Dec. 26, 1950 W. H. BENNETT 2,535,032

RADIO FREQUENCY MASS SPECTROMETER

Filed Aug. 19, 1948 4 Sheets-Sheet 1

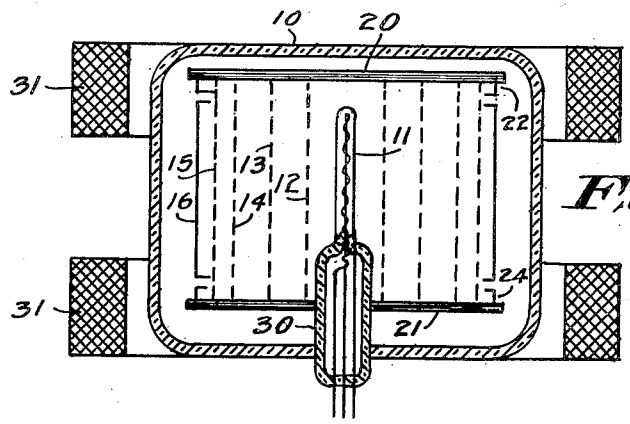


Fig. 1.

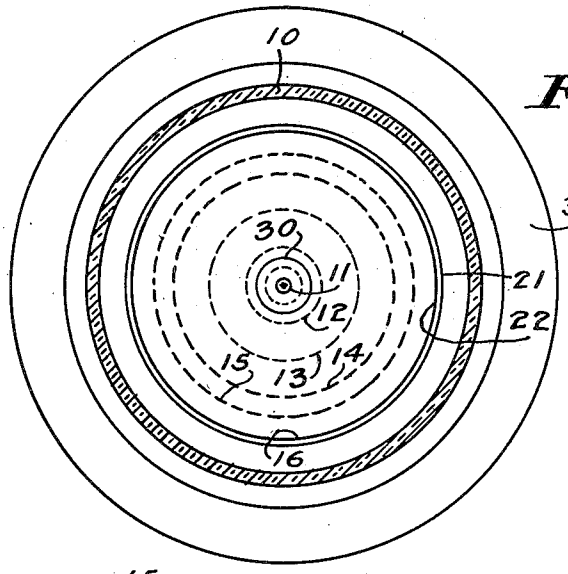


Fig. 2.

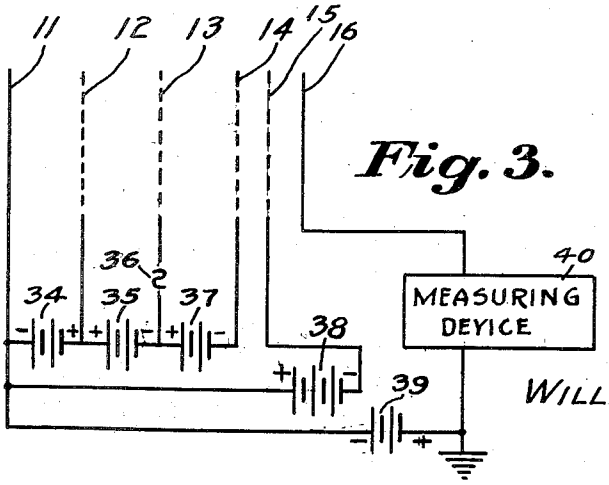


Fig. 3.

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RADIO FREQUENCY MASS SPECTROMETER

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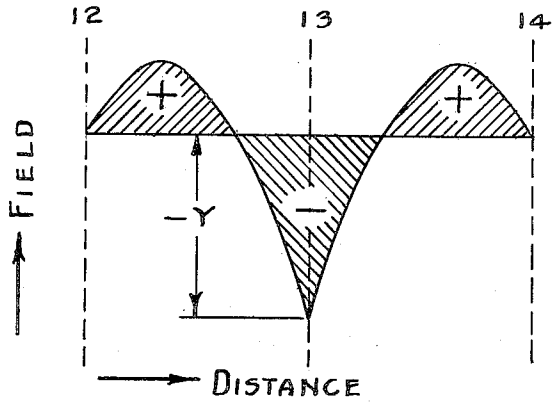


Fig. 4.

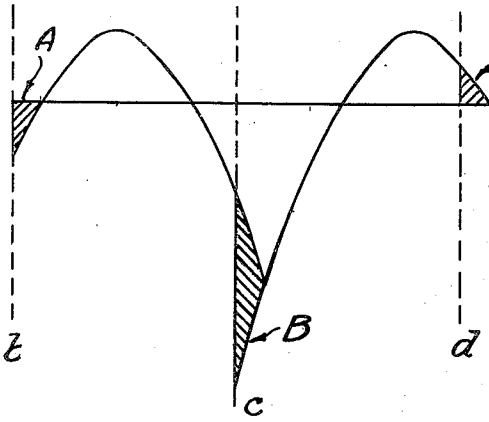


Fig. 5.

Fig. 7.

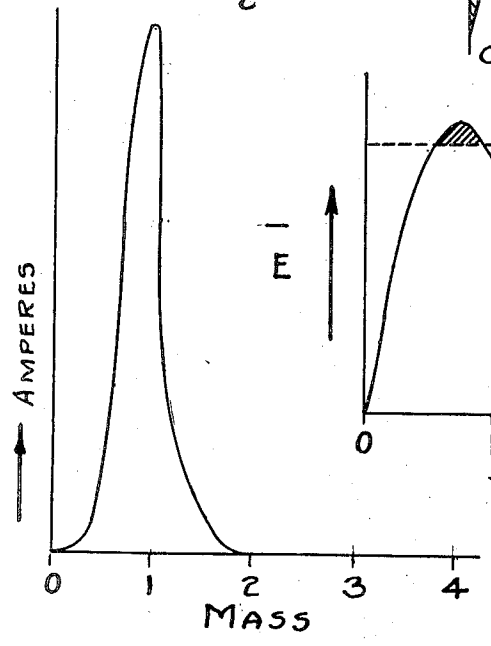
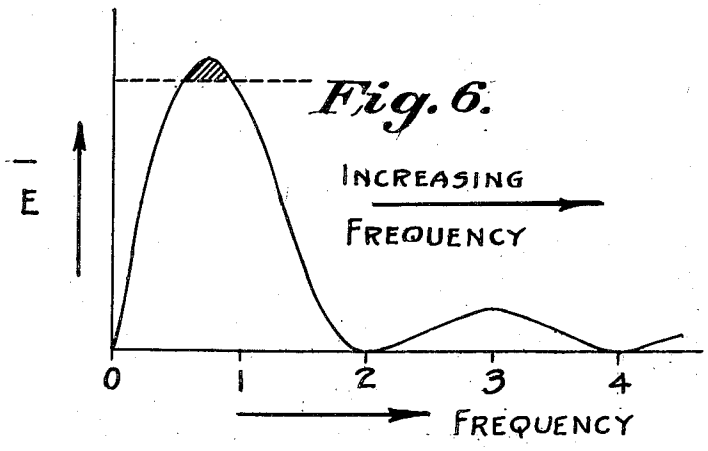


Fig. 6.



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RADIO FREQUENCY MASS SPECTROMETER

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Fig. 8.

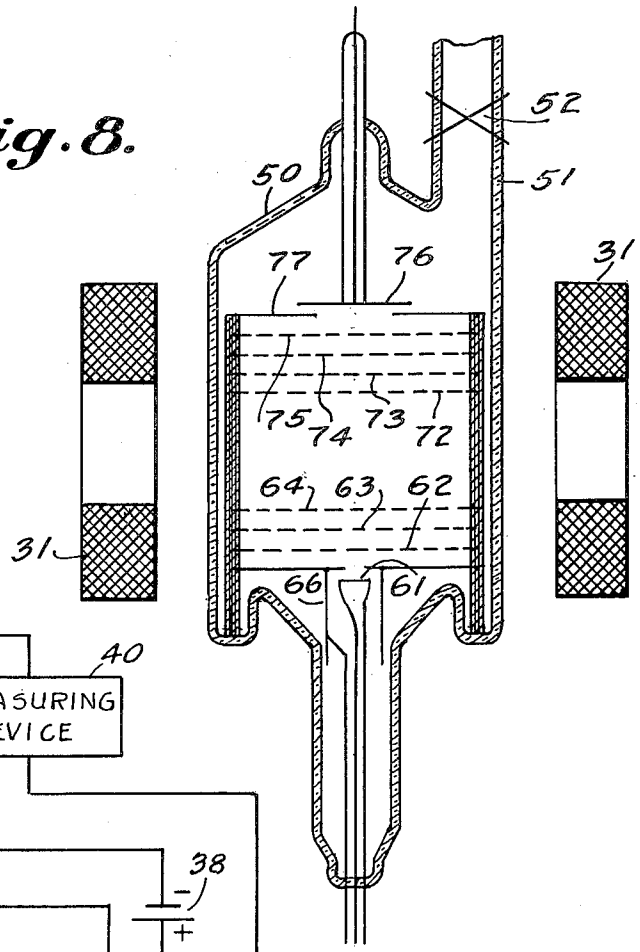
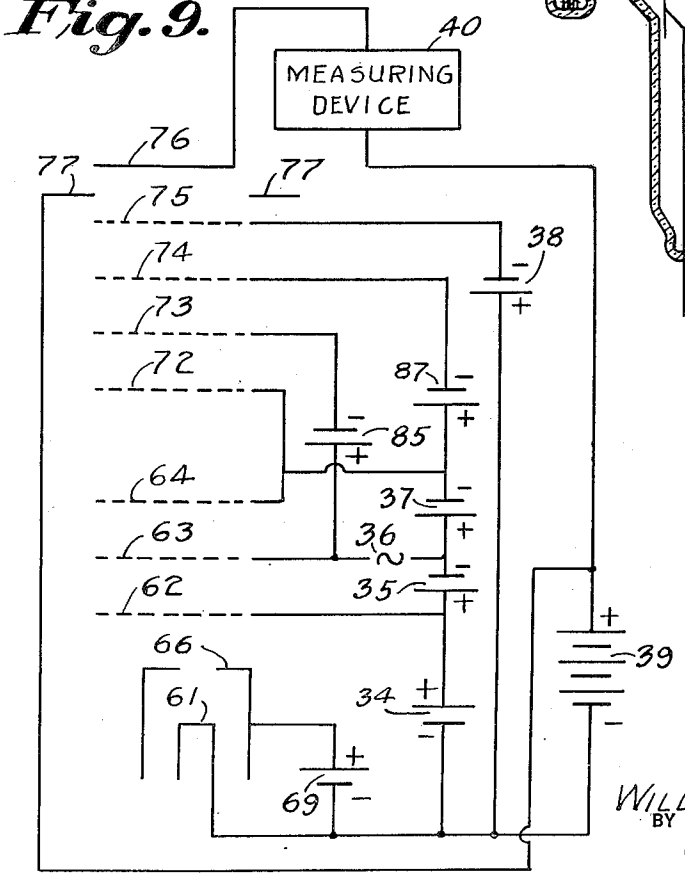


Fig. 9.



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RADIO FREQUENCY MASS SPECTROMETER

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Fig. 10.

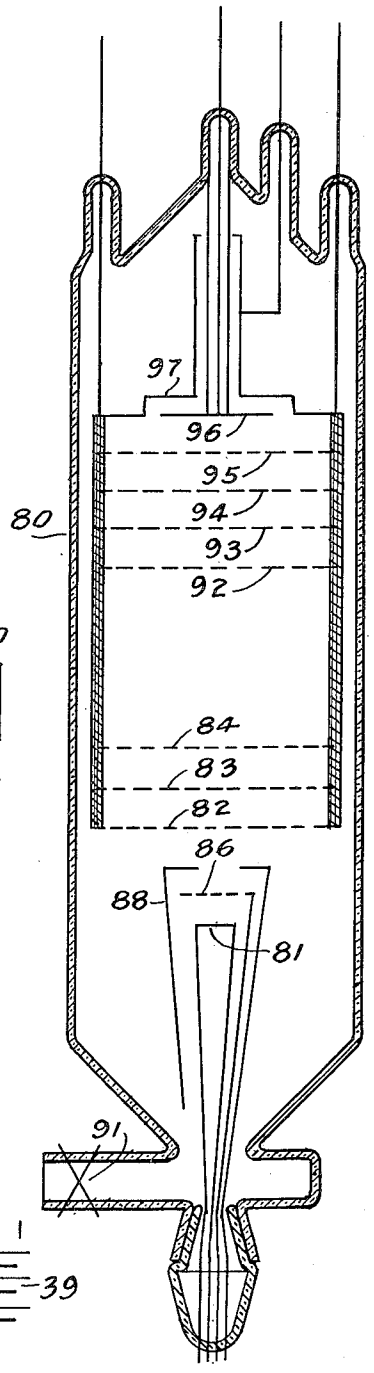
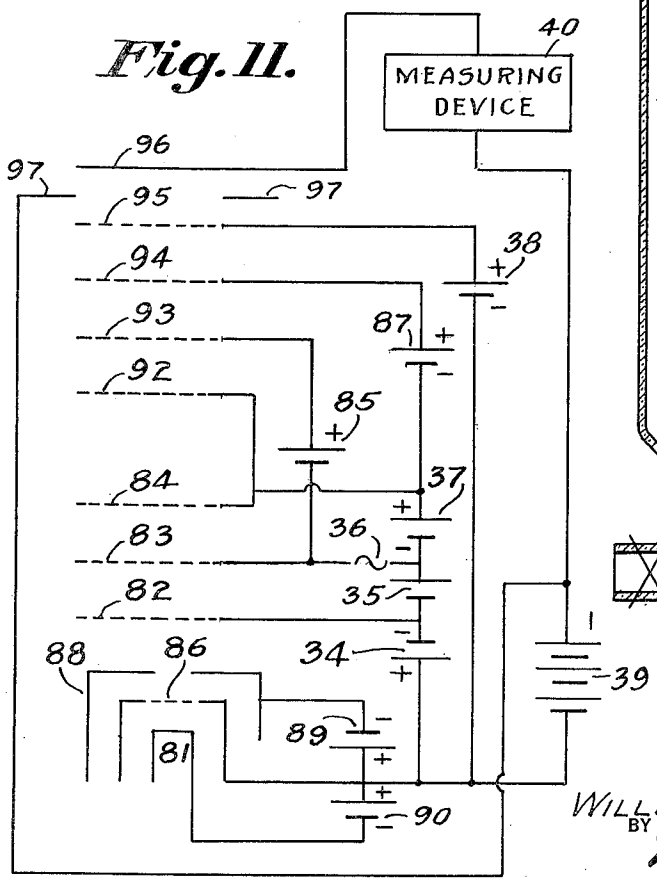


Fig. 11.



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UNITED STATES PATENT OFFICE

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RADIO-FREQUENCY MASS SPECTROMETER

Willard H. Bennett, Washington, D. C.

Application August 19, 1948, Serial No. 45,163

6 Claims. (Cl. 250—41.9)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to mass spectral analysis, and more particularly to a method of and means for analyzing mass components in accordance with their velocity.

In the methods used heretofore for obtaining the isolation and identification of the negatively charged mass components in an electrical discharge at reduced pressures, either there has not been as complete separation of the ions from electron backgrounds as was desirable, or else the ions were almost entirely lost either by collision with residual gas molecules or positive ions or by photo-dissociation.

Negative atomic ions in general have much smaller electron attachment energies than the more familiar atomic and molecular ionization energies, and as a result the dissociation cross-sections are in general much larger than the ionization cross-sections. Negative ions in collision with positive ions are attracted toward the positive ions during a collision. This has the result of increasing still further the dissociation cross-section of a negative ion in collision with a positive ion, particularly at lower energies as compared with the ionization cross-section of corresponding neutral components.

Another factor which can contribute to make the rate of loss of these negative ions in high vacuum much greater than that for positive ions or neutral atoms under similar conditions is that radiations which can produce dissociation are in the visible or infrared and ordinarily are present near hot cathodes at much higher density than are the ultraviolet radiations necessary for photo-ionization of neutral atoms or of positive ions.

Although residual gas pressures of the order of 10^{-5} mm. of mercury may be tolerable for positive ions in mass spectrometers using the magnetic resolution of beams where the ions must travel a distance of the order of magnitude of a meter, such pressures and path lengths would be prohibitive for any negative ions except for such electro-negative substances as the halogens or oxygen whose electron attachment energies exceed one volt.

Another difficulty which is peculiar to negative ion studies is that the ions are usually accompanied by electron currents which may be 10^{-12} or more times as large as the ion currents being

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analyzed. Not only must these electron currents be entirely separated but also all electrons arising from collisions and other processes must be separated.

Another difficulty in prior methods has been that the electrical discharge which is the source of the ions to be analyzed has had to be confined behind a narrow aperture or slit through which the ions to be observed must pass. Only a very small fraction of the total supply of ions from the discharge can pass through the small aperture and as a result the entire analysis must be made on a very small part of the total supply of ions.

It is an object of this invention to provide a method for separating mass components of an electric discharge in accordance with the velocity of said components.

It is a further object to provide an apparatus for mass spectral analysis in which the mass components are required to travel a relatively short path.

It is a further object to provide an apparatus for mass spectral analysis in which a large fraction of the total supply of ions from the discharge can be analyzed.

It is a further object to provide a method of and apparatus for the mass spectral analysis of positive ions.

Other objects of this invention will become apparent from the following specification taken in connection with the drawing in which

Fig. 1 is a sectional side view of a tube constructed in accordance with the principles of this invention.

Fig. 2 is a sectional top view of the tube shown in Fig. 1.

Fig. 3 is a schematic diagram showing the application of potentials to the electrodes of the tube shown in Figs. 1 and 2.

Figs. 4, 5, 6 and 7 are graphs explaining the operation of the tube of Figs. 1 and 2.

Fig. 8 is a sectional side view of another embodiment of a tube embodying the principles of this invention.

Fig. 9 is a schematic diagram showing the application of potentials to electrodes of the tube shown in Fig. 8.

Fig. 10 is a sectional side view of a tube embodying the principles of this invention, said tube being specially adapted for the study of positive ions.

Fig. 11 is a schematic diagram showing the application of potentials to the tube of Fig. 10.

As seen in Figs. 1 and 2, a partially evacuated

envelope 10, which may be of glass, encloses a cathode 11, grids 12, 13, 14 and 15 and plate 16. Envelope 10 is substantially cylindrical. Cathode 11 is long and thin and positioned at the axis of envelope 10. Grids 12—15 and plate 16 are cylindrical and are coaxially placed about cathode 11. The ends of the cylindrical electrodes are closed by non-conducting discs 20 and 21 which may be of mica. The distance between grids 12 and 13 is the same as the distance between grids 13 and 14.

Plate 16 in Fig. 1 does not extend all the way to the discs 20 and 21 and short conducting cylinders 22 and 24 of the same diameter as plate 16, and coaxial therewith, extend from the plate to the discs but do not contact the plate. Alternatively, plate 16 may extend from disc 20 to disc 21, dispensing with guard rings 22 and 24. Cathode 11, which has a lead 28, is of the "heater" type and has a heating filament terminating in leads 29. Leads 28 and 29 are surrounded by glass tube 30. The leads of grids 12—15 and plate 16 are not shown.

Envelope 10 is surrounded by coaxial coils 31—31 supplied by a source of direct current (not shown) for producing a magnetic field extending axially of said envelope 10 and its electrode. This field is held at sufficient intensity to restrain the electrons from the cathode from reaching the first grid, in order to hold down the production of positive ions throughout the tube which otherwise would result. This magnetic field gives the negative ion trajectories a curvature away from the straight radial paths which is too small to affect the operation of the tubes and so is neglected in the following discussion.

In Fig. 3, cathode 11, grids 12—15, and plate 16 are schematically shown with their potential supplies. A battery 34 is applied between cathode 11 and the first grid 12 so that the first grid is at a higher potential than the cathode.

A radio frequency alternating potential source 36 has its first terminal connected to the second grid 13 and its second terminal connected in series with battery 35, the positive terminal of battery 35 being connected to the first grid 12. The second terminal of alternating potential source 36 is also connected in series with battery 37 to the third grid 14, the negative terminal of battery 37 being connected to the third grid 14. The potentials supplied by batteries 35 and 37 are each approximately equal to 0.730 times the peak value of the alternating potential supplied by source 36. Alternating potential source 36 is preferably adjustable as to frequency.

The positive terminal of battery 38 is connected to the cathode 11 while its negative terminal is connected to the fourth grid 15. The potential of battery 38 is a little less than twice 0.730 times the peak value of the alternating potential supplied by source 36.

The negative terminal of battery 39 is connected to the cathode 11. The positive terminal of battery 39 is connected to the plate 16 through a measuring device 40. The potential of battery 39 is greater than a value equal to the potential of battery 34 plus twice 0.730 times the peak value of the alternating potential supplied by source 36. The measuring device 40 may be any device capable of detecting and measuring the minute amounts of currents caused by the impingement of the ions on plate 16. Measuring device 40 preferably includes a direct current amplifier feeding a sensitive current meter.

The following discussion of the operation of the tube is a fairly close approximation but not exact, because both the curvature of the electrodes and the variations in speed of the ions while passing from the first to the third grid are neglected. In the operation of the device disclosed in Figs. 1–3, electrons, positive ions, and negative ions are emitted from cathode 11. Positive and negative ions will also be produced by collision of the emitted components and those of the residual gas. It is assumed with respect to Figs. 1–3 that the negative ions are under study and are to be collected on plate 16.

The potential supplied to the first grid 12 by battery accelerates the negative ions toward the plate 16 but retards positive ions. While this potential also tends to accelerate electrons toward the plate 16, the axial magnetic field produced by winding 31 causes the electrons to take a spiral or circular course and prevents them from reaching directly the first grid 12.

If the analysis is to be limited to only those negative ions which arise at the cathode 11, the magnetic field produced by coil 31 is applied in sufficient intensity to keep the electrons from reaching a radial distance from the cathode 11 at which the potential drop through which the electrons have fallen exceeds any ionization potential of any of the residual gases present in the tube.

The negative ions accelerated by the potential on the first grid 12 pass through that grid and into the fields set up between the grids 12, 13 and 14. The fields produced by batteries 35 and 37 always tend to retard negative ions (when negative ions are being collected on electrode 16). The fields produced by the alternating potential retard or accelerate negative ions in dependence on their time of entry in the fields.

Fig. 4 is a graph showing the field intensity acting upon a negative ion plotted against position relative to grids 12, 13 and 14 for a negative ion entering the fields between these grids with such a velocity and at such a time with respect to the phase of the alternating potential that the ion picks up the maximum amount of energy. It can be calculated that an ion picks up maximum energy if it passes the first grid 12 at 45° 27.5′ phase, passes second grid 13 at 180° and reaches third grid 14 at 314° 32.5′ phase. The energy pick-up is then equal to the energy obtained in falling through 0.730 of the peak value of the alternating potential supplied by source 36 and the velocity of the ion is such that during one-quarter of a cycle of the alternating potential the ion travels 0.67 times the distance from first grid 12 to the second grid 13, which is equal to the distance from second grid 13 to third grid 14.

Since the alternating potential is applied to grids 12 and 13 in oposite sense to that in which it is applied to grids 13 and 14, the alternating field between grids 12 and 13 is inverted with respect to, or in effect, 180° out of phase with, the alternating field applied between grids 13 and 14. Hence, an ion passing grid 13 at 180° phase, as in Fig. 4, will tend to be accelerated by the half of the wave when grid 13 is positive with respect to grid 12 and further accelerated when it passes grid 13 because grid 14 is then positive to grid 13.

However, the fields produced between grids 12 and 13 and between grids 13 and 14 by batteries 35 and 37, respectively, are approximately equal and are both retarding to a negative ion. The magnitude of these steady fields is indicated in Fig. 4 by the quantity —Y. Y is chosen so that

the portions hatched above the zero axes, in which the ion is accelerated, equal the portions hatched below the zero axis, in which the ion is retarded. The value of Y, the magnitude of battery 35 and also the magnitude of battery 37, is thus equal to the root-mean-square value of the curve. In this case the value Y is 0.730 times the peak value of the alternating potential.

Such a plot is, of course, only an approximate representation, which should be close for initial velocity at grid 12 much greater than the changes in velocity produced by the R. F. fields. The phase of entry of the ion at grid 12 for maximum energy pick-up is readily found by integrating for the average height of the curve above $-Y$ and finding the phase angle for maximum height.

That the maximum energy pick-up occurs for ions passing c at 180° phase, can be seen from Fig. 5, which is a plot for an ion of proper velocity but a somewhat earlier phase of entry at grid 2. The energy lost to the ion due to this phase error is proportional to the cross-hatched areas A, B, and C.

Thus, for initial energy eV materially larger than the maximum pick-up of energy from the alternating field, the ion giving maximum energy keeps essentially a constant speed in traveling from grids 12 to 14 while other ions slow down.

The retarding potential for negative ions applied to the fourth grid 15 by battery 38 is nearly equal to the maximum pick-up of energy from the alternating fields between grids 12, 13 and 14. This retarding potential on the fourth grid 15 stops all ions except those which traversed the first grid 12 at nearly the optimum phase and having such a mass that the energy received from the accelerating potential on second grid 13 has of a maximum optimum value.

The unidirectional potential on the second grid, in addition to which the radio frequency potential was applied, and the unidirectional potential on the third grid, are each successively reduced below the unidirectional potential on the preceding grid by just the amount that will hold the ion velocity the same upon passage through each of the first three grids for those ions which can acquire the maximum energy from the R. F. field.

The positive potential on plate 16 attracts, and causes to be collected, the negative ions to be measured. This positive plate potential, being greater than the potential on the first grid 12 plus twice the maximum energy pick-up from the alternating fields between grids 13, 14 and 15, stops positive ions which may arise near the first grid 12 or anywhere else in the tube. Such positive ions cannot reach plate 16 even though they may also pick up some energy from the alternating field.

Representing the field between the two grids due to the ratio frequency alternating potential on the second grid as $E \sin(\omega t+\theta)$ where E is the peak value of the field, ω is 2π times the frequency, and θ is the phase angle of the alternating potential when an ion passes the first grid, the force acting on this ion is

$$m\ddot{x}=Ee \sin(\omega t+\theta)$$

The force on this ion after it passes the second grid and before it reaches the third grid is

$$m\ddot{x}=-Ee \sin(\omega t+\theta)$$

Taking for a first approximation the case when the alternating potential is small compared with the D. C. potential used in accelerating the ion to the first grid, variations in the velocity of the ion due to the A. C. field will be small compared with the average velocity of the ion from the first to the third grid. The energy acquired by the ion from the alternating field is approximately:

$$\Delta W=\Delta\left(\frac{mv^2}{2}\right)=v\cdot\Delta(mv)$$

and the transit time for the ion to travel from each grid to the next is a/v where a is the distance between grids. Then

$$W=v\left\{\int_0^{a/v} Ee \sin(\omega t+\theta)dt+\int_{a/v}^{2a/v}-Ee \sin(\omega t+\theta)dt\right\}=\frac{Eev}{\omega}\left[\cos\theta-2\cos\left(\frac{av}{\omega}+\theta\right)+\cos\left(\frac{2av}{\omega}+\theta\right)\right]$$

This expression is a maximum when

$$\frac{av}{\omega}+\theta=180°$$

and when $\theta=45°$ (more precisely 45° 27.5′), so the transit angles between grids is

$$\frac{av}{\omega}=135°$$

The velocity of the ion is obtained from $eV=\frac{1}{2}M\cdot m_0v^2$, where V is the potential difference between the cathode and the first grid, M is the atomic mass number of the ion, and m_0 is the mass of an atom of unit atomic number. Eliminating v between the last two equations, and substituting 2π times the frequency, f, for ω gives

$$M=0.271\times10^{12}\frac{V}{a^2f^2}$$

where V is in volts.

It was found by experiment that the above approximate treatment was inadequate and irregular curves for each mass component resulted when the applied alternating potential was more than about twenty percent of the D. C. potential on the first grid. It was found, however, that clean symmetric curves for each mass were obtained if the D. C. potentials on the second and third grids were each reduced below that on the preceding grid by approximately the amount that would make the ion velocity have the same value upon passage through each of the first three grids, for those ions having the proper velocity and phase to acquire the maximum energy from the A. C. field. The required decrease in D. C. potential on the two grids is approximately equal to the root-mean-square value of the alternating potential.

As the frequency of the alternating field is varied, the pick-up of energy of the ions of a particular mass can be plotted as in Fig. 6 where the energy pick-up is plotted as a function of the number of cycles through which the alternating field has moved while the ion has travelled from grid 12 to grid 14. If a potential Z is the stopping potential applied by battery 38 between cathode 11 and fourth grid 15, the ions at proper phase can pass only over the frequency range of that portion of the curve above the horizontal dotted line. Ions which pass at a little different phase can pass only over a narrower range of frequency and hence the current received at plate 16 as a

function of frequency has a sharper form than the cross-hatched portion in Fig. 6. An experimentally observed curve is shown in Fig. 7.

The mica discs 20 and 21 closing the ends of the grids are for the purpose of preventing ions from escaping from the ends of the cylindrical electrodes and producing ionization outside the grids which can then drift toward grid 15 and plate 16. The glass cover 30 on cathode leads 28 and 29 is similarly provided to prevent ionization at the end of the tube. Guard rings 22 and 24 are provided to prevent current from leaking from the electrode leads to the plate 16.

Although the theory of the single-stage tube as discussed in the above assumed the use of radio frequency potential which is small compared with the potential difference applied to the first grid, experimental measurements with the tube have shown that the tube operates well when the radio frequency potential has the same order of magnitude as the unidirectional potential. Good mass line forms have been obtained using a radio frequency potential as low as 3 volts while the unidirectional potentials were, respectively:

	Volts
1st grid	+5.0
2nd grid	+2.0
3rd grid	−1.0
4th grid	−5.8
Collector	+10

with respect to the cathode.

Potentials up to 120 volts have been used on the first grid and no reason is foreseen for not increasing the voltage to as high values as can be insulated for in the tube.

It is to be noted that the tube can be calibrated once and for all with one kind of ion, after which the calibration holds for the entire mass range, both in regard to frequency dependents and in regard to mass line form.

It is further to be noted that in the calibration formula

$$M=0.271.10^{12}\frac{V}{d^2f^2}$$

the potential, V, is the potential difference between the point of origin of the ion and the first grid. Consequently, if the mass of some kind of ion is measured both at a high voltage and at a low voltage, the difference between the value of V which must be used to make the low voltage measurement of mass agree with the high voltage measurement, and the known applied V to the first grid gives the energy of the electron, the collision of which with residual vapor gave rise to the ion.

From the foregoing description it is seen that this tube is adequate for the separation and measurement of negative ions when the masses to be separated differ by at least 20 per cent, which is the case for many negative ion studies. For cases where a higher order of mass resolution is needed, it is necessary to go to a two-stage modification shown in Fig. 8, in which there are two stages of analyzing grids.

In Fig. 8, gas impervious envelope 50 has a tube 51 provided with a valve 52 to allow for evacuation or for ingress of selected gases.

Inside envelope 50 is a cathode 61, grids 62—64 and 72—75 and plate 76. Grids 62—64 of Fig. 8 correspond, respectively, to grids 12—14 of the embodiment of Figs. 1–3. Grids 72—75 of Fig. 8 correspond, respectively, to grids 12—15 of the embodiment of Figs. 1–3. An electrode 66 having cylindrical and annular components surrounds the cathode 61 and an annular electrode 77 lies between plate 76 and the last grid 75.

The distance between grids 62 and 63, 63 and 64, 72 and 73, 73 and 74, are all equal. The distance between grids 64 and 72 is approximately .66+(2.66) (n) times the distance between grids 62 and 63, n being an integral number. A suitable number for n is 5, so that, for an ion at optimum phase and frequency, the alternating fields pass through six cycles while the ion travels from grid 63 to grid 73.

In Fig. 9, in which is shown schematically the electrodes of the tube of Fig. 8, the positive terminal of battery 34 is connected to the first grid 62 while its negative terminal is connected to cathode 61. Battery 35 is connected with its positive terminal to 1st grid 62 and its negative terminal to one terminal of alternating potential source 36, said last mentioned terminal being also connected to the positive terminal of battery 37. The other terminal of source 36 is connected to 2nd grid 63. The negative terminal of battery 37 is connected to 3rd grid 64 and 4th grid 72.

The terminal of alternating potential source 36 connected to 2nd grid 63 is also connected through battery 85 to 5th grid 73, the negative terminal of battery 85 being connected to grid 73. The negative terminal of battery 37 is connected through battery 87 to 6th grid 74, the negative terminal of battery 87 being connected to grid 74.

A negative potential is applied to 7th grid 75 with respect to cathode 61 by battery 38. Plate 76 is maintained at a positive potential with respect to cathode 61 by a battery 39 connected in series with measuring device 40 between plate 76 and cathode 61. The negative terminal of battery 39 is connected to cathode 61 and electrode 77 is connected to the positive terminal of battery 39.

Battery 69 supplies to electrode 66 a negative potential with respect to cathode 61 which may be varied by means not shown to collimate the ions flowing from cathode 61.

The use of seven grids in tandem is not a very practical device if the ordinarily available woven wire screens are to be used in their construction. However, there is available a kind of knitted wire fabric with which a screen can be made with less than five per cent of the area covered by wire (cover factor) and with which an open area of seventy per cent can be obtained with seven grids.

The relative magnitudes of the potentials of Fig. 9 and the operation of the tube shown in Fig. 8 are similar to that described above for the tube of Figs. 1–3. However, the tube of Fig. 8 provides two stages for analyses of mass components. Since there will be collected on plate 76 only those negative ions which have twice been accelerated at the right velocity to traverse the alternating and retarding fields, there is obtained a very sharp line of division between the mass components.

In the use of the tube of Fig. 8, the potential of collimating electrode 66 is varied until the ions are electrically collimated well enough to put most of the ion current on collecting plate 76. Since plate 76 is exposed through a relatively small opening in annular electrode 77, it is thus insured that the ions which reach plate 76 have travelled along paths which are approximately perpendicular to the grids.

Electrode 77 is introduced for shielding the collecting electrode 76 from stray radio frequency fields from the leads to the radio frequency grid 74, and also to stop leakage currents along the

inner surface of the glass if that surface should become contaminated in some of the vapor studies.

The coils 31 produce a steady magnetic field at right angles to the direction of ion flow from the cathode 61 to the plate 76. The purpose of this field is, as in the tube of Fig. 1, to prevent electrons from flowing directly from the cathode 61 to the first grid 62.

There is provided a long leakage path over glass for currents from plate 76 to the other electrodes and to provide a portion of the leakage path which could be heated without the necessity of heating any leads through glass. This is to permit using the caseium positive ions from a hot tungsten filament in caseium vapor for calibrating the tube. The caseium condenses on the tube walls forming a leakage path which must be removed by evaporating some of the caseium by application of heat.

By varying the stopping potential on the last grid 75, the potentials for the appearance successively of various mass components can be determined. The differences between these potentials and the potential for those mass components arising at the cathode represent the threshold electron energies for the ionization processes responsible for producing the corresponding mass components.

Similar critical potential determinations could be made by replacing the cathode 61 at the axis with a pencil of electrons surrounded by an additional grid. The type of tube shown in Fig. 8 having plane grids can be used with a trough-shaped cathode containing molten material the ions of which are to be studied.

The mass scale is related to the distance between grids 62 and 63, 63 and 64, 72 and 73, and 73 and 74, the frequency of source 36, and the potental of battery 34 on the first grid by

$$M=\frac{0.279eV}{m_0d^2\cdot f^2}$$

where M is the mass number, m_0 is the mass of an ion of unit mass number. For those mass components which appear at reduced stopping potentials, the value of V in the equation must be reduced by the amount of potential through which the electrons must fall before producing the ionization reaction responsible for those mass components.

From the formula, it is evident that the mass scale can be traversed equally readily by traversing the frequency, or by traversing the voltage, V, on the first grid keeping the other D. C. voltages in the proper relationship. Calibration for any one mass fixes the calibration for the entire mass range. Small errors in dimensions of the tube can not distort the mass scale but can only broaden the lines.

While the foregoing description has been directed to a method of and apparatus for analyzing negative ions, it will be understood that by reversing the potential of the batteries, an analysis of the positive ions will be obtained. In Fig. 10 is shown a tube modified for investigation of positive ions. In this tube the envelope 80, grids 82—86 and 92—95, plate 96 and electrode 97 correspond to grids 62—64 and 72—75, plate 76 and electrode 77 of the tube in Fig. 8. Outlet means 91 having a valve is provided as in Fig. 8. In the tube of Fig. 10, however, an auxiliary grid 86 has been interposed between cathode 81 and grid 82. An apertured electrode 88 surrounds grid 86.

As seen in Fig. 11 the potentials are applied to the electrodes of tube 80 in substantially the reverse manner in which they are applied to the electrodes of the tube of Fig. 8. However, in the tube of Fig. 10, grid 86 is maintained by battery 90 at a positive potential with respect to cathode 81. Electrode 88 is maintained by battery 89 at a negative potential with respect to grid 86.

In the operation of the tube of Fig. 10 electrons emitted from the hot cathode 81 are attracted toward positive grid 86 and pass through the meshes of grid 86. After passing grid 86 the electrons collide with atoms of the rarified gas contained in envelope 80, dislodging electrons from some of said atoms and thereby forming positive ions. The electrons passing through grid 86 are repelled by negative electrode 88 and return toward grid 86. It will be noticed that a magnetic field is not necessary in the investigation of positive ions. In the tube of Figs. 10 and 11 the stopping grid 95 may also be eliminated since the stopping potential can be applied to the plate 96.

The positive ions formed between grid 86 and electrode 88 are attracted to negative grid 82 and given a velocity thereby in accordance with their mass. Positive ions having other than a critical mass, which is predetermined by the potentials applied to the various electrodes and the frequency of source 36, are retarded in passing from grid 82 to grid 94. The retarded ions are stopped by the potential applied to grid 95 but those of the critical mass and phase are collected on plate 96 and measured by device 40.

It will be apparent to those skilled in the art that, while batteries have been shown as sources of unidirectional potential, any other suitable source could be used such as an alternating current with a rectifying means used with potentiometers or other potential dividing or varying means. It will also be seen that the single stage tube of Fig. 1 could be made with plane parallel electrodes and that the double stage tube of Fig. 8 could be made with cylindrical grids and plate.

Undoubtedly numerous specialized applications exist for such a tube. One such is as a leak detector where the voltages and frequencies are set for positive ions of the particular gas to be used in searching for leaks as, for example, helium; and provision is made for ionizing the helium. In such an application fewer grids than four would be needed because uniform velocity from the first to the third grid is not essential. The radio frequency field might also be used for ionizing the gas. When this is done, multiple peaks appear for each kind of ion, but this need not spoil the use of the tube as a leak detector if peaks of possible residual gases are kept away from the helium peak by the proper selection of potentials.

The invention set forth above provides a mass spectrometer in which the mass components must travel only a relatively short distance and in which a substantially full angle of the emitting medium can be used. The device requires only unidirectional potentials and an alternating potential, which is preferably a sine wave, all of which are easy to provide. This invention provides a mass spectrometer which may be used for the investigation of positive or negative ions and which may be calibrated by the use of one type of ion having a known mass.

The modifications described above are exemplary only and many changes will occur to those skilled in the art within the scope of the invention as defined by the appended claims.

What is claimed is:

1. In combination, a gas impermeable envelope enclosing a cathode, an anode and seven grids, said grids being spaced from each other and from the cathode and the anode, said grids being consecutively placed between said cathode and anode, with the first grid adjacent said cathode and the seventh grid adjacent said anode, the spacings between the first and second grids, the second and third grids, the fourth and fifth grids, all being equal and the distance between the third and fourth grids being .659 plus 2.66 times an integral number, times any one of said equal spacings.

2. The combination of claim 1 in which there is provided means for producing a magnetic field extending parallel to said grids.

3. The combination of claim 1 in which the envelope has an outlet for evacuation of said envelope and for the introduction of gases at selected pressures.

4. The combination of claim 1 in which the cathode, the anode and the seven grids are in substantially parallel planes.

5. In combination, a cathode, four grids and an anode, said grids being placed in order between said cathode and anode, the first grid being adjacent the cathode, the fourth grid being adjacent the anode, a first unidirectional potential applied between said cathode and said first grid, an alternating potential applied between said first and second grids and between said second and third grids so that the alternating fields produced between said first and second grids are 180 degrees out of phase with the alternating field produced between said second and third grids, a second unidirectional potential applied between the first and second grids, a third unidirectional potential applied between said second and third grids, said second and third potentials being each in series with said alternating potentials and each producing a field in opposition to the field of said first unidirectional potential, said second and third unidirectional potential being approximately .730 times the peak

value of the alternating potential with which they are in series, a fourth unidirectional potential applied between said cathode and fourth grid of such polarity that its field opposes the field of said first unidirectional potential, and having a magnitude a little less than .730 times the peak of said alternating potential, a fifth unidirectional potential applied to the anode, said potential being a polarity that its field aids that of the first unidirectional potential, and having a magnitude greater than the sum of the first potential plus twice .740 times the peak of the alternating potential.

6. The combination of claim 5 in which a coil for producing a magnetic field is placed around said cathode, anode and four grids.

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