Sept. 4, 1956 M. C. BURK ET AL 2,761,974

MASS SPECTROMETER

Filed Jan. 10, 1955 4 Sheets-Sheet 1

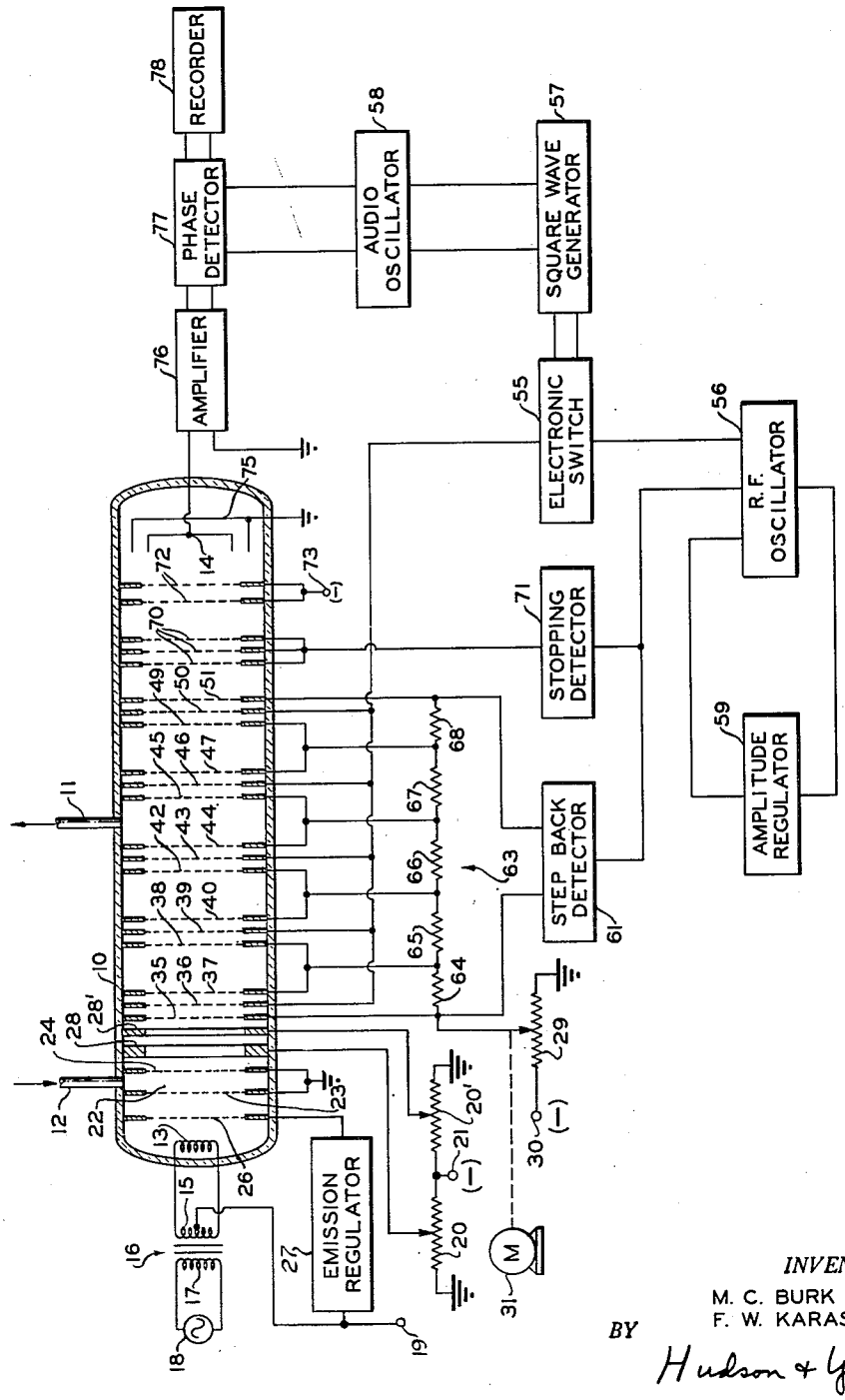


FIG. 1

INVENTORS.
M. C. BURK
F. W. KARASEK

BY Hudson & Young

ATTORNEYS

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MASS SPECTROMETER

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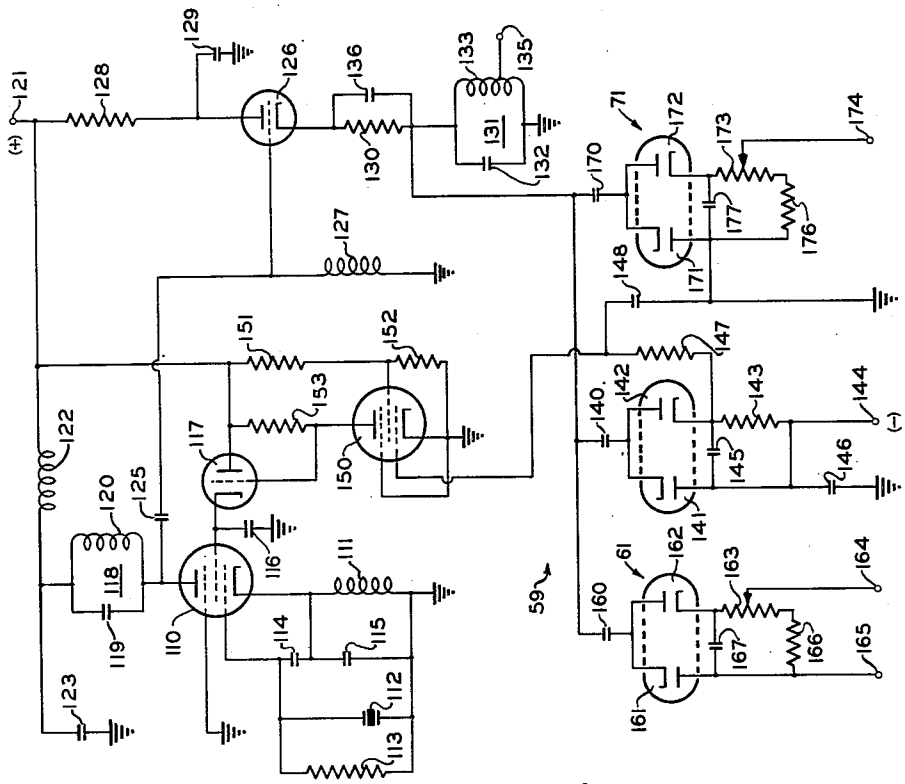


FIG. 3

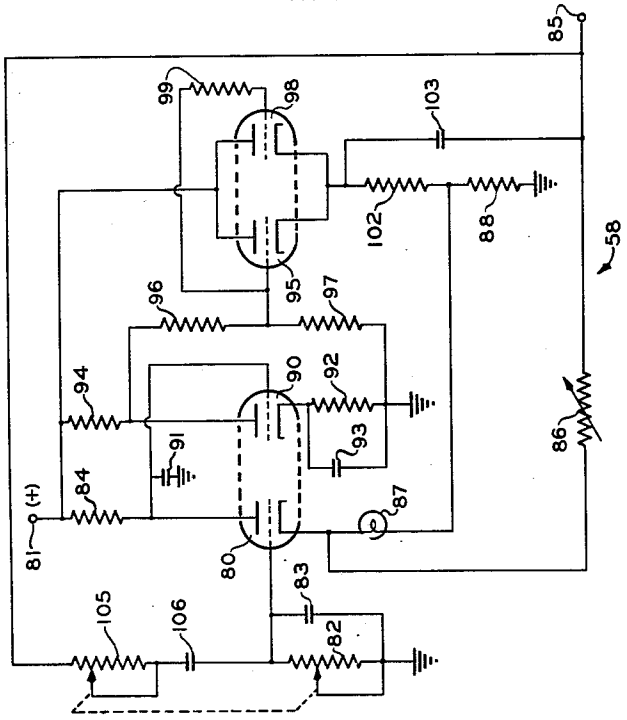


FIG. 2

INVENTORS
M. C. BURK
F. W. KARASEK

BY Hudson & Young

ATTORNEYS

Sept. 4, 1956 M. C. BURK ET AL 2,761,974

MASS SPECTROMETER

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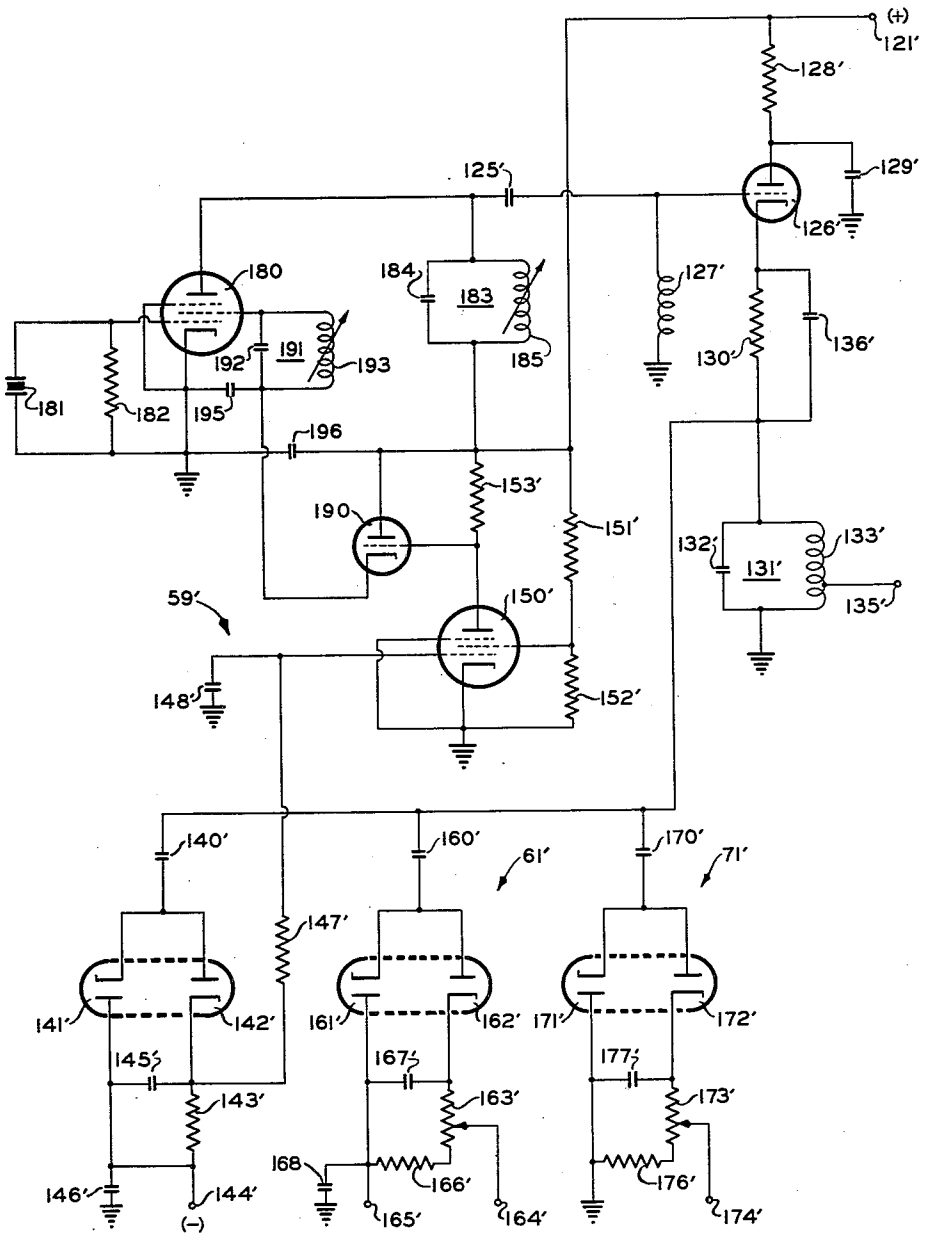


FIG. 4

INVENTORS.
M. C. BURK
F. W. KARASEK

BY Hudson & Young

ATTORNEYS

Sept. 4, 1956 M. C. BURK ET AL 2,761,974

MASS SPECTROMETER

Filed Jan. 10, 1955 4 Sheets-Sheet 4

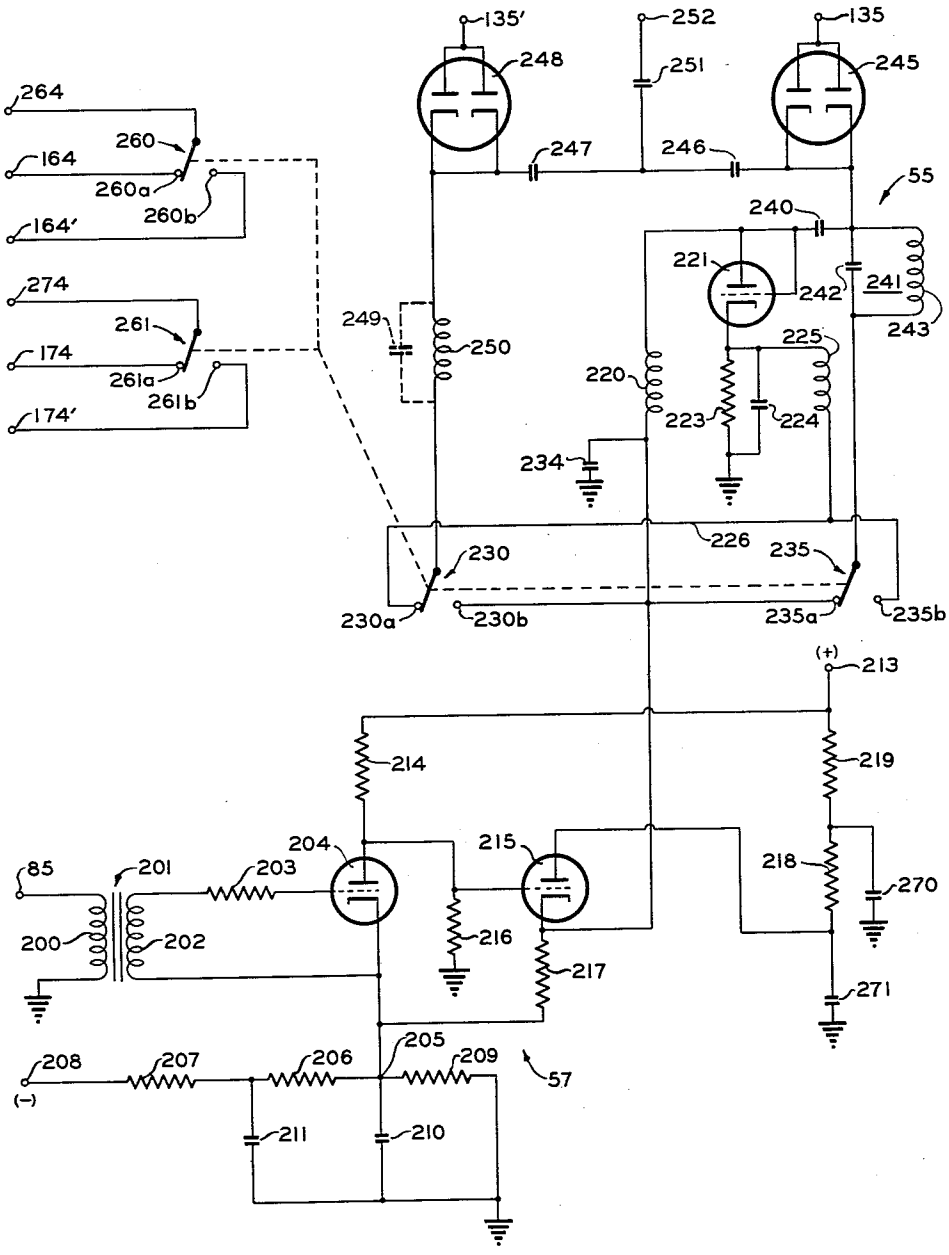


FIG. 5

INVENTORS.
M. C. BURK
F. W. KARASEK

BY Hudson & Young

ATTORNEYS

United States Patent Office

2,761,974

Patented Sept. 4, 1956

2,761,974

MASS SPECTROMETER

Marvin C. Burk, Bartlesville, and Francis W. Karasek, Dewey, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

Application January 10, 1955, Serial No. 480,698

14 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometers. In one specific aspect it relates to switching means to control the application of accelerating potentials of a first frequency to selected grids of a mass spectrometer.

In recent years mass spectrometers have been developed from highly specialized academic research instruments for measuring the relative abundance of isotopes into analytical tools of extreme sensitivity and accuracy. At the present time, applications are being found for the use of mass spectrometers in process monitoring and control. Mass spectrometery comprises, in general, ionizing a sample of material under investigation and separating the resulting ions according to their masses to determine the relative aboundance of ions of selected masses. The material to be analyzed usually is provided as a gas which is bombarded by a stream of electrons to produce the desired ions. Although both positive and negative ions may be formed by such electrical 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 negative potentials. Such potentials impart equal kinetic energies to 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 types and the velocity or energy selection types. The momentum selection instruments sort the ions into beams of different masses by the use of magnetic and/or electrical deflecting fields. Ions of selected masses are allowed to impinge upon a collector plate to which is connected an indicating circuit. The velocity or energy selection instruments sort the ions according to the velocities or energies imparted to ions of selected masses by electrical accelerating fields. The present invention is directed primarily toward improving a mass spectrometer of the latter type.

United States Patent 2,535,032 describes a mass spectrometer which is provided with two sets of three equally spaced accelerating grids. Direct potentials are applied to the outer two grids and a radio frequency potential is applied between the center grid and the outer two grids of each set. Ions which enter the space between the first two grids in proper phase receive maximum energy and are accelerated through the field between the first and second grids and the field between the second and third grids. The ions subsequently pass through a field-free drift space and enter the second group of three grids. The spacing between the grids, the frequency of the radio frequency voltage, and the magnitudes of the accelerating potentials are such that ions of predetermined mass receive sufficient energy to overcome a potential barrier and impinge upon a collector plate.

The mass spectrometer of the present invention is an improvement over the mass spectrometer disclosed in said Patent 2,535,032. Five sets of accelerating grids are employed to provide four separate drift spaces. This

greatly improves the resolving power of the spectrometer. The radio frequency applied to the accelerating grids is turned on and off at a frequency, preferably in the audio range, which modulates the flow of ions through the spectrometer tube. An electronic switch actuated by the output of a square wave generator is provided for this purpose. The modulated ion current which impinges upon the collector plate is amplified and detected in a measuring circuit. The stopping potentials and the D. C. step back potentials applied to the grids of the mass spectrometer tube are derived from the output of the radio frequency oscillator so that the potentials applied to the grids are maintained constant relative to one another.

Accordingly, it is an object of this invention to provide an improved mass spectrometer which operates upon the principle of energy selection of ions of a predetermined mass.

Another object is to provide a mass spectrometer wherein accelerating potentials of a first frequency are applied to the ions periodically at a second lower frequency so that the ion beam is modulated at the lower frequency.

A further object is to provide a mass spectrometer of the energy selection type wherein the potentials applied to the several grids of the tube are derived from a common source.

Other objects, advantages, and features of the 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 schematic circuit diagram of the audio oscillator of Figure 1;

Figure 3 is a schematic circuit diagram of one embodiment of the radio frequency oscillator and detectors of Figure 1;

Figure 4 is a schematic circuit diagram of a second embodiment of the radio frequency oscillator and detectors of Figure 1; and

Figure 5 is a schematic circuit diagram of the square wave generator and electronic switch of Figure 1.

Referring now to the drawing in detail and to Figure 1 in particular, there is shown a mass spectrometer tube **10** comprising a gas impermeable envelope, the interior of which is maintained at a reduced pressure by a vacuum pump, not shown, which communicates with the interior of tube **10** through a conduit **11**. A sample of gas to be analyzed is directed into tube **10** through a conduit **12**. An electron emitting filament **13** is disposed in one end of tube **10** and an ion collector plate **14** is disposed in the second end of the tube. The end terminals of filament **13** are connected to the respective end terminals of the secondary winding **15** of a transformer **16**. The end terminals of the primary winding **17** of transformer **16** are connected to an alternating current source **18**. The center tap of the secondary winding **15** of transformer **16** is connected to a negative potential terminal **19**.

The gas sample supplied through conduit **12** is directed into an ionization chamber **22** in tube **10** which is defined by a pair of spaced grids **23** and **24** that are maintained at ground potential. Electrons emitted from filament **13** are accelerated into chamber **22** by the potential difference between filament **13** and grids **23** and **24**. A grid **26** is positioned between filament **13** and grid **23**. Grid **26** is connected to the output of an emission regulator circuit **27**, which can be of the type disclosed in the copending application of M. C. Burk, Serial No. 412,790, filed February 26, 1954. The input of emission regulator **27** is connected to the center tap of transformer winding **15**. This emission regulator is provided for the purpose of applying a potential to grid **26** of magnitude such as to maintain a constant flow of electrons

into ionization chamber 22 irrespective of minor fluctuations in the electron emission from filament 13. In this manner the rate at which gas molecules are ionized in chamber 22 by electron bombardment is a function of only the gas pressure in the chamber.

A first collimating electrode 28 is positioned on the second side of ionization chamber 22 and is connected to the contactor of a potentiometer 20. One end terminal of potentiometer 20 is connected to a negative potential terminal 21, the second end terminal of potentiometer 20 being grounded. A second collimating electrode 28' is spaced from electrode 28. Electrode 28' is connected to the contactor of a potentiometer 20'. The end terminals of potentiometer 20' are connected to terminal 21 and ground, respectively.

The positive ions produced in ionization chamber 22 are accelerated by the negative potentials applied to electrodes 28 and 28' so as to travel through the tube toward collector plate 14. A first set of three equally spaced grids 35, 36 and 37 is positioned in tube 10 between grid 28 and collector plate 14; a second set of equally spaced grids 38, 39 and 40 is positioned in spaced relation with the first set of grids; a third set of equally spaced grids 42, 43 and 44 is positioned in spaced relation with the second set of grids; a fourth set of equally spaced grids 45, 46 and 47 is positioned in spaced relation with the third set of grids; and a fifth set of equally spaced grids 49, 50 and 51 is positioned in spaced relation with the fourth set of grids. Grid 35 is connected to the contactor of a potentiometer 29. One end terminal of potentiometer 29 is connected to a negative potential terminal 30, the second end terminal of potentiometer 29 being connected to ground. The contactor of potentiometer 29 can be adjusted manually or by a motor 31 to apply selected negative accelerating potentials to grid 35. Grids 36, 39, 43, 46 and 50 are connected to one another and to the output terminal of an electronic switch 55. The input terminal of switch 55 is connected to one output terminal of a radio frequency oscillator 56. Switch 55 is controlled by the output of a square wave generator 57, which in turn is energized by the output of an audio oscillator 58. Switch 55 is thus turned on and off at the frequency of oscillator 58 to apply the output of oscillator 56 to grids 36, 39, 43, 46 and 50. Grid 35 is connected to one output terminal of a step back detector 61, which in turn is connected to an output terminal of oscillator 56. The second output terminal of detector 61 is connected to grid 51. Grids 35 and 51 are connected to one another by a voltage dividing network 63 which comprises five resistors 64, 65, 66, 67 and 68 that are connected in series relation. Grids 37 and 38 are connected to one another and to the junction between resistors 64 and 65; grids 40 and 42 are connected to one another and to the junction between resistors 65 and 66; grids 44 and 45 are connected to one another and to the junction between resistors 66 and 67; and grids 47 and 49 are connected to one another and to the junction between resistors 67 and 68.

A plurality of closely spaced stopping grids 70 is positioned between grid 51 and collector plate 14. Grids 70 are connected to one another and to the output of a stopping detector 71, which in turn is connected to an output of oscillator 56. A plurality of suppressor grids 72 is positioned between grids 70 and collector plate 14. Grids 72 are connected to a negative potential terminal 73 to suppress secondary electrons which may result from ions impinging upon metal parts of the tube. A grounded shield 75 is positioned adjacent collector plate 14.

Collector plate 14 is connected to one input terminal of an amplifier 76 which is tuned to pass signals of the same frequency as the frequency of oscillator 58. The second input terminal of amplifier 76 is connected to ground. The output terminals of amplifier 76 are connected to first input terminals of a phase detector 77. The second input terminals of phase detector 77 are connected to output terminals of oscillator 58. The output terminals of phase detector 77 are connected to a suitable indicating means such as a recorder 78.

The positive ions formed in chamber 22 are accelerated toward collector plate 14 by the negative potential applied to grid 28. During one half cycle of the output signal from oscillator 56, the electrical field between grids 35 and 36 is of such phase that the ions entering this field are accelerated. Ions which enter the field during a particular phase of this half cycle receive maximum energy. During the following half cycle of the signal from oscillator 56, the field between grids 35 and 36 is reversed such that the ions are further accelerated. These ions then drift through the field-free space between grids 37 and 38. The masses of the individual ions determine their times of arrival at grid 38. The ions which arrive at grid 38 at the proper time are again accelerated a maximum amount by the field applied between grids 38 and 39, thereby receiving additional energy. The same accelerating procedure continues as the ions pass through the next ten grids. The positive potential applied to grids 70 is adjusted such that only those ions which receive a predetermined maximum energy are able to pass through grids 70 to impinge upon collector plate 14. The ions impinging upon collector plate 14 cause current to flow through the input circuit of amplifier 76 to ground. This current, which is proportional in magnitude to the number of ions impinging upon the collector plate, is amplitude modulated at the same frequency as audio oscillator 58. It is this modulated component of the current which is measured in accordance with the present invention by recorder 78. The output voltage from step back detector is applied to potential dividing network 63 to decelerate the ions so that the velocity of the selected ions remains substantially constant, whereas the ions of other masses are decelerated in passing through tube 10.

A suitable audio oscillator 58 is illustrated schematically in Figure 2. This oscillator can be tuned to provide output signals of a frequency of approximately 25 cycles per second, for example. The oscillator comprises a first triode 80 having the anode thereof connected to a positive potential terminal 81 through a resistor 84. The control grid of triode 80 is connected to ground through a variable resistor 82 which is shunted by a capacitor 83. The cathode of triode 80 is connected to an output terminal 85 through a variable resistor 86. The cathode of triode 80 is also connected to ground through a lamp 87 and a resistor 88. The anode of triode 80 is connected directly to the control grid of a second triode 90 and to ground through a capacitor 91. The cathode of triode 90 is connected to ground through a resistor 92 which is shunted by a capacitor 93. The anode of triode 90 is connected to positive potential terminal 81 through a resistor 94 and to the control grid of a third triode 95 through a resistor 96. The control grid of triode 95 is connected to ground through a resistor 97 and to the control grid of a fourth triode 98 through a resistor 99. The cathodes of triodes 95 and 98 are connected to one another and to ground through series connected resistors 102 and 88. The anodes of triodes 95 and 98 are connected to positive potential terminal 81. The cathodes of triodes 95 and 98 are also connected to output terminal 85 through a capacitor 103. Output terminal 85 is connected to the control grid of triode 80 through a variable resistor 105 and a capacitor 106 which are connected in series relation.

The oscillator of Figure 2 operates such that triodes 80 and 90 conduct in unison, as do triodes 95 and 98. These two pairs of triodes conduct alternately so that the resulting current flows therethrough produce pulses which initiate operation of the other pair of triodes after a predetermined time delay. The frequency of oscillations is determined by the resistance-capacitance network which provides regenerative coupling between the output of triodes 95 and 98 and the input of triode 80.

This regenerative network is formed by resistors **105** and **82** and capacitors **106** and **83**. The circuit produces oscillations at a frequency f defined by the following equation:

$$f=\frac{1}{2\pi\sqrt{R_{105}R_{82}C_{106}C_{83}}}$$

where R_{105}, R_{82}, C_{106} and C_{83} represent values of resistors **105** and **82** and capacitors **106** and **83**, respectively. In one embodiment of this invention, resistors **105** and **82** each have total resistances of approximately 716,000 ohms and capacitors **106** and **83** are each 0.01 microfarad. Thus, by varying resistors **105** and **82**, which are mechanically coupled to one another, an output frequency of the order to 25 cycles per second can readily be obtained. The amplitude of the voltage appearing between terminal **85** and ground can be adjusted by variable resistor **86**.

The particular ion mas detected by the mass spectrometer of this invention is determined in part by the frequency of oscillator **56**. In Figure 3 there is shown an oscillator which provides an output signal at a frequency of approximately 3.9 megacycles per second. This frequency is useful in detecting ions having masses in the range of approximately thirteen to one hundred twenty-four. The oscillator of Figure 3 comprises a pentode **110** having the cathode thereof connected to ground through an inductor **111**. The control grid of pentode **110** is connected to one terminal of a crystal **112** which oscillates at a frequency of approximately 3.9 megacycles per second. The second terminal of crystal **112** is connected to ground. A resistor **113** is connected in shunt with crystal **112**. A pair of capacitors **114** and **115** is connected in series relation between the control grid of pentode **110** and ground. The junction between capacitors **114** and **115** is connected to the cathode of pentode **110**. The screen grid of pentode **110** is connected directly to the cathode of a triode **117** which is described in detail hereinafter. The screen grid of pentode **110** is also connected to ground through a capacitor **116**. The suppressor grid of pentode **110** is connected to ground. The anode of pentode **110** is connected to one terminal of a tank circuit **118** which comprises a capacitor **119** and an inductor **120** connected in parallel relation. The second terminal of tank circuit **118** is connected to a positive potential terminal **121** through an inductor **122** and to ground through a capacitor **123**. The anode of pentode **110** is connected through a capacitor **125** to the control grid of a triode **126**. The control grid of triode **126** is connected to ground through an inductor **127**. The anode of triode **126** is connected to positive potential terminal **121** through a resistor **128** and to ground through a capacitor **129**. The cathode of triode **126** is connected through a resistor **130** to one terminal of a second tuned circuit **131** which comprises a capacitor **132** and an inductor **133** connected in parallel relation. The second terminal of tuned circuit **131** is connected to ground. An output terminal **135** is connected to a point on inductor **133**. The oscillations produced by pentode **110** and its associated circuit are amplified by triode **126** such that the signal appearing between terminal **135** and ground has a frequency of approximately 3.9 megacycles per second.

The amplitude regulator circuit **59** of Figure 1 is provided to maintain the output voltage from oscillator **56** constant. This regulator is illustrated in detail in Figure 3. The junction between resistor **130** and tank circuit **131** is connected through a capacitor **140** to the cathode of a diode **141** and to the anode of a diode **142**. The cathode of diode **142** is connected through a resistor **143** to a terminal **144** which is maintained at a negative potential of constant magnitude by a suitable voltage regulating circuit, not shown. A capacitor **145** is connected between the cathode of diode **142** and the anode of diode **141**. The anode of diode **141** is connected to ground through a capacitor **146**. The cathode of diode **142** is also connected

through a resistor **147** to the control grid of a pentode **150**. The cathode and the suppressor grid of pentode **150** are connected to ground. The screen grid of pentode **150** is connected to positive potential terminal **121** through a resistor **151** and to ground through a resistor **152**. The anode of pentode **150** is connected through a resistor **153** to positive potential terminal **121** and directly to the control grid of triode **117**. The anode of triode **117** is connected to positive potential terminal **121**.

Diodes **142** and **141** and capacitors **140** and **145** form a voltage doubling circuit. During the half cycle of the output signal from triode **126** when the cathode thereof is the most positive, capacitor **140** is charged by current flow through diode **142**, which current flow also charges capacitor **145**. During the following half cycle of the output signal from triode **126**, diode **141** conducts current to discharge capacitor **140** and to charge capacitor **145** further to a voltage approximately twice that previously applied across the capacitor. The rectified doubled voltage appearing at the cathode of diode **142** is applied to the control grid of pentode **150**. If the output voltage appearing at the cathode of triode **126** tends to increase in value, for example, then the rectified voltage applied to the control grid of pentode **150** is also increased, which increases the current flow through the pentode. The increased current flow results in a greater voltage drop across anode resistor **153**, such that the potential applied to the control grid of triode **117** becomes more negative. This negative change in potential decreases the current flow through triode **117** such that the potential applied to the screen grid of pentode **110** becomes more negative. This potential change tends to reduce the output voltage of the oscillator by an amount sufficient to maintain said output voltage constant. If the oscillator output voltage tends to decrease, the potential changes previously mentioned are all reversed such that the screen grid of pentode **110** becomes more positive to increase the output of the oscillator back to the desired value.

Step back detector **61** is illustrated in Figure 3. The junction between resistor **130** and tank circuit **131** is connected through a capacitor **160** to the cathode of a diode **161** and to the anode of a diode **162**. The cathode of diode **162** is connected to one end terminal of a potentiometer **163**. The contactor of potentiometer **163** is connected to a first output terminal **164**. The second end terminal of potentiometer **163** is connected through a resistor **166** to a second output terminal **165**. A capacitor **167** is connected between the cathode of diode **162** and the anode of diode **161**. Diodes **161** and **162** and capacitors **160** and **167** also form a voltage doubling circuit which provides a rectified voltage between terminals **164** and **165**.

Stopping detector **71** is illustrated in Figure 3. The junction between resistor **130** and tank circuit **131** is connected through a capacitor **170** to the cathode of a diode **171** and the anode of a diode **172**. The cathode of diode **172** is connected to one end terminal of a potentiometer **173**. The contactor of potentiometer **173** is connected to an output terminal **174**. The second end terminal of potentiometer **173** is connected through a resistor **176** to ground. A capacitor **177** is connected between the cathode of diode **172** and the anode of diode **171**. Diodes **171** and **172** and capacitors **170** and **177** thus form a third voltage doubling circuit to provide a rectified output voltage between terminal **174** and ground.

In Figure 4 there is shown a second embodiment of oscillator **56** which provides an output signal having a frequency of approximately ten megacycles per second. A frequency in this range is useful in detecting ions having masses up to approximately sixteen. The oscillator comprises a pentode **180** having the cathode and suppressor grid thereof connected to ground. The control grid of pentode **180** is connected to one terminal of a crystal **181** which vibrates at a frequency of approximately ten megacycles per second. The second terminal of crystal **181** is connected to ground. A resistor **182** is connected in par-

allel with crystal 181. The anode of pentode 180 is connected to a positive potential terminal 121' through a tank circuit 183 which comprises a capacitor 184 connected in parallel with a variable inductor 185. The anode of pentode 180 is also connected to the control grid of a triode 126' through a capacitor 125'. Triode 126' and the circuit associated therewith are similar to the corresponding triode and circuit of Figure 3; corresponding elements are designated by like primed reference numerals. Detectors 61' and 71' are also similar to corresponding elements in Figure 3. The oscillator amplitude regulator 59' is likewise similar to the corresponding regulator circuit in Figure 3. The anode of pentode 150' is connected to the control grid of a triode 190. The cathode of triode 190 is connected to one terminal of a tank circuit 191 which comprises a capacitor 192 connected in parallel with a variable inductor 193. The second terminal of tuned circuit 191 is connected to the screen grid of pentode 180. The first terminal of tuned circuit 191 is also connected to ground through a capacitor 195. The operation of the circuit illustrated in Figure 4 is substantially the same as the operation of the corresponding circuit in Figure 3.

The square wave generator 57 and electronic switch 55 are illustrated in Figure 5. Output terminal 85 of audio oscillator 58 of Figure 2 is connected to one end terminal of the primary winding 200 of a transformer 201. The second end terminal of transformer winding 200 is connected to ground. One end terminal of the secondary winding 202 of transformer 201 is connected through a high ohmic value resistor 203 to the control grid of a triode 204. The second end terminal of transformer winding 202 and the cathode of triode 204 are connected to a negative potential terminal 205. Terminal 205 is connected through a pair of series connected resistors 206 and 207 to a negative potential terminal 208. Terminal 205 is also connected to ground through a resistor 209. A capacitor 210 is connected between terminal 205 and ground and a capacitor 211 is connected between ground and the junction between resistors 206 and 207. The circuit comprising resistors 207 and 206 and capacitors 211 and 210 thus filters the negative potential at terminal 208, which can represent the output of a current rectifier, not shown. The anode of triode 204 is connected to a positive potential terminal 213 through a high ohmic value resistor 214. The anode of triode 204 is also connected to the control grid of a triode 215. The control grid of triode 215 is connected to ground through a resistor 216 which has a considerably smaller ohmic value than resistor 214. The cathode of triode 215 is connected to terminal 205 through a resistor 217. The anode of triode 215 is connected to positive potential terminal 213 through series connected resistors 218 and 219. The junction between resistors 218 and 219 is connected to ground through a capacitor 270 and the anode of triode 215 is connected to ground through a capacitor 271.

The circuit of Figure 5 thus far described functions to generate substantially square waves of the same frequency as the sinusoidal output of oscillator 58. The high ohmic value resistors 203 and 214 function to limit the current flow through triodes 204 and 215 such that the potential appearing at the cathode of triode 215 varies in substantially a square wave form.

The cathode of triode 215 is connected through an inductor 220 to the anode of a triode 221 which functions as a diode because the control grid thereof is connected to the anode. Triode 221 will be referred to hereinafter as a diode. The cathode of triode 215 is also connected to ground through a capacitor 234. The cathode of diode 221 is connected to ground through a resistor 223 which is shunted by a capacitor 224. The cathode of diode 221 is also connected through an inductor 225 to a lead 226 which is connected to terminals 230*a* and 235*b* of respective switches 230 and 235. The anode of diode 221 is connected through a capacitor 240 to one terminal of a tank circuit 241 which comprises an inductor 243 connected in parallel with a capacitor 242. The second terminal of tank circuit 241 is connected to the movable arm of switch 235. Terminal 235*a* of switch 235 is connected to a terminal 230*b* of switch 230. The first-mentioned terminal of tank circuit 241 is connected to the cathodes of a double diode 245. The anodes of double diode 245 are connected to output terminal 135 of the oscillator illustrated in Figure 3. The first terminal of tuned circuit 241 is also connected through a pair of series connected capacitors 246 and 247 to the cathodes of a second double diode 248. The anodes of double diode 248 are connected to one another and to output terminal 135' of the oscillator illustrated in Figure 4. The cathodes of double diode 248 are connected through an inductor 250 to the movable arm of switch 230.

The junction between capacitors 246 and 247 is connected through a capacitor 251 to an output terminal 252 which is applied to grids 36, 39, 43, 46 and 50 of mass spectrometer tube 10 illustrated in Figure 1.

The electronic switch of Figure 5 functions to apply the output signals from terminals 135 and 135' selectively to output terminal 252 at the same frequency as the signal applied to the input of the square wave generator through transformer 201. The output square wave signal from triode 215 is applied to the anode of diode 221. Inductor 220 presents low impedance to this audio frequency signal, but presents high impedance to radio frequency signals. The current flow through diode 221 results in a positive potential appearing on the cathode thereof, which potential is applied through inductor 225, switch 230, and inductor 250 to the cathodes of diode 248. This positive biasing potential prevents current flow through diode 248. The square wave output signal from triode 215 is also applied through switch 235 and inductor 243 to the cathode of diode 245. During the negative half cycle of this square wave, diode 245 conducts such that the radio frequency signal applied to terminal 135 is applied through diode 245 and capacitors 246 and 251 to output terminal 252. The cathodes of diode 245 are connected to ground through tank circuit 241, switch 235 and a capacitor 234. However, circuit 241 is tuned to the same frequency as the signal applied to terminal 135 from the oscillator of Figure 3 and thus presents high impedance to this signal. The radio frequency current flow through diode 245 is applied to terminal 252 through capacitors 246 and 251.

When it is desired to apply the signal at terminal 135' from the oscillator of Figure 4 to output terminal 252, switches 230 and 235 are moved to their right-hand positions to engage respective contacts 230*b* and 235*b*. This applies the D. C. bias potential on the cathode of diode 221 to the cathodes of diode 245 through inductor 225, switch 235 and inductor 243. This bias potential prevents current flow through diode 245. The square wave signal from triode 215 is applied through switch 230 and inductor 250 to the cathodes of diode 248. This square wave signal permits current flow through diode 248 during alternate half cycles. The radio frequency current flow through diode 248 is thus applied to ouput terminal 252 through capacitors 247 and 251. Inductor 250 has stray capacitance in parallel therewith which forms a second tank circuit.

Output terminals 164 and 164' of Figures 3 and 4 are connected to the contacts 260*a* and 260*b*, respectively, of a switch 260. Switch arm 260 is connected to an output terminal 264. Terminals 174 and 174' of Figures 3 and 4 are connected to the contacts 261*a* and 261*b*, respectively, of switch 261. Switch arm 261 is connected to an output terminal 274. The movable arms of switches 260, 261, 230 and 235 are mechanically coupled to one another as illustrated. Terminal 264 is connected to grid 51 of mass spectrometer tube 10; terminals 165 and 165' are connected to grid 35 of tube 10; and terminal 274 is connected to grids 70 of tube 10. In this manner the mass spectrometer can readily be adjusted for the analysis

of ions of different mass ranges by moving the arms of these switches.

The over-all operation of the mass spectrometer of this invention should now become apparent. With reference to Figure 1, electrons emitted from heated filament **13** are accelerated into ionization chamber **22**. The electron flow into this ionization chamber is maintained constant by emission regulator **27**, which is desirable but not essential to operation of the mass spectrometer of this invention. The positive ions formed in chamber **22** are accelerated toward collector plate **14** by the negative potential applied to grid **28**. Ions of a particular mass receive maximum energy as they pass through the radio frequency fields applied to the next fifteen grids in the tube. The ions which acquire sufficient energy to overcome the positive potential barrier applied to grids **70** impinge upon collector plate **14** and are detected by the circuit connected thereto. The amplifier **76**, phase detector **77** and recorder **78** preferably are of the type described in the copending application of M. C. Burk, Serial No. 431,805, filed May 24, 1954, although other circuits to measure the component of the output signal of the same frequency as oscillator **58** can be employed.

In the operation of the mass spectrometer tube of this invention it is important that a fixed relationship be maintained between the radio frequency accelerating voltages and the D. C. step back potentials. It has been found that the use of a square wave signal to actuate electronic switch **55** is advantageous. If a sinusoidal signal were employed for this modulation, then the radio frequency signal envelope would vary in a sinusoidal fashion. Under such circumstances the radio frequency potential at which the tube is designed to operate would be realized for only a very short interval at the peak of the envelope. The square wave signal, however, permits the radio frequency envelope to remain at the proper level for substantially one-half of the period. This permits an output signal of greater magnitude from the collector plate than could be obtained with the use of a sine wave.

In the mass spectrometer tube of Figure 1, the spacings s between grids **35** and **36**, **36** and **37**, **38** and **39**, **39** and **40**, **42** and **43**, **43** and **44**, **45** and **46**, **46** and **47**, **49** and **50**, and **50** and **51** are maintained equal. The spacings r between the centers of grids **37** and **38**, **40** and **42**, **44** and **45**, and **47** and **49** can be represented by the expression:

$$r=2s\left(\frac{n}{0.742}-1\right)$$

where n is an integral number, all dimensions being in inches. In one embodiment of this invention, s was 0.118 inch and the four n's, proceeding from filament **13** to collector plate **14**, were five, nine, four and seven, respectively. The values of n can be varied, they may be equal, and more or fewer drift spaces can be provided, if desired.

The circuit components of oscillator **58** were as follows: resistor **84**, 470,000 ohms; resistor **99**, 470 ohms; resistor **94**, 180,000 ohms; resistor **92**, 220,000 ohms; resistor **96**, 560,000 ohms; resistor **97**, 820,000 ohms; resistor **102**, 10,000 ohms; resistor **88**, 56 ohms, resistor **86**, 3,250 ohms; capacitor **91**, 0.02 microfarad; capacitor **93**, 8 microfarads; capacitor **103**, 25 microfarads; triodes **80** and **90**, each one-half of a tube type 12AX7; and triodes **95** and **98**, each one-half of a tube type 12AU7. The voltage supplied to terminal **81** was obtained from a terminal at approximately 450 volts through filter resistors of 10,000 ohms. The values of resistors **82** and **105** and capacitors **83** and **106** are described heretofore.

In Figure 3, the circuit components were as follows: resistor **113**, 47,000 ohms; resistor **153**, 470,000 ohms; resistor **151**, 68,000 ohms; resistor **152**, 10,000 ohms; resistor **128**, 5,600 ohms; resistor **130**, 330 ohms; resistors **143**, **147** and **176**, 1,000,000 ohms each; resistor **166**, 175,000 ohms; potentiometer **163**, 50,000 ohms; potentiometer **173**, 300,000 ohms; crystal **112** vibrates at 3.9 megacycles per second; capacitors **116**, **123**, **145**, **167** and **177**, 0.0033 microfarad each; capacitor **114**, 10 micro-microfarads; capacitor **115**, 220 micro-microfarads; capacitor **119**, 68 micro-microfarads, capacitor **125**, 100 micro-microfarads; capacitors **129** and **136**, 0.01 microfarad each; capacitor **132**, 300 micro-microfarads; capacitors **140**, **160** and **170**, 100 micro-microfarads each; capacitor **148**, 0.1 microfarad; pentodes **110** and **150**, tube type 6AU6 each, triodes **117** and **126**, each one-half of a tube type 12AU7; diodes **161**, **162**, **141**, **142**, **171** and **172**, each one-half of a tube type 6AL5; inductors **111**, **122** and **127**, 2.5 millihenries each; inductor **120**, 45 turns of No. 28 wire on an XR–50 form; and inductor **133**, 30 turns of No. 24 wire on an XR–50 form, tap **135** being seven turns from the bottom. Terminal **121** was maintained at 300 volts, and terminal **144** was maintained at —90 volts.

In Figure 4, the circuit components were as follows: resistor **182**, 100,000 ohms; resistor **128'**, 5,600 ohms, resistor **130'**, 330 ohms; resistor **153'**, 470,000 ohms; resistor **151'**, 68,000 ohms; resistor **152'**, 10,000 ohms; resistors **147'** **143'** and **176'**, 1,000,000 ohms each; resistor **166'**, 175,000 ohms; potentiometer **163'**, 50,000 ohms; potentiometer **173'**, 300,000 ohms: capacitors **192** and **184**, 47 micro-microfarads each; capacitors **195** and **196**, 0.005 microfarad each; capacitor **125'**, 100 micro-microfarads; capacitors **129'**, **146'**, **148'** and **168**, 0.01 microfarad each; capacitors **140'**, **160'**, **170'**, **145'**, **167'** and **177'**, 100 micro-microfarads each; crystal **181** vibrates at ten megacycles per second; pentodes **180** and **150'** and diodes **141'**, **142'**, **161'**, **162'**, **171'** and **172'**, same as their counterparts in Figure 3; triodes **190** and **126'**, each tube type 6C4; inductor **127'**, 2.5 millihenries; and inductors **193**, **185** and **133'**, each 12 turns of No. 18 wire on an XR–50 form tap **135'** being three turns from the bottom of inductor **133'**. Terminal **121'** was maintained at 300 volts and terminal **144'** was maintained at —85 volts.

In Figure 5, the circuit components were as follows: resistors **203** and **214**, 1,000,000 ohms each; resistors **218** and **219**, 8,200 ohms each; resistor **216**, 68,000 ohms; resistor **217**, 15,000 ohms; resistor **223**, 10,000 ohms, resistors **206** and **207**, 15,000 ohms each; resistor **209**, 20,000 ohms; capacitors **210** and **270**, 20 microfarads each; capacitor **211**, 40 microfarads; capacitors **246**, **247**, **234** and **251**, 0.01 microfarad each; capacitor **240**, 0.001 microfarad, capacitor **224**, 50 microfarads; capacitor **242**, 82 micro-microfarads; inductor **220**, 2.5 millihenries; inductor **250**, four turns of No. 18 wire on an XR–50 form; inductor **243**, thirty turns of No. 24 wire on an XR–50 form; inductor **225** was a choke coil formed of No. 34 wire on a one-half inch form; triodes **215** and **221**, each one-half of a tube type 12AU7; triode **204**, tube type 6AB4; and diodes **245** and **248**, each tube type 6AL5. Terminal **213** was maintained at 300 volts, and and terminal **208** was maintained at —600 volts.

In Figure 1, the circuit components were as follows: resistors **64**, **65**, **66**, **67** and **68**, 120,000 ohms each, and potentiometer **29**, 300,000 ohms. The potentials applied to terminals **73** and **30** were approximately —600 volts, and the potential applied to terminal **19** was approximately —60 volts. Adjustment of potentiometer **29** enables ions of selected masses to impinge upon collector plate **14**.

From the foregoing description it should be apparent that there is provided in accordance with this invention an improved mass spectrometer. The instrument is particularly useful for process analysis and control because of its small size. The spectrometer does not require a magnetic deflecting field and is therefore less bulky and less expensive to operate than conventional mass spectrometers. While the invention has been described in conjunction with present preferred embodiments, it should be evident that the invention is not limited thereto.

What is claimed is:

1. A mass spectrometer comprising a gas impermeable envelope enclosing a source of ions, a collector plate spaced from said source of ions, a plurality of groups of

grids spaced in a line between said source of ions and said plate, each of said groups comprising three grids in spaced relation with one another, the spacings between adjacent grids being equal, the spacings between adjacent groups of said grids being substantially

$$2s\left(\frac{n}{0.742}-1\right)$$

inches, where n is an integral number and s is the spacing between adjacent grids in each group, all of said dimensions being in inches, and a second grid positioned between said collector plate and said groups of grids; means applying steady potentials to the two end grids in each of said groups of grids; means applying a potential to said second grid of polarity opposite the polarity of the ions being detected; a source of potential which fluctuates in magnitude at a first frequency; switching means connecting said source of potential to the center grid in each of said groups of grids; means to actuate said switching means at a second frequency whereby said source of potential is applied to the center grid in each of said groups at said second frequency; and means connected to said collector plate to measure ions impinging thereon at said second frequency.

2. The combination in accordance with claim 1 wherein said switching means comprises an electronic switch adapted to pass current from said source of potential when energized by a voltage of predetermined magnitude, means producing a fluctuating voltage of substantially sinusoidal wave form at said second frequency, a square wave generator, means energizing said square wave generator by the output of said means producing a fluctuating voltage whereby the output of said square wave generator is of said predetermined magnitude during alternate half cycles, and means applying the output of said square wave generator to said switch.

3. The combination in accordance with claim 2 wherein said switch comprises a diode, means connecting the anode of said diode to said source of potential, means connecting the cathode of said diode to the center grids of each of said groups of grids, said diode normally being non-conductive, and means applying the output of said square wave generator to the cathode of said diode, the magnitude of the output signal of said square wave being of such magnitude to render said diode conductive during alternate half cycles.

4. The combination in accordance with claim 3 further comprising a second source of potential which fluctuates in magnitude at a third frequency, a second diode, means connecting the anode of said second diode to said second source of potential, means connecting the cathode of said second diode to the center grids of each of said groups of grids, a source of bias potential, and switching means to apply said bias potential selectively to the cathodes of said diodes and to apply the output of said square wave generator selectively to the cathodes of opposite ones of said diodes.

5. The combination in accordance with claim 14 wherein said means applying a potential to said second grid of polarity opposite the polarity of the ions being detected comprises current rectifying means, and means connecting said source of potential to the input of said current rectifying means.

6. The combination in accordance with claim 5 wherein said current rectifying means comprises a first diode, a second diode, a first capacitor having one terminal thereof connected to the cathode of said first diode and to the anode of said second diode, the second terminal of said first capacitor being connected to said source of potential, a second capacitor having one terminal thereof connected to the anode of said first diode and the second terminal thereof connected ot the cathode of said second diode, the first terminal of said second capacitor also being connected to a point of reference potential, a potentiometer, means connecting one end terminal of said potentiometer to the cathode of said second diode, means connecting the second end terminal of said potentiometer to the anode of said first diode, and means connecting the contactor of said potentiometer to said second grid.

7. The combination in accordance with claim 1 wherein said means applying steady potentials to the two end grids in each of said groups of grids comprises current rectifying means, means connecting said source of potential to the input of said current rectifying means, a voltage dividing network, and means applying the output of said current rectifying means across said voltage dividing network, said steady potentials being obtained from selected points on said voltage dividing network.

8. The combination in accordance with claim 7 wherein said current rectifying means comprises a first diode, a second diode, a first capacitor having one terminal thereof connected to the cathode of said first diode and to the anode of said second diode, the second terminal of said first capacitor being connected to said source of potential, a second capacitor having one terminal thereof connected to the anode of said first diode and the second terminal thereof connected to the cathode of said second diode, the first terminal of said second capacitor also being connected to a point of reference potential, a potentiometer, means connecting one end terminal of said potentiometer to the cathode of said second diode, means connecting the second end terminal of said potentiometer to the anode of said first diode, means connecting the contactor of said potentiometer to one end terminal of said voltage dividing network, and means connecting said point of reference potential to the second end terminal of said voltage dividing network.

9. The combination in accordance with claim 1 wherein said means applying a potential to said second grid of polarity opposite the polarity of the ions being detected comprises first current rectifying means, and means connecting said source of potential to the input of said first current rectifying means, and wherein said means applying steady potentials to the two end grids in each of said groups of grids comprises second current rectifying means, means connecting said source of potential to the input of said second current rectifying means, a voltage dividing network, and means applying the output of said second current rectifying means across said voltage dividing network, said steady potentials being obtained from selected points on said voltage dividing network.

10. A mass spectrometer comprising a gas impermeable envelope enclosing an electron emitting filament, an ionization chamber spaced from said filament, means to introduce gas molecules to be detected into said ionization chamber, means applying a potential difference between said filament and said chamber to direct electrons from said filament into said chamber, a collector plate spaced from said chamber, a first grid positioned between said chamber and said plate, means applying a first potential to said first grid to direct ions from said chamber toward said plate, a plurality of groups of second grids spaced in a line between said first grid and said plate, each of said groups comprising three grids in spaced relation with one another, the spacings between adjacent grids being equal, the spacings between adjacent groups of said grids being substantially

$$2s\left(\frac{n}{0.742}-1\right)$$

inches, where n is an integral number and s is the spacing between adjacent grids in each group, all of said dimensions being in inches, a third grid positioned between said groups of second grids and said plate; a voltage dividing network, the two end grids in each of said groups of second grids being connected to selected points on said network; means applying a second potential across said voltage dividing network; means applying a third potential to said third grid of polarity opposite the polarity of the ions being detected; a source of alternating

potential of first frequency; switching means connecting said source of alternating potential to the center grid in each of said groups of second grids; means to actuate said switching means at a second frequency whereby said source of potential is applied to the center grid in each of said groups at said second frequency; and means connected to said collector plate to measure ions impinging thereon at said second frequency.

11. The combination in accordance with claim 10 further comprising first and second current rectifying means, and means connecting said source of alternating potential to the inputs of said current rectifying means, the output of said first current rectifying means supplying said second potential, and the output of said second current rectifying means supplying said third potential.

12. The combination in accordance with claim 11 wherein each of said current rectifying means comprises a first diode, a second diode, a first capacitor having one terminal thereof connected to the cathode of said first diode and to the anode of said second diode, the second terminal of said first capacitor being connected to said source of alternating potential, a second capacitor having one terminal thereof connected to the anode of said first diode and the second terminal thereof connected to the cathode of said second diode, the first terminal of said second capacitor also being connected to a point of reference potential, a potentiometer, means connecting one end terminal of said potentiometer to the cathode of said second diode, and means connecting the second

end terminal of said potentiometer to the anode of said first diode.

13. The combination in accordance with claim 10 further comprising a second source of alternating potential of a third frequency, second switching means to apply said second source of alternating potential to the center grid in each of said groups of grids selectively in place of said first-mentioned source of alternating potential, and means to vary the magnitude of said first potential applied to said first grid.

14. A mass spectrometer comprising a gas impermeable envelope enclosing a source of ions, a collector plate spaced from said source of ions, a plurality of first grids spaced in a line between said source of ions and said plate, a second grid positioned between said collector plate and said plurality of first grids, means applying a potential to said second grid of polarity opposite the polarity of the ions being detected, a source of potential which fluctuates in magnitude at a first frequency, switching means to connect said source of potential between selected pairs of said first grids, means to actuate said switching means at a second frequency so that said source of potential is applied between said selected pairs of first grids at said second frequency, and means connected to said collector plate to measure ions impinging thereon at said second frequency.

No references cited.