March 28, 1961 C. F. ROBINSON 2,977,470

MASS SPECTROMETRY

Filed April 14, 1955 2 Sheets-Sheet 1

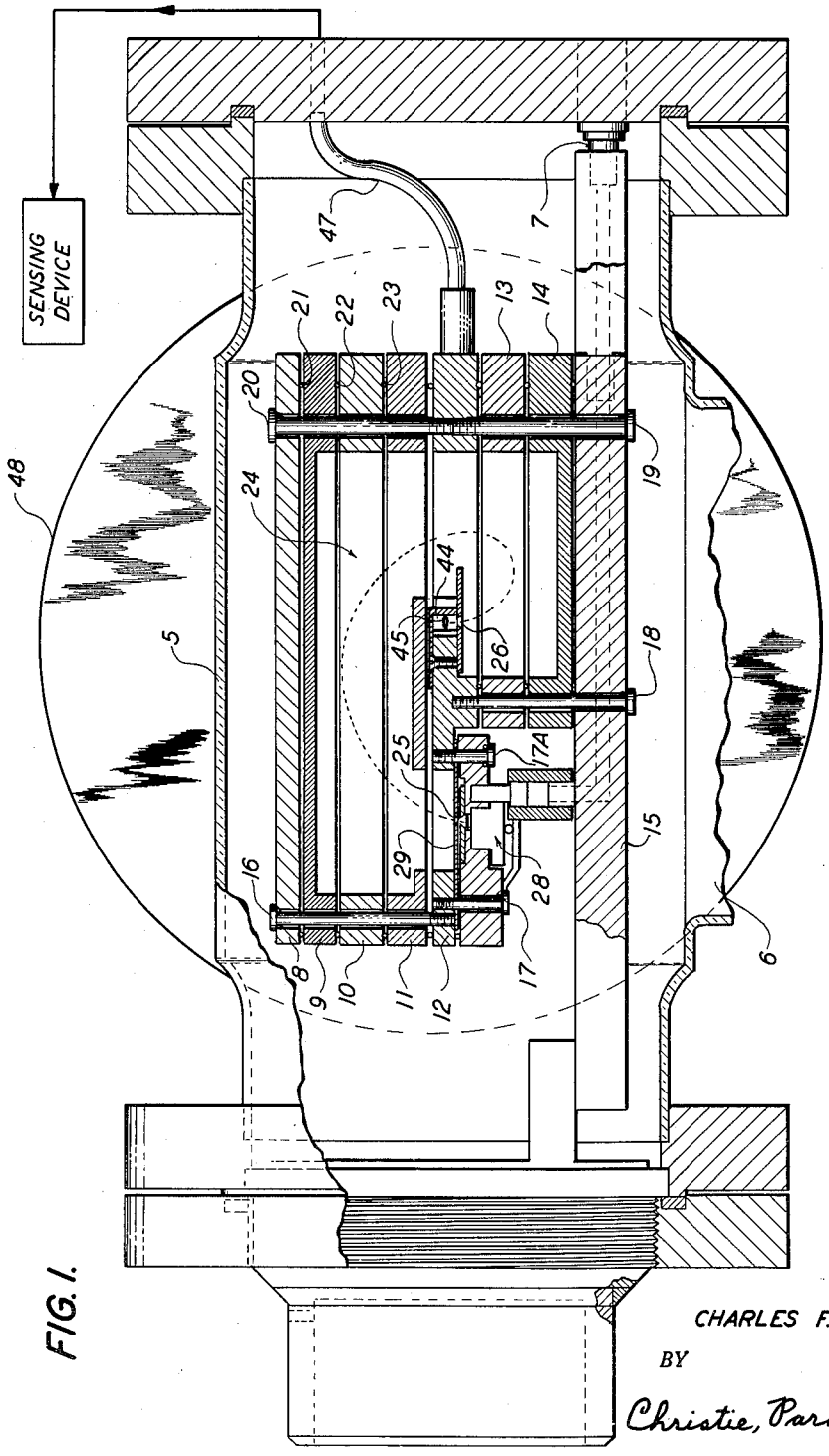


FIG. 1.

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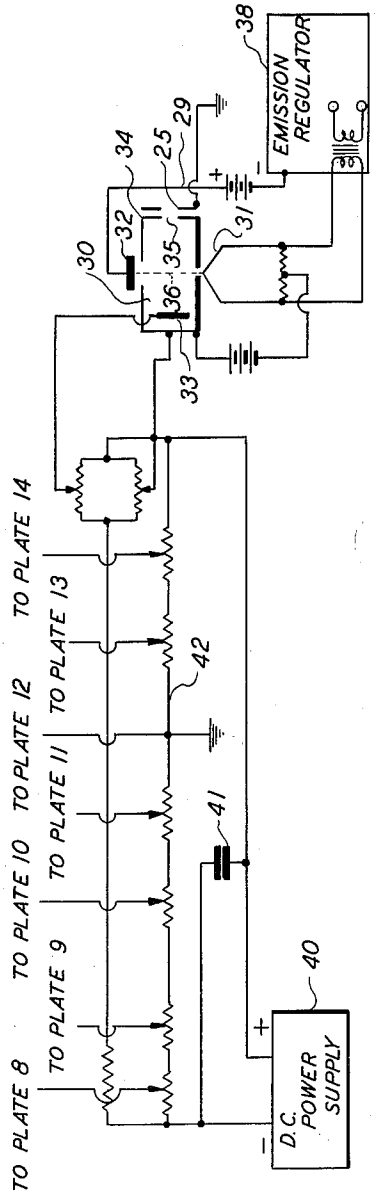


FIG. 2.

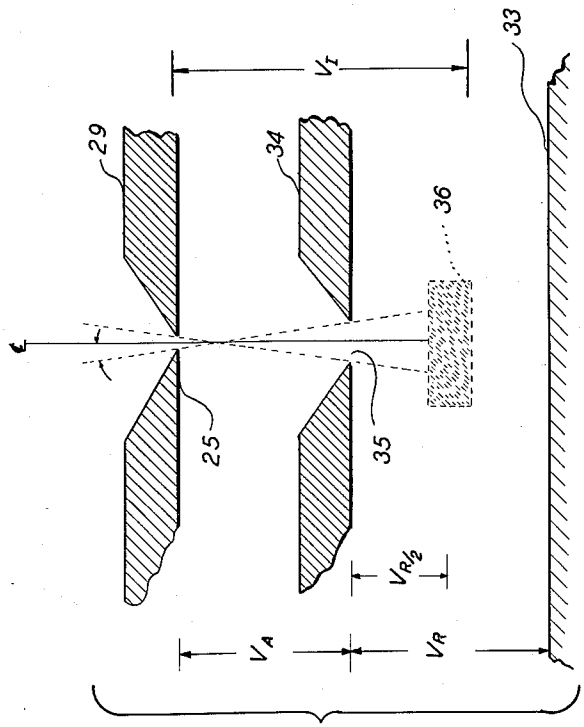


FIG. 3.

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MASS SPECTROMETRY

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4 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometry and particularly to improvement in the methods of operation of a cycloidal or crossed field mass spectrometer.

The principle of operation of a cycloidal mass spectrometer is as follows: If a charged particle is introduced into a magnetic field it will move in a circular path to return to its point of origin. This is true regardless of the mass of the particle, with particles of increasing mass traveling in circles of increasing radius, but in each instance returning to the point of origin. If a uniform electric field is imposed across the space defined by the magnetic field and normal to the magnetic field, the ions pursue a path which may be considered as rigorously circular in a coordinate system moving with uniform velocity. The movement of the coordinate system is a function of the ratio of the electric and magnetic field strengths. If ions of a particular mass are introduced into such a field system they will complete one turn of their circular motion in a time which depends directly on the mass of the particle and, if the electric field strength is uniform so that the coordinate systems corresponding to each particle move at the same velocity, the particles will converge to a series of rigorous point foci after any integral number of turns in the magnetic field and regardless of their velocity or direction of travel at the moment of introduction into the field. Since the time required for ions to complete one turn of their circular motion depends directly on mass, and since under the conditions of uniform field strength specified the rate of motion of the coordinate system is invariant to the mass of the particles involved, the focal point of the heavy particles will be displaced farther from the point of origin than the focal point of the lighter particles. This is the basic concept of the cycloidal mass spectrometer.

A mass spectrometer of this type has a principal characteristic advantage. Because of the fact that ions of a given mass will converge to a rigorous point foci after any integral number of turns regardless of their velocity or direction of travel at the moment of introduction into the crossed field, the instrument is not subject to aberration and is insensitive not only to the energy spread of ions introduced into the field but also to the angular divergence of the ion beam at the point of introduction into the field.

The present invention takes advantage of this unique characteristic of a cycloidal mass spectrometer in an unusual manner of operating the ion source. The invention involves the distribution of potentials in the ion source such that the ions are propelled from the point of formation into the region of crossed fields under different influences than are conventionally possible in an ion source. The region of crossed fields in the cycloidal mass spectrometer is referred to herein as the cycloidal analyzer.

In terms fo structure and electrode arrangement, the ion source with which the invention is involved may include the usual repeller electrode, a first apertured accelerating electrode, means for developing an ionizing electron beam traversing the region between the repeller and first accelerating electrode, and a second apertured accelerating electrode, the aperture of which represents an exit slit through which ions emerge from the ion system into the cycloidal analyzer, and means for supplying potentials to these electrodes.

The present invention contemplates a method of mass spectrometry comprising the formation of ions in an ionizing region by means of an electron beam, the boundaries of which define the ionizing region, propelling the ions into an analyzer region spaced from the ionizing region by means of an electrical propelling field of such configuration that the field strength in the ionizing region is at least 25% as high as the field strength at any point between the ionizing region and the analyzer region, maintaining in the analyzer region transversely oriented magnetic and electrical fields whereby ions entering the region are caused to pursue cycloidal trajectories with ions of any given mass converging at a point after one cycle of motion and collecting the convergent ions of a given mass.

In essence the invention involves maintaining a field strength in the region ionization many, many times greater than that possible in forms of mass spectrometry other than the double focusing cycloidal instruments. Another way of expressing this relationship is to state that the repeller voltage established between the repeller electrode and the first accelerating electrode, this being the potential developing a repelling field in this region, is at least one-fourth as great as the injection voltage, this being defined as the potential existing between the median plane of the ionizing electron beam and the point of entry of the ions into the cycloidal analyzer, i.e. the aperture in the second accelerating electrode. In mass spectrometers other than the cycloidal mass spectrometer with which this invention is concerned, effort is made to maintain the electric field in the region of ionization as small as practical. This is because these other types of mass spectrometers are extremely sensitive to differences in the initial energies of the ions. Since the ionizing electron beam has a finite width, the greater the potential drop across this finite width the greater will be the variation in initial energies in ions formed in different regions of the electron beam. Because of the fact that the cycloidal mass spectrometer is characteristicly insensitive to initial energies, it is possible, and at the same time very advantageous, to maintain a very high field strength, comparatively speaking, in the region of the electron beam. This high field strength, which may be ten times that acceptable in other forms of mass spectrometers, greatly reduces adverse space charge effects, the magnitude of which is proportional to the residence time of ions in the ion source and hence inversely related to the magnitude of the repelling field.

Also, subjecting the ions to potentials as herein defined reduces discrimination effects. In any mass spectrometer ion source, conditions are adjusted so that a particular ion mass will emerge therefrom under conditions which are optimnm for that ion. The same set of conditions will not be optimum for another ion which differs appreciably in mass or in initial velocity from the first, so that it is inherent that any source will show discrimination between ions of different mass.

It follows that the longer the ions remain in the source, the greater is the opportunity for the ion source to create these discrimination effects. The present invention reduces these effects by minimizing the residence time of the ions in the source.

The invention will be clearly understood from the following detailed description taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a longitudinal section elevation through a cycloidal focusing mass spectrometer;

Fig. 2 is a schematic diagram of the electrical circuitry of the spectrometer of Fig. 1; and

Fig. 3 is a greatly enlarged schematic view of an ion source showing the critical conditions above defined.

The cycloidal mass spectrometer shown in Fig. 1 comprises an evacuable envelope 5 provided with conduit means 6 for connection to an evacuating system (not shown) and sample inlet means 7. A plurality of electrodes 8, 9, 10, 11, 12, 13 and 14 are supported in the envelope from a framework 15 by a series of pins 16, 17, 17A, 18, 19, 20. The several electrodes are spaced and insulated from each other by insulating spheres 21, 22, 23, etc. The electrode structure defines a chamber 24 having an inlet slit 25 and a resolving slit 26 spaced from each other on a common or so-called focal plane. An ion source 28 is supported adjacent the chamber 24 and includes a terminal accelerating electrode 29 defining the above mentioned inlet slit 25.

As shown schematically in Fig. 2, the ion source includes a chamber 30, electron gun 31, an electron target 32, a repeller electrode 33, and a first accelerating electrode 34 having an aperture 35 and the electrode 29 defining the inlet aperture 25 to the cycloidal analyzer. The above recited elements of the ion source are arranged so that molecules in the chamber 30 are ionized by electron beam 36 traveling between the gun 31 and target 32 and, under the influence of the potential between the repeller electrode 33 and the accelerating electrodes 34 and 29, the ions are propelled through aperture 25 into the cycloidal analyzer.

Electron gun 31 and target 32 are conventionally interconnected through an emission regulator circuit 38 so that the ionizing electron beam 36 is maintained at substantially uniform density. Many emission regulator circuits are known in the art as conventional adjuncts to a great number of commercial mass spectrometers.

Appropriate potentials are impressed on the several electrodes 8, 9, 10, etc. by means of a voltage divider network also shown schematically in Fig. 2. A D.C. power supply 40 is connected across a capacitor 41. A voltage divider 42 is connected in parallel across the capacitor 41 and the several electrodes 8, 9, 10, 11, 12, 13 and 14 are connected to the divider network 42 as illustrated. A mass spectrum can be scanned by charging the capacitor 41 and allowing the charge to decay across the voltage divider 42. The several field forming electrodes will remain at the same relative potentials but the field strengths will diminish as the capacitor 41 discharges and different ion trajectories will be brought to focus at the resolving aperture 26.

Electrode 12 is provided with a cavity 44 into which the resolving aperture 26 opens and in which a collector electrode 45 is mounted. Ions focusing on the resolving aperture 26 will collect on and discharge at the collector electrode 45. Suitable electrical leads are brought through a wall of the envelope 25 in conventional manner for connection to the various portions of the ion source of the field forming electrodes and the collector electrode. An electrical conduit 47 is shown as accomplishing this purpose, the individual electrical leads brought into the conduit not being distributed in the drawing for purposes of clarity.

The entire instrument is immersed in a magnetic field developed between magnet pole 48 and a companion pole piece (not shown) disposed on the opposite side of the envelope 5. The two magnet poles develop a magnetic field normal to the electrical field existing between the several electrodes 8, 9, 10, etc.

Operation of the mass spectrometer in accordance with the present invention is best described with relation to the enlarged schematic view of a typical ion source as shown in Fig. 3. The source includes repeller electrode 33, electron beam 36 shown in cross-section, first accelerating electrode 34 provided with aperture 35 and the second accelerating electrode 29 provided with the aperture 25, this being the inlet slit into the cycloidal analyzer. Various notations are illustrated on the drawing relative to potentials established in the ion source. The potential existing between the median plane of the electron beam 36 and the inlet aperture 25 is known as the injection voltage, represented by the notation V_I, this being the potential influence to which the average ions formed in the electron beam are subjected. The repeller voltage is that potential existing between repeller electrode 33 and accelerating electrode 34 and is designated by the symbol V_R. A component of the injection voltage is that potential existing between electrodes 34 and 29 and is designated by the symbol V_A.

In accordance with the invention, a mass spectrometer as illustrated in Fig. 1, that is, a cycloidal type mass spectrometer having an ion source of the type shown schematically in Fig. 3, is so operated that the repeller voltage V_R is at least equal to one-fourth the injection voltage V_I and preferably to one-half the injection voltage V_I. This means that the field strength in the ionizing region, that is, in the region of formation of the ions defined by the boundaries of the electron beam, is at least one-fourth as high as the field strength anywhere else in the ion source, and again preferably one-half as high as the field strength anywhere else in the ion source. As above explained, the result of these conditions is that the ions at the moment of formation are subjected to a repelling potential approximately ten times the magnitude of that acceptable in other forms of mass spectrometry, and accordingly are removed from the source a great deal more rapidly. This also means that ions formed adjacent the rear boundary of the electron beam will have much greater initial energies than those formed adjacent the forward boundary of the electron beam.

Typical values of operating potentials in accordance with the invention are as follows:

Magnetic field strength=3400 gauss

V_I:

For m/e 100=8.4 volts

For m/e 16=52.5 volts

V_R:

For m/e 100=4.2 volts

For m/e 16=26.25 volts

In the operation of the illustrated device, sample molecules introduced to the ion source are ionized by the electron beam and, under the influence of the injector, are expelled from the source into the cycloidal analyzer. Responsive to the transversely oriented magnetic and electrical fields impressed across the analyzer, the ions pursue cycloidal trajectories in the chamber. The pitch of the ion trajectories is a function both of mass and electrical and magnetic field strengths, the latter being controlled to focus ions of a given predetermined mass at the resolving slit. The in-focus ions are collected at the collector electrode and the resultant discharge current is sensed in any conventional fashion. To scan a mass spectrum, either of the transverse magnetic and electrical fields may be varied to successively focus ions of a different mass on the resolving slit. The ion source meeting the structural limitations herein specified greatly improves the operation of an instrument of this type in avoiding ion discrimination normally encountered in the source, reducing the sensitivity of the instrument to space charges in the ion source and increasing the absolute sensitivity of the instrument by passing a greater number of the total formed ions in the source into the cycloidal analyzer.

One form of cycloidal mass spectrometer has been illustrated and described in detail. However, it is understood that the invention is not directed to the specific form of instrument as presented apart from the specific construction of the ion source as recited. The particular

ion source is applicable to any of the many forms of cycloidal mass spectrometers, the source being limited only to use with a double focusing instrument of this particular generic type.

I claim:

1. In a cycloidal mass spectrometer having an ion source, an analyzer separated from and communicating with the source through a first apertured accelerating electrode, means for forming in the analyzer crossed magnetic and electric fields, a repeller electrode in the ion source spaced from said first apertured accelerating electrode, a second accelerating electrode disposed in the source between the repeller electrode and the first accelerating electrode and means for directing an ionizing electron beam through the ion source between the repeller electrode and second accelerating electrode, the combination comprising means for developing a relatively high repeller voltage V_R between the repeller electrode and the second accelerating electrode, means for developing a voltage V_A between the second accelerating electrode and the first accelerating electrode, means for establishing the voltages V_R and V_A such that the voltage V_R is at least ¼ the magnitude of the injection voltage V_I which is that voltage existing between the median plane of the electron beam and the first accelerating electrode and the voltages V_A and V_R comprise the components of the injection voltage, and means for establishing a strong magnetic field in the ion source to collimate the electron beam to compensate for the relatively high repeller voltage.

2. In a cycloidal mass spectrometer having an ion source, an analyzer separated from and communicating with the source through a first apertured accelerating electrode, means for forming in the analyzer crossed magnetic and electric fields, a repeller electrode in the ion source spaced from said first accelerating electrode, a second apertured accelerating electrode disposed in the source between the repeller electrode and the first accelerating electrode and means for directing an ionizing electron beam through the ion source between the repeller electrode and second accelerating electrode, the combination comprising means for developing a relatively high repeller voltage V_R between the repeller electrode and the second accelerating electrode, means for developing a voltage V_A between the second accelerating electrode and the first accelerating electrode, means for establishing the voltages V_R and V_A such that the voltage V_R is at least ½ the magnitude of the injection voltage V_I which is that voltage existing between the median plane of the electron beam and the first accelerating electrode and the voltages V_A and V_R comprise the components of the injection voltage, and means for establishing a magnetic field in the ion source to collimate the electron beam to compensate for the relatively high repeller voltage.

3. In a cycloidal mass spectrometer having an ion source, an analyzer separated from and communicating with the source through a first apertured accelerating electrode, means for forming in the analyzer crossed magnetic and electric fields, a repeller electrode in the ion source spaced from said first apertured accelerating electrode, a second accelerating electrode disposed in the source between the repeller electrode and the first accelerating electrode and means for directing an ionizing electron beam through the ion source between the repeller electrode and second accelerating electrode, the improvement which comprises the steps of establishing a relatively high repeller voltage V_R between the repeller electrode and the second accelerating electrode, establishing a voltage V_A between the first and second accelerating electrodes, maintaining the voltages V_R and V_A such that the voltage V_R is at least one-quarter the magnitude of the injection voltage V_I which is the voltage existing between the median plane of the electron beam and the first accelerating electrode, the components of the injection voltage V_I comprising V_A and V_R, and simultaneously producing a strong magnetic field in the ion source to collimate the electron beam to compensate for the co-existing relatively high repeller voltage.

4. In a cycloidal mass spectrometer having an ion source, an analyzer separated from and communicating with the source through a first apertured accelerating electrode, means for forming in the analyzer crossed magnetic and electric fields, a repeller electrode in the ion source spaced from said first apertured accelerating electrode, a second accelerating electrode disposed in the source between the repeller electrode and the first accelerating electrode and means for directing an ionizing electron beam through the ion source between the repeller electrode and second accelerating electrode, the improvement which comprises the steps of establishing a relatively high repeller voltage V_R between the repeller electrode and the second accelerating electrode, establishing a voltage V_A between the first and second accelerating electrodes, maintaining the voltages V_R and V_A such that the voltage V_R is at least one-half the magnitude of the injection voltage V_I which is the voltage existing between the median plane of the electron beam and the first accelerating electrode, the components of the injection voltage V_I comprising V_A and V_R, and simultaneously producing a strong magnetic field in the ion source to collimate the electron beam to compensate for the co-existing relatively high repeller voltage.

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