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MASS SPECTROMETERS

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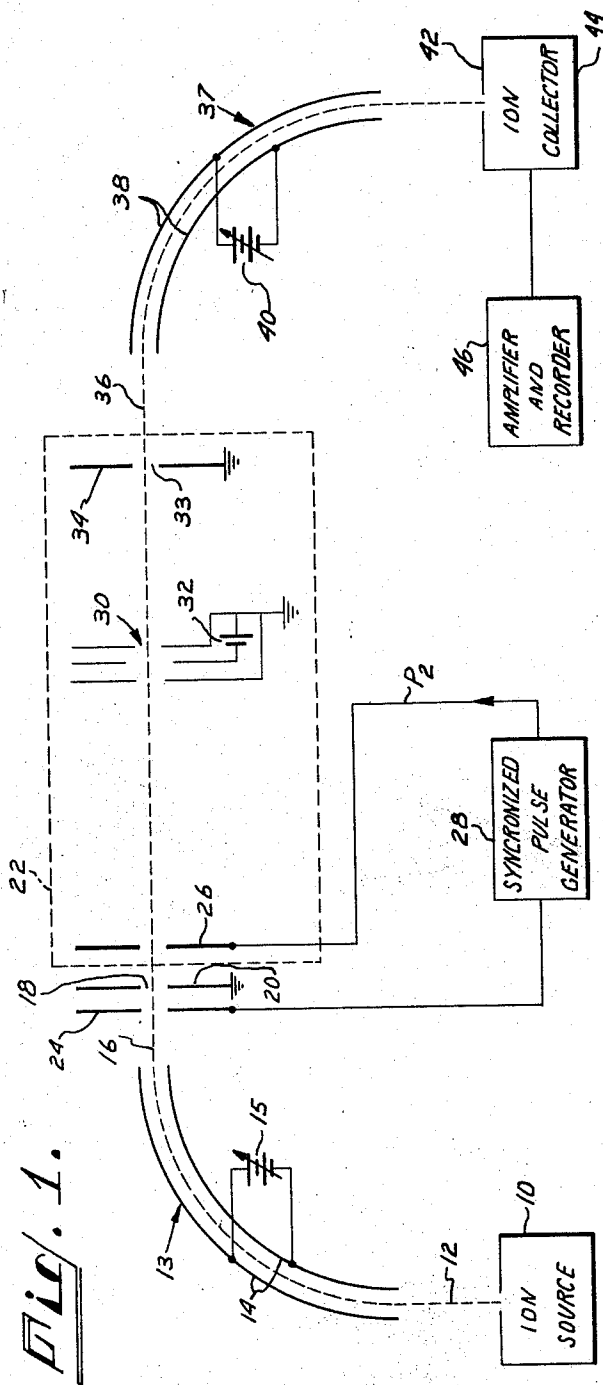


Fig. 2B.

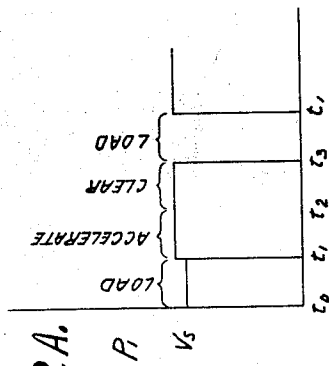
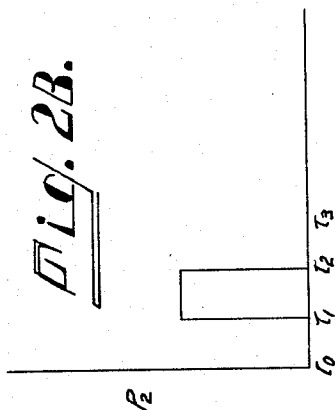


Fig. 2A.

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MASS SPECTROMETERS

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This invention relates to mass spectrometry, and more particularly to methods and apparatus for analyzing a sample of material by separating the ions according to their specific mass.

In mass spectrometry, a sample of material to be analyzed is ionized by any one of several known means and the ions thus formed are separated as a function of mass-to-charge ratio. Separation of the ions in accordance with mass-to-charge ratio is generally accomplished under the influence of electric or magnetic fields, or both, to effect spatial separation. Ions of a given mass-to-charge ratio may then be directed upon an ion collector or target and discharged, whereby a measure of the resulting current may be obtained. The ion current in turn is a function of the partial pressure of the components in the original sample from which the ions of the given mass-to-charge ratio are derived.

In many instances a non-magnetic spectrometer would be preferred to a magnetic type because of the undesirable effect of the magnetic field on the sample of material to be analyzed, or because the magnetic field interferes with surrounding instruments or other equipment, or because of disadvantages due to the bulk and weight of magnets used to produce the magnetic field, e.g. in airborne equipment generally and rockets in particular.

The most common non-magnetic spectrometer is the spectrometer which has become known as the "time-of-flight" mass spectrometer. One particular type of time-of-flight mass spectrometer employs bunching grids adjacent the point of ion formation, i.e. ion source whereby ions are bunched to proceed along a drift tube. In this type of instrument, a gate grid is conventionally employed adjacent a collector electrode. The gate grid is triggered with respect to the acceleration system whereby ions of a preselected transit time and hence a preselected mass are passed through to the collector, to the exclusion of other ions. Such selective gating provides a degree of resolution between the spatially separated ion bunches.

A disadvantage of the time-to-flight mass spectrometer of the type referred to is that expensive high transmission, closely spaced, and low electrical leakage grids are required for bunching of the ions. Another disadvantage is that the performance of the instrument is dependent upon the precise relation between the position of the bunch of ions in the instrument and the time of application of a steep wavefront voltage pulse to the gating grids and the waveform of the voltage pulse. A serious disadvantage is the dependence of the instrument upon ions of different masses becoming separated in space along the optical axis of the spectrometer, requiring precise electronic timing circuits for gating and an instrument having a greater length to maximize the resolution of ions according to their specific mass.

I have developed a novel non-magnetic mass spectrometer which is not subject to any of the foregoing disadvantages. It produces good resolution of a heterogeneous beam of ions into a mass spectrum by sequential arrangement of static and pulsed electric fields.

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The present invention is directed to methods and apparatus for analyzing an unsorted heterogeneous ion beam by first separating the heterogeneous ions to form a beam of ions within a predetermined relatively narrow energy band, thereafter periodically interrupting the selected ion beam to form ion pulses, accelerating the ion pulses to add substantially the same momentum to ions in each pulse and finally separating the ions in the pulses of different energy to resolve the ions according to their specific mass. The resolved ions may then be collected and sensed.

The apparatus for carrying out the described method includes in combination an ion source for producing an ion beam, first energy filter means including deflection means producing a radial electrostatic field for sorting the ions into beams of differing energies, and an electrode having an energy-resolving aperture disposed in the path of the beams for passing a selected beam into an impuser. In the impuser region, means are provided for periodically interrupting the selected beam to produce ion pulses and individually accelerating each pulse to add substantially the same increment of momentum to the ions in the pulse. Serially following the impulses there is provided a non-magnetic mass resolving system for separating the ions in the pulses according to their specific mass, and means to selectively detect ions of a given mass. The non-magnetic mass resolving system may comprise a second energy filter and the invention is hereafter described as thus embodied.

These and other aspects of the invention will be understood completely in the light of the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic diagram of a preferred mass spectrometer of my invention; and

Figs. 2A and 2B are typical pulse waveforms for illustrating the operation of the instrument shown schematically in Fig. 1.

The mass spectrometer illustrated schematically in the drawings includes an ion source 10 producing an unsorted heterogeneous ion beam 12 which is propelled into a first energy filter 13 involving arcuate deflection plates 14 between which an electrostatic field is established by means of a voltage source 15 connected across the plates. This energy filter is herein referred to as an electric sector. The field in the electric sector separates the heterogeneous ion beam 12 transversely to the beam axis into diverging beams of ions of different energy, including a selected beam 16 which is passed to the impuser 22. The first electric sector limits the ions passed into the impuser to a narrow energy band. Any desired energy band can be selected by variation of the field strength in the filter or by variation of the accelerating potentials in the ion source in accordance with conventional practice.

The impuser 22 includes pulse forming electrodes 24, 26 arranged on either side of a grounded electrode 18 and connected to opposite sides of a pulse generating circuit 28. A serially arranged electrostatic lens 30 focuses ion pulses produced by the electrode array 24, 18, 26 on an aperture 33 of an electrode 34 forming the outlet barrier of the impuser. This electrode is theoretically unnecessary in the instrument, but in practice functions to sharpen the ultimate image. The impuser functions in the following manner.

Voltage pulses P_1 on the apertured grid 24 gates groups of ions into the impulsing region. The gate is closed by the application of positive potential on grids 24, 26. The electric field between grid 26 and the lens 30 accelerates the ions of the groups. The potential of grid 26 is reduced to zero before any of the ions in the group reach the lens. Thus, all ions of the group receive the same impulse, or increment of momentum. The energy re-

ceived by the ions in the impulser is directly proportional to the distance the ions move while the field is on. The light ions therefore receive more energy than do the heavier, slower ions. The pulses P_1 and P_2 applied to grids 24 and 26 are illustrated by the waveforms in Figs. 2A and 2B.

A typical cycle goes as follows. Starting with an impulsing region free of ions, at time t_0 , the potential of grid 24 is brought to zero, thus opening the gate for a new group of ions. Grid 26 is also at zero potential. During the interval t_1-t_0 ions are admitted to the impulser. At time t_1 the potentials of grids 24 and 26 are raised by pulses P_1 and P_2 , respectively. The potential of grid 24 closes the gate when it reaches the potential of the ion source V_s . The potential of pulse P_1 exceeds the source potential V_s . The potential of pulse P_2 may be either more or less than the potential of the source V_s . During the time interval t_2-t_1 the ions are accelerated. At time t_2 the potential of grid 26 is returned to zero, and during the interval t_3-t_2 the ions of the group all clear the impulsing region, leaving it ready for a new group of ions. At time t_3 the potential of grid 24 returns to zero, thus opening the gate and admitting another group of ions for a new cycle.

The lens 30 including three electrodes focuses the ions passing through the apertured grid 26. The potential applied to the center electrode of the lens by the D.C. supply source 32 determines the energy band of the ions which are focused or concentrated on slit 33 of a grounded electrode 34 forming the exit aperture of the analyzer region.

The pulsed ion beam passing through the exit slit 33 and indicated by the reference numeral 36 is directed into the entrance of a second energy filter 37 in the form of an electric sector which separates the ions in the pulses according to their specific mass. The electric sector is shown as radially spaced deflection plates 38 connected to a variable voltage source 40. The ions in the pulsed beam 36 traversing the energy filter 37 are focused on resolving aperture 42 in an ion collector 44. The output of the ion collector is coupled to an amplifier and recorder 46 for amplifying and recording the ion current output of the ion collector.

As is conventional in mass spectrometry, the entire system including the ion source, first energy filter, analyzer, second energy filter and ion collector are immersed in an envelope (not shown) which may be evacuated by conventional means.

In the operation of the instrument, static electric fields in the first and second energy filters are combined with a time-varying electric field produced in the impulser for mass separation of the ions in an unsorted heterogeneous ion beam. The new and novel arrangement of static and time-varying or pulsed electric fields effects the separation of the ion beam into a mass spectrum. The first electric sector limits the ions passed into the impulser to ions whose energy is within a narrow preselected energy band. The spaced pulsed grids in the impulser pass ions during the loading time period (t_0-t_1) when the potential of the grids 24 and 26 is below the voltage of the ion source indicated on the graph in Fig. 2A at V_s . Preferably these grids are reduced to zero voltage during this interval so as not to affect the energies of the ions. At a later time t_1 , the voltage pulse P_1 is applied to the grid 24 to interrupt the beam of ions entering the impulser as the potential of the grid is raised above the voltage of the ion source V_s . Since the voltage pulse P_2 is applied to grid 26 at t_1 , as indicated in both Figs. 2A and 2B, an electrical potential gradient is set up between grid 26 and lens 30 which accelerates the ions previously passed into the impulser during the period t_1-t_0 . The accelerating impulse is maintained for the period t_2-t_1 . During the period of acceleration t_2-t_1 , all ions in the pulse are given an equal increment of momentum, after which the energy of the ions is mass dependent. The pulsing of the ions enables the potential gradient set up between the spaced

grids to apply an equal momentum to all the ions to be analyzed. No new ions enter the region between the grids after time t_1 and during the time interval (t_3-t_2) the heaviest, slowest moving ions clear the region and the analyzing region is prepared to handle a new pulse of ions for a subsequent cycle of operation. The ions in the impulser region (the region between the grid 26 and the lens 30) become separated due to the difference in velocities of the ions. However, the ions need not be, and preferably are not, separated into spaced bunches as is the case in the drift tubes of time-of-flight mass spectrometers. The second energy filter or detector 37 resolves each group of ions leaving the exit slit 33 in accordance with the energy (and mass) of the individual ions. The separation of the ions according to their energies in the energy filter 37 does not depend upon any spacial separation between ions of different mass in any one group and thus is not concerned with the time of flight of the individual ions in any one group between two spaced points.

Since ions within a narrow energy band but different masses are given equal increments of momentum by the electrical potential gradient set up between grid 26 and lens 30, the resulting energies are a function of their masses. However, it may be noted that ions of a given mass may not have exactly the same energy due to the fact that the first energy filter has passed ions having a finite energy interval. This represents a minor limitation on the resolution of the instrument.

In the preferred embodiment of the invention as shown in Fig. 1, a second energy filter is shown as an electric sector having deflection plates 38. Preferably, the ions pass through a defining aperture as described above, before entering the second sector. In the preferred arrangement, therefore, the ions in the pulses are focused by the lens 30 on the defining slit 33 in the electrode 34. The ion pulses which reach the lens have energies which are a function of their masses. By the application of the proper potential to the lens, ions of the desired mass are concentrated on the defining slit 33 and are admitted thereby to the second energy filter. The ions of the other masses focus either in front of or behind the resolving slit and are thereby attenuated.

The energy and mass discrimination of the lens and energy slit in the electrode 34 reduces the space charge effects in the second energy filter 38, providing for improved mass and energy filtering.

Mass scanning of a sample of material in the ion source 10 can be made in several ways. For example, the voltage applied to the ion source 10 and the voltage applied to the deflection plates 14 of the first energy filter may be varied for selection of different energy bands. Another method of scanning the masses of the ions is to maintain the lens voltage constant and to change the magnitude of the pulse voltage applied to grid 26 and hence the magnitude of the equal momentum impulses applied to the ion pulses whereby ions of different energy masses are focused on the defining slit to the second energy filter 38. A third method of scanning the mass of the ions in the sample to be analyzed is to vary the potential of the lens 30 and the second energy filter 38 proportionally whereby the lens focuses ions of different energies and mass sequentially to the second energy filter 38 which in turn passes the ions onto the ion collector 44 through the final resolving slit 42.

The foregoing apparatus should not be considered as limiting the invention but only as the preferred embodiment of a method and apparatus for analyzing an unsorted heterogeneous ion beam by separating a beam of ions having energies within a predetermined energy band and periodically interrupting the selected ion beam to form ion pulses and passing the pulses individually through an electric field for adding substantially the same momentum impulse to ions in each pulse, which is followed by separating the ions within a selected energy band

from the pulses. Once a group of ions of the narrow energy band has been separated from an unsorted heterogeneous ion beam and substantially the same momentum has been added to the ions passed, there are many ways in which the mass dependence of the energy can be made manifest. A second electric sector providing a second energy filter is the preferred arrangement as illustrated, but any of several other kinds of deflections in electrostatic fields may be used, or the ions may be reflected by a potential barrier.

From the foregoing disclosure it is apparent that a new and novel type of non-magnetic mass spectrometer has been set forth in which the need for expensive high transmission and low electrical grids for gating, as in time-of-flight spectrometers, are not required, but rather only electrodes having resolving slits as in conventional magnetic mass spectrometers. Also, the need for ion grouping or space focusing along the optical axis in a non-magnetic instrument has been eliminated and the ions are resolved according to mass transverse to the beam axis of the instrument, as in magnetic mass spectrometers, providing better resolution of the ions according to their mass without increasing the size of the instrument and/or the complexity of the timing circuits such as would be required for equivalent resolution in a time-of-flight mass spectrometer. Further, the performance of the instrument presented herein is not as dependent upon the steep wavefront of pulses generated and applied to the grids for pulsing the ion beam as in time-of-flight instruments, and it is only necessary that an easily generated wavefront be repeated from cycle to cycle, i.e. the frequency and amplitude be maintained relatively constant. It should be noted that the position of a train of ions between the spaced grids of the present instrument is not critical to the performance of the instrument, because the final separation is transverse to the axis of the beam rather than along the axis of the beam. In many instances, therefore, the need for gating systems which greatly increase the complexity of the instrument due to the problems of timing and synchronization between the accelerating and gating functions has been eliminated.

I claim:

1. In a mass spectrometer, the combination comprising an ion source for producing ions, energy filter means for selecting a beam of ions falling in a predetermined energy band, an impulser arranged to receive said beam from the energy filter, means in the impulser for periodically interrupting the selected beam to produce ion pulses and accelerating the ions in each pulse by substantially the same momentum impulse, resolving means adapted to receive ions from the impulser and separate these ions according to their energy whereby ions of a given mass may be selected, and sensing means for sensing ions of said given mass.

2. In a mass spectrometer, the combination comprising an ion source for producing ions, energy filter means for selecting a beam of ions falling in a predetermined energy band, an impulser arranged to receive said beam from the energy filter, means in the impulser for adding substantially the same momentum to all ions in the selected energy band whereby the energy of the ions is mass dependent, resolving means adapted to receive pulses from the impulser and to separate the ions in the pulses according to their energy whereby ions of a given mass may be selected, and sensing means for sensing ions of said given mass.

3. In a mass spectrometer, the combination comprising an ion source for producing ions, a first energy filter for passing ions in a beam within a selected narrow energy band, an impulser arranged to receive ions passed by the filter, means in the impulser for periodically interrupting the selected beam received into the impulser to produce ion pulses and to accelerate each ion in a pulse by the same momentum impulse, a second energy filter arranged to receive ions from the analyzer and to separate the ions in the pulses received from the analyzer, and sensing means for selectively sensing ions of a given mass.

4. In a mass spectrometer, the combination comprising in serial arrangement an ion source for producing ions, first energy filter means for selecting a beam of ions falling in a given energy band, an impulser arranged to receive said beam of ions from the first energy filter, the impulser including a pair of spaced grids and means for producing between the grids a pulsed electric field for periodically interrupting the selected beam to produce ion pulses and for applying substantially an equal momentum to the ions in each pulse, second energy filter means for separating the ions in the pulses according to energy whereby ions of a given mass may be selected, and sensing means for sensing ions of said given mass.

5. In a mass spectrometer, the combination comprising in serial arrangement an ion source for producing ions, first energy filter means including deflection means producing a radial electrostatic field for selecting a beam of ions falling in a predetermined energy band, an electrode having a resolving aperture disposed in the path of ions emerging from the filter for passing said selected beam, an impulser including said electrode and having means for periodically interrupting the selected beam to produce ion pulses and individually accelerating the ions in each pulse by a momentum impulse, second energy filter means arranged to receive ion pulses from the analyzer and to separate the ions in the pulses according to their energy whereby ions of a given mass may be selected, and sensing means for sensing ions of said given mass.

6. In a mass spectrometer the combination comprising an ion source for producing ions, means for selecting a group of ions from the ion source having substantially equal energies, means for receiving said group of ions and for accelerating each of the ions in said group by substantially the same momentum impulse to impart substantially equal increments of momentum to each of the ions, energy detecting means for receiving the ions from the last named means and for separating the ions according to their energy whereby ions of a given mass may be selected, and means for sensing ions of said given mass.

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