

July 12, 1949.

B. W. THOMAS
ANALYTICAL APPARATUS

2,476,005

Filed Aug. 6, 1945

3 Sheets-Sheet 1

FIG. 1.

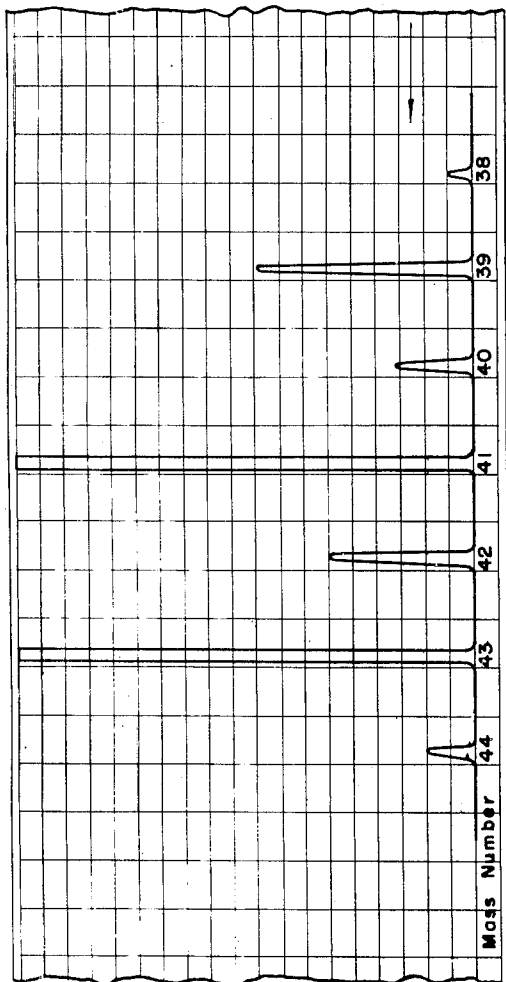
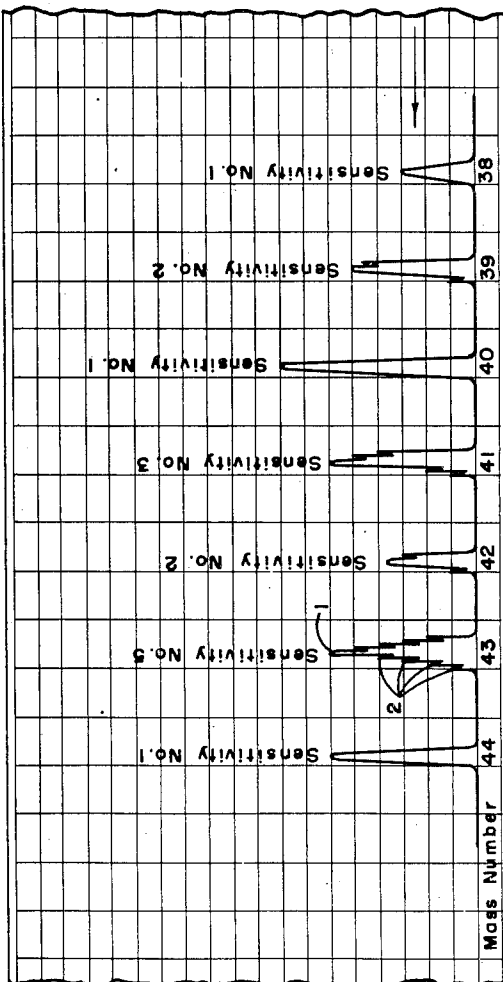


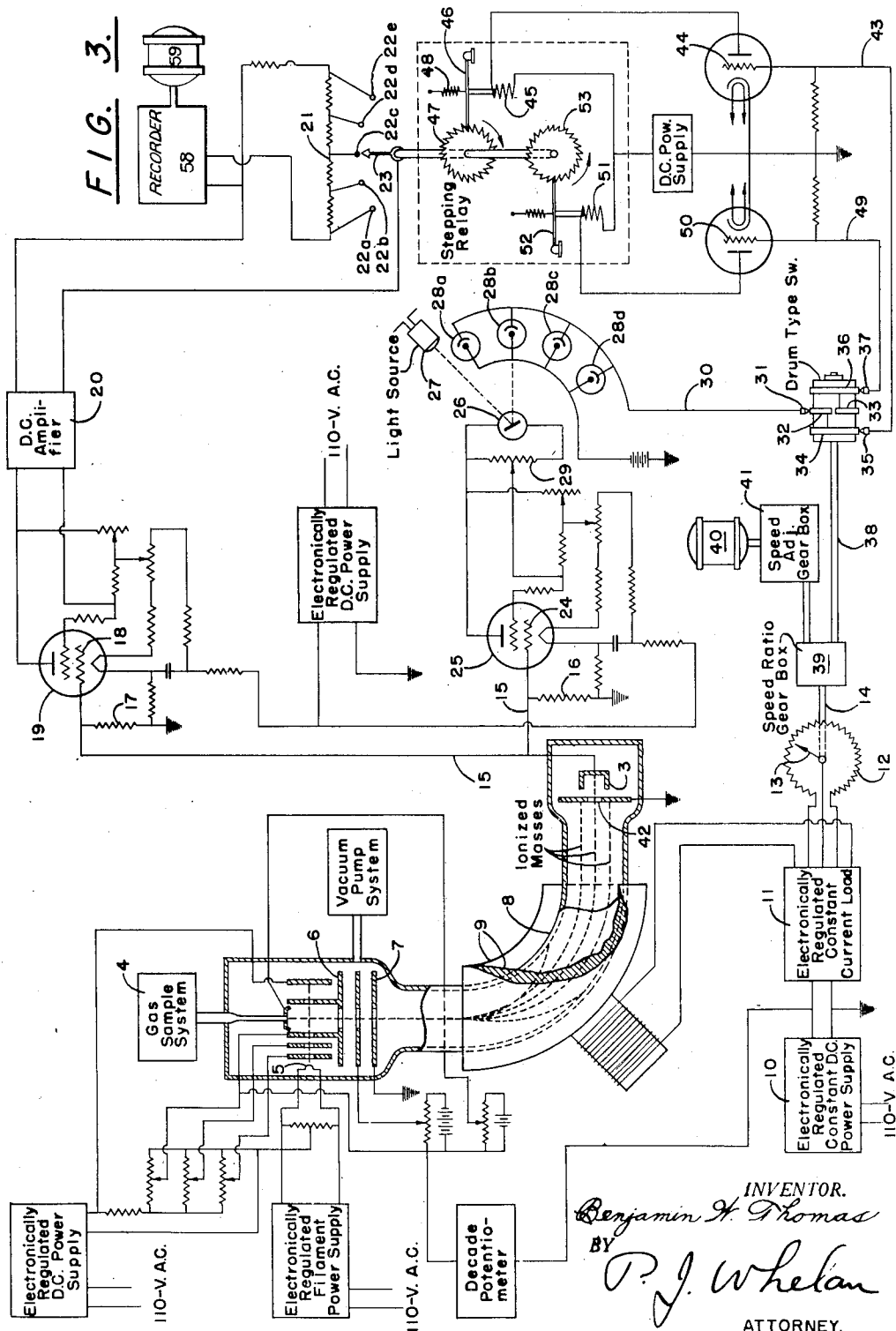
FIG. 2.



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3 Sheets-Sheet 2



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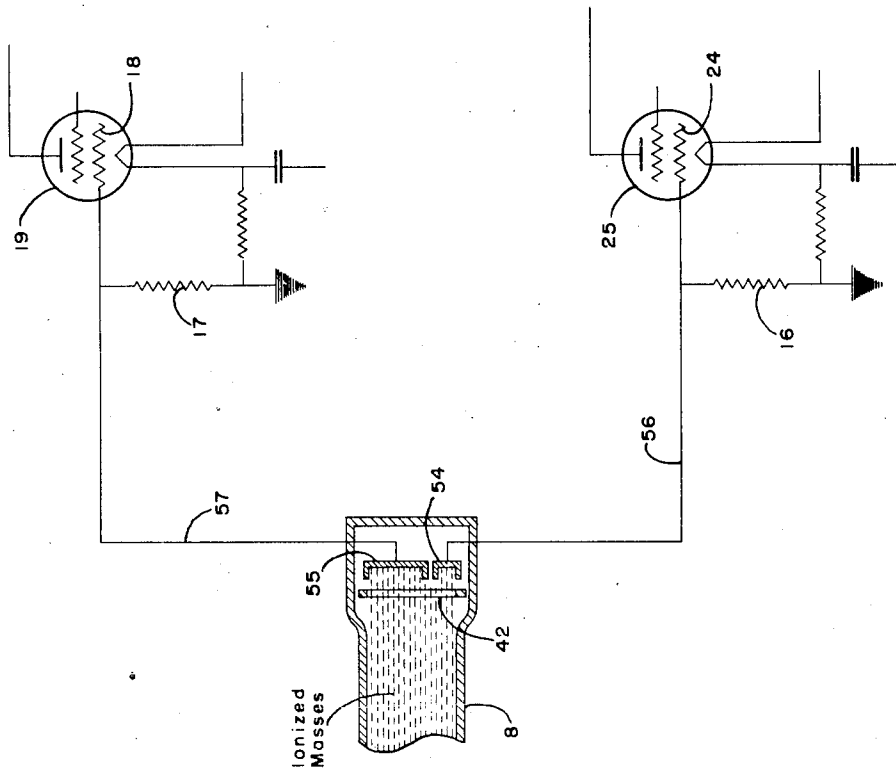
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3 Sheets-Sheet 3

FIG. 4.



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UNITED STATES PATENT OFFICE

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ANALYTICAL APPARATUS

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4 Claims. (Cl. 346—33)

1

The present invention is directed to a method and apparatus for analyzing mixtures of gases of different molecular weights. More specifically, the present invention is directed to an improvement in mass spectroscopy.

As is known, in analyses of gas mixtures by a mass spectrometer, the gas mixture is introduced into the zone of influence of an accelerating voltage under a reduced pressure. As the gas mixture comes into the zone of influence of this voltage, it is ionized by electron bombardment. The electrons are produced by a hot filament. The accelerating voltage drives the ions at a speed proportional to the voltage into a curved conduit in which is maintained a crossed magnetic field. As the ionized fragments pass through this magnetic field, the line of travel of the individual components thereof is determined by their velocity, mass (or molecular weight) and the magnitude of the magnetic field. As a result, some of the ions are able to navigate the curved conduit, whereas other ions of different molecular weights strike against the grounded walls of the conduit, lose their charge and are pumped out of the tube. The magnetic field can be so regulated that the ions representing only one mass emerge from the curved path. Upon emergence these ions encounter a metal shield having a slit. By controlling the magnetic field and accelerating voltage precisely, these ions can be made to pass through this slit, where they enter a Faraday cage, which is grounded through a resistance. The neutralization of the charge carried by the ions causes a current to flow from the ground through the resistance, setting up a potential drop, which may be used to operate recording means. As will be evident, by manipulation of the magnetic field, ions representing components of different molecular weights or masses can be caused to pass through the slit in sequence. As a result, the voltage across the aforesaid resistance changes with time, depending on the quantity of the different ionized masses which pass through the slit, giving a record which is a spectrum representing the composition of the gases.

In using the mass spectrometer for the analyses of gases of different molecular weights, limitations are imposed on the range of measurable ion currents produced from the gases. The principal limitation arises out of the fact that a chart re-

2

recorder is employed, the sensitivity range of which is insufficient. If the sensitivity of the recorder is sufficiently high to record minute ion currents for one molecular weight, it may be so high that the chart will not accommodate the peak representing some other molecular weight present in the same spectrum. Conversely, if the sensitivity of the instrument is adjusted so that the largest peaks in the spectrum are accommodated, then the smaller peaks in the spectrum will be so small, if they appear at all, that computation of the quantity of gas represented by these minor peaks will be unreliable.

According to the present invention, this difficulty is eliminated by incorporating in the recording circuit an electrical means operated from the Faraday cage for adjusting the amplification of the peaks on the spectrum to a degree inversely proportional to the magnitude of the peaks. In other words, according to the present invention, a portion of the energy carried by the ions of any given mass entering the Faraday cage is utilized to adjust the degree to which the voltage generated across the resistor connected to the Faraday cage by said mass is amplified before being recorded. Where the mass is present in large quantity, its ions are used to set the recording apparatus at a low sensitivity, whereas, when a mass is present in minute quantity, its ions are used to set the sensitivity of the recording apparatus at a high value.

The object of the present invention can be realized in many ways, of which two may be mentioned as illustrative. One way is to ground the Faraday cage through two separate resistors, whereby each resistor draws current from the ground to an extent proportional to its size in order to neutralize the ions in the Faraday cage. Thus, there will be correlated across each resistor a current inversely proportional to its size. One of these resistors can be made many times larger than the other, the smaller being used to transmit the main signal to the recorder, and the larger being used to control the degree of amplification or the sensitivity of the recorder for the main signal.

The same effect can be produced by employing two Faraday cages behind the slit in the spectrometer. By proportioning the sizes of these cages, the contribution of the beam to the sensi-

tivity device and to the recording device can be varied as desired. Here, again, the cage used for regulation will be small in comparison to the cage used for recording.

The nature of the present invention will be more clearly understood in the following detailed description of the accompanying drawing, in which

Fig. 1 is a replica of a spectrum obtained with a mass spectrometer without any sensitivity regulation of the recorder;

Fig. 2 is a replica of the spectrum obtained from a mass spectrometer with the sensitivity regulated in accordance with the present invention;

Fig. 3 is a diagrammatic view of the electrical circuits in a mass spectrometer embodying the present invention; and

Fig. 4 is a similar view of a modification of the sensitivity control means.

In order to facilitate description of this invention, reference will be made first to the type of spectrum produced with a conventional recorder and with the improved recorder, respectively. Figs. 1 and 2 represent the spectra, each being part of the spectrum of pure isobutane. As will be understood, the ionization of pure hydrocarbons in the spectrometer produces a wide variety of masses, such as H , H_2 , C , CH , CH_2 , CH_3 , CH_4 , C_2 , C_2H , C_2H_2 , C_2H_3 , etc. Only the heavier of these masses are represented on the spectra shown.

The spectrum shown in Fig. 1 was produced on a 10 inch chart with a recorder having a single sensitivity. On this spectrum the voltages generated by the positively charged masses are represented by ordinates, while the mass numbers are represented as abscissae. In this recorder, every inch on the ordinate scale represents six millivolts. It will be observed that the peaks representing several of the masses went "off scale" entirely, so that it is impossible to tell what was the magnitude of these peaks.

In the spectrum shown in Fig. 2 five sensitivity adjustments of the recorder are represented. This made it possible to have a varying ordinate scale, the sensitivity on one extreme being such that one inch represents two millivolts (high sensitivity), and the sensitivity of the other extreme being such that one inch represents 1250 millivolts (low sensitivity). Here the peak of the 44 mass was recorded at highest sensitivity. It will be observed that this peak in this spectrum is three times as high as the corresponding peak in the spectrum in Fig. 1 and can be measured with a greater percentage of accuracy. In the recording of the mass 43 peak in the spectrum shown in Fig. 2, the whole range of sensitivity of the recorder comes into play. It will be seen that this peak is actually composed of a main peak, indicated by numeral 1, and a number of satellites, indicated by numeral 2. Each of these satellites is produced when the sensitivity of the recorder is changed. It will be seen that, with the chart moving in the direction of the arrow, the peak front is on the left of the spectrum. As the spectrum was scanned by the slit of the spectrometer, the quantity of mass 43 increased to the point where it reduced the sensitivity of the recorder, producing the first satellite. As the quantity of mass 43 passing through the slit continued to increase, it again reduced the sensitivity of the recorder, to produce the second satellite, and so on, until the sensitivity of the recorder was reduced to its lowest level, to produce the main peak, which was accommodated by the chart.

In like manner, it will be observed that the quantity of mass 39 was sufficient to cause one reduction in the sensitivity of the recorder. Although this peak was accommodated by the chart in the spectrum of Fig. 1, it could not be accommodated by the chart in the spectrum of Fig. 2 at the No. 1 or highest sensitivity of the recorder, equivalent to one inch of deflection for a 2 millivolt peak which is a considerably higher sensitivity than that represented by Fig. 1. Consequently, in order for this peak to stay on the chart, there had to be a reduction in sensitivity of the recorder. Before leaving these peaks with satellites, it will be observed that the same number of satellites appear on the rear face of the peak as appear on the front face; that is, after the mass passes the point of maximum concentration passing through the slit, the voltage it generates reduces, and as these reductions are passed on to the recorder, the sensitivity of the recorder increases stepwise until, at the bottom of the rear face of the peak, it is back at maximum sensitivity.

With these differences in the spectra produced, reference is made to Fig. 3, in which is illustrated one embodiment of the present invention. In this figure the Faraday cage is designated by numeral 3. Everything to the left of this cage is conventional in the art. For the sake of completeness, however, it may be pointed out briefly that the gas sample supply is designated by numeral 4, the electron supply filament is designated by numeral 5, and the ion accelerating plates are designated by numerals 6 and 7, respectively. It will be noted that these plates have aligned slits through which the ions must pass in their motion toward the magnetic field. Plate 7 is grounded, while plate 6 is connected to a high voltage source. The ions which pass through the slits in the ion accelerating plates then enter the curved conduit 8, which, in conventional apparatus, may represent a 90° angle. The curved conduit conventionally is made of glass provided with a grounded, internal, non-magnetic metal shield and is surrounded by suitable electromagnets 9 to set up a magnetic field, the magnitude of which is controlled by power supply 10, between which and the magnets is arranged a control device 11, including a potentiometer 12. The potentiometer is of a helipot type, with a radial contact 13, the rotation of which, about the center, is controlled by a shaft 14, to which reference will hereinafter be made. It may be mentioned that the purpose of this variable potentiometer is, as before indicated, to change the field strength of the magnetic field across the curved conduit 8 to successively higher or lower values, depending upon the end from which the spectrum is being scanned.

Everything to the right of the Faraday cage 3 is part of the recording means, in which applicant's improvement resides. Here it will be observed that the Faraday cage 3 is connected by a conductor 15 to two grounded resistors 16 and 17, respectively. In this embodiment, the resistor 17 has a value which is small in comparison to that of resistor 16, such as about one-tenth or even one-hundredth thereof. The ratio between these resistors is a matter of choice, depending upon the nature of the instrument itself and the degree of sensitivity desired. This proportioning of these resistors makes resistor 17 the one which produces the voltage which may be considered the main signal. The voltage set up across resistor 17, as a result of the entry of ions into cage 3, is

utilized as the biasing voltage of the grid 18 of an electrometer tube 19, the plate voltage of which constitutes the signal. This plate voltage is fed into a D. C. amplifier 20, one output terminal of which is connected directly to one input terminal of any conventional recorder 58, such as a Leeds & Northrup electronic "Speedomax" recorder. The other output terminal of the D. C. amplifier is connected to the other input terminal of the recorder through a tapped variable resistance 21 of the type commonly known as an Ayrton shunt, which includes a number of contact points 22a, b, c, d and e and a rotating contact 23 arranged to contact the points 22 in sequence. It is to the control of the movement of this contact 23 that the present invention is directed.

The voltage drop through resistor 16 is used as a biasing voltage for the grid 24 of a second electrometer tube 25, the plate current of which is fed to a mirror galvanometer 26. A suitably located light source 27 plays on the mirror of galvanometer 26 to produce a reflected beam, which plays on a bank of photocells 28a, b, c and d. As the mirror of the galvanometer moves from one position to the other, the reflected beam moves from one photocell to the other, and while it is not playing directly on a photocell there is no current flowing in the conductor 30 which carries the current output from the photocells. The sensitivity of galvanometer 26 is set by the resistor 29 so that the highest peak to be recorded causes this galvanometer to reflect the light beam to photocell 28a.

The conductor 30 terminates in a contact 31, riding on a drum-type switch which has two disconnected semi-circumferential contacts 32 and 33, respectively. Contact 32 is connected to a ring 34, on which rides a contact 35. Element 33 is connected to a second ring 36, on which rides a contact 37. This drum is driven by a shaft 38, which is connected to a gear in a proportioning gear box 39. The prime mover for the proportioning gears is a synchronous motor 40, which is operated from the same power source (not shown) as a synchronous motor 59, connected with recorder 58, which drives the chart on which the spectrum is recorded. If desired, motor 40 may also replace and perform the functions of motor 59. Between the proportioning gears and the synchronous motor is a set of reducing gears 41.

It will be observed that shaft 14 is also driven by one of the proportioning gears in gear box 39. Shaft 14 moves the moving contact 13 of potentiometer 12 at a rate selected to provide a desired time interval between the passage of the several masses by the slit 42 in front of the Faraday cage 3. At the same time, shaft 38 is driven at such a rate that the drum-type switch makes one complete revolution for each peak. Since the distance between peaks is regulated, it is possible to control the revolutions of the drum-type switch so that half way between each peak the contact 31 will be just between the contacts 32 and 33, so that for approximately one half the peak the contact 31 rides on the strip 32, and for the other half of the peak it rides on the strip 33.

Contact 35 is connected by conductor 43 to the grid 44 of an electronic switch. This switch is a vacuum tube of one of the common types used for making and breaking circuits. For example, it can be a trigger-type tube which causes a current to flow in the plate circuit when a current flows in the conductor 43. The current in the plate circuit passes through a solenoid 45 which

actuates a pawl 46. This pawl coacts with a ratchet 47 which is mounted on the same shaft as the contact arm 23. This pawl is urged upwardly by a spring 48. Thus, when a current flows in conductor 43 the solenoid pulls the pawl downwardly, causing it to move the ratchet wheel one notch. As soon as current flow in 43 stops, the pawl is released and pulled upwardly by the spring into a position to contact another notch in the ratchet. Each time the ratchet is moved one notch it moves the contact arm 23 from one contact 22 to the next.

The contact 31 in the arrangement shown makes contact with the strip 34 during the first half of the peak. At the beginning of the peak, the contact arm 23 is in contact with the point 22a, to the extreme left. As the galvanometer 26 moves the light beam from the zero position onto photocell 28a, a current flow in conductor 43 starts. When the beam reaches the photocell 28a current begins to flow in conductor 43, actuating the ratchet 47 in the direction shown, and moving the contact arm from the point 22a to the next point 22b. If the quantity of the mass is sufficient, the galvanometer beam will move to the next photocell 28b. As the galvanometer moves the beam from photocell 28a to photocell 28b, the current flow in conductor 43 stops and the pawl is released into position to contact the next higher notch. Then, when the photocell 28b is reached by the beam, the performance is repeated and contact arm 23 is moved to the next contact point 22c.

During the second half of the peak the contact 31 rides on the strip 33. The contact 37, which is connected to strip 33 through ring 36, is also connected by conductor 49 to the grid 50 of another vacuum tube switch. The plate current of this tube likewise flows through a solenoid 51 which actuates a pawl 52, which coacts with a ratchet 53, also mounted on the same shaft as contact arm 23. In this case, each time the pawl is actuated it moves the contact arm 23 in the direction opposite to that indicated above. Thus, if we assume that a certain mass had caused the contact arm 23 to move to the position shown in the drawing in arriving at its peak value, it would have moved the mirror of galvanometer 26 to a point where the beam would shine on the photocell 28b. As the concentration of the mass began to decrease, the mirror of the galvanometer would rotate counter-clockwise and the drum-type switch would have turned so that contact 31 had come in contact with the strip 33 thereby actuating solenoid 51, with the result that the beam would be restored to the zero position above the topmost photocell 28a when the mass had completely passed the slit 42. During this period the pawl 52 would be actuated twice, and restore the contact arm 23 to the contact point 22a.

The stepping relay comprising the elements 45, 46, 47, 48, 51, 52 and 53 may be the commercial add and subtract relay, series R, as manufactured by Guardian Electric Co., Chicago, and shown at page 24 of the 1944 catalog of this company.

Referring back to Fig. 2, each one of the satellites 2 is the result of the movement of the beam from the mirror of galvanometer 26 from one photocell to the next, with a consequent movement of the contact arm 23 from one contact point 22 to the next toward the right. In like manner, the right hand side of each peak represents the movement of the contact arm 23 in the reverse direction.

To illustrate the effect of the improvement of

the present invention on the type of spectrum produced, reference may be made again to Figs. 1 and 2. The following table demonstrates the relative sensitivity and peak height ranges of the standard recorder and the recorder according to the present invention.

Mass	Figure 1 (1 Sensitivity)		Figure 2 (5 Sensitivities)	
	Final Sensitivity Factor of Recorder ¹	Peak Height, mv.	Final Sensitivity Factor of Recorder ¹	Peak Height, mv.
44-----	6	6±0.5	2	6±0.1
43-----	6	off scale	1250	3750±30
42-----	6	18±1.0	10	18±0.2
41-----	6	off scale	50	150±1.5
40-----	6	8±0.5	2	8±0.1
39-----	6	25±1.5	10	25±0.2
38-----	6	3±0.5	2	3±0.1

¹ 1 inch=mv.

In the above table, the first column lists the mass numbers shown as abscissae in Figs. 1 and 2. The second column indicates that the recorder used in recording the spectrum of Fig. 1 had a uniform final sensitivity of 6 millivolts per inch; that is, a mass which would produce an amplified voltage of 6 millivolts across the input of the recorder would cause the recording stylus to move one inch across the chart. The third column of the table shows, in millivolts, the heights of the peaks for the respective masses as recorded on the chart shown in Fig. 1 and the accuracy, expressed in millivolts, with which the peak height could be read from the chart.

The last two columns of the table refer to Fig. 2. Column 4 indicates the final sensitivity, expressed in millivolts per inch, which was employed to produce the chart of Fig. 2 with the same sample as used to produce the chart of Fig. 1. However, instead of having a single uniform sensitivity as in the case of the recorder employed in connection with Fig. 1, the recorder in this instance had a variable sensitivity in accordance with the present invention. Thus, sensitivity No. 1 was equal to 2 millivolts per inch, sensitivity No. 2 was one fifth of this amount or 10 millivolts per inch, and sensitivity Nos. 3, 4 and 5 were, respectively, 50, 250, and 1250 millivolts per inch on the chart. That is, at sensitivity No. 5, a voltage of 1250 millivolts at the input of the recorder caused the recording stylus to move only one inch across the chart.

As in the case of column 3, column 5 indicates in millivolts the heights of the peaks for the respective masses as recorded on the chart of Fig. 2 and the accuracy with which the peak heights could be read from the chart.

It will be observed that, because of the much higher sensitivity which can be imparted to the recorder by the improvement of the present invention for recording minor peaks, the quantity of these masses can be recorded much more accurately. Mass 44, for example, according to these spectra, can be evaluated to one-tenth of a millivolt by the improved recorder, whereas it can be evaluated only to one-half a millivolt with the standard recorder. On the other hand, mass 43, which went entirely off the scale with the standard recorder, can be recorded by the recorder of the present invention to the same relative accuracy as the minor peaks.

In Fig. 4 is illustrated another embodiment of the present invention. This embodiment differs from that illustrated in Fig. 3 only in the manner in which the ions passing through the slit 42 are utilized to actuate the electrometer tubes 19 and 25. In this figure the single Faraday cage 3 of

the embodiment shown in Fig. 3 is replaced by two Faraday cages 54 and 55. The ratio between the sizes of these cages can be set at any desired value and the resistors 16 and 17 adjusted accordingly. Ordinarily, the cage 54 will be of a size to collect about one-tenth of the ions passing through the slit and the cage 55 will collect about nine-tenths of the ions. The Faraday cage 54 is connected to resistor 16 by conductor 56, resistor 16, in turn, being connected to the ground and to the grid of electrometer tube 25 in the same manner as in Fig. 3. Cage 55 is connected to resistor 17 by conductor 57, resistor 17 being connected to the ground and to the grid 18 of electrometer tube 19 in the same manner as in Fig. 3.

It will be evident that the present invention is capable of assuming a number of concrete embodiments, of which the two specifically described and illustrated are examples. It is intended to embrace such other embodiments in the appended claims so long as they operate on the principle that a portion of the energy contained in the ions of a given mass passing through the exit slit 42 of the spectrometer tube is utilized for controlling the sensitivity of the recorder during the recording of the peak of that mass.

The present invention has been described in connection with the operation of a mass spectrometer. It will be evident that the invention is directly applicable to the recording of any signals where the variation between the maximum and minimum value on the recorder is so great as to render it impractical to record them both on the same chart with a single sensitivity. For example, the invention may be applicable in the same way to spectrometric analyses of the infrared and the ultra violet type. In each case a portion of the energy which represents the value to be recorded is utilized for controlling the sensitivity of the recorder. Another application of this invention is in the recording of seismic disturbances. In seismic prospecting, the waves which reach the pickups produce currents which vary over a wide range. In this art much attention has been given to automatic volume (sensitivity) control of the recorders. The present invention is directly applicable to such operations.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. An apparatus for recording a signal which varies in intensity between wide limits, comprising means for receiving the signal, means for diverting a fixed portion of said signal, means for delivering the remainder of said signal to a recorder, and means actuated by the diverted portion of said signal for varying the response of said recorder to the transmitted portion inversely as the said transmitted portion varies.

2. An apparatus for recording a signal from a mass spectrometer having an exit slit through which the ions pass, comprising means for collecting the ions passing through the exit slit representing a given mass, means electrically connected to said collecting means for diverting a fixed portion of the energy derived from said ions, means electrically connected to said collecting means for delivering a signal to a recorder which is a function of the remainder of the energy derived from the ions, and means actuated by the diverted portion of the energy for varying the response of said recorder to the signal as a function of the transmitted portion of the energy.

9

3. An apparatus for recording a signal from a mass spectrometer having an exit slit through which the ions pass comprising a member arranged to receive energy from the ions passing through the exit slit representing a given mass, a conductor electrically connected to said member, a recorder electrically connected to said conductor for producing a record which is a function of the energy received by the member from the ions, and means electrically connected to said conductor for varying the response of the recorder as a function of the energy received by said member from the ions.

4. A recorder for a mass spectrometer provided with an exit slit through which the ions pass, comprising, in combination, a first member for collecting the major portion of the energy from the ions passing through the exit slit representing a given mass, a second member for collecting the

10

remainder of the energy from the ions, a recorder, means electrically connecting the first member with the recorder whereby a signal which is a function of the energy received by the first member from the ions is recorded by the recorder, and means electrically connected to the second member arranged for varying the response of said recorder as a function of the energy received by the second member from said ions.

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