June 30, 1970 G. G. WANLESS ET AL 3,518,424
ION BEAM INTENSITY CONTROL FOR A FIELD IONIZATION MASS SPECTROMETER EMPLOYING VOLTAGE FEEDBACK TO THE ION SOURCE
Filed Sept. 13, 1967 2 Sheets-Sheet 1

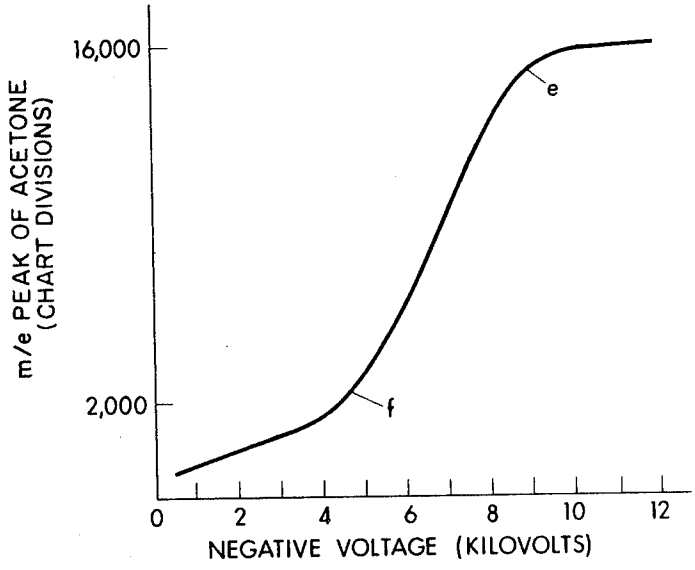


FIG. 1

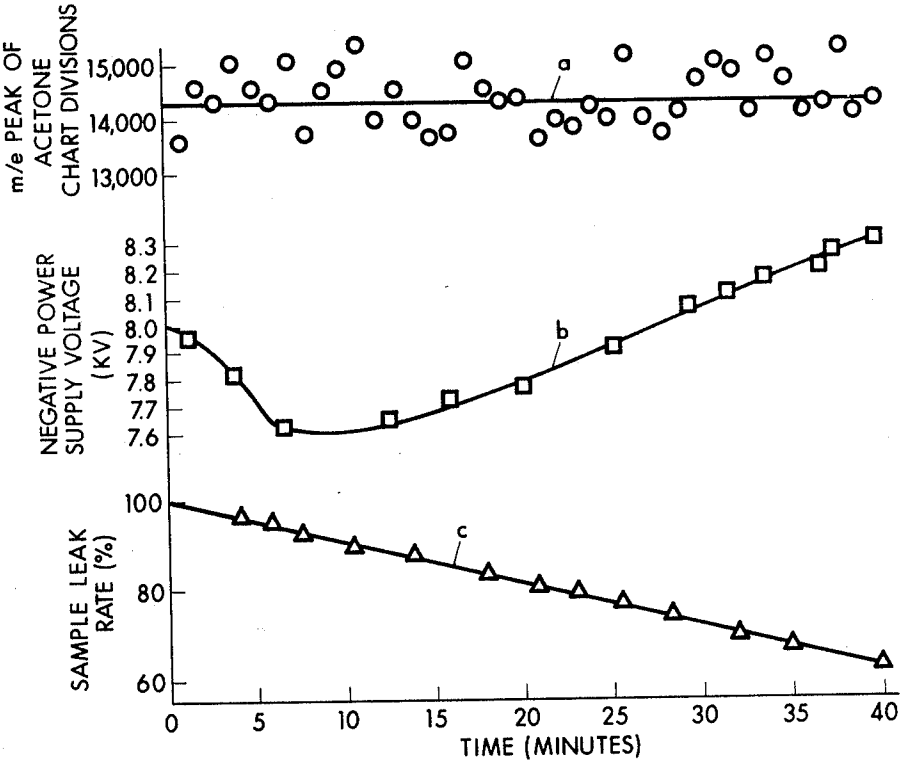


FIG. 4

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ION BEAM INTENSITY CONTROL FOR A FIELD IONIZATION MASS SPECTROMETER EMPLOYING VOLTAGE FEEDBACK TO THE ION SOURCE

Filed Sept. 13, 1967 2 Sheets-Sheet 3

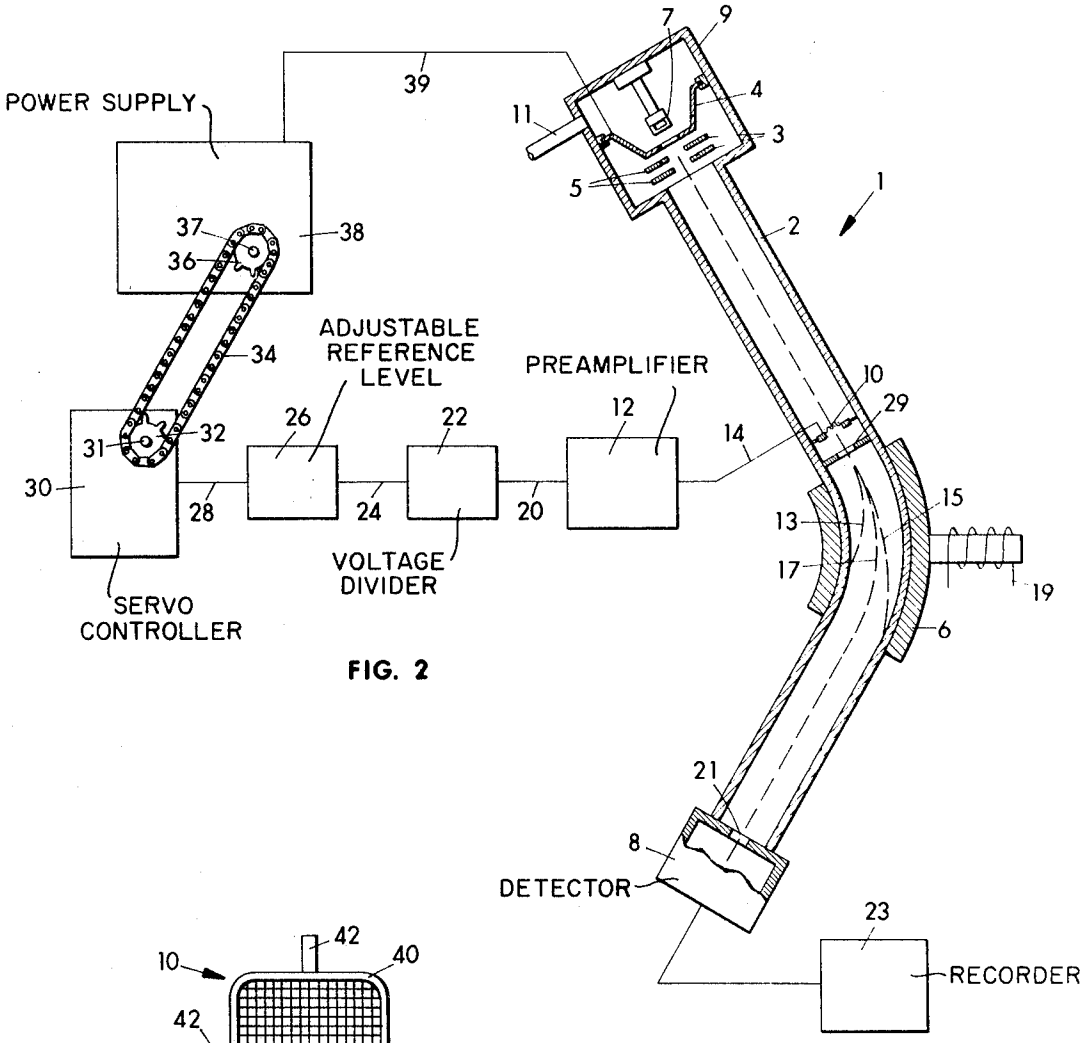


FIG. 2

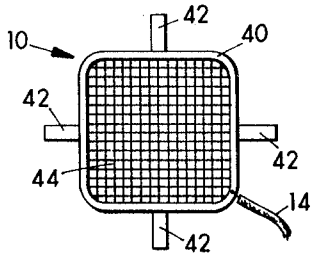


FIG. 3

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3,518,424

ION BEAM INTENSITY CONTROL FOR A FIELD IONIZATION MASS SPECTROMETER EMPLOYING VOLTAGE FEEDBACK TO THE ION SOURCE

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Int. Cl. H01j 39/36
U.S. Cl. 250—41.9 3 Claims

ABSTRACT OF THE DISCLOSURE

In a field-ionization mass spectrometer a controller which varies the cathode potential with respect to the anode in the mass spectrometer source to compensate for fluctuations in output of ion source. The system of the instant invention also compensates for the bleeding down of the sample under examination which is encountered over the course of a mass spectrometric determination.

FIELD OF THE INVENTION

This invention relates to mass spectrometry and to means and methods for controlling the ion beam produced by the mass spectrometer source. More particularly, the invention relates to the use of controlled field-ionization in mass spectrometers and is specifically concerned with a controller for the ion beam output of a field-ionization source.

Mass spectrometry is one method of determining the chemical or elemental composition of a material. In the conventional mass spectrometer, the material to be examined is introduced into an ionization chamber and subjected to electron bombardment which causes the material to ionize. The ions thus formed are accelerated in a mass tube by an electrostatic field and are resolved into successive groups of individual mass by the dispersing power of a magnetic field. The relative abundance of each mass group is then measured and recorded in peaks on an oscillographic chart. Every ionized mass group has a distinct mass-to-charge (m/e) ratio and, therefore, should appear as a separate peak on the oscillographic record.

In contrast to the more conventional spectrometers which use electron bombardment for providing an ion source, the instant invention relates in particular to improvements in those spectrometers which make use of a field-ionization source. Field-ionization is a preferred kind of mass spectrometry which leads to simpler spectra. In this process, the sample of material to be analyzed is vaporized and the vaporized molecules are allowed to pass into a region of very high electrostatic field strength between an anode and a cathode which are 0 to 2 mm. apart. In the region between the anode and the cathode an electrostatic field gradient on the order of about 10^8 volts per centimeter is generated. This field gradient results in a stress which is sufficient to abstract an electron from a molecule. As a result, a positive ion is formed and this ion is then quickly ejected from the region of high stress by the repulsion of the field-ion anode. From this point the mixture of ions is analyzed by any of the conventional mass spectrometric methods known to those skilled in the art. The field-ionization technique yields a greater abundance of parent ions and lesser amounts of fragment ions as compared to the electron bombardment techniques and, hence, is of greater advantage in the analysis of mixtures of molecules.

The large field gradient of about 10^8 volts per centimeter referred to above may be established by using an

anode possessing a very small radius of curvature. For example, it may be calculated that a field-ion anode in the form of a thin wire having a diameter of 0.25 micron can create a field stress of 76×10^6 volts near the surface of the wire, while using a potential difference between the thin wire anode and cathode of 10,000 volts.

In the past three basic types of field-ionization anodes have been used in mass spectrometers. The first of these is in the form of an individual small radius tip made of some refractory material such as tungsten, platinum or gold, the radius of curvature of the tip being about 500 to 1000 angstroms and being obtained by electrolytically etching the tip. Most of the published literature in this field is based on such tip anodes. The second type of anode employed in the past makes use of a razor blade as an anode; however, the use of this type anode has been restricted because of the limitations on the field stresses which may be applied to the blade. Still another type of anode employs the small diameter wire referred to above. It should be appreciated that these fine anode wires, known in the art as Beckey-Wollaston wires, are very fragile and difficult to make and to use. Off-setting thees disadvantages in the past has been the fact that sensitivities using such wire anodes could be 100 to 1000 times greater than those obtained with single anode tips. In spite of the fact that these single wires result in the greater sensitivities just mentioned, at the present stage of their development the signal strength obtainable from such sources are still too low and are subject to unwanted fluctuations. These fluctuations are in part due to the well-known statistical variants of weak electrical signals and in part due to inherent properties of the field-ionization process and the wire source used to carry it out. In applicants' co-pending application, Ser. No. 674,040, a method and apparatus for producing a stronger signal from a field-ionization anode is described. This device was referred to as a tip-array anode. The instant invention, which is directed to a control system for a mass spectrometer utilizing a field-ionization source has as one of its objectives the minimization of the ion beam fluctuations referred to above. In this regard it will be understood that the device and method of the instant invention may be used to control the ion beam fluctuations from any of the anodes previously mentioned and will produce excellent results with the tip-array anode of applicant's co-pending application, Ser. No. 674,040.

SUMMARY OF THE INVENTION

The instant invention is directed to an improved controller for use in a field-ionization mass spectrometer. The controller automatically varies the cathode potential with respect to the field anode in the mass spectrometer source thereby compensating for fluctations in the output of the ion source. The system of the instant invention also compensates for the bleeding down of the sample which is normally encountered over the course of a mass spectrometric determination. It will be understood by those skilled in the art that increases in the potential difference between the anode and cathode of a mass spectrometer ion source will increase the number of ions obtainable from the source. Thus, by controlling this potential difference it is possible to correct fluctations in the ion beam output. When a field-ionization source, as opposed to an electron bombardment source, is used, it is significant to point out that the changes in potential required do not cause a significant change in the overall nature of the mass spectrometric pattern. If this type of operation were carried out with an electron bombardment source, the changing potential would result in highly detrimental changes to the cracking pattern, and hence, the overall mass spectrometric pattern would be untenable. The above discussed ability to control the fluctations in an ion beam

are achieved by use of a unique ion beam sample probe in combination with a preamplifier of the vibrating reed electrometric type, a voltage divider, a zero adjust circuit, a servo controller circuit with direct chain drive and clutch and a negative power supply which is controlled by this servo system and which is connected to and controls the power supply to the cathode. As will be more fully explained hereinafter, the ion beam sample probe has a current generated therein which is about two orders of magnitude greater than the signal it is intended to control. Thus, the probe possesses a favorable electrical "leverage" despite the fact that in a preferred embodiment it is using only about 10% of the ion beam for operation of the control circuit while allowing about 90% of the beam to pass through unhindered. The design of the sample probe, which must constantly examine the weak ion beam which may vary between 10^{-14} and 10^{-11} amperes without "stealing" too much of the signal from the mass spectrometer detector, will be discussed hereinafter.

Using the device of the instant invention, it becomes possible to control ion beam fluctations so that the readings obtained vary by $\pm 3\%$–4%, whereas without the use of the control, mean deviations of $\pm 18\%$ have often been observed.

Thus, an object of the invention is to provide a system for controlling the statistical fluctations in a weak signal system such as a field-ionization mass spectrometer.

Another object of the invention is to provide a sample probe for such a system which constantly samples an ion beam without "stealing" more than 10%–15% of the original ion beam signal strength.

Still another object is to provide a system which compensates for the leaking down of sample with time in the sample chamber of a mass spectrometer. It will be immediately apparent to those skilled in the art that to obtain this last mentioned advantage in the manner to be discussed is unique to a field-ionization mass spectrometer; for, if such a system were applied to a conventional electron impact mass spectrometer, the difference in applied potential between the anode and cathode would cause untenable changes in the cracking pattern.

The above and further objects as well as a fuller understanding of the instant invention may be had by reference to the accompanying detailed descriptions and by referring to the drawings in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting the strength of the ion beam versus applied voltage.

FIG. 2 is a schematic representation of the controller of the instant invention.

FIG. 3 is a schematic illustration of an ion beam probe for use in the control depicted in FIG. 2.

FIG. 4 is a graph which plots ion beam signal strength, negative voltage supply, and sample system leak rate all against time.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be had to the figures in detail and particularly to FIG. 1, which illustrates a typical current/voltage curve which is obtained while employing a field-ionization mass spectrometer source. To obtain this curve, a sample of acetone was introduced into the ionization head; and the negative voltage supplied to the cathode in the head was varied. The ordinate of FIG. 1 is a measure in chart divisions on a standard mass spectrometric chart of the *m/e* 58 peak of acetone. The value on the ordinate is directly proportional to the strength of the ion beam composed of this particular ion of acetone. The abcissa of the chart indicates the negative voltage which was supplied to the cathode. During the course of determining this graph, the anode was kept at a potential of about

+3000 volts. It may readily be understood from FIG. 1 that increasing the potential difference between the anode and cathode (by varying the negative voltage applied to the cathode) increases the abundance of the ions obtainable from the source. This result holds true up to a point generally indicated at *e* where the curve begins to level off. The device of the instant invention is designed to have an operating range which corresponds to the steep portion of the current voltage range between *e* and *f*. When operating in this region, the voltage changes required do not cause a significant change in the overall nature of the mass spectrometric pattern. As pointed out above, such a controller finds maximum utility in a field-ionization ion beam source as marked changes in the cracking pattern would result if a similar device was employed in an electron bombardment mass spectrometer source.

Referring now in detail to FIG. 2 wherein a schematic illustration of the controller of the instant invention is depicted, reference numeral **1** indicates diagrammatically a mass spectrometer. Mass spectrometer **1** has an ionization head **9** containing therein a cathode **4** and an anode **7**. A plurality of plates indicated generally at **3** and **5** are also positioned within the head beneath cathode **4**. The function of these plates will be explained hereinafter. Mass spectrometer **1** is provided with a spectrometer tube **2** having a detection end with a detector located thereon indicated at **8** and passing through an electromagnetic field generated by the electromagnet **6**. In operation the tube works as follows:

The material to be analyzed is admitted into the ionization head **9** via the line **11** wherein the sample is ionized and the ions produced in the head are expelled from the ionization chamber and into the tube **2**. As the ionized particles travel through the mass tube **2**, they are resolved into separate homogenous beams such as **13**, **15** and **17**, by means of magnetic field produced between the poles of the electromagnet **6**. The strength of the magnetic field in magnet **6** may be controlled and is a function of the current flowing through the windings **19**. At any given strength of the imposed magnetic field only that homogenous ion beam, e.g. beam **17**, whose mass-to-charge ratio (*m/e*) corresponds to the strength of the magnetic field can negotiate the curved section of the mass tube and pass through the collector slit **21**, leading to the detector **8**. The ions passing through the collector slit **21** impinge on a collecting electrode (not shown) within detector **8** and produce a small current. This current is amplified by means of a series of multiplier dynodes (not shown) and recorded by means of a suitable apparatus **23**. An oscillographic chart (again not shown) may then be produced by the recording apparatus to indicate the presence and amount of the particular ion of interest.

An ion beam probe **10** (to be discussed in further detail hereinafter) is positioned in mass tube **2** in the region between the ion beam source and the electromagnet **6**. Probe **10** should be located within the range of from about 3 to about 35 and preferably about 25 centimeters below the ion source and positioned so that it is substantially normal to the direction of travel of the ion beam. This probe which constantly examines the weak ion beam which varies from about 10^{-14} to 10^{-11} amperes must be of such construction so as to avoid attenuating too much of the signal which is to be picked up by the mass spectrometer detector **8**.

In order to make the sampling screen reflect ion beam changes more faithfully, two sets of beam limiting "blinders" or guide plates are placed within mass spectrometer ion source **9**. The first of these sets is designated by the reference numeral **3** while the second set is indicated at **5**. The distance between the plates comprising each of the sets is on the order of about 2.5 mm. Thus, the two pairs of plates limit the beam width to approximately 2.5 mm., which is the width of the beam which sampling probe **10** sees. This prevents the probe from

picking up signals from the edge of the frame used to support it within tube **2**.

Located beneath the sample probe **10** is a slotted plate **29**, having a slot of approximately 30 mm. in length and 2.5 mm. in width. This plate fixes the dimension of the beam leaving the probe **10** to allow more accurate determinations to be made at detector **8**.

In operation the apparatus of FIG. 2 works as follows:

The ion beam is sensed by the probe **10** which generates an extremely small current in the range of from about 10^{-13} to 10^{-9} amps and normally about 10^{-13} to 10^{-11} amps. This current will, of course, vary depending on the strength of the ion beam which is being monitored. The current so generated is fed via the lead **14** to a preamplifier **12** which is mounted in close proximity to probe **10**. Preamplifier **12** is preferably of the type known in the art as a vibrating reed electrometer, which is a high quality device of exceptional electrical stability which is normally used for detecting weak electrical signals at the detector end **8** of the mass tube **2** (currents encountered here are in the range of 10^{-15} to 10^{-7} amps). Suitable types of vibrating reed electrometers include the Cary Model 36 vibrating reed electrometer and the Victoreen Model 475 Femtometer. It is to be noted that a short, vibration-free and fully shielded connection **14** is required between the probe **10** and the preamplifier **12** due to the sensitivity of the latter device. The preamplifier **12** senses the current generated by probe **10** and produces a voltage which is directly proportional to the detected current. This voltage is normally in the range of from about 10^{-2} to 10^{-3} volts. This voltage is then fed via the conduit **20** to a voltage divider **22** and from divider **22** to a zero adjust device **26** via the line **24**. The voltage divider is used to select the proper voltage for the servo controller **30**, while the zero adjust device allows a suitable base or reference point to be fixed. The signal leaving the zero adjust device **26** is fed via the line **28** to the servo controller **30**. A suitable servo controller for the instant invention may be obtained by modifying a Leeds and Northrup Model G Speedomax Recorder, by removing the chart pen assembly and by attaching to the main potentiometer drive shaft **31** a clutch (not shown) and a gear **32**, for the chain drive **34**. The chain drive **34**, which may be equipped with a suitable take-up tensioning device (not shown) causes the gear **36** to rotate a voltage adjustment shaft **37** on the negative power supply source **38**, thereby adjusting the power supplied via the line **39** to the cathode **4** in field-ionization source **9**. Thus, for example, if the intensity of the ion beam is reduced (due to sample leakage or momentary statistical fluctuations) the signal from probe **10** will decrease. This smaller sginal will then result in the feeding of an appropriately proportional correction signal to the servo controller **30**. Controller **30** will then cause the negative power supply **38** to increase the negative voltage supplied to the cathode **4**, thereby increasing the ion beam strength bringing it back to the desired norm. The ratio of gears **32** and **36** are dependent on the sensitivity of the servo controller and the leak rate of the sample system and may be suitably adjusted depending on these variables.

FIG. 3 illustrates schematically a preferred configuration for ion beam probe **10**. Probe **10** is comprised of a mesh screen **44** of molybdenum or tungsten wires having diameters of about 0.025 mm. with spacings of about 0.225 mm. Screen **44** is supported within a suitable metal frame **40** which in turn is supported within mass tube **2** by a plurality of insulating support members **42**. The transparency of the screen to the ion beam is in the range of about 85%–90%. As the ion beam impinges on the wires comprising mesh screen **44**, a current proportional to the number of impingements (and hence proportional to the strength of the beam itself) is generated by the probe. This current is then fed via the lead **14** to the vibrating reed amplifier as hereinabove discussed.

The nature of the sampling problem, which is successfully solved by the device of the instant invention, may be more fully appreciated by reference to the following example and the attendant current measurements.

EXAMPLE

A sample charge of .00076 ml. of acetone (16.6 micromoles) was introduced into field-ionization head **9**. The voltage across the dynode multiplier (not shown) within the detector **8** was set at 1800 volts.

The total anode to cathode voltage was set at 14,000 volts. Under these conditions the following currents were determined:

	Amps
(a) Ion beam sample probe current	3.5×10^{-11}
(b) Estimated current through probe mesh	2.3×10^{-10}
(c) Ion beam current at the first dynode of the electron multiplier in detector **8**	2.2×10^{-13}
(d) Current at last dynode of electron multiplier in detector **8**	2.9×10^{-7}

Thus, it may be seen that the ion beam sample probe current is about two orders of magnitude greater than the signal it is intended to control (compare items .a) and (c) above). It thus possesses a favorable electrical "leverage" despite the fact that only 10%–15% of the ion beam is being used for operation of the control circuit.

It is also to be pointed out that the above described control system will automatically compensate for the bleeding down of the sample with time as well as for the aforesaid statistical fluctuations. This is exemplified by the graphs illustrated in FIG. 4.

FIG. 4 illustrates results obtained over a 40 minute test period again using an acetone sample and obtaining readings for its *m/e* 58 peak. As may be seen from the line indicated by the reference letter *b*, the negative power supply voltage, while fluctuating slightly, gradually increased from 7600 volts to about 8300 volts while the sample (as shown by line *c*) leaked down by 30%. The line *a* indicates the fluctuations in 40 readings (in chart divisions) of the *m/e* 58 peak of acetone taken over the 40 minute period of the test. The scatter of points about line *a* is random and shows essentially no drift with time. These points and the data they represent indicate that the mean deviation for the 40 successive readings of the *m/e* 58 peak of acetone over the 40 minute test period was held to approximately ±3.3%. It is of prime importance to realize that without the control device of the instant invention, mean deviations of about ±18% are often observed.

It has thus been shown that the device herein disclosed functions as an effective means for controlling the statistical fluctuations in a weak signal system such as a field-ionization mass spectrometer as well as a device which automatically compensates for the leaking down of a mass spectrometer sample with time. The above highly desirable results are obtained without significantly detracting from the original signal strength of the ion beam produced.

It should be understood that although the above embodiments of the instant invention have been described with a certain degree of particularity, the present disclosure has been by way of example and that obviously changes in the methods of construction and arrangement of various components may be resorted to without departing from the spirit of the disclosed teachings. Accordingly, for the full scope of the instant invention, reference should be made to the following appended claims.

What is claimed is:

1. In a mass spectrometer of the type having a field-ionization source having a field anode and cathode, an apparatus for controlling fluctuations in the strength of the ion beam produced by said source which comprises in combination; a fine wire mesh screen probe for sensing the strength of said beam, said probe producing an electrical signal proportional to the strength of said ion beam, means for detecting and amplifying the electrical signal so

produced, servo controller means responsive to the amplified signal, and a negative voltage supplier for feeding voltage to said cathode, the output of said voltage supplier being controlled by said servo controller, said output fixing the potential difference between said cathode and said field anode whereby the strength of said ion beam is adjusted.

2. The apparatus of claim 1 wherein said probe is positioned within the tube of said mass spectrometer at a distance of about 25 cm. below said field-ionization source and said detecting and amplifying means is a vibrating-reed electrometer.

3. In a mass spectrometer of the type having a field-ionization source having a field anode and a cathode, an apparatus for controlling fluctuations in the strength of the ion beam produced by said source which comprises in combination; a probe having a fine wire mesh detecting screen for sensing said ion beam, said screen producing an electrical signal which is proportional to the strength of said beam means for amplifying said signal, a servo controller means responsive to a second signal which is proportional to said first signal, said second signal being produced by a voltage divider and adjustable reference level means, said divider and adjustable reference level means receiving said first signal from said amplifying means, and

a negative voltage supplier for feeding voltage to said cathode, the output of said voltage supplier being controlled by said servo controller means, said output fixing the potential difference between said cathode and said field anode whereby the strength of said ion beam is adjusted.

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