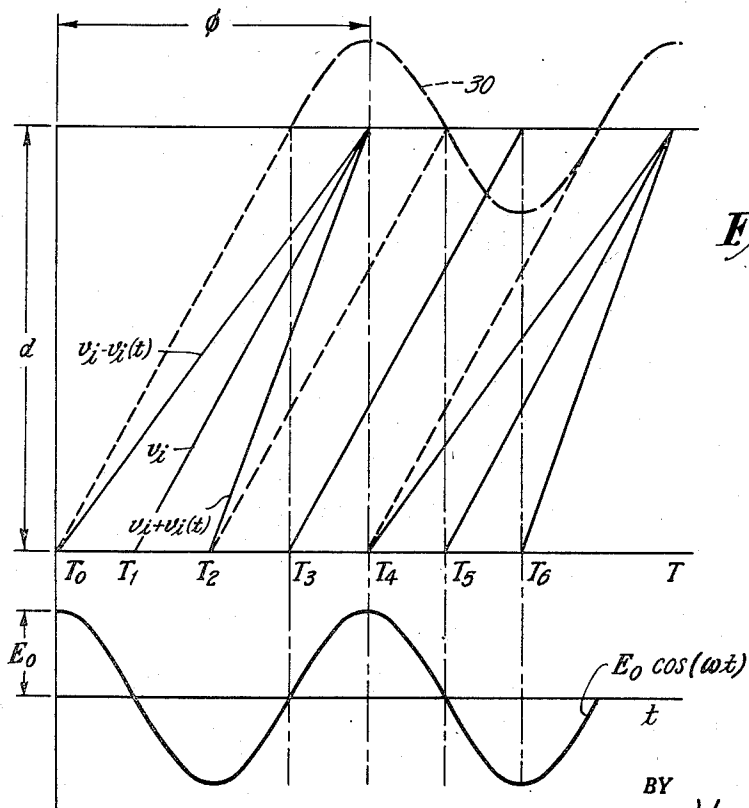
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MASS SPECTROMETRY

Filed Nov. 13, 1953

2 Sheets-Sheet 1



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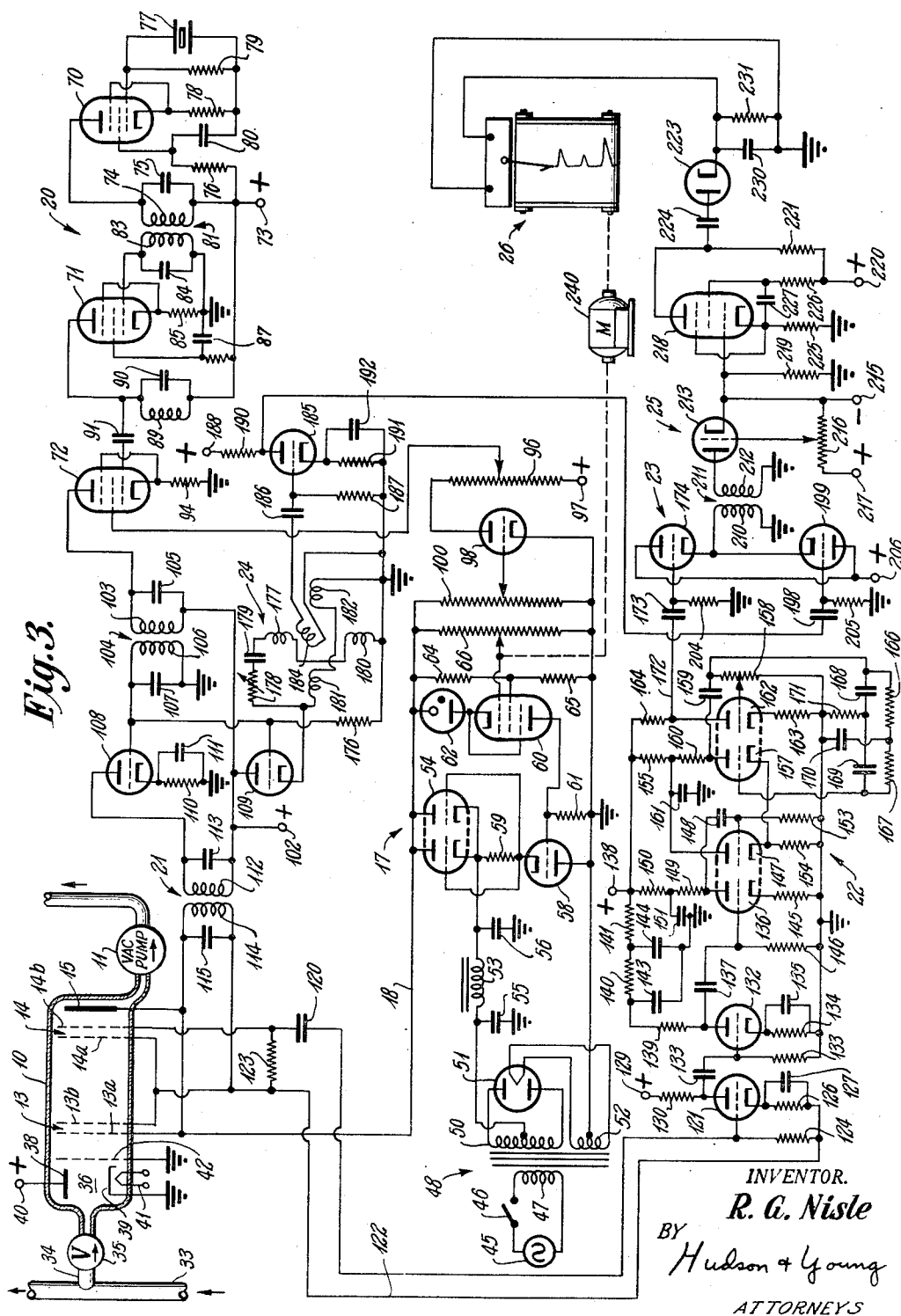
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MASS SPECTROMETRY

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14 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometry. In one specific aspect it relates to a mass spectrometer which indicates the time of flight of selected ions over a path of predetermined length.

Mass spectrometry comprises, in general, ionizing a sample of the material under investigation and separating the resulting ions according to their masses to determine the relative abundance of the ions of selected masses. The material to be analyzed usually is provided as a vapor, and this vapor is bombarded by a stream of electrons to produce the desired ions. The bombarded vapor is maintained at a relatively low pressure, but at sufficient pressure to provide the required number of ions needed for the analysis. The molecules may be ionized by removal of an electron, or by breaking up the molecules, or both. Although both positive and negative ions may be formed by such bombardment, most mass spectrometers make use of only the positive ions. These positive ions are accelerated out of the region of the electron beam by means of a negative electrical potential applied thereto. This electrical potential imparts equal kinetic energies to the ions having like charges such that ions of different masses have different velocities after passing through the electrical field, and consequently have different momenta.

The presently known mass spectrometers can be classified in one of two general groups, the momentum selection type and the velocity selection type. The momentum selection instruments sort the ions into beams of different masses by means of a magnetic deflecting field, an electrical deflecting field, or by a combination of the two. Ions of a selected mass are allowed to impinge upon a collecting plate to which is connected a suitable indicating circuit. The velocity selection instruments sort the ions according to their velocities in terms of the times required to travel through a path of predetermined length. These latter instruments are referred to generally as time-of-flight mass spectrometers.

In recent years the mass spectrometer has been developed from a highly specialized academic research instrument for measuring the relative abundance of isotopes to an analytical tool of extreme sensitivity and accuracy. At the present time, applications are being found for use of the mass spectrometer in process monitoring and control. For such use of the mass spectrometer, the conventional instruments commercially available have not been found to be entirely satisfactory. This has resulted from the large size and relative complexity of these instruments. A fairly strong magnetic field usually is required which increases the size of the instrument and its operating cost. In order to employ a mass spectrometer in the field for process control it is necessary that the instrument be rugged, compact, relatively inexpensive, and explosion proof. The commercial instruments have not met these requirements.

It is an object of this invention to provide an improved method of separating ions of different masses by means of a velocity selection of the ions under consideration.

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Another object is to provide a mass spectrometer that does not require a magnetic deflecting field.

A further object is to provide a mass spectrometer that is free of spurious signals due to multiples and sub-multiples of the indicated mass.

A still further object is to provide a relatively simple, compact mass spectrometer that can readily be adapted for process monitoring or control purposes.

The mass spectrometer of the present invention includes an ion source to provide ions of the material under analysis. Ions emitted from this source are directed through a first set of bunching grids, across which is applied an alternating electrical field of radio frequency. The ions subsequently are allowed to pass through a field-free drift space, thence through a set of collector grids and finally to a collecting electrode. The positive ions are bunched when they pass beyond the first set of grids since the ions which enter the bunching grids during the negative half cycle of the applied field are accelerated whereas the ions which pass through the bunching grids during the positive half cycle of the applied field are decelerated. In this manner, ions of a particular mass arrive at the collector grids in bunches. The bunches of ions passing through the collector grids give up a portion of their energy to the collector grids. The resulting signal induced between the collecting grids is amplified and compared with a signal proportional to and in phase with the electrical field applied to the bunching grids. A phase correcting network is included in the collector grid circuit, and a detector circuit is connected to the output of the comparing circuit to indicate the presence of ions of a predetermined mass.

Other objects, advantages and features of this invention should become apparent from the following detailed description taken in conjunction with the accompanying drawing in which:

Figure 1 is a schematic representation of the mass spectrometer of this invention;

Figure 2 is a graphical representation of an operating feature of the invention; and

Figure 3 is a detailed schematic circuit diagram of one embodiment of the mass spectrometer shown in Figure 1.

Referring now to the drawing in detail and to Figure 1 in particular, there is shown a mass spectrometer tube 10, the interior of which is maintained at a reduced pressure by a vacuum pump 11. An ion source 12 is disposed in one end of tube 10 to provide ions of the sample of material to be analyzed. These ions are directed through a set of bunching grids 13 and a set of collector grids 14 to a collecting electrode 15. Bunching grids 13 comprise a pair of closely spaced grids 13a and 13b, the planes of which are substantially perpendicular to the direction of ion propagation through tube 10. Collecting grids 14 comprise a pair of closely spaced electrodes 14a and 14b, the planes of which are also disposed substantially perpendicular to the direction of ion propagation through tube 10. Grid 13a is maintained at an adjustable constant potential which is of polarity opposite that of the ions under consideration. This potential is supplied by a power supply circuit 17 having one output terminal thereof grounded. The second output terminal of power supply 17 is connected directly to grid 13a. If positive ions are to be measured, the non-grounded output terminal of power supply 17 is maintained at an adjustable constant negative potential.

An alternating voltage is applied between grids 13a and 13b from an oscillator 20, the output terminals of which are connected to respective grids 13a and 13b through a transformer 21. Collector grids 14a and 14b are connected to the respective input terminals of an amplifier 22 that is tuned to pass signals of the same fre-

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quency as the output of oscillator 20. Collector electrode 15 is connected to the non-grounded output terminal of power supply 17. The output terminals of tuned amplifier 22 are applied to a first pair of input terminals of a mixer circuit 23. The output terminals of oscillator 20 are applied to the input terminals of a phase correction network 24, and the output terminals of network 24 are connected to a second pair of input terminals of mixer circuit 23. The output terminals of mixer circuit 23 are connected to the input terminals of a limiter circuit 25, and the output terminals of limiter circuit 25 are connected to the input terminals of a detector 26. Power supply 17, oscillator 20 and detector 26 are coupled to one another in a manner which is described in detail hereinafter.

Ions preferably are formed in source 12 by bombardment of a gaseous sample to be analyzed by a stream of electrons emitted from a heated filament. The positive ions thus produced are accelerated by a negative potential applied to grid 13a. These ions are velocity modulated by the voltage applied between grids 13a and 13b from the output of oscillator 20. This modulating voltage can be represented by the term $E_0 \cos(\omega t)$. The ions then drift through the space between grids 13 and 14 and finally impinge upon negative collector plate 15 where they are discharged, the resulting neutral molecules being removed from tube 10 by vacuum pump 11. Within the drift space between grids 13 and 14, ions of the same mass tend to form into bunches. These bunches of ions induce an electrical signal between collector grids 14a and 14b by giving up a portion of their energy to the output circuit connected to grids 14a and 14b.

The process of forming the ions into bunches is illustrated schematically in Figure 2. At the bottom of the figure, the output voltage signal from oscillator 20 is represented by a cosine curve of maximum amplitude E_0 . The abscissa of the upper portion of Figure 2 represents time and the ordinate d represents the distance between the mid-point of grids 13 and the mid-point of grids 14. Positive ions which pass between bunching grids 13a and 13b at time T_0 are decelerated since E_0 is positive at this time. These ions follow the path $v_i - v_i(t)$ and arrive between collector grids 14a and 14b at time T_4 . Ions passing through the bunching grids at time T_1 are not affected by the modulating voltage because E_0 is of zero amplitude at this time. These ions continue at the same velocity v_i as they had prior to their passage through bunching grids 13a and 13b and arrive between collector grids 14a and 14b at time T_4 . This path is represented by line v_i . Positive ions passing through bunching grids 13a and 13b at time T_2 are accelerated because E_0 is negative. These ions of a particular mass also arrive between the collector grids at time T_4 , their path being represented by line $v_i + v_i(t)$. This procedure is repeated during subsequent cycles of the voltage $E_0 \cos(\omega t)$ applied to the bunching grids. Thus, the ions of a selected mass are concentrated between collector grids 14a and 14b at the same frequency as the voltage applied between the bunching grids 13a and 13b. In this manner, a fluctuating voltage signal is established between the input terminals of amplifier 22, which signal is represented by the dotted curve 30 in the upper portion of Figure 2. Voltage curve 30 is displaced from the voltage curve $E_0 \cos(\omega t)$ by the phase angle ϕ .

This bunching process can be explained mathematically in the following manner. Ions with mass m_i initially arrive at bunching grid 13a with kinetic energy represented as

$$K. E. = eE = \frac{1}{2} m_i v_i^2 \quad (1)$$

where e is the charge on the individual ions, E is the accelerating potential supplied by power supply 17 and v_i is the velocity of the individual ions. During their

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passage from grid 13a to grid 13b, the kinetic energies of the ions are changed as follows:

$$\Delta K. E. = eE_0 \cos(\omega t) \quad (2)$$

- 5 The velocities of the ions are changed by an amount which is a function of the time required to make the passage from grids 13a to grids 13b, and this change in velocity is represented by $v_i(t)$. The energy balance of the velocity modulated ions is represented as:

$$K. E. + \Delta K. E. = \frac{1}{2} m_i [v_i + v_i(t)]^2 \quad (3)$$

which can be rewritten as:

$$\frac{1}{2} m_i v_i^2 - eE_0 \cos(\omega t) = \frac{1}{2} m_i [v_i + v_i(t)]^2 \quad (4)$$

- 15 At $\omega t = 0$, the ions are decelerated by the positive potential E_0 , so that $\Delta K. E.$ is negative. If equation 4 is solved for $v_i(t)$ there is obtained:

$$v_i(t) = -v_i \pm \sqrt{v_i^2 - \frac{2eE_0}{m_i} \cos(\omega t)} \quad (5)$$

Referring again to Figure 2 it can be seen that for a particular bunch of ions to arrive at the collector grids, the accelerated and decelerated ions must arrive at the same time. The times of flight of ions passing between the two sets of grids at different times must therefore be different. The time of flight for the decelerated ions can be written as:

$$\tau_1 = T_4 - T_0 = \frac{d}{v_1} \quad (6)$$

where τ_1 represents the time of flight and v_1 represents the velocity of the decelerated ions. The time of flight for the ions which are neither accelerated nor decelerated is represented as:

$$\tau_2 = T_4 - T_1 = \frac{d}{v_2} \quad (7)$$

where τ_2 represents the time of flight and v_2 represents velocity. The time of flight of the accelerated ions is represented as:

$$\tau_3 = T_4 - T_2 = \frac{d}{v_3} \quad (8)$$

where τ_3 is the time of flight of the accelerated ions and v_3 represents velocity.

The velocity of any given ion after being velocity modulated is represented as:

$$v = v_i + v_i(t) \quad (9)$$

- 50 Substituting Equation 5 in Equation 9 there is obtained:

$$v = v_i + v_i(t) = \sqrt{v_i^2 - \frac{2eE_0}{m_i} \cos(\omega t)} \quad (10)$$

- 55 At time T_0 , ωt is zero, so that $\cos(\omega t)$ is unity. If both e and E_0 are positive, Equation 10 becomes:

$$v_1 = \sqrt{v_i^2 - \frac{2eE_0}{m_i}} \quad (11)$$

At time T_1 , ωt is

$$\frac{\pi}{2}$$

- 65 so that $\cos(\omega t)$ is zero. Equation 10 then becomes:

$$v_2 = v_i = \sqrt{\frac{2eE_0}{m_i}} \quad (12)$$

- 70 At time T_2 , ωt is π , so that $\cos(\omega t)$ is -1 . Equation 10 then becomes:

$$v_3 = \sqrt{v_i^2 + \frac{2eE_0}{m_i}} \quad (13)$$

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If Equations 11, 12 and 13 are substituted in respective Equations 6, 7 and 8, there are obtained:

$$\tau_1 = \frac{d}{\sqrt{\frac{2eE}{m_i} - \frac{2eE_0}{m_i}}} \quad (14)$$

$$\tau_2 = \frac{d}{\sqrt{\frac{2eE}{m_i}}} \quad (15)$$

$$\tau_3 = \frac{d}{\sqrt{\frac{2eE}{m_i} + \frac{2eE_0}{m_i}}} \quad (16)$$

The difference in times between τ_1 and τ_3 can be expressed as follows:

$$\tau_1 - \tau_3 = (T_4 - T_0) - (T_4 - T_2) = T_2 - T_0 = \frac{1}{2} P \quad (17)$$

where P is the period of $E_0 \cos(\omega t)$. P is equal to

$$\frac{1}{f}$$

where f is the frequency of $E_0 \cos(\omega t)$.

Equation 17 can be rewritten as:

$$\frac{d}{\sqrt{\frac{2eE}{m_i} - \frac{2eE_0}{m_i}}} - \frac{d}{\sqrt{\frac{2eE}{m_i} + \frac{2eE_0}{m_i}}} = \frac{1}{2f} \quad (18)$$

which when rewritten becomes:

$$f = \frac{1}{2d} \sqrt{\frac{2e}{m_i} \left(\frac{\sqrt{E^2 - E_0^2}}{\sqrt{E + E_0} - \sqrt{E - E_0}} \right)} \quad (19)$$

The phase relation between the modulating voltage applied from oscillator 20 and the signal established between collector electrodes 14a and 14b can be derived from a consideration of Figure 2. If τ is the time delay between these signals, and ϕ is the phase shift between the signals, then

$$\phi = 2\pi f \tau \quad (20)$$

From a consideration of Figure 2 and Equations 6 and 14, τ can be expressed as follows:

$$\tau = T_4 - T_0 = \frac{d}{\sqrt{\frac{2e}{m_i}} \sqrt{E - E_0}} = d \sqrt{\frac{m_i}{2e}} \left(\frac{1}{\sqrt{E - E_0}} \right) \quad (21)$$

Combining Equations 19, 20 and 21 gives:

$$\phi = 2\pi f \tau =$$

$$2\pi \frac{1}{2d} \sqrt{\frac{2e}{m_i} \left(\frac{\sqrt{E^2 - E_0^2}}{\sqrt{E + E_0} - \sqrt{E - E_0}} \right)} d \sqrt{\frac{m_i}{2e}} \left(\frac{1}{\sqrt{E - E_0}} \right) \quad (22)$$

Equation 22 can be simplified as:

$$\phi = \pi \left(\frac{1}{1 - \sqrt{\frac{E - E_0}{E + E_0}}} \right) \quad (23)$$

If ϕ becomes 2π or $n2\pi$ there is, in effect, no delay between the modulating voltage and the collector grid signal, whereby these two signals are in phase with one another. Under this condition it is found that the following relationship is obtained from Equation 23:

$$E_0 = \frac{3}{5} E \quad (24)$$

If the value of E_0 is substituted into Equation 19, the following relationship is obtained for the mass of the individual ions being bunched:

$$m_i = \frac{4}{5} \frac{eE}{f^2 d^2} \quad (25)$$

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the particular mass spectrometer tube. This equation can be modified by the introduction of the following constants:

$$e = 4.8024 \times 10^{-10} \text{ e. s. u.}$$

$$E \text{ (e. s. u.)} = \frac{E \text{ (volts)}}{300}$$

$$m_i \text{ (grams)} = M_i \text{ (mass units)} \times 1.6603 \times 10^{-24}$$

to obtain:

$$M_i = 0.77133 \frac{E}{f^2 d^2} \quad (26)$$

where d is expressed in centimeters and f is in megacycles.

If the tube is constructed such that d is 10 centimeters and f is 0.2 megacycle, then

$$m_i = 0.1928E \quad (27)$$

Under these conditions it can be seen, for example, that if ions of mass 50 are to be analyzed, voltage E should be 259 volts and voltage E_0 should be 156 volts.

The foregoing analysis is based on the assumption that the time for the ions to travel between bunching grids 13a and 13b is small compared to the period P of modulating voltage $E_0 \cos(\omega t)$. In designing the tube 10, grids 13a and 13b should be as closely spaced as practical. In practice, the frequency of oscillator 20 preferably is maintained at a selected value and the ratio between the output voltages from this oscillator and power supply 17 is maintained constant as indicated by Equation 24. By varying the amplitudes of these voltages it is possible to scan a particular sample for ions of the various masses present. The signal induced between collector grids 14a and 14b is amplified, filtered and mixed with a portion of the output of oscillator 20 which has been delayed by ϕ . The limiter circuit suppresses all signals except those resulting from a sum of the voltage E and E_0 which are in phase. The peak value of this sum is measured by detector 26 to indicate the presence of particular ions under investigation.

In Figure 3 there is shown in detail one embodiment of electrical circuitry provided to operate the spectrometer of Figure 1. A gaseous sample to be analyzed is passed through a conduit 33, a portion of the sample being transmitted into tube 10 through a conduit 34 which communicates with conduit 33 and through a valve 35. This gas sample drifts into a region 36 which has an anode 38 and a cathode 39 disposed therein in spaced relation with one another. Anode 38 is connected to a positive potential terminal 40 and cathode 39 is grounded. Cathode 39 is heated by a filament 41, and electrons emitted from the cathode pass through the region 36 toward anode 38. The gas sample in region 36 is thereby bombarded by the stream of electrons which results in the formation of ions from the gas molecules. A grounded grid 42 is positioned within tube 10 to shield region 36 from grid 13a. The positive ions formed in region 36 are accelerated toward bunching grids 13 by the negative potential applied to grid 13a by a lead 18.

Lead 18 is maintained at a predetermined negative potential by the power supply circuit 17. This circuit comprises a source of alternating current 45 which is applied through a switch 46 to the primary winding 47 of a transformer 48. Current source 45 can be obtained from a 110 volt, 60 cycle power line, for example. The end terminals of a first secondary winding 50 of transformer 48 are applied to the respective anodes of a double diode 51. A secondary winding 52 of transformer 48 is applied across the filament of double diode 51 and the center tap of transformer winding 52 is maintained at ground potential. The center tap of transformer winding 50 is connected to one end terminal of a filter inductor 53. The second end terminal of inductor 53 is connected to the two cathodes of a double triode 54. The junction between the center tap of transformer winding 50 and inductor 53 is connected to ground through a filter capacitor 55, and the junction between inductor 53 and the cathodes of double

Equation 25 thus constitutes the design equation for 75

triode 54 is connected to ground through a filter capacitor 56.

Both anodes of double triode 54 are connected to lead 18. The two control grids of double triode 54 are connected to the cathode of a triode 58, and the two cathodes of double triode 54 are connected to the cathode of a triode 58 through a common resistor 59. The anode of triode 58 is grounded, and the control grid of triode 58 is connected to the anode of a pentode 60. The anode of pentode 60 is connected to ground through a resistor 61. The suppressor grid of pentode 60 is connected to the cathode thereof, and this cathode is connected to lead 18 through a gas filled voltage regulating tube 62. A pair of series connected resistors 64 and 65 is connected between lead 18 and ground to form a voltage dividing network. The junction between these resistors is connected to the screen grid of pentode 60. The end terminals of a potentiometer 66 are connected to lead 18 and to ground, respectively, and the contactor of potentiometer 66 is connected to the control grid of pentode 60.

The power supply circuit thus far described serves to maintain an adjustable constant negative potential on lead 18. Double diode 51 forms a full wave rectifier, the output of which is filtered and applied to the cathodes of double triode 54 and to the cathode of triode 58. Voltage regulating tube 62 maintains a constant potential on the cathode of pentode 60. The potential on the control grid of pentode 60 is adjustable by movement of the contactor of potentiometer 66. The current flow through pentode 60 controls the current flow through triode 58, which in turn regulates the current flow through double triode 54. In this manner the several tubes cooperate with one another to maintain a constant negative potential at lead 18 with respect to ground.

The modulating voltage applied between grids 13a and 13b is supplied by oscillator 20. This oscillator comprises a first pentode 70 which forms a portion of the oscillator itself, a second pentode 71 which forms a portion of a buffer oscillator and a third pentode 72 which forms a portion of a power amplifier. The anode of pentode 70 is connected to a positive potential terminal 73 through a tuned circuit comprising an inductor 74 shunted by a capacitor 75. Inductor 74 forms the primary winding of a transformer 81. The screen grid of pentode 70 is connected to potential terminal 73 through a resistor 76. One terminal of a frequency regulating crystal 77 is connected to the control grid of pentode 70, and the second terminal of crystal 77 is connected to the cathode of pentode 70 through a cathode resistor 78. A resistor 79 is connected in shunt with crystal 77. The junction between crystal 77 and cathode resistor 78 is grounded, and a capacitor 80 is connected between the screen grid of pentode 70 and ground.

The secondary winding 83 of transformer 81 is shunted by a capacitor 84. One end terminal of transformer winding 83 is connected to the control grid of pentode 71 and the second end terminal of transformer winding 83 is grounded. A cathode resistor 85 is connected between the cathode of pentode 71 and ground. The suppressor grid of pentode 71 is connected to the cathode thereof, and the screen grid of pentode 71 is connected to ground through a capacitor 87. The anode of pentode 71 is connected to positive potential terminal 73 through a tuned circuit comprising an inductor 89 shunted by a capacitor 90.

The anode of pentode 71 is also connected to the control grid of pentode 72 through a capacitor 91. The suppressor grid of pentode 72 is connected to the cathode thereof, and this cathode is grounded through a resistor 94. The screen grid of pentode 72 is connected to the contactor of a potentiometer 96. One end terminal of potentiometer 96 is connected to a source of positive potential 97 and the second end terminal of potentiometer 96 is connected to the anode of a triode 98. The cathode of pentode 98 is grounded, and the control grid of triode

98 is connected to the contactor of a potentiometer 100. The end terminals of potentiometer 100 are connected between lead 18 in the power supply circuit and ground, respectively. In this manner the power supply circuit is coupled to the oscillator such that a predetermined ratio can be maintained between the power supply circuit output and the oscillator output by adjustment of either potentiometer 96 or potentiometer 100.

The anode of pentode 72 is connected to a source of positive potential 102 through the primary winding 103 of a tuned transformer 104. A capacitor 105 is connected in shunt with transformer winding 103. The secondary winding 106 of transformer 104 is shunted by a capacitor 107. One end terminal of transformer winding 106 is connected to the control grid of a triode 108 and to the control grid of a triode 109. The second end terminal of transformer winding 106 is grounded. The cathode of triode 108 is grounded through a resistor 110 which is shunted by a capacitor 111, and the anode of triode 108 is connected to positive potential terminal 102 through the primary winding 112 of tuned transformer 21. A capacitor 113 is connected in shunt with transformer winding 112. One end terminal of the secondary winding 114 of transformer 21 is connected to grid 13a of spectrometer tube 10, and the second end terminal of transformer winding 114 is connected to grid 13b. A capacitor 115 is connected in shunt with transformer winding 114.

Collector grid 14b of spectrometer tube 10 is connected through a capacitor 120 to the control grid of a triode 121, the latter forming the first stage of tuned amplifier 22. Collector grid 14a is connected to a lead 122 which forms the second input terminal of amplifier 22. A resistor 123 is connected between grids 14a and 14b, and a resistor 124 is connected between the control grid of triode 121 and lead 122. The cathode of triode 121 is connected to lead 122 through a resistor 126 which is shunted by a capacitor 127. The anode of triode 121 is connected to a positive potential terminal 129 through a resistor 130 and to the control grid of a triode 132 through a capacitor 133.

Triode 132 forms the second stage of amplifier 22. The control grid of triode 132 is connected to ground through a resistor 133, and the cathode of triode 132 is connected to ground through a resistor 134 which is shunted by a capacitor 135. The anode of triode 132 is connected to the control grid of a third triode 136 through a capacitor 137 and to a positive potential terminal 138 through series connected resistors 139, 140 and 141. A capacitor 143 is connected between ground and the junction between resistors 139 and 140, and a second capacitor 144 is connected between ground and the junction between resistors 140 and 141.

The cathode of triode 136 is connected to ground through a resistor 145, and the control grid of triode 136 is connected to ground through a resistor 146. The anode of triode 136 is connected to the control grid of a fourth triode 147 through a capacitor 148, and to positive potential terminal 138 through series connected resistors 149 and 150, the junction between resistors 149 and 150 being connected to ground through a capacitor 151. The control grid of triode 147 is connected to ground through a resistor 153, and the cathode of triode 147 is connected to ground through a resistor 154. The anode of triode 147 is connected to positive potential terminal 138 through a resistor 155. The cathode of triode 147 is connected directly to the cathode of a fifth triode 157. The anode of triode 157 is connected to one end terminal of a potentiometer 158 through a capacitor 159 and to positive potential terminal 138 through series connected resistors 160 and 155, the junction between resistors 160 and 155 being connected to ground through a capacitor 161. The contactor of potentiometer 158 is connected to the control grid of a sixth triode 162, and the second end terminal of potentiometer 158 is connect-

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ed to ground. The cathode of triode 162 is connected to ground through a resistor 163, and the anode of triode 162 is connected to positive potential terminal 138 through a resistor 164.

The first-mentioned end terminal of potentiometer 158 is connected to the control grid of triode 157 through a pair of series connected resistors 166 and 167. A pair of capacitors 168 and 169 are connected in series relation with one another and in parallel with series connected resistors 166 and 167. The junction between resistors 166 and 167 is connected to ground through a capacitor 170, and the junction between capacitors 168 and 169 is connected to ground through a resistor 171. Resistors 166, 167 and 171 and capacitors 168, 169 and 170 thus form a parallel-T filter which serves to minimize the transmission through amplifier 22 of signals at frequencies other than the frequency of oscillator 20. If oscillator 20 provides 0.2 megacycle signals, this parallel-T filter is tuned to 0.2 megacycle so as to present high impedance to two tenths megacycle signals and relatively low impedance to signals of other frequencies. Amplifier 22 is, therefore, tuned to pass only signals of a predetermined frequency, which frequency is the frequency of oscillator 20.

A lead 172 is connected to the anode of triode 162, and thus constitutes one output terminal of amplifier 22, the second output terminal of which is represented by ground. Lead 172 is connected through a capacitor 173 to the control grid of a first triode 174 which forms a portion of mixer circuit 23, the control grid of triode 174 being connected to ground through a resistor 204. The second signal applied to mixer circuit 23 is obtained from the output of oscillator 20 through cathode follower triode 109. The anode of triode 109 is connected to positive potential terminal 102, and the control grid of triode 109 is connected directly to the first end terminal of transformer winding 106. The control grid of triode 109 also is connected to ground through a resistor 176.

The output signal from triode 109 is applied to mixer circuit 23 through phase correction network 24. To this end, the cathode of triode 109 is connected to one end terminal of a coil 177 through a variable resistor 178 and a capacitor 179 connected in series relation. The second end terminal of coil 177 is connected to the first end terminal of a second coil 180, the second end terminal of which is grounded. The cathode of triode 109 also is connected to the first end terminal of a third coil 181. The second end terminal of coil 181 is connected to the first end terminal of a coil 182, the second end terminal of which is grounded. Series connected coils 177 and 180 are positioned at right angles to series connected coils 181 and 182, and a rotatable coil 184 is positioned at the center of coils 177, 180, 181 and 182. One end terminal of coil 184 is grounded and the second end terminal of coil 184 is connected to the control grid of a triode 185 through a capacitor 186, the control grid of triode 185 being connected to ground through a resistor 187. The anode of triode 185 is connected to a positive potential terminal 188 through a resistor 190, and the cathode of triode 185 is connected to ground through a resistor 191 which is shunted by a capacitor 192. The anode of cathode 185 is connected to the control grid of a second triode 199 of mixer circuit 23 through a capacitor 198, the control grid of triode 199 being connected to ground through a resistor 205.

Phase correction network 24 is thus constructed such that equal current flows through the two sets of coils which are mounted at right angles. However, these current flows are 90° out of phase with one another because of capacitor 179. The phase of the voltage induced in coil 184, with respect to the output signal from triode 109, is, therefore, a function of the angular position of coil 184. The purpose of this phase correction network 24 is to compensate for any phase distortion which may take place in amplifier 22 so that the signals applied to the

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control grids of triodes 174 and 199 are maintained in phase with one another. If the mass spectrometer tube is designed such that ϕ is 2π , then the only phase correction needed is to compensate for any phase distortion in the spectrometer circuitry. If the tube is designed such that ϕ is other than 2π , then a phase correction factor can be introduced by network 24 to maintain the two signals applied to mixer circuit 23 in phase with one another. The phase of the output signal from network 24 is adjusted by rotating coil 184.

The cathodes of triodes 174 and 199 are connected to one another. The anodes of triodes 174 and 199 are connected to one another and to a positive potential terminal 206. The interconnected cathodes of triodes 174 and 199 are connected to one end terminal of the primary winding 210 of a transformer 211, the second end terminal of transformer winding 210 being grounded. One end terminal of the secondary winding 212 of transformer 211 is connected to the anode of a triode 213, and the second end terminal of transformer winding 212 is grounded. The cathode of triode 213 is connected to a negative potential terminal 215, and the control grid of triode 213 is connected to the contactor of a potentiometer 216. One end terminal of potentiometer 216 is connected to negative potential terminal 215, and the second end terminal of potentiometer 216 is connected to a positive potential terminal 217. The cathode of triode 213 also is connected to the control grid of a pentode 218 which forms a power amplifier, the control grid of pentode 218 being connected to ground through a resistor 219.

The two triodes in mixer circuit 23 are connected such that the input signals applied thereto are effectively added. The total current flow through triodes 174 and 199 passes through the primary winding 210 of transformer 211 and induces a corresponding signal in the secondary winding 212. The control grid of triode 213 is maintained at a predetermined potential by potentiometer 216 such that current flows through triode 213 only when a potential greater than a predetermined value is applied to the anode thereof. In this manner only a peak signal representative of the sum of the two signals applied to mixer circuit 23 is transmitted through limiter circuit 25 to the control grid of power amplifier pentode 218.

The anode of pentode 218 is connected to a positive potential terminal 220 through a resistor 221 and to the anode of a diode rectifier 223 through a capacitor 224. The cathode of pentode 218 is grounded through a resistor 225, and the suppressor grid of pentode 218 is connected to the cathode thereof. The screen grid of pentode 218 is connected to positive potential terminal 220 through a resistor 226, and a capacitor 227 is connected between the cathode of pentode 218 and the screen grid thereof. The cathode of diode 223 is connected to one input terminal of recorder 26, the second input terminal of which is grounded. A capacitor 230 and a resistor 231 are each connected in parallel with the input terminals of recorder 26.

The chart of recorder 26 is mechanically coupled to the contactor of potentiometer 66 which controls the magnitude of the voltages applied to bunching grids 13a and 13b. From a consideration of Equations 24 and 27, it can be seen that the magnitude of the accelerating potentials determines the particular mass being detected. Adjustment of the contactor of potentiometer 66 advances the chart of recorder 26 so that a particular sample under analysis can be scanned for ions of various masses. Detector 26 obviously can comprise any of several indicating devices. It can be a conventional recorder, or an indicating meter such as a galvanometer or an oscilloscope. If desired, scanning of a sample can be made automatic by use of a motor such as 240 which progressively or sequentially varies the contactor of potentiometer 66 and moves the recorder chart. The magnitude of the indicated signal is an indication of the abundance of the detected ions.

From the foregoing description it should be apparent that there is provided in accordance with this invention an improved mass spectrometer. The instrument does not require a magnetic field, and as such can be made much smaller than the commercially available instruments. This is of considerable importance if it is necessary to enclose the instrument in an explosion-proof compartment. Obviously, numerous modifications can be made in the electronic circuitry without departing from the scope of this invention. While the device has been described in conjunction with the analysis of positive ions, negative ions can be analyzed by reversing the polarity of the accelerating potentials. Thus, while the invention has been described in conjunction with a present preferred embodiment thereof, it should be apparent that the invention is not limited thereto.

What is claimed is:

1. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be analyzed, first and second closely spaced grids; means for applying a voltage between said first grid and a point of reference potential to accelerate the resulting ions in a path through said first grid and through said second grid, means for applying an alternating voltage between said first and second grids, third and fourth closely spaced grids spaced from said first and second grids in the path of said accelerated ions, and means to measure the voltage induced between said third and fourth grids by the passage of said ions therethrough.

2. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be analyzed, first and second closely spaced grids, means for applying a constant voltage between said first grid and a point of reference potential to accelerate the resulting ions in a path through said first grid and through said second grid, means for applying an alternating voltage between said first and second grids, third and fourth closely spaced grids spaced from said first and second grids in the path of said accelerated ions, means to compare the voltage induced between said third and fourth grids by the passage of said ions therethrough with the voltage applied between said first and second grids, and means to vary the magnitude of voltage applied between said first grid and said point of reference potential and the voltage applied between said first and second grids.

3. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be analyzed; first and second closely spaced grids; a source of direct voltage applied between said first grid and a point of reference potential; a source of alternating voltage applied between said first and second grids; means to vary the magnitudes of said direct and alternating voltages whereby a fixed ratio is maintained between said magnitudes; third and fourth closely spaced grids positioned in spaced relation with said first and second grids whereby ions are directed successively through said first, second, third and fourth grids; and means to measure the voltage induced between said third and fourth grids by the passage of ions therethrough.

4. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be ionized; first, second, third and fourth grids mounted in spaced relation with one another whereby ions emitted from said means can be passed successively through said grids in the order named, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; a source of alternating voltage applied between said first and second grids; circuit means connected between said third and fourth grids to provide a voltage of magnitude proportional to the voltage induced between said third and fourth grids by the passage of ions therebetween;

and circuit means to compare said last-mentioned voltage with said alternating voltage.

5. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be ionized; first, second, third and fourth grids mounted in spaced relation with one another whereby ions emitted from said means can be passed successively through said grids in the order named, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; a source of alternating voltage applied between said first and second grids; a tuned amplifier to pass signals of the same frequency as said source of alternating voltage, the input terminals of said amplifier being connected to said third and fourth grids, respectively; a mixer circuit, the output terminals of said amplifier being connected to first input terminals of said mixer circuit; a phase shift circuit connected between said source of alternating voltage and second input terminals of said mixer circuit; and indicating means connected to the output terminals of said mixer circuit.

6. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be ionized; first, second, third and fourth grids mounted in spaced relation with one another whereby ions emitted from said means can be passed successively through said grids in the order named, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; a source of alternating voltage applied between said first and second grids; a tuned amplifier to pass signals of the same frequency as said source of alternating voltage, the input terminals of said amplifier being connected to said third and fourth grids, respectively; a mixer circuit, the output terminals of said amplifier being connected to first input terminals of said mixer circuit; a phase shift circuit connected between said source of alternating voltage and second input terminals of said mixer circuit; a voltage limiter circuit connected to the output terminals of said mixer circuit to pass signals of magnitude greater than a predetermined value; and an indicating circuit connected to the output terminals of said limiter circuit.

7. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be ionized; first, second, third and fourth grids mounted in spaced relation with one another whereby ions emitted from said means can be passed successively through said grids in the order named, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; a source of alternating voltage applied between said first and second grids; means to vary the magnitudes of said direct and alternating voltages whereby a fixed ratio is maintained between the magnitudes of said direct and alternating voltages; circuit means connected between said third and fourth grids to provide a voltage of magnitude proportional to the voltage induced between said third and fourth grids by the passage of ions therebetween; and circuit means to compare said last-mentioned voltage with said alternating voltage.

8. A mass spectrometer comprising, in combination, means for ionizing a sample of material to be ionized; first, second, third and fourth grids mounted in spaced relation with one another whereby ions emitted from said means can be passed successively through said grids in the order named, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a

point of reference potential to accelerate ions through said first grid; a source of alternating voltage applied between said first and second grids; means to vary the magnitudes of said direct and alternating voltages whereby a fixed ratio is maintained between the magnitudes of said direct and alternating voltages; a tuned amplifier to pass signals of the same frequency as said source of alternating voltage, the input terminals of said amplifier being connected to said third and fourth grids, respectively; a mixer circuit, the output terminals of said amplifier being connected to first input terminals of said mixer circuit; a phase shift circuit connected between said source of alternating voltage and second input terminals of said mixer circuit; a voltage limiter circuit connected to the output terminals of said mixer circuit to pass signals of magnitude greater than a predetermined value; and an indicating circuit connected to the output terminals of said limiter circuit.

9. The combination in accordance with claim 8 further comprising means coupling said indicating circuit with said means to vary the magnitudes of said direct and alternating voltages whereby the signal measured by said indicating circuit is correlated with the magnitudes of said direct and alternating voltages.

10. A mass spectrometer comprising, in combination, a chamber; means for maintaining said chamber at a reduced pressure; means disposed in said chamber to ionize a sample of material to be analyzed; first, second, third and fourth grids and a collector electrode mounted in spaced relation with one another in said chamber whereby ions emitted from said ionizing means can be passed through said grids in the order named to impinge upon said collector electrode, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; means for maintaining said collector electrode at a potential of polarity opposite that of the ions being measured; a source of alternating voltage applied between said first and second grids; circuit means connected between said third and fourth grids to provide a voltage of magnitude proportional to the voltage induced between said third and fourth grids by the passage of ions therebetween; and circuit means to compare said last-mentioned voltage with said alternating voltage.

11. The combination in accordance with claim 10 wherein said means to ionize a sample of material comprises a pair of spaced electrodes, means for establishing an electrical discharge between said pair of spaced electrodes, and means for introducing the sample of material to be analyzed between said spaced electrodes as a gas.

12. A mass spectrometer comprising, in combination, a chamber; means for maintaining said chamber at a reduced pressure; means disposed in said chamber to ionize a sample of material to be analyzed; first, second, third and fourth grids and a collector electrode mounted in spaced relation with one another in said chamber whereby ions emitted from said ionizing means can be passed through said grids in the order named to impinge upon said collector electrode, said first and second grids being closely spaced to one another and said third and fourth grids being closely spaced to one another; a source of direct voltage applied between said first grid and a point of reference potential to accelerate ions through said first grid; means for maintaining said collector electrode at a potential of polarity opposite that of the ions being measured; a source of alternating voltage applied between said first and second grids; a tuned amplifier to pass signals of the same frequency as said source of alternating voltage, the input terminals of said amplifier being connected to said third and fourth grids, respectively; a mixer circuit, the output terminals of said amplifier being connected to first input terminals of said mixer circuit; a phase shift circuit connected between said source of alternating voltage and second input terminals of said mixer circuit; a voltage limiter circuit connected to the output terminals of said mixer circuit to pass signals of magnitude greater than a predetermined value; and an indicating circuit connected to the output terminals of said limiter circuit.

13. The combination in accordance with claim 12 wherein said means to ionize a sample of material comprises a pair of spaced electrodes, means for establishing an electrical discharge between said pair of spaced electrodes, and means for introducing the sample of material to be analyzed between said spaced electrodes as a gas.

14. A mass spectrometer comprising, in combination, an ion source, first and second closely spaced grids, means to apply an electrical potential to said ions to accelerate said ions from said ion source through said first and second grids, means to apply an alternating potential between said first and second grids, third and fourth closely spaced grids spaced from said first and second grids in the path of said accelerated ions, and means to measure the voltage induced between said third and fourth grids by the passage of said ions therethrough.

References Cited in the file of this patent

UNITED STATES PATENTS

2,582,216	Koppius	Jan. 15, 1952
2,642,535	Schroeder	June 16, 1953