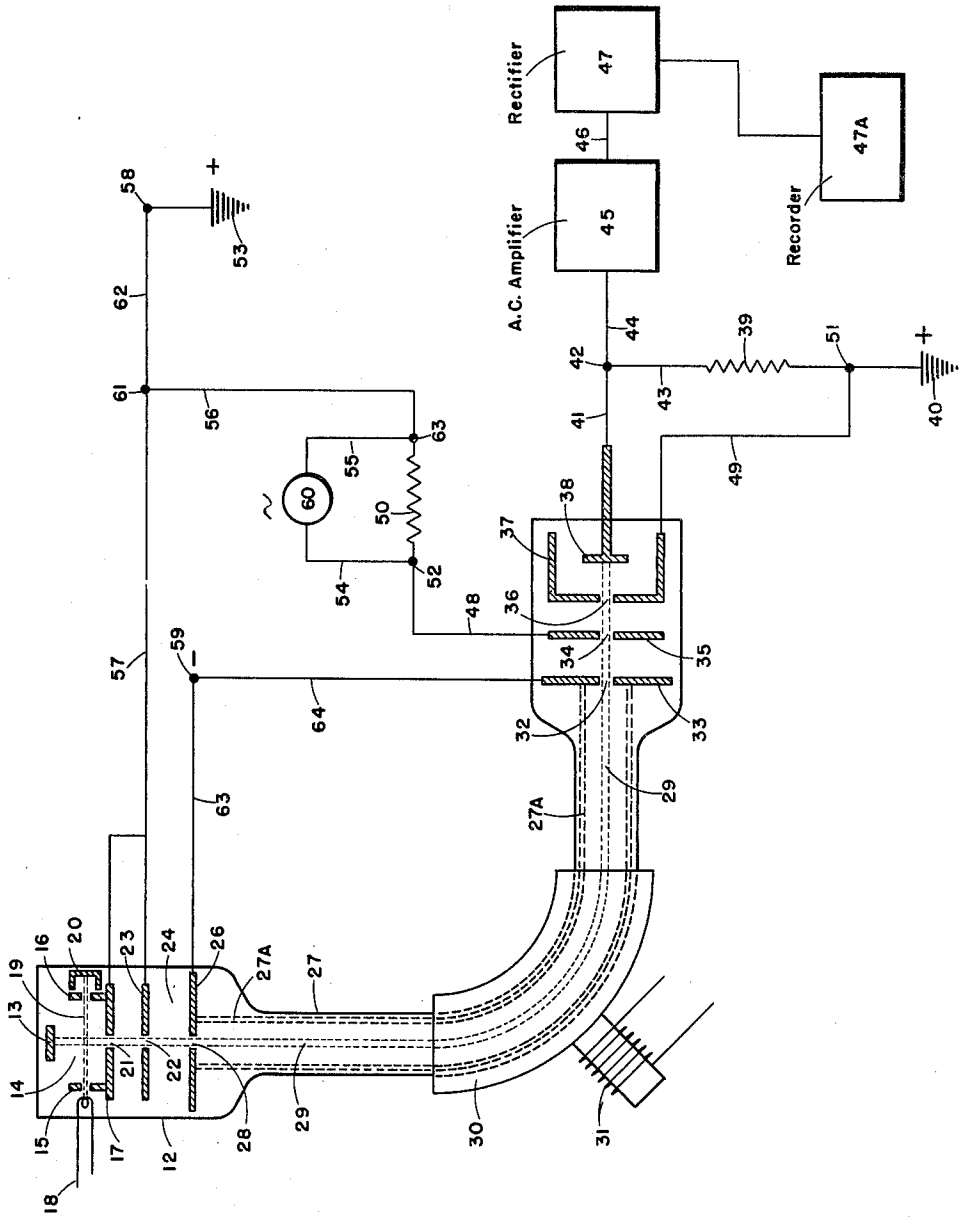
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METHOD AND APPARATUS FOR ANALYZING SUBSTANCE BY MASS SPECTROMETRY

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METHOD AND APPARATUS FOR ANALYZING SUBSTANCE BY MASS SPECTROMETRY

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The present invention relates to the field of mass spectrometry. More particularly, the present invention is directed to a method for analysis wherein ions are obtained from a substance to be analyzed and are formed into a pulsating beam, and to apparatus suitable for use in performing the method of anaylsis.

The art of analyzing gaseous mixtures by means of a mass spectrometer is well known. The analysis is usually carried out by admitting a gas under reduced pressure into an ion source contained in a high vacuum spectrometer tube. The molecules of the gas are bombarded with high speed, fixed energy electrons emitted from a hot filament such that a small portion of the molecules are converted into parent ions and fragments of many different masses. Each ion usually possesses a unit of positive electricity. The charged ions pass from the ion source into an ion accelerating field where they are accelerated to high velocities. The ions are caused to pass from the ion source into the accelerating field by means of a small auxiliary electrostatic field. The ions in the accelerating field acquire equal kinetic energies and thus their velocities are inversely proportional to the square roots of their masses. The accelerated ions then pass through an entrance slit into an analyzing portion of the mass spectrometer which comprises a curved conduit within an external magnetic field.

The ions moving at a high velocity constitute an electric current and a magnetic field is produced simultaneously by the moving ions. The magnetic field caused by the moving ions is acted upon by the external, crossed magnetic field which causes a deflection of the ions in the curved conduit. The magnitude of the magnetic field and the accelerating voltage creating the accelerating field may be controlled precisely such that ions representing only one mass may navigate the curved conduit of the analyzer. This is because ions of different masses are deflected by different amounts. Consequently, ions of any one mass will follow a path having a radius of curvature of magnitude different from the radii of curvature of paths of ions having any other masses. The number of ions of any given mass are thus caused to focus on an exit slit of the analyzer and from the exit slit they enter a Faraday cage or other collecting means which is grounded through a resistance. The neutralization of the charge carried by the ions causes a current to flow through the resistance setting up a potential drop. This potential drop may then be amplified in a D. C. amplifier and measured by means of a sensitive galvanometer or a recorder. The current set up by neutralization of the ions impinging on the collector plate is proportional to the number of ions of a particular mass striking the plate per unit time. By manipulation of the external magnetic field and/or the accelerating electric field

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strengths, ions representing components of different molecular weights or masses can be caused to pass through the analyzer exit slit in sequence. Therefore, the voltage across the aforementioned resistance changes with time depending on the quantity per unit time of the different ionized masses passing through the exit slit, and a record or mass spectrum representing the composition of the gases will be obtained. If a chart recorder is employed, a mass spectrum will be obtained having peaks corresponding to ions of any particular mass and will show the relative abundance of these particular ions.

In the conventional type of mass spectrometer positive ions produced at the ion source are usually measured. Because a slightly greater positive potential is maintained in the ion source than for the ion accelerating field, positive ions are caused to pass into the ion accelerating field and are eventually passed through the analyzer portion of the mass spectrometer, whereas negative ions formed at the ion source are repelled. Thus the ions passing through the anaylzer form a direct or steady positive ion beam which eventually impinges on the collector plate as mentioned above and are neutralized by a flow of electrons from ground. The electron flow is directly equivalent to the positive ion charge flow onto the collector plate and thus the I (current) $\times$R (Resistance) =E (voltage) difference across the ends of the grounded resistor is directly related to the current through the resistor. As previously mentioned, this current is related to the number of ions collected per unit time. Hence, the variations of the number of ions collected per unit time are converted into signals represented by voltage changes which are impressed on an electronic tube designed to amplify the magnitude of the original current to a magnitude more amenable to standard measuring devices or recorders.

It is thus seen that direct currents set up by the neutralization of the direct positive ion beam on the collector plate are amplified and measured in the conventional equipment. Direct current amplification of the voltage change, however, has certain drawbacks. It is known, for example, that A. C. amplifiers are inherently more stable than D. C. amplifiers. D. C. amplifiers also are subject to what is known as "zero drift" resulting from the fact that aging of filament, minute changes of potentials within the electronic tubes, and similar disturbances upset the balance of conditions previously established causing a new set of operating parameters to exist. These new parameters obviously produce a shift of the apparent balance which is interpreted as a "zero drift." A. C. amplifiers respond only to signals of periodic character and have no output for no input signal; hence in the quiescent period no output is obtained which means that no shift of

balance can appear. Direct current amplification is also known to have less usable sensitivity and to respond more slowly to voltage fluctuations than does an A. C. amplifier. It would, therefore, be extremely desirable to devise a means for using A. C. amplification of the ion beam currents in order to eliminate the aforementioned difficulties.

It is, therefore, an object of my invention to provide a means for improving the operation of a mass spectrometer.

Another object of my invention is to provide a method of modulating the ion beam in a mass spectrometer such that A. C. amplification of the beam currents may be employed.

It is a further object of my invention to improve the stability and sensitivity of a mass spectrometer as regards the amplification and recording of ion beam currents produced therein.

I accomplish the objects of the present invention by the interruption of the ion beam produced in the mass spectrometer by applying repelling voltages in such a manner as to cause a periodic variation of the steady ion beam. The interruption of the ion beam causes a pulsing or grouping of the ions and produces a periodic voltage change corresponding to the frequency of the pulsating ion beam. In other words, the direct ion beam passing through the analyzer is converted into a pulsating ion beam, the magnitude of which is directly related to the number of ions per unit time reaching the collector plate. A pulsating voltage is set up in the ion collecting system which is more easily controlled and amplified than the direct voltage set up in conventional mass spectrometers. By using a conventional "peaked" response A. C. amplifier tuned to the interruption frequency imposed on the ion beam or other A. C. amplifier systems, variations due to changes of the ion beam intensity are readily amplified.

An added advantage of the "peaked" response system is that voltage changes arising from interfering sources will be minimized because such voltage changes do not have the proper frequency to be amplified to the full amount by the system tuned to the interruption frequency of the ion beam. Therefore, a very stable and sensitive amplifying system is obtained which is not subject to "zero drift" and which has a considerably shorter response time than conventional D. C. amplifier systems.

One embodiment of the device of the present invention will now be described in detail in conjunction with the accompanying drawing in which the sole figure is an elevation, partly in section, with conventional electrical units comprising the assembly indicated by conventional symbols.

In the figure, numeral 12 designates a spectrometer tube which is maintained under an extremely low pressure and which is of the 90° type frequently used in the analysis of gaseous mixtures. It is to be noted, however, that my invention is not limited to any specific type of mass spectrometer tube, but is applicable to analysis in the 60°, 180° and other types of spectrometer tubes.

The mass spectrometer tube comprises a means for supplying the gas to be analyzed into the tube, an ion source for forming ions of various masses, an ion accelerating field, an analyzer in the form of a curved conduit in which ions of various masses are deflected by means of an external magnetic field, a focusing means for focusing the ions of a desired mass on a collecting means, means for modulating the direct beam of ions so focused on the collecting plate into a pulsating beam of ions, and suitable A. C. amplification and measuring means for determining the relative abundance of ions of a given mass produced at the ion source.

Turning now specifically to the drawing, a small amount of gas under a reduced pressure such as, for example, from 10^{-3} to 10^{-6} millimeters of mercury is introduced into drawout electrode 13 by conventional means, not shown, such that the gas under reduced pressure is discharged downwardly into dissociation region 14, defined by electrodes 15, 16 and 17. Electrons emitted from heated filament 18 flow through small apertures in electrodes 15 and 16 as a beam designated by 19 in a direction perpendicular to the flow of gas emitted downwardly through drawout electrode 13. Electron beam 19 is maintained in a horizontal flat ribbon through dissociation region 14 by means of an externally applied magnetic field, not shown, such that the electrons impinge on electron collector 20.

A portion of the electrons in electron beam 19 bombard molecules of gas in region 14 and cause ionization of a fraction of the molecules. Thus, region 14 may be considered as a source of ions. If positively charged ions are to be analyzed, the ions formed in region 14 are slowly moved toward accelerating field entrance slit 21 in electrode 17 by means of a small electric potential difference between electrode 17 and drawout electrode 13. The ions pass through slit 22 in focusing electrode 23 before reaching the accelerating field 24 existing between electrodes 23 and 26. Accelerating field 24 is produced by a voltage applied to electrode 26 such that a potential difference is maintained between electrodes 23 and 26. It is to be pointed out that in the method of operation to be described, electrodes 17 and 23 are grounded while electrode 26 is connected to a high voltage source at junction 59. This method of operation will be referred to as the ion source grounded. Slits 21 and 22 are aligned and define the path of the useful portion of the ions to be analyzed, and, for the purpose of definition electrodes 17 and 23 will be termed the ion source. Electrode 23 may, if desired, be split into two sections such that one portion is connected electrically to electrodes 15, 16 and 17, while the other electrode may be supplied a voltage from a voltage network. Under some conditions, control in the focusing of ions of various masses into the analyzer is improved by employing a split focusing electrode. Leaving slit 22, the ions are accelerated in the field existing between electrodes 23 and 26.

The accelerated ions then enter the analyzer section 27 of the mass spectrometer through entrance slit 28 in electrode 26, slit 28 being aligned with slits 21 and 22. Ions passing through slit 28 in a beam designated as 29 are eventually deflected by an external crossed magnetic field 30 produced by a suitable electromagnet 31. Analyzer 27 in the form of a curved conduit representing a 90° angle may be made of glass provided with internal, nonmagnetic shield 27A. The magnitude of the magnetic field is controlled by a power supply not shown. Ions of a given mass which navigate the curved conduit as beam 29 are focused on analyzer exit slit 32 in electrode 33. The ions of a desired mass are focused as beam 29 on slit 32 by controlling the magnitude of the magnetic field 30 and/or the strength of

the accelerating field 24. It is pointed out that electrodes 26 and 33 are electrically connected by means of the aforementioned internal shield within analyzer tube 27 and in the figure are connected through leads 63 and 64 at junction 59. Ions of either less or greater mass than those in beam 29 are discharged by striking the walls of the analyzer and are pumped out of the tube by means not shown.

In a conventional system, ions of a given mass passing through exit slit 32 in the form of a direct beam also pass through slit 34 of electrode 35, slit 36 of electrode 37, and eventually impinge on collector plate electrode 38. Collector plate 38 and shield electrode 37 constitute a Faraday cage and the collector plate 38 is electrically connected through leads 41, 43 and resistor 39 to ground 40.

As pointed out previously, electrodes 26 and 33 are electrically connected as represented by junction 59 and are at a potential negative with respect to ground in the operation with ion source at ground potential. Electrodes 35, 37, and 38 are at substantially ground potential. Therefore, the electrical field existing between electrode 33 and electrodes 35, 37 and 38 is a retarding field for the positively charged ions. It is only because the ions are given a greater energy due to the slightly different potentials maintained between drawout electrode 13 and ion source electrodes 17 and 23 do the ions reach collector plate 38.

Normally, the voltage difference between electrode 13 and electrodes 17 and 23 is in the order of a few volts (approximately 5 volts); hence, if electrode 35 and/or electrode 37 are made positive with respect to ground 53, the positive ions in beam 29 may be prevented from reaching collector plate 38. Furthermore, if the voltage (of proper polarity) applied across electrodes 35 and/or 37 is made periodic in character, the direct ion beam is modulated into pulses. Therefore, a pulsating voltage rather than a direct voltage is produced across grounded resistor 39, the amount of voltage being dependent upon the number of ions per unit time collected on plate 38. To retain the true identity and operation of the Faraday cage, electrode 37 is usually near the same potential as the collector plate 38 and not varied with time.

The method of modulating the direct positive ion beam passing through exit slit 32 before said beam impinges on collector plate 38 will now be described in greater detail. The revised system comprises, as shown in the figure, a lead 41 to junction 42 from which point lead 43 is attached to resistor 39, and lead 44 is attached to A. C. amplifier 45. Amplifier 45 is then connected through suitable connections such as is represented by 46 to rectifier 47 and then to galvanometer or recorder 47A. Resistor 39 is connected through junction 51 to ground 40 and shielding electrode 37 is connected through lead 49 to junction 51. Thus, shielding electrode 37 and collector plate electrode 38, which constitute the Faraday cage system, are substantially at ground potential.

Electrode 35 is connected through lead 48 to resistor 50 at terminal 52. Terminal 63 of resistor 50 is connected through lead 56 to lead 57 at junction 61. Lead 57 electrically connects electrodes 17 and 23. When the ion source comprising electrodes 17 and 23 is at ground potential, lead 62 from junction 61 will be connected to ground 53 at junction 58.

Terminals 52 and 63 of resistor 50 are connected through leads 54 and 55 to a source of alternating current and voltage 60, such as an oscillator or a multivibrator circuit. Oscillator 60 is incorporated in the circuit to supply alternating current and voltage to resistor 50, said alternating current and voltage having any desired wave form. Thus, a wave form best suited for optimum modulation of the direct ion beam may be applied. The potential at junction 61 is common to the ion source comprising electrodes 17 and 23 and to the modulating electrode 35. It will be obvious to those skilled in the art that the magnitude of resistor 50 will depend upon the operating parameters desired. It will also be obvious that when no voltage is applied through leads 54 and 55, there will be no current through resistor 50 and, therefore, electrodes 35 and 37 will be at a common potential as both are connected to ground at 53 and 40 which are electrically identical.

In order to modulate the positive ion beam, the alternating voltage from oscillator 60 is applied through leads 54 and 55 such that the ion beam is modulated into pulses of a certain frequency. The positive half-cycle of the alternating voltage from the oscillator 60 will repel incoming positive ions whereas the negative half-cycle will offer no repelling influence. This then interrupts the ion beam into pulses. The direct ion beam which is converted into a pulsating ion beam impinges on collector electrode 38 causing a pulsating signal to occur across grounded resistor 39. The pulsating signal passes to A. C. amplifier 45 for amplification and subsequently the amplified signal is rectified in rectifier 47 and received by the galvanometer or recorder 47A.

It is possible, in some instances, that only the crest or peak of the modulation voltage applied to electrode 35 is responsible for the greatest interrupting influence. For example, in the case of a wave form with 10 volts peak value, of which approximately the first 8 volts contribute little to stopping the ion beam, it usually is desirable to insert a bias voltage of 8 volts in series with the alternating voltage and reduce the swing of the alternating voltage to 2 volts. This bias voltage could be applied between junctions 63 and 61 in place of lead 56. The source of this voltage may be batteries or a small A. C. operated power supply.

Although the above-mentioned mode of operation applies to the modulation of the ion beam when ion source electrodes 17 and 33 are at ground potential, it is to be pointed out that the present invention is applicable to the modulation of an ion beam when these electrodes are at high potential with respect to ground. In order to effect a change from operation with ion source at ground potential to ion source at high potential, it is merely necessary to interchange ground 53 from junction 58 to junction 59. Upon making this change, analyzer electrodes 26 and 33 are at ground potential and ion source electrodes 17 and 23 are at the desired high potential. Oscillator 60 must be insulated if it is desired to operate such that junction 58 is at a high potential.

It is pointed out that the modulation of the ion beam reduces the number of ions reaching collector electrode 38. The pulsating ion beam, however, permits much greater amplification than is possible when amplifying a direct ion beam by conventional methods. Since the amplification possible in A. C. amplifiers is considerably more stable than that obtained in D. C. amplifiers, resistor 39 may have a much lower value in the

practice of my invention than is normally required in the case of conventional systems. Obviously, the reduction of the input resistance 39 decreases the time constant for amplification and recording the signal produced by neutralization of the pulsating ion beam. Therefore, much more rapid scanning of the mass spectrum may be obtained when the ion beam is modulated in accordance with my invention.

My invention is applicable to the analysis of either positive or negative ions. Proper regard to polarity throughout the entire system must be considered for the measurement of either type of ions. As previously mentioned, if positive ions are to be measured, a positive repelling voltage is applied at electrode 13 in order to introduce the positive ions into accelerating field 24. If it is desired to measure negative ions, a negative potential will be applied to electrode 13 such that negative ions are repelled into the accelerating field. If a negative ion beam is introduced into the retarding field existing between electrodes 33 and 35, a periodic negative retarding voltage is applied to electrode 35 in the manner hereinbefore described wherein a positive ion beam is subjected to a positive retarding voltage.

It is seen, therefore, that my invention may be carried out for the measurement of either positive or negative ions with the ion source at either ground potential or high potential, permitting four different modes of operation to be effected depending on the type of analysis desired.

It will be obvious to those skilled in the art that other arrangements may be made to accomplish the desired modulation of the ion beam produced in a mass spectrometer. For example, if electrodes 35 and 37 are electrically connected, another electrode may be placed in the intervening space between electrodes 33 and 35. This new electrode merely substitutes for the function of electrode 35 as described previously. It is also possible to modulate the ion beam produced at the ion source. For example, a pulsating voltage may be applied to ion drawout electrode 13 to secure the desired modulation of ions introduced into accelerating field 24. Also, an auxiliary electrode may be inserted between electrodes 17 and 23 with a periodic voltage applied thereto. This would accomplish the desired interruption of the ion beam. The extent to which this latter-mentioned method may be applied will depend on the mass range of the ions to be analyzed and on the sizes of the entrance and exit slits employed in the analyzer tube. I do not intend to restrict this invention to any one particular mass spectrometer but rather intend that it apply for improving the results obtained in any mass spectrometer used in the analysis of gases or vaporized solids or liquids.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. In a method for analyzing a substance in a mass spectrometer, the steps of obtaining ions from said substance, forming at least a portion of the ions into a beam comprising ions corresponding to a plurality of different masses, separating from said beam a selected ion beam consisting essentially of ions corresponding to a single mass, periodically interrupting said selected beam with a repelling voltage to form a pulsating beam, employing said pulsating beam to produce a signal which is a function of a characteristic of said substance, and displaying said signal.

2. In a method for analyzing a substance in a mass spectrometer, the steps of treating a sample of said substance to obtain a beam of ions, periodically interrupting said beam with a repelling voltage to obtain a pulsating beam of ions and collecting said pulsating beam.

3. In the operation of a mass spectrometer including means for forming a beam of ions, the steps of periodically interrupting said beam with a repelling voltage to form a pulsating beam of ions and subsequently collecting said pulsating beam.

4. In a method for operating a mass spectrometer wherein a beam of ions is produced, the step of periodically interrupting the ion beam with a repelling voltage.

5. In a mass spectrometer including a means for producing a direct beam of ions and means for collecting same, in combination, a means for periodically interrupting the direct ion beam with a repelling voltage to form a pulsating ion beam.

6. A mass spectrometer in accordance with claim 5 in which said interrupting means includes a source of alternating voltage and a resistance element adapted to supply a periodic repelling voltage to an electrode adjacent said direct beam of ions.

7. In the operation of a mass spectrometer including a means for focusing a direct current ion beam on an ion collector to produce an electric signal, the improvement which comprises the steps of periodically subjecting said ion beam to a repelling voltage to produce a pulsating current ion beam, collecting said pulsating ion beam, employing said collected beam to produce a pulsating electric signal and amplifying said pulsating electric signal.

8. In the operation of a mass spectrometer including an analyzer through which a direct current ion beam passes and a member for collecting the charge from said ion beam, the improvement which comprises subjecting said direct current ion beam to a periodic repelling voltage to produce a pulsating current ion beam.

9. A method for operating a mass spectrometer including the steps of subjecting a gasiform fluid to bombardment by electrons to produce ions, forming a portion of said ions into a beam, subjecting said beam to a periodic repelling voltage to convert said beam to a pulsating beam, collecting said pulsating beam, and displaying a signal which is a function of said collected pulsating beam.

10. A mass spectrometer which comprises, in combination, means for producing a beam of ions, means for imposing a periodic repelling voltage on said beam to convert it to a pulsating beam, means for collecting said pulsating beam, and means for displaying a signal which is a function of a characteristic of the collected pulsating beam.

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