In a mass spectrometer wherein gases of a mixture are ionized and respective ion beams are directed to collector plates or cups to generate proportional signals for determining the relative amounts of the several gases in the mixture, the sensitivity of the collector cup signals is maintained by adjusting the ionizing power supply as required to maintain the total of the signals from the collector plates or cups substantially equal to a reference signal. The total of the collector signals are compared with the reference signal by a summing amplifier. When the compared signals differ from a predetermined relation (e.g., equality) a proportional output signal is generated and applied to power control means to vary the level of power applied to ionize the mixture, and hence the levels of the collector signals, until the total of the collector signals is in said predetermined relation to the reference signal. Resistors associated with the collector plates or cups and with the reference signal source are selected so that the total of the collector signals and the reference signal are in said predetermined relation when the ion species collected are related to the gas species of interest.

7 Claims, 2 Drawing Figures
The present invention relates to mass spectrometers adapted for measuring the proportional quantity of particular gases in a mixture by measuring the relative abundance of the respective gases at each mass position of interest. In particular, the invention is such a mass spectrometer incorporating means for maintaining uniform sensitivity of the instrument.

In a mass spectrometer of the type under consideration a sample of the gas is fed into an ionizing chamber which is under a vacuum and through which a beam of electrons passes from an emissive cathode to an anode. The sample gas is admitted to the ionizing chamber through a suitable inlet, such as a conventional molecular leak, so that its gas pressure is reduced, without disturbing the composition of the gas, to a level compatible with the vacuum in the ionizing chamber. The beam of electrons ionizes the gas by electron bombardment and the resulting gas ions are accelerated out of the ionizing chamber into an analyzing chamber by a suitable ion accelerating and focusing system. In the analyzing chamber, which is also under a vacuum, the ions of the respective gases are directed by a magnetic field into separate curved paths, the curvature of which are determined by the mass to charge ratio of the respective ions, the ion velocity and the magnetic field strength. Ion current collector plates or cups are placed to receive ions of particular gases to be measured and to generate signals proportional to amounts of the particular gases present in the mixture.

The initial sensitivity of the instrument may vary due to aging or drift from environmental conditions, such variations being substantially uniform for the several output signals from the respective collectors. More specifically, the effectiveness of the sensitivity control concept of this invention is based on the realization that most of the sensitivity variations which limit the reliability of mass spectrometers for many purposes are due to factors which effect the outputs in a common mode and that by appropriately balancing the configurations of the several ion current measuring circuits these factors can be related to the total of the input partial pressures of the mixed gases so as to be compensated for by a closed loop system incorporating a feedback control of the generation of ions or of the delivery of ions to the collector plates or cups. Examples of such interrelated sensitivity variations include variations due to aging or movement of the cathode or anode to changes in the level of vacuum in the ionizing chamber, to aging of the surfaces of the collector plates or cups, and/or to changes in the ambient temperature.

A principal object of the present invention is to provide automatic correction of common-mode variations of the sensitivity of a mass spectrometer from its initial sensitivity. This object is accomplished in accordance with the invention by comparing the total of the signals proportional to the partial pressures of the ionized gases being measured with a reference signal and generating an error signal if the compared signals vary from a predetermined relation. The error signal is applied to control the level of ionization of the gas, and thereby vary the signals produced by the ionized gases until the total of the latter signals is again in the aforementioned predetermined relation with respect to the reference signal, at which point the initial sensitivity of the instrument is restored.

The sensitivity control in accordance with this invention is adapted to operate effectively even though only the ions of selected gases, less than all the component gases, of a sample mixture are collected and summed.

In one embodiment of this invention a total pressure transmitter is connected into the supply of the gas mixture and produces a reference signal that is proportional to the total pressure of the gases in the mixture and directs the signal to a summing amplifier for comparison with the sum of ion signals. In another embodiment an arbitrary reference signal is supplied from a reference voltage source.

In both embodiments the signals from the collectors and the reference signal are directed to a summing amplifier which is adapted to compare the total of the output signals with the reference signal, and, if they vary from a predetermined relation, suitably equally, the summing amplifier generates an error signal proportional to the variation. This error signal is applied to the level of the ionization until the total of the collector output signals is again in the predetermined relation to the reference signal. In a preferred embodiment the ionization level is controlled by means of an emission regulator coupled to an electron beam generator which ionizes the gas mixture. Any of a number of known means for ionizing gases may be used, however, and the level of ionization or the number of ions directed to the collectors may be varied by a variety of suitable means, such as by varying the power input to a gain element of the ionization means or by control grids or repeller electrodes.

The predetermined relationship (equality) between the total of the collector signals, which are proportional to the vapor pressures of the respective gases, and the reference signal is established by the appropriate selection of resistors of appropriate value between the summing amplifier and the reference signal source and the collector outputs, respectively. The resistors between the collector outputs and the summing amplifier are selected so that the several currents which are produced at the summing junction are equal to each other at unit partial pressures of the respective gases. The value of the resistor between the reference voltage source and the summing amplifier is selected so that the current at the output side of this resistor equals the total current to the summing amplifier from all the collectors when the sample gas mixture supplied to the instrument contains (in any proportions) all the gases to be measured.

Further objects, advantages and features of the invention will be apparent from the following more detailed description of preferred embodiments of the invention illustrated in the accompanying drawings in which:

FIG. 1 is a partly schematic diagram of a mass spectrometer incorporating sensitivity control means in accordance with one embodiment of the invention, and

FIG. 2 is a partial diagram illustrating an alternative source of reference voltage for the instrument shown in FIG. 1.

Referring to FIG. 1, a mass spectrometer for analyzing the proportionate quantities of several gases in a mixture includes an ionizing chamber 10 under a vacuum through which an electron beam 11 is passed from an emissive cathode 12 to an anode 13, the cathode 12 being energized by power from a source indicated at 14. A mixture of gases to be analyzed from a source not shown, is conducted by a conduit 15 to a suitable sample inlet device 16, such as a conventional type of molecular leak, which admits a sample of the gas into the ionizing chamber 10 at reduced pressure. The inlet device 16 reduces the pressure of the gas sample, without disturbing its composition, to a level compatible with the degree of vacuum provided in the ionizing chamber and the ion currents required. The gas sample in the ionizing chamber is ionized by electron bombardment and the resulting ions are accelerated through an aperture 17 into an analyzing chamber 18 by ion focusing lenses (electrodes) indicated at 19 between the outlet from the ionizing chamber 10 and the aperture 17.

In the analyzing chamber 18, which is also under vacuum, the stream of gas ions are segregated by a magnetic field indicated at 20 into separate curved paths 21a, b and c of different curvature in accordance with their respective mass to charge ratios. Ion current collector cups illustrated by the collector cups 23a, b and c are placed for ions of the particular gases of interest in the mixture to impinge upon them and produce signal currents proportional to the masses of the respective gases. Electroemeters 23a, b and c connected respectively to the collector cups 23a, b and c amplify the collector currents and apply them to signal indicators 24a, b and c which read the relative strengths of the signals and which may suitably be calibrated to show the proportional amounts of the particular gases.

The operating pressures, namely vacuums in the ionizing chamber 10 and the analyzing chamber 18, are provided by a
vacuum pump 25 connected into the analyzing chamber 18. The vacuum pump 25 may be an ion pump utilized in combination with a roughing pump, not shown, for starting the creation of the vacuum in the conventional manner.

The above-described apparatus is conventional and well known in this art.

In accordance with the present invention means for maintaining the initial sensitivity of a mass spectrometer of the type described above includes a summing amplifier 30 connected to receive the total of the output signals from electrometers 23a, b and c through resistors R1, R2 and R3, which are in series with the respective electrometers, and to receive a reference signal through a resistor R4. In the embodiment shown in FIG. 1 the reference voltage is supplied by a total pressure transducer 31 connected into the conduit 15 to produce a reference signal proportional to the total pressure of the gas mixture of the supply. The summing amplifier 30 is adapted to compare the total of the signals from the electrometers 23a, b, and c with the reference signal from the total pressure transducer 31 and to supply a signal proportional to any difference to a power control device 32 which is connected between the emissive cathode 12 and the power source 14 therefore. As illustrated, the power control device 32 can suitably be an emission regulator adapted to vary the power input to the (thermonic) cathode 11 accordingly to maintain the signal from the summing amplifier 30 so as to vary the cathode temperature and thereby vary the level of ionization of the gas mixture. Thus the strengths of the collector output signals from the electrometers 23a, b and c are varied until their total is brought into equality with the reference signal at which point the original sensitivity of the instrument is restored and the summing amplifier 30 no longer generates an error signal. The level of ionization then remains constant until the sensitivity changes to initiate the generation of error signals again.

Other, alternative means may also be utilized for varying the ionization level in accordance with an error signal. For example, the error signal could be applied to vary a resistance which converts the current of anode 13 to voltage for the power control device, power control means could be connected for varying the potential of the focusing lenses, a split electrode could be provided in the approximate position of the lenses 19 and be connected for deflecting the ions in proportion to the strength of the error signal, a repeller electrode could be provided to adjust the flow of ions from the chamber 10 by altering the voltage of the repeller electrode, or control grids could be placed in the path of the electron beam 11 and be connected to vary the beam intensity.

It should also be appreciated that other ionizing means could be substituted for the electron beam generating arrangement illustrated, for example, a cold cathode emitter such as an electron multiplier which produces electrons at its output in proportion to an input signal and voltage. In this case the number of electrons produced, and hence the level of ionization, could be varied by controlling either the input signal or the voltage. Another alternative would be to ionize the gas mixture by means of a point source of high voltage in the proximity of the sample of the gas mixture in chamber 10 and to control the flow of ions to the collectors by means of an accelerating grid whose potential would be varied in proportion to the error signal. Still another alternative would be to apply ultraviolet light to ionize the gases and to vary the ionization level by a shutter for controlling the light applied or by varying the intensity of the light source.

In order to assure that the signal produced by each of the electrometers 23a, b, and c represents the true partial pressures of the gases, whose ions are collected at the collector cups 22a, b, and c, feedback resistors R5a, b, and c connected across the respective electrometers are chosen to provide a maximum electrometer output consistent with the operating range of the instrument.

In order for the signals from the electrometers 23a, b, and c to remain related to true partial pressures of the mixed gas when the proportions of the gas components change, their values are selected so that equal currents are produced at the output side of each of them by equal partial pressures of the respective gases in the mixture. In selecting the values for these resistors, the value of one of them, preferably one which will have an intermediate value, is selected to pass current in response to ions of a minimum expected quantity of the pertinent gas component of a representative sample mixture.

When the values of the resistors R1, R2 and R3 are selected as aforesaid, the value of the resistor R4 which is between the summing amplifier 30 and the total pressure transducer 31 (or other reference voltage source as in FIG. 2) is selected so that the current from the resistor R4 equals the total of the currents from the resistors R1, R2 and R3 for a sample gas mixture containing all the gases for which ion current collectors are provided. The several components may be present in any proportion.

With this arrangement of resistances selected in the manner described, the spectrometer is adapted to measure relative quantities of any one or more of the component gases of a mixture, for which ion current collectors are provided. And the sensitivity of the instrument will be kept constant despite variations in the sensitivity as previously explained.

In the apparatus illustrated in FIG. 1 the spectrometer is shown adapted for determining the proportional amounts of three component gases of a mixture, such as a mixture of N2, O2 and CO2. It may of course be adapted for determining the proportional amounts of any selected number of particular gases in different gas mixtures.

The following example illustrates the relative values of the resistors R1, R2 and R4 in a spectrometer that is adapted for measuring the proportionate parts of N2, O2 and CO2 of a mixture of these gases in which a reference sample of this mixture consists of 70 percent N2, 25 percent O2 and five percent CO2 at a pressure of 800 torr so that the partial pressures would therefore be 560, 200 and 40 torr, respectively. In order to obtain the largest outputs possible from the electrometers 23a, b, and c for this mixture in the test spectrometer, the values of the feedback resistors R5a, b, and c were five (109), two (108) and 107 ohms, respectively.

For obtaining the appropriate values of the resistors R1, R2 and R3 the instrument is operated by itself, disconnected from the sensitivity control circuitry of this invention. Feeding a gas sample containing the above three components in the stated reference proportions to the instrument, produced voltages of 4.6, 5.1 and 3.75 volts, respectively, at the output of the electrometers 23a, b, and c. As described above the values of the resistors should be such that the currents from the respective resistors for gas ions at each of the collectors are equal for equal partial pressures of the respective gases. This relationship may be expressed:

\[
\frac{V(N_2)P(N_2)}{R_1} = \frac{V(O_2)P(O_2)}{R_2} = \frac{V(CO_2)P(CO_2)}{R_3}
\]

for the voltages (V) from the electrometers associated with the collectors for ions of the indicated gases at the partial pressures (P) of the indicated gases. Assigning the value of 50K ohms to the intermediate resistor R2 and inserting the above-specified voltages and pressure figures, the relationship is:

\[
\frac{4.60/7}{5.10/25} = \frac{3.75/0.65}{50} = \frac{50}{R_3}
\]

from which it is determined that R3 should be 16.10K ohms and R3 should be 183.82K ohms.

The value of resistor R4, which sets the scale of the system, is then selected so that for a gas containing N2, O2 and CO2 the current from the output side of the resistor R4 will equal the total of the currents from the resistors R1, R2 and R3. For ex-
ample, if the voltage from the transducer 31 is 5 volts the relationships will be:

\[ \frac{5}{R_t} = \frac{4.6}{16.1} + \frac{5.10}{50} + \frac{3.75}{181.8} \]

from which it is determined that the value of resistor R4 should be 12.28k ohms.

With the foregoing resistor relationships, when the voltage outputs from the collectors vary in accordance with variations in the proportions of the component gases of the mixture, the outputs of the collectors will always be related to the true partial pressures of the component gases by a constant. Consequently, the instrument will accurately measure variations in the proportions of the component gases of the mixture so long as the total of the collector output signals equal the output signal of the total pressure transducer 31 at the summing amplifier 30.

FIG. 2 shows an alternative embodiment of the invention that is adapted for use in systems in which the gas mixture is supplied to the spectrometer at a constant pressure. In this embodiment the reference signal, instead of being supplied by a total pressure transducer 31 connected to the gas supply as in FIG. 1, is supplied by a reference voltage source 35 and a variable resistor 36. From the variable resistor 36 the reference voltage is coupled through the resistor R4 to the summing amplifier 30 as in the FIG. 1 embodiment. In this instance the value of the resistor R4 is selected in the same manner as described above for the FIG. 1 embodiment except that here the level of current through the resistor R4 is arbitrarily selected in accordance with the voltage from the source 35 by adjusting variable resistor 36. Mass spectrometers incorporating sensitivity control means in accordance with this invention are adapted for accurately monitoring one or more components of a gas mixture and are useful for many varied purposes including, for example, monitoring the components of the atmosphere in aircraft, spacecraft and undersea craft and monitoring components of anesthetic or other special gas mixtures used for medical purposes.

What is claimed is:

1. A mass spectrometer comprising an electrically actuated source of ions of the gases contained in a sample mixture, a plurality of ion collectors for receiving, respectively, ions of the gases in the mixture, said collectors discharging ions received thereby and producing electric output signals proportional to the number of ions received, means for directing ions from the source to the respective collectors, means for measuring the electric signals from the collectors as means for measuring the relative amounts of the respective gases in the sample mixture, and means for maintaining the sensitivity of the spectrometer comprising electrically actuated control means controlling the number of ions supplied to the collectors from the source, circuit means associated with the collectors for adjusting their output signals to be equal at unit partial pressures of the gases whose ions are received, respectively, at the collectors, signal summing means connected to receive the electric signals from the collectors, and means producing a reference signal from a reference voltage source and connected to apply the reference signal to the signal summing means, said signal summing means producing an output signal proportional to variations of the total of the signals of the collectors from a predetermined relation to the reference signal, and being connected to apply its output signal to said control means to vary the number of ions supplied to the collectors in proportion to said output signal.

2. The mass spectrometer of claim 1 including resistance means respectively between each of the ion collectors and the signal summing means and between the reference signal producing means and the signal summing means, the resistance means associated with the respective collectors being selected so that the signal current produced at the collectors are equal to each other at the outputs of these resistance means, the resistance means associated with the reference voltage signal producing means being selected so that the current received therefrom is in a predetermined relation to the total of currents received from the resistance means associated with the collectors when the gas mixture is one containing each gas whose ions are collected.

3. The mass spectrometer of claim 2 in which the reference voltage source comprises a variable resistor coupled to a source of voltage.

4. The mass spectrometer of claim 1 in which said reference voltage source is a total pressure transducer connected into said gas mixture and producing a reference voltage proportional to the total pressure of the gas mixture.

5. The mass spectrometer of claim 4 including resistance means respectively between the ion collectors and the signal summing means and between the transducer and the signal summing means, the resistance means associated with the respective collectors being selected so that the optimum signal currents, as produced per unit partial pressure of the respective gases at the collectors by ions of the gases of the mixture, are equal to each other, the resistance means associated with the transducer being selected so that the current received therefrom is equal to the total of the signal currents received from the resistance means associated with the collectors when the gas mixture being analyzed is one containing each gas whose ions are collected.

6. The mass spectrometer of claim 1 including means for ionizing a sample gas mixture comprising an electron beam generator having a cathode and an anode connected to a power source for producing a beam of electrons therebetween, for ionizing gases in the proximity of the beam, said control means being coupled to the electron beam generator for adjusting the intensity of said electron beam to be in proportion to an output signal from the signal summing means.

7. The mass spectrometer of claim 6 in which said control means is connected to adjust the power input to the cathode from said power source.