March 17, 1953 H. W. WASHBURN ET AL 2,632,112

MASS SPECTROMETRY

Filed Aug. 3, 1950

FIG. 1.

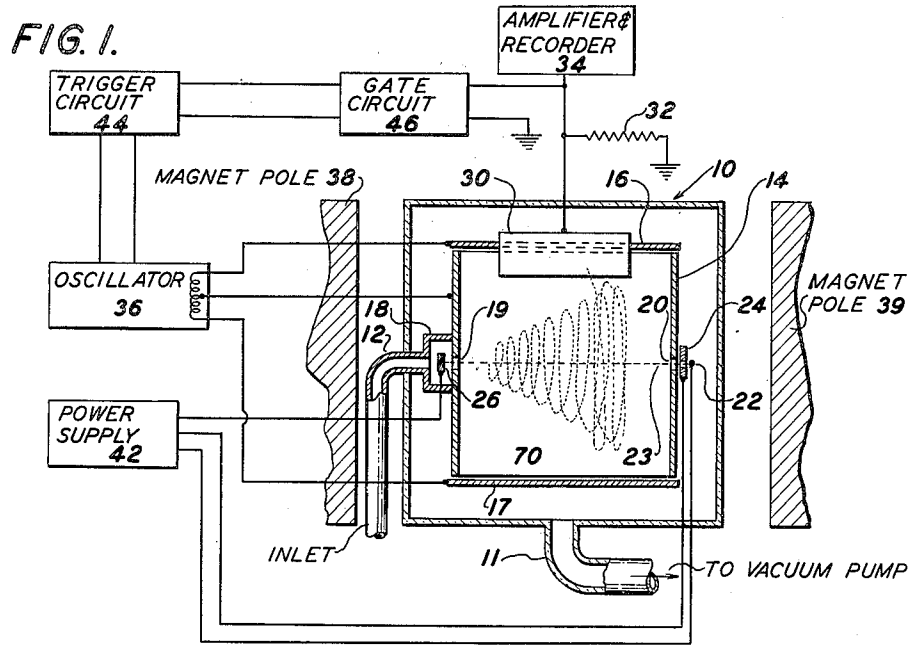
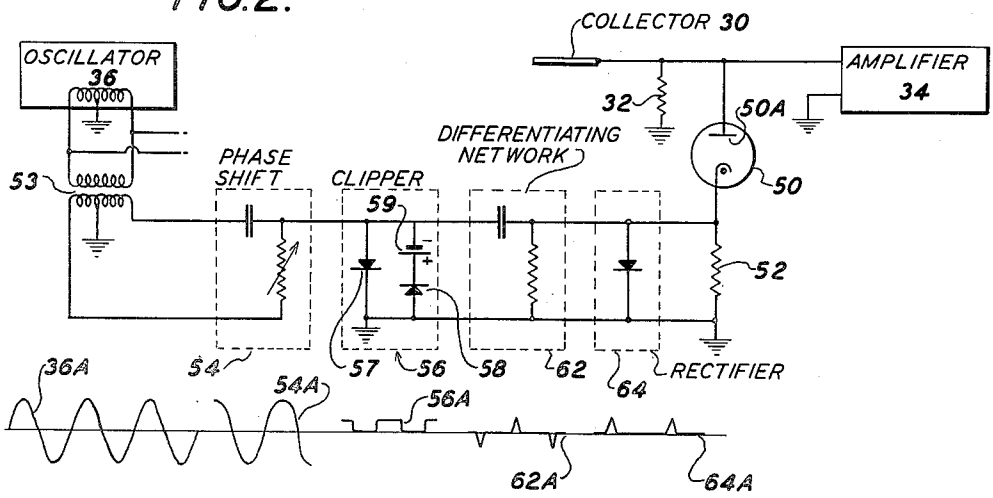


FIG. 2.



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Patented Mar. 17, 1953

2,632,112

UNITED STATES PATENT OFFICE

2,632,112

MASS SPECTROMETRY

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Application August 3, 1950, Serial No. 177,502

5 Claims. (Cl. 250—41.9)

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This invention relates to mass spectrometry and particularly to mass spectrometry wherein charged particles of differing mass-to-charge ratio are segregated according to their periodicity of motion in a magnetic field.

Mass spectrometry in general involves ionization of a sample to be analyzed, as by bombardment with an electron beam, and segregation of the resultant ions in accordance with their mass-to-charge ratio. The measured magnitude of the current developed by discharge of the ions of the given mass-to-charge ratio provides a basis for calculating the partial pressure of those molecules in the sample from which these particular ions were derived. Where a sample is to be analyzed for more than one component, the practice is to scan the mass spectrum by successively discharging and measuring ions of different mass-to-charge ratio. The spectrum is scanned by varying one or more of the parameters which determine the paths of travel of the ions.

One means of segregating or sorting the ions comprises introducing them into or forming them in a space traversed by a magnetic field and a high frequency alternating field normal to the magnetic field. It has been found that ions will assume characteristic paths of motion in the space traversed by these fields, the orbits of which depend primarily upon whether or not the ions are in resonance with the alternating field. At any given magnetic field strength and at any given frequency of the alternating field, only ions of a given mass-to-charge ratio will be in resonance with the alternating field.

Under these circumstances, the so-called resonant ions will pursue a path from their origin in the form of an ever expanding spiral of uniformly increasing radius, the radius being normal to the magnetic field. The non-resonant ions, on the other hand, will be driven in an expanding and contracting spiral, i. e. the radius of travel will increase in decreasing increments to a maximum and will thereupon commence to decrease in increasing increments so that the ion path collapses back to the origin. The origin may be considered as the axis of ion flow into the space, or as the axis of an ionizing electron beam projected through the space parallel to the magnetic field.

As might be expected, the non-resonant ions of mass most closely adjacent the mass of the resonant ions will have the largest orbital radii, and for this reason the degree of resolution depends upon the selectivity with which the resonant ions are measured to the exclusion of the non-resonant ions of closely adjacent mass-to-

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charge ratio. To scan the mass spectrum, it is only necessary to vary the frequency of the alternating field so that ions of a different mass-to-charge ratio will become in resonance therewith.

It can be shown that all ions of resonant mass starting at arbitrary times at the origin and with no initial energy, lie in a roughly radial band.

In other words, the resonant ions orient themselves into a radial spoke with the axis of rotation coinciding with the axis of origin. Phase differences with respect to the time of formation are substantially eliminated within the first few revolutions of the spiral path. In practice the origin may be anywhere along the ionizing electron beam. As a result of initial energies and stray fields ions may move parallel to the beam, a small retaining D. C. field generally being applied to limit this movement within the confines of the crossed fields. The longitudinal movement does not affect the characteristic spiral paths of the ions, and at any given instant all of the ions of resonant mass will lie in a radial plane intersecting the beam, the beam being the axis of origin as well as the axis of rotation.

Non-resonant ions, that is, ions whose mass-to-charge ratio does not fit the condition

$$q/m=\omega/B \qquad (1)$$

where:

q=the charge of the ion;

m=the mass of the ion;

ω=the angular frequency of the alternating field; and

B=the transverse magnetic field;

will also move in bands. However, the non-resonant bands are bent in a curvilinear configuration and do not lie on a radius of the axis of origin as does the band of resonant ions. Since the effect of initial energy in either the ions of resonant mass or non-resonant mass is only to obscure or spread the boundaries of the respective bands leaving their angular orientation unaffected, these do not require special consideration in this instance.

As mentioned above, the resolution depends upon the selectivity with which the resonant ions are discharged with respect to the non-resonant ions of closely adjacent mass. From the foregoing considerations, it is seen that resonant ions do not continuously strike a collector electrode which may be located in the field and spaced from the axis of origin for the reason that the resonant ions are disposed in a radial spoke and will hence strike the collector electrode only once for each revolution of the spoke. Non-resonant ions of adjacent mass will interfere with the resolution

of the instrument by discharging at the electrode in the periods intervening between successive impingement of the spoke of resonant ions on the electrode. Theoretically, by placing the collector electrode far enough from the axis of origin, non-resonant ions will not achieve a sufficient radius of travel to attain the collector electrode. However, in practice, the ideal situation is not achieved and some non-resonant ions will discharge at the collector interfering with the resolving power of the instrument.

We have now discovered a method for increasing the resolving power of a mass spectrometer of this type by an appreciable factor, which method is based upon the discovery that the resonant ions will travel in a radial spoke as described.

Thus, the invention contemplates in mass spectrometry involving the formation of ions and the separation thereof in an analyzer region by causing them to travel in different paths under the influence of a magnetic field and a transverse alternating electrical field, and measuring ions by means of a collector electrode, the improvement which comprises maintaining the collector electrode and the alternating electrical field in matched relationship whereby only ions of a given mass-to-charge ratio will be measured at the collector electrode.

To accomplish this method, the collector electrode and associated amplifier and recorder are electrically gated so that the electrode is responsive to ion discharge only during a small fraction of the period of operation, the sensitive period being synchronized with the alternating electrical field so as to coincide with the instant at which ions of resonant mass impinge on the collector electrode. By so operating the collector electrode, all ions which impinge thereon in the comparatively longer period during which the ions of resonant mass are revolving through an angle of approximately 360° will not be sensed. In this way, non-resonant ions of closely adjacent mass can be excluded from the collection and amplification system and the resolution of the instrument may be increased by a comparatively large factor.

Our invention contemplates improvements in instrumentation which facilitate the practice of the method of the invention involving in a mass spectrometer the combination which comprises an analyzer chamber, means for ionizing a gas sample introduced into the chamber, collector means disposed in the chamber for discharging ions impinging thereon, amplification means connected to the collector, means for amplifying discharge current developed at the collector means, electrodes disposed at opposite ends of the chamber, a high frequency oscillator connected to the electrodes to establish a high frequency alternating field across the chamber, means for establishing a magnetic field across the chamber normal to the alternating electrical field and means in association with the collector means for rendering the same insensitive to ion discharge during the period in which ions of a given mass-to-charge ratio do not strike the collector means.

Many means may be employed for controlling the sensitivity of the collector electrode and amplification system. One convenient means comprises gating the collector in synchronism with the high frequency alternating field responsive to an impulse delivered to the collector and amplification system from the high frequency oscillator.

The invention will be more clearly understood with reference to the following detailed description taken in conjunction with the accompanying drawing wherein:

Fig. 1 is a schematic diagram of one form of instrument in accordance with the invention; and

Fig. 2 is a circuit diagram showing in greater detail one means of gating the collector and amplification system of the apparatus of Fig. 1 in synchronism with the high frequency electrical field.

The apparatus of Fig. 1 includes an envelope **10** having an exhaust line **11** for connecting the envelope to an evacuating system (not shown) and a sample inlet line **12** for introduction of a gas sample to be analyzed. An open ended conductive box **14** is disposed within the envelope and electrodes **16, 17** are mounted at opposite ends of the box. The electrodes **16, 17** are insulated from the box, as by the illustrated gap, and substantially enclose the open ends of the box. The sample inlet line **12** connects to an inlet chamber **18** formed on an outside wall of the box **14** midway between the electrodes **16** and **17**. An opening **19** in the wall of the box gives access from the inlet chamber **18** to the interior of the box, and a similar opening **20** in the opposite wall of the box permits an electron beam **23** to be directed across the box from a gun **22** and into the inlet chamber **18**. An electrode **24** propels electrons from the gun **22** through the box and into the inlet chamber **18** where they impinge and are discharged at a target electrode **26**. The same propelling potential may be developed between the gun and the box itself so as to eliminate electrode **24** if desired.

A collector electrode **30** is mounted through electrode **16** and is insulated therefrom. The collector electrode is grounded through a resistor **32** and is connected to an amplifying and recording network **34**. Operation of the collector electrode at ground potential is not necessary to the practice of the invention.

A high frequency oscillator **36** is connected across electrodes **16** and **17** to develop in the analyzer region defined by the box **14**, a high frequency alternating electrical field transverse to the electron beam. Magnetic pole pieces **38, 39** are mounted outside the envelope **14** and develop a magnetic field across the analyzer region parallel to the electron beam. A power supply network **42** is connected to the various propelling electrodes, electron gun and electron target to supply the necessary potentials thereto.

The oscillator **36** is connected through a trigger circuit **44** and a gate circuit **46** to the amplification and recording network **34** so as to gate the collector electrode **30** in the manner and for the reasons above described.

One circuit by means of which the amplifier and recorder may be gated in synchronism with the alternating electrical field is shown in greater detail in the diagram of Fig. 2. Referring to this figure, collector electrode **30** is connected to the amplifier **34** and is grounded through the resistor **32**. A diode **50** is connected to the circuit between the collector and the amplifier, cathode **50A** of the diode being grounded through a resistor **52**. The collector is hence normally grounded through the diode which bleeds any signal from the collector electrode before it is applied to the amplifier **34**. Oscillator **36** develops an A. C. signal shown by the trace **36A**, which is applied through a step up transformer **53** to a phase shift network **54** which shifts the phase of the signal **36A**

as shown in 54A, this signal being applied to a clipper 56. The phase shift network is preferably variable as shown so that the relationship of collector sensitivity to the alternating electrical field may be adjusted at will. The clipper comprises rectifier elements 57, 58 and a bias battery 59 biasing the rectifier element 58. The output signal from clipper 56 as represented by the trace 56A is differentiated in a differentiating network 62 to convert it into a series of pips as illustrated at 62A. The signal 62A is in turn rectified in a rectifier element 64 erasing the negative pips to give a signal illustrated by the trace 64A. The output of the rectifier is applied to the cathode of diode 50 so that during the interval of each of these pips, voltage developed across resistor 32 responsive to discharge current at the collector electrode will not be shorted through the diode and will be amplified in the amplifier 34.

The signal applied to the gate tube 50 is so synchronized with the alternating voltage delivered by the oscillator 36 that the collector and amplification system is sensitive only when the resonant ions are in the vicinity of the collector electrode and not otherwise. If the collector electrode is differently oriented in the analyzer region, for example if it projected into the region at a point 90° from the position shown, the same gate circuit could be applied with suitable adjustment of the phase shift to vary the periods at which the collector is energized to again correspond to the time intervals in which resonant ions are in the vicinity of the collector.

The operation of the illustrated apparatus is as follows. A gas sample introduced through inlet line 12 diffuses from the inlet chamber into the analyzer region defined by the box 14 in substantially an un-ionized state. In the analyzer region any gas molecules intersecting the electron beam 23 are ionized and under the influence of the transverse magnetic and alternating fields are set in motion which is characterized by rotation around the electron beam. Ions of resonant mass will travel in a spiral path 70 of ever increasing radius and will strike the collector electrode 30. The conductive walls of the box are conveniently provided with a slight positive bias so as to prevent ion discharge at the walls. The effect of this bias is to cause ions formed along the electron beam to oscillate between the opposite walls of the box. This oscillation, however, does not affect the spiral paths of the ions. During the intervals in which no resonant ions are discharging at the collector electrode, the electrode and amplification network are rendered insensitive by the gate tube 50 so that any non-resonant ions which may strike the electrode in this interval are not measured.

The effect of the invention is to bring about a time separation as well as a space separation between resonant and non-resonant ions, it having been found that the space separation alone is not entirely satisfactory because of the closely approximating radii of non-resonant ions of mass approaching the mass of the resonant ions. Particularly is this true when the spectrum is scanned by varying the frequency of the alternating field. By gating the collector advantage is taken of the phase differences between the resonant and non-resonant ions. Moreover, in passing from one mass peak to an adjacent mass peak as the frequency of the alternating field is varied, the bases of the adjacent peaks are narrowed as a result of the gating and undesirable overlap of the adjacent peaks is minimized.

Another factor which ordinarily has a bearing on the resolution achieved is the existence of ions having small initial energies. These ions tend to spread the ion bands so that ions having an initial energy and of mass adjacent the resonant mass may strike the collector electrode. However, such initial kinetic energy does not alter the phase relationship between the resonant and non-resonant masses and by gating the collector as described some of the non-resonant ions having initial kinetic energy may be excluded from the measurement.

We claim:

1. In a mass spectrometer the combination which comprises an analyzer chamber, a collecting system including a collector electrode disposed in the chamber for discharging ions impinging thereon a sensing circuit connected to the collector, means including a high frequency oscillator for establishing an alternating electrical field across said chamber, means for establishing a magnetic field across said chamber transverse to the alternating electrical field, and means in association with said collecting and sensing systems to render the sensing circuit insensitive to ion discharge at the collector electrode for a part of each cycle of the alternating field.

2. In a mass spectrometer the combination which comprises an analyzer chamber, a collecting system including a collector electrode disposed in the chamber for discharging ions impinging thereon a sensing circuit connected to the collector, means including a high frequency oscillator for establishing an alternating electrical field across said chamber, means for establishing a magnetic field across said chamber transverse to the alternating electrical field, and means for matching the sensing circuit with the oscillator for rendering the sensing circuit insensitive to ion discharge at the collector electrode for a part of each cycle of the alternating field.

3. In a mass spectrometer the combination which comprises an analyzer chamber, a collecting system including a collector electrode disposed in the chamber for discharging ions impinging thereon a sensing circuit connected to the collector, means including a high frequency oscillator for establishing an alternating electrical field across said chamber, means for establishing a magnetic field across said chamber transverse to the alternating electrical field, and means for matching the sensing circuit with the oscillator for rendering the sensing circuit insensitive to ion discharge at the collector electrode for a major part of each cycle of the alternating field.

4. In a mass spectrometer the combination which comprises an analyzer chamber, a collecting system including a collector electrode disposed in the chamber for discharging ions impinging thereon a sensing circuit connected to the collector, means including a high frequency oscillator for establishing an alternating electrical field across said chamber, means for establishing a magnetic field across said chamber transverse to the alternating electrical field, and a gate circuit connected between the oscillator and the sensing circuit for rendering the sensing circuit insensitive to ion discharge at the collector electrode for all but a fraction of each cycle of the alternating field.

5. In a mass spectrometer including an analyzer region, means for establishing across the analyzer region an alternating electrical field and a transverse magnetic field, the combination comprising a collector electrode disposed in the region for discharging ions thereon, a sensing circuit connected to receive discharge signals from the collector electrode, and means rendering the sensing circuit insensitive to discharge signals from the collector electrode during a part of each cycle of the alternating electrical field.

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No references cited.