Sept. 15, 1953 H. W. WASHBURN 2,652,495

PROCESS MONITOR MASS SPECTROMETER MINIMIZING HIGH-VOLTAGE HISTORY EFFECTS

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FIG. 1

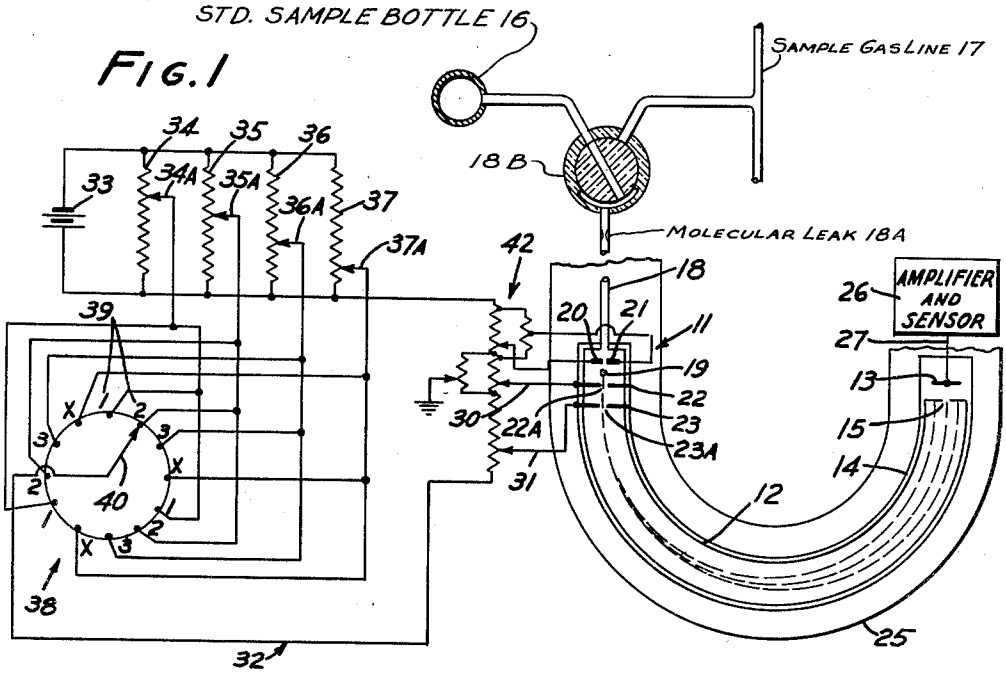


FIG. 2

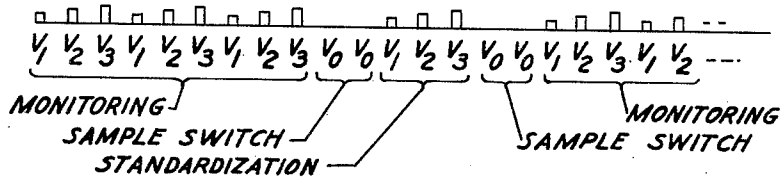
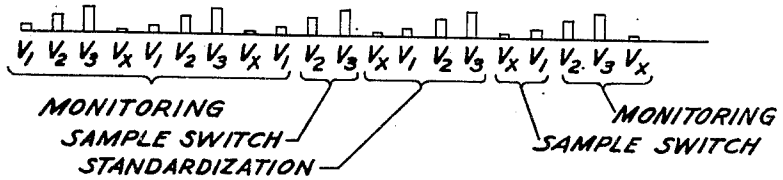


FIG. 2A



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PROCESS MONITOR MASS SPECTROMETER MINIMIZING HIGH-VOLTAGE HISTORY EFFECTS

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8 Claims. (Cl. 250—41.9)

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This invention relates to a mass spectrometer and to a method of mass spectrometry particularly directed to elimination of high voltage history effects.

A mass spectrometer is an analytical apparatus which functions to sort and measure ions. Ordinarily, it includes an ionization chamber in which molecules of a sample to be analyzed are bombarded by a stream of electrons and thereby converted into ions. Other means may be used to ionize sample molecules, but electron bombardment represents the most common expedient. The ions are propelled by so-called repelling and accelerating electrodes into and through an analyzer chamber. During passage through the analyzer chamber, the ions are subjected to a transverse magnetic field, or to crossed magnetic and electric fields to separate them according to their mass-to-charge ratios into a plurality of diverging ion beams. Each beam is composed of ions of the same specific mass and differing from the specific mass of ions forming the other beams. The diverging beams may be successively focussed as by adjustment of the potential applied to the accelerating electrodes, on and are discharged at an ion collector. The current produced by each beam as it strikes the ion collector is indicative of the amount of ions in the beam and thus becomes a measure of the partial pressure of the molecules from which the ions of the particular beam were derived.

In another type of mass spectrometer, the ion beams are focussed on the collector electrode by variation of the strength of the transverse magnetic field in the analyzer chamber, or an electric field perpendicular to the magnetic field. In this type of instrument, ion focus is substantially independent of the velocity of the ions propelled into the analyzer chamber and hence, the potential applied to the accelerating electrodes. The present invention is directed to mass spectrometers in which focussing of the ion beams is brought about by a lateral electric field induced by the accelerating electrodes or a field in the analyzer chamber, i. e. a transverse magnetic field or a perpendicular electric field, the latter being present in the so-called "crossed field" mass spectrometer.

For purposes of description, however, the invention is described with relation to its application to the more conventional mass spectrometer and the more conventional methods of operating a mass spectrometer in which the focussing of the ion beams on the collector electrode is determined by a lateral electric field by variation

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in the voltage applied to the accelerating electrodes to produce this field.

In conventional practice, the current produced by ions discharge at the ion collector is amplified in either an A. C. or D. C. amplifier and the current magnitude is recorded as a continuous curve in a suitable recorder. The peaks in the record corresponding to the ions of differing specific mass are commonly referred to as "mass peaks."

An important industrial application of mass spectrometer is in the continuous monitoring or control of industrial processes. In this type of analysis, a gas stream, as for example, a plant feed stream or an effluent stream, is continuously or intermittently sampled. The composition thereof with respect to one or more, but generally less than all of the components of the gas stream, is determined on a substantially continuous basis. The continuity of analysis is, of course, a function of the frequency of sampling and becomes continuous when a sample stream is continuously introduced into the spectrometer. Generally, in this type of operation there is a certain previously determined composition which represents an optimum for the specific process involved. A mixture having such a composition, at least with respect to the constituents of interest, is commonly referred to as a "standard" sample.

In the application of mass spectrometry to continuous monitoring, one or more of the components of the gas stream are analyzed and a continuous record of the "mass peaks" for each of the components is obtained. The primary function of continuous monitoring is to detect variations in the concentration of the particular component or components from the theoretical standard composition. As long as the composition of the sample remains standard with respect these components, the mass peak for a given component will theoretically fall at the same point on the recording scale each time the record is sensing on that mass. Any deviation of the peaks should be an indication in the change of relative abundance in the sample stream of the component represented by that peak.

However, this is not always the case since a variation in power supply voltage beyond a given tolerance will, among other factors, cause a variation in peak height independent of sample composition. For this reason, a continuous monitor mass spectrometer is frequently standardized by introducing a standard sample containing known amounts of the constituents under investigation.

Any deviation in the peak heights in the constituents in the standard sample from one period of standardization to the next will evidence a change in the various factors which control the peak heights relative to ion discharge. As a general proposition, correction need not be made since a new peak height representative of a given constituent concentration is ascertained and usuable as a standard with each new standardization.

The conventional manner of operating a continuous monitor instrument is to vary the accelerating voltage step-wise to successively focus the ion beams of interest on the collector electrode, repeating this voltage sequence through a number of cycles, adjusting the accelerating voltage to a value at which no ions are focussed on the collector for a short period during which a switch is made from the unknown to a standard sample, repeating the same stepwise voltage cycle to successively focus the ion beams of the same constituents in the standard sample on the collector, again adjusting the accelerating voltage to a value at which no ions are focussed on the collector while the instrument is switched from the standard to the unknown sample, and thereafter repeating the voltage sequences throughout a number of cycles.

After a mass spectrometer has been operated over a period of time, I have found that the height of any particular mass peak will depend in part upon the time and magnitude variations of accelerating voltage which have preceded the measurement of the particular peak. This effect, which may be called the high-voltage history effect, is probably due, at least in the case where the accelerating voltage is varied, to semi-conducting layers which are formed on any of the various electrodes in the ion source and can be minimized by proper design of the ion source and by proper treatment of the surfaces. Heretofore, it has not been possible to completely eliminate the high voltage history effect which is found to be particularly pronounced after the mass spectrometer has been operated for a considerable period of time on a continuous basis.

In present continuous monitor mass spectrometers, sensitivity of the instrument is automatically adjusted as described above, by running a standard sample of gas through the instrument and by adjusting the output of a D. C. amplifier at each mass of interest by means of a servomechanism so that the amplifier output will correspond to a predetermined voltage respectively for each significant mass. Heretofore the schedule of the positive ion accelerating voltage increments has been different during the standardizing period than it has during the monitoring period. Since the voltage schedule was different, the high voltage history effects are different during and immediately following the standardizing period than they are during the final cycles of the monitoring period, thus causing errors in the analysis obtained from the record. The present invention contemplates operation wherein the time and magnitude schedule of the positive ion accelerating voltage is maintained the same during the standardizing period as it is during the monitoring period. In other words, the positive ion voltage is set to a value where no ions reach the collector, which value may be zero or some voltage at which no ions are in focus. Following this, the accelerating voltage is set successively at the particular values which focus the ions of the desired masses on the ion collector. In the present operation this sequence is continuously repeated regardless of whether the unknown sample or the monitoring sample is being run through the instrument and is uninterrupted even during the time intervals of switching from one sample to another.

In one aspect, therefore, the invention contemplates in a method of mass spectrometry wherein a sample stream is substantially continuously analyzed for at least one preselected constituent by ionizing the sample, causing the ions to pass through a magnetic field by subjecting the ions to an accelerating potential, focussing the particular ions produced from said constituent on collector means and discharging said particular ions at said collector means, and periodically substituting a sample containing a known quantity of said constituent, the improvement comprising successively focussing each constituent to be analyzed on the collector means for a fixed period of time, altering the focus so that no ions fall on the collector electrode for a like period of time and repeating this procedure for succeeding voltage cycles without altering the voltage pattern during operation on the sample stream and on the sample containing a known concentration of said constituent.

The invention also contemplates in a mass spectrometer for continuous sequential analysis of preselected constituents in a sample stream and including an ionization chamber, accelerating electrodes, analyzer chamber, means for establishing a magnetic field across the analyzer chamber, and a collector electrode, a voltage supply circuit comprising a source of D. C. voltage, a plurality of potentiometers connected in parallel across the source, a switch having a plurality of contacts and a single movable contactor, means connecting the sliders of each potentiometer in a given pattern to the switch contacts, a voltage divider network connected between the voltage source and the switch contactor whereby successive contact of the contactor with the several contacts in repeating cycles will successively impress the voltage output of the several potentiometers in the pre-selected sequence and in repeating cycles across the voltage divider network and means connecting the accelerating electrodes to the divider network.

The invention will be clearly understood from the following detailed description thereof taken in relation to the accompanying drawings wherein:

Fig. 1 is a diagrammatic illustration of a mass spectrometer provided with an accelerating voltage supply circuit in accordance with the present invention;

Fig. 2 is a diagram of the voltage pattern presently employed in continuous monitor mass spectrometers; and

Fig. 2A is a diagram of the voltage pattern in accordance with the apparatus and methods of the present invention.

In Fig. 1, the invention is shown in association with a mass spectrometer wherein the ion beams are focussed by varying the potential applied to accelerating electrodes. As pointed out above and as will be apparent from the following description, the invention is equally adaptable to incorporation in a mass spectrometer wherein the ion beams are focussed by variation in a transverse magnetic field or a crossed electric field. In short, the invention finds use in any mass spectrometer operation dependent upon sequential changes in ion focus, whether these changes are

brought about by variation of the accelerating voltage or by variation of the strength of a magnetic or electrical field in the analyzer chamber.

Referring to Fig. 1, it will be observed that it shows diagrammatically a mass spectrometer having an ion source 11, an analyzer tube 12, and an ion collector 13, disposed within an envelope 14 which is maintained at low pressure during the operation of the instrument. The analyzer chamber 12 is provided at the end thereof adjacent collector 13 with an exit slit 15 through which the ion beams are focussed on the collector 13. An inlet line 18 provides means for introducing a sample to be analyzed either continuously or intermittently into the ion source. One system for selective introduction of the sample gas of interest and a sample of standardized composition is shown diagrammatically in Fig. 1. Sample inlet line 18 is connected through a conventional molecular leak 18A to a three-way stop cock 18B. The inlet ports of the stop cock are connected respectively to a standard sample bottle 16 and to a source 17 of the gas of interest, illustrated in this instance as a gas flow line. The switch from unknown to standard sample and vice versa is easily accomplished by manipulation of the stock cock.

A pumping system (not shown) is connected to the envelope 14 to evacuate the analyzer tube and ion source. An electron gun (not shown) is mounted in or adjacent to the ion source to develop an electron beam 19 traversing the ion source. The ion source 11 includes repeller electrodes 20, 21 and accelerating electrodes 22, 23, the latter being provided with slits 22A, 23A, respectively, through which ions are propelled from the chamber defined by the repeller electrodes and first accelerating electrode into the analyzer tube.

Representation of this particular ion source is for illustrative purposes only, there being many modifications thereof equally applicable to this invention. The analyzer tube 12 and surrounding envelope 14 are disposed between the poles of a magnet 25 whereby a transverse magnetic field is developed across the analyzer tube 12.

A gas sample introduced through inlet 18 passes between the repeller electrodes 20, 21 and is ionized by electron beam 19 in the ionization chamber. The repeller electrodes 20, 21 urge the ions as they are formed towards the first accelerating electrode 22, and the ions passing through slit 22A therein are accelerated between electrodes 22, 23 to issue from slit 23A at high velocity into the analyzer tube 12. The ions thus propelled into the analyzer tube are formed therein into diverging beams of ions of given specific mass under the influence of the transverse magnetic field developed by the magnet 25. By adjustment of the potential impressed between accelerating electrodes 22, 23, a given one of the diverging ion beams may be focused on the ion collector 13 through the exit slit 15. The ion collector 13 is electrically connected by lead 27 to an amplifier and sensing circuit 26. The sensing means is conveniently a recorder but may be any type of sensing device adapted to indicate either the amplifier output or deviation from a normal peak condition. In any event, the amplifier and sensor circuit form no part of the present invention apart from their essential relationship to the mass spectrometer. The accelerating electrodes 22, 23 are connected through leads 30, 31, respectively, to a voltage supply circuit 32. The voltage supply circuit 42 is particularly adapted

to impress on the accelerating electrodes 22, 23 a voltage pattern of the type shown in Fig. 2A.

Referring to Figs. 2 and 2A, the former is a diagram of the voltage pattern impressed on accelerating electrodes in the conventional operation of a continuous monitor mass spectrometer and the latter is a diagram of the voltage pattern impressed on the accelerating electrodes in accordance with the present invention. In Fig. 2 each monitoring period comprises repetitive cycles of the voltage sequence V_1, V_2, V_3, wherein each of these voltages is applied to the accelerating electrodes for a fixed and uniform time interval to focus a different ion beam on the collector electrode. When standardization is required, no voltage is impressed on the accelerating electrodes during the period of switching between the subject sample and the standard sample, this period being represented by two time intervals of voltage V_0. During standardization, voltages V_1, V_2, V_3 are sequentially impressed on the accelerating electrodes for time intervals corresponding to the time intervals on the monitoring cycle and thereafter no voltage is impressed on the accelerating electrodes for another switching period for the time required to return to another monitoring cycle.

In the chart of Fig. 2A it will be seen that the voltage sequence is uniform, the pattern of each cycle being voltages V_1, V_2, V_3 and V_x where V_x may be either zero or any voltage at which no ions are focused through the exit slit onto the collector electrode. In this operation, voltage is applied to the accelerating electrodes even during the sample switching period so that a cyclic voltage pattern is impressed on the accelerating electrodes throughout the monitoring, switching and standardization periods. As described above, the effect of the repetitive continuity is to entirely eliminate high voltage history effects and hence, the analytical errors attendant on such effects.

Referring again to Fig. 1, the voltage supply circuit 32 is specifically designed to develop on the accelerating electrodes the voltages V_1, V_2, V_3, V_x in continuous repetitive cycles independent of the switch from unknown to standard sample. A voltage source 33 is connected across a plurality of parallel coupled potentiometers 34, 35, 36, 37, each of which has an adjustable tap 34A, 35A, 36A, 37A, respectively. A selector switch 38 has a plurality of stationary contacts 39 and a rotary contactor 40. The several taps of the potentiometers 34, 35, etc., are connected to the stationary contacts of the switch 38 in repeating sequence identified on the switch as 1, 2, 3, X, 1, 2, 3, X, etc. A conventional voltage divider network 42 is connected between the voltage source 33 and the rotary contactor 40 so that rotation of the contactor 40 develops across the divider network 42 a voltage, dependent upon the position of the contactor switch 40 and of the respective tap of the potentiometers 34, 35, etc. Leads 30, 31 connect the accelerating electrodes 22, 23, respectively, to the voltage divider network 42. By means of this circuit, the voltages V_1, V_2, V_3, V_x are impressed on the accelerating electrodes 22, 23 in step-wise repeating cycles. Of course, voltages impressed on the two electrodes differ but their relationship remains constant, and the representation of both of these voltages by the designation V_1, V_2, V_3, V_x is not intended to imply that the same voltage is impressed on each of the two electrodes.

As mentioned above, there are some mass spectrometers in which ion focus is brought about by adjustment of a transverse magnetic field,

while the lateral electric field developed by the accelerating electrodes is held constant. In such an instrument the voltage supply circuit 42 may be connected directly to an electro-magnet developing the transverse magnetic field or electrodes developing a "crossed" electric field, while the accelerating electrodes are supplied with a constant voltage from a conventional voltage source. Alternatively, a transverse magnetic field may be varied stepwise in accordance with the invention by mechanical variation of the shunt of a permanent magnet.

I claim:

1. In a mass spectrometer for continuous analysis of preselected constituents in a sample stream including an ionization chamber, analyzer chamber, means for propelling ions from the ionization chamber through the analyzer chamber, means for establishing a magnetic field across the analyzer chamber, a collector electrode and focussing means for focussing ions on the collector electrode, a voltage supply circuit comprising a source of D. C. voltage, a number of potentiometers exceeding by one the number of preselected constituents and connected in parallel across the source, a switch having a plurality of contacts and a single movable contractor, means connecting the taps of the potentiometers in preselected sequence to the contacts, a voltage divider network connected between the source and the contactor whereby successive contact of the contactor with the contacts will successively impress the voltage output of the potentiometers in said preselected sequence and in repeating cycles across said voltage divider network, and means connecting the focussing means to the divider network.

2. In a mass spectrometer for continuous analysis of preselected constituents in a sample stream including an ionization chamber, analyzer chamber, means for propelling ions from the ionization chamber through the analyzer chamber, means for establishing a magnetic field across the analyzer chamber, a collector electrode and focussing means for focussing ions on the collector electrode, a voltage supply circuit comprising a source of D. C. voltage, a number of potentiometers equal to the number of preselected constituents and connected in parallel across the source, a switch having a plurality of contacts in a single movable contactor, means connecting the taps of said potentiometers in preselected sequence to said contacts with one switch contact left open for each group of contacts connected in said preselected sequence to the potentiometers, a voltage divider network connected between the source and the contactor whereby successive contact of the contactor with the contacts will successively impress across the divider network the voltage output of the potentiometers and the open switch contact in said preselected sequence and in repeating cycles, and means connecting the focussing means to the divider network.

3. In apparatus for monitoring a sample stream for at least one preselected constitutent thereof and including means for ionizing the sample, means for producing a magnetic field, means for causing the resulting ions to pass through the magnetic field, means for discharging ions having masses of interest on a collector electrode, and means for periodically substituting a sample containing a known concentration of said constituent, the combination comprising control means operable in a control sequence to successively focus ions of each mass of interest on the collector electrode and thereafter to defocus the ions of all the masses of interest with respect to the collector electrode, and means for cycling the control means for repeating the same control sequence.

4. In apparatus for monitoring a sample stream for at least one preselected constituent thereof and including means for ionizing the sample, means for producing a magnetic field, means for producing an accelerating potential to cause the ions to pass through the magnetic field, means for discharging ions on a collector electrode, and means for periodically substituting a sample containing a known concentration of said constituent, the combination comprising means varying the accelerating potential step-wise in a sequence including potential values adapted to respectively focus each ion mass of interest on the collector electrode and a potential value at which none of the ions of interest are focused on the collector electrode, said means being adapted to repeat the same sequence of step-wise voltage variations without interruptions throughout the monitoring period.

5. In apparatus for monitoring a sample stream for at least one preselected constitutent thereof and including means for ionizing the sample, means producing a magnetic field, means developing an accelerating potential to cause the ions to pass through the magnetic field, and means for discharging ions on a collector electrode, the combination which comprises control means operable to successively focus each ion mass of interest on the collector electrode for a fixed period of time and operable after the ion masses of interest have been focused on the collector electrode to alter the focus so that none of the ions of interest fall on the collector electrode for said fixed period of time, means operative to cycle the control means without interrupting the sequence or timing, and means operable to substitute a sample containing a known concentration of said constituent for said sample stream.

6. In apparatus for monitoring a sample stream for at least one preselected constituent thereof and including means for ionizing the sample, means developing an accelerating potential acting on the ions to cause them to pass through a magnetic field, and means for discharging ions on a collector electrode, the combination comprising means operable to vary the accelerating potential step-wise in a uniform repeating sequence, each sequence including potential values adapted to respectively focus each ion mass of interest on the collector electrode, and a potential value at which no ions are focused on the collector electrode.

7. Apparatus according to claim 6 including means operable to periodically substitute a standard sample containing the constituents of interest in known concentration for the sample stream.

8. In apparatus for monitoring a sample stream for at least one preselected constituent and including means for ionizing the sample stream, means producing a magnetic field, means developing an accelerating potential operable on the ions to cause them to pass through the magnetic field, and means for discharging ions on a collector electrode, the combination comprising means varying the accelerating potential step-wise in an uninterrupted uniform repeating sequence, each sequence including potential

values such as to respectively focus each ion mass of interest on the collector electrode and a potential value at which no ions are focused on the collector electrode, and means operable to periodically substitute for the sample stream a standard sample containing the constituents of interest in known concentration.

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