Dec. 8, 1953 L. P. ROBINSON ET AL 2,662,185

MASS SPECTROMETRY

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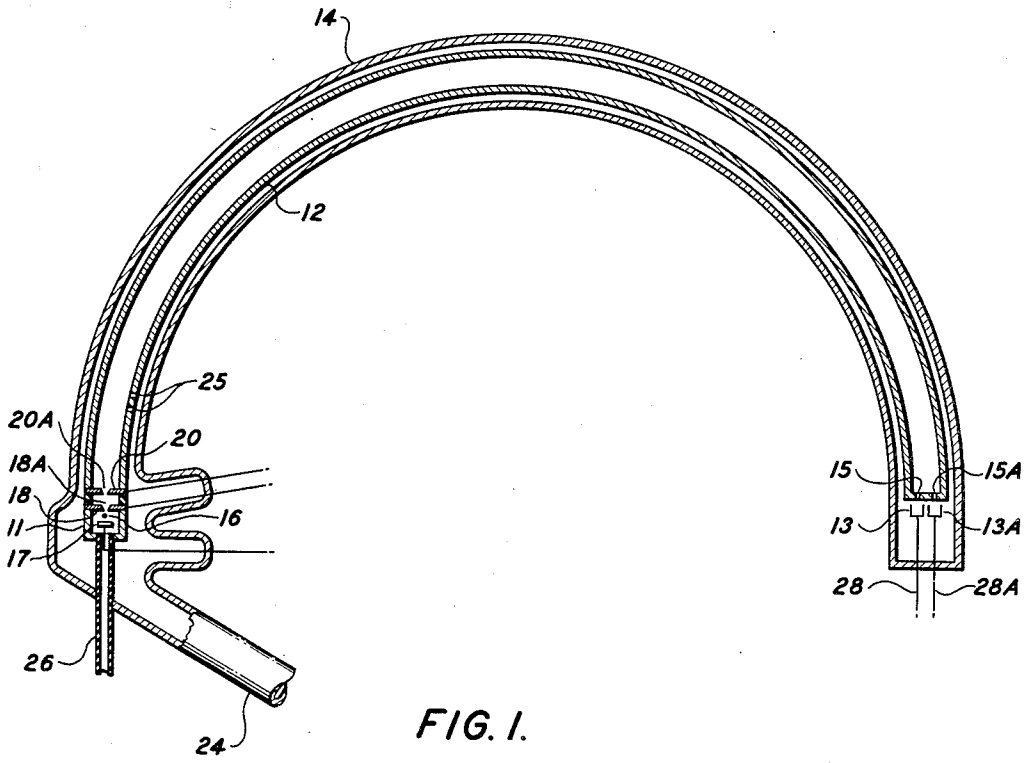


FIG. 1.

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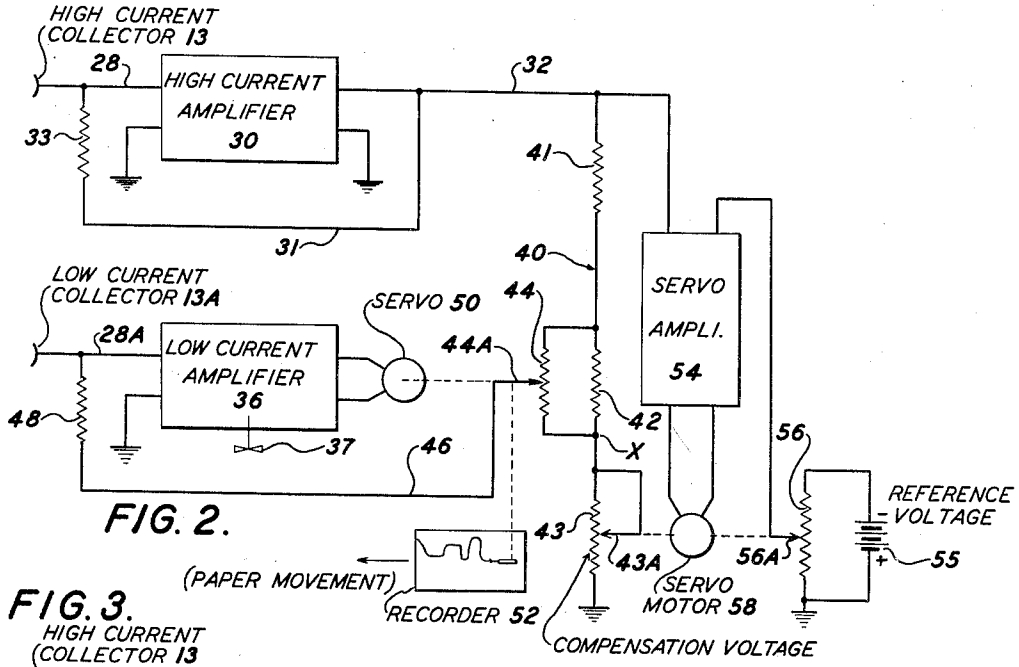
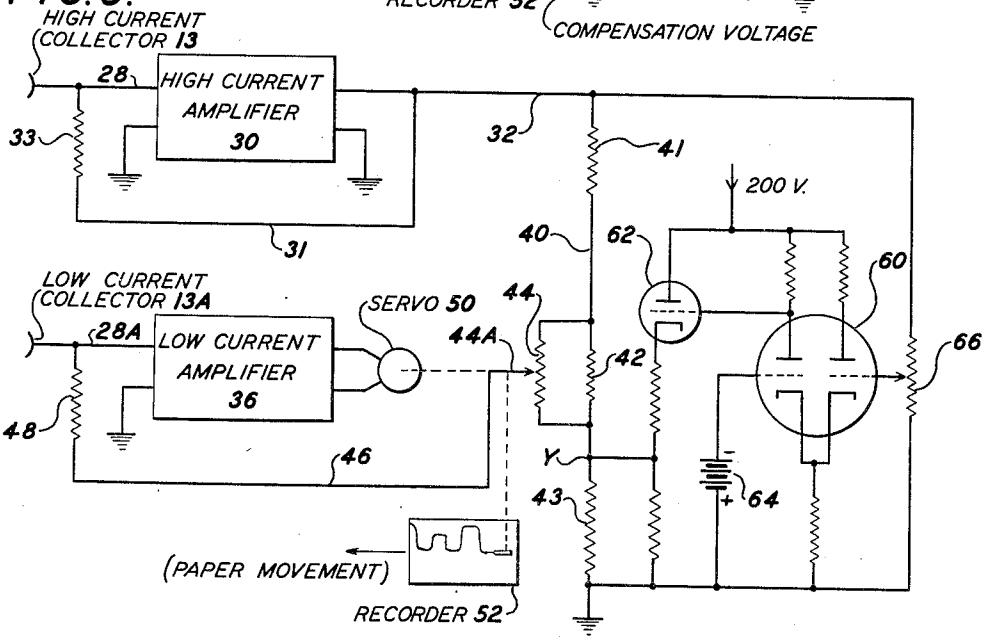


FIG. 2.

FIG. 3.



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Patented Dec. 8, 1953

2,662,185

UNITED STATES PATENT OFFICE

2,662,185

MASS SPECTROMETRY

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Application June 28, 1951, Serial No. 234,088

9 Claims. (Cl. 250—41.9)

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This invention relates to mass spectrometry and particularly to improved methods and apparatus for measuring isotope ratios.

In the practice of mass spectrometry a sample to be analyzed is first ionized, as by bombardment, with an electron beam. The resulting ions are segregated according to their mass-to-charge ratio, i. e. specific mass, and the ions of a given specific mass are selectively discharged. The current produced by such selective ion discharge gives a measure of the partial pressure in the sample of the parent molecules from which the particular ions derived.

In terms of apparatus, a mass spectrometer generally includes an ion source, an analyzer chamber, and a collector electrode together with associated power supply circuits, amplification and sensing circuits, and the like. The sample is introduced into the ion source wherein it is ionized and the ions are propelled from the source into the analyzer chamber as a heterogeneous beam. In the analyzer chamber the heterogeneous beam is subjected to a transverse magnetic field whereby ions of differing mass-to-charge ratio are caused to follow different paths through the chamber. A single resulting beam may be focused on the collector electrode or a plurality of beams may be successively focused on the collector by varying the parameters determinative of the ion paths through the analyzer.

Recently mass spectrometers have been adapted to measurement of isotope ratios by inclusion therein of a pair of collector electrodes. One of these electrodes is referred to as the "low current electrode" and at which the ion beam derived from molecules of a low abundance isotope is discharged. The other electrode is referred to as the "high current electrode" and the ion beam or beams of the more abundant isotope or isotopes are focused on and discharged at this electrode. For example, consider the analysis of a sample of carbon dioxide to determine the relative abundance of the C^{13} and C^{12} isotopes. C^{12} being the most abundant, the CO_2^{44} ions will be focused on the high current collector and the CO_2^{45} ions will be focused on the low current collector.

In isotope ratio analysis it is generally desired to measure the ratio of the ion currents rather than the absolute value of each of the components. Accordingly, the amplification and recording circuit connected to the two collector electrodes is often arranged as a null balance network, wherein the current developed at one collector is effectively divided by the current developed at the other collector to give a recorded value representative of the indicated ratio.

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Collector circuits of this character are illustrated and described in some detail in United States Patent 2,456,426 issued to Alfred O. C. Nier on December 14, 1948, and in co-pending United States Patent Application, Serial No. 104,030, filed July 11, 1949 by Robert L. Sink. In the network described in said co-pending application, first and second amplifiers are connected to the high and low current electrodes respectively, a potentiometer is connected across the first amplifier and the tap of the potentiometer is connected to the input resistor of the second amplifier. A servo system is connected to be operable responsive to the output of the second amplifier to adjust the tap of the potentiometer to the point where there is no output from the second amplifier. Recording means record the excursions of the potentiometer tap in maintaining the null balance.

In this system a signal is fed from the high current amplifier through the potentiometer to the input of the low current amplifier for the purpose of balancing the current fed to the low current amplifier from the low current collector. When there is any change in the relative abundance of the ion striking the two collectors, the balance in the system will be disturbed so that a signal appears at the output of the low current amplifier. This signal drives the servo system to adjust the potentiometer tap to return the system to a null condition.

It has now been found that pressure variation in the ion source may have an appreciable effect on the isotope ratio measurement independent of isotopic abundance. For example, if it is desired to continuously measure and record the concentration of deuterium in water samples, the ratio of deuterium to the sum of deuterium plus hydrogen is recorded. In practice the desired result is accomplished by measuring the ratios of m/e 19 to m/e 18 ion currents generated by ionization of the water sample in the ion source. The significant contribution to the m/e 19 ion current is HDO; the significant contribution to the m/e 18 ion current is H_2O.

As an undesirable by-product of the ionization of the water sample, H_3O ions are generated. These ions, which are termed "isobaric ions," have the same specific mass as do the HDO ions; therefore, in order to obtain a true indication of deuterium concentration, the contribution of these isobaric ions must be compensated for by some method. It has been found that the ion current produced by these isobaric ions is proportional to

the square of the partial pressure of water vapor within the ion source; the error introduced in the sensed ratio being therefore proportional to this partial pressure.

It has been proposed as a means of eliminating the error factor due to isobaric ions that the total inlet sample pressure ahead of the molecular leak into the ion source be maintained very nearly constant, as for example at 100 microns plus or minus 2½% and electrically subtract out the isobaric ion contribution to the desired ratio. This method has a number of disadvantages. Apparatus for maintaining total inlet pressure within the allowable tolerance is extremely expensive. The method contemplates only regulation of the total pressure. If there should be any significant quantities of impurities in the sample, the partial pressure of water vapor will vary with variations in impurity concentration, and since the isobaric ion contribution is a function of the partial pressure of the water vapor, error may be introduced independent of total pressure variation. Moreover, the error resulting from the presence of isobaric ions is, as mentioned above, proportional to water vapor pressure inside the ion source and rigorous control of the pressure on the downstream side of the sample leak will not necessarily result in equally rigorous control of the pressure within the ion source. It is quite possible that variations in leak rate may occur, as for example due to partial plugging of the extremely small leak orifice, or that pressure in the ion source may vary independently of sample pressure due to temperature fluctuations or other factors.

In accordance with the present invention we propose to sense variations in partial pressure of water within the ion source itself rather than by means of a separate external transducer, and to accomplish this sensing based on m/e 18 ions. The magnitude of the m/e 18 ion current as measured by the output voltage of the corresponding amplifier, is a function of various parameters, as follows:

(*a*) Directly proportional to the partial pressure of water vapor within the ionization region of the ion source;

(*b*) Directly proportional to the intensity of the ionizing electron beam;

(*c*) Directly proportional to the resistance of the input resistor of the respective amplifier;

(*d*) Directly proportional to the gain of this amplifier; and

(*e*) Some undetermined function of the relative potentials applied to the various electrodes in the ion source.

Under normal operating conditions, the last four of the above listed parameters will be held essentially constant over at least a 24 hour period so that magnitude of the m/e 18 ion current becomes dependent solely on the partial pressure of water vapor within the ionization chamber. As a result, variations in the output voltage of the high current amplifier will be an accurate measure of variations in the partial pressure of water vapor within the ionizing region of the ion source.

The present invention contemplates utilization of the variation in output voltage of the amplifier connected to the high current collector, i. e. the collector on which the m/e 18 ions are discharged to apply a compensating factor to the ratio measurement of the null balance network. This method is applicable to eliminate error due to isobaric ions when the ratio between the isotopes to be measured is extremely large, as for

example where the total concentration of HDO in the water is 0.1% or less. When relative concentration of HDO and H_2O is less than $\frac{1}{10}$ of 1%, a significant change in HDO concentration does not appreciably vary the H_2O concentration so that for all practical purposes any change in partial pressure of water vapor will not be as a result of change in concentration of H_2O but will be due to fluctuations in inlet pressure or the variations in impurities in the sample. As a result, any variation in the H_2O partial pressure, as reflected in variation in the output of the high current amplifier, will be reflected in variation of the abundance of isobaric ions, and the total variation in the amplifier output may be used to determine the applied correction factor.

The invention therefore contemplates in mass spectrometry wherein isotope ratios are determined by ionizing a sample, segregating ions of the isotopes to be determined, separately discharging the ions of these isotopes and determining the ratio of the discharge currents thereby produced, the improvement which comprises separately sensing variations in one of the discharge currents and varying the determined ratio in proportion to such variation.

In another aspect the invention contemplates in an isotope ratio mass spectrometer having dual ion collectors and electrical means for determining the ratio of discharge currents developed at the collectors, the combination comprising means operable responsive to variation in the discharge current at one of the collectors to vary the ratio in proportion to such variation.

Several means may be employed to introduce the compensating factor to the null balance network. The simplest of these means comprises manual adjustment of a compensating resistor in proportion to variation of the output of the high current amplifier. This means is relatively unsatisfactory, particularly where continuous analysis is sought. In preferred practice compensation is carried out automatically, as for example by means of a servo system operative responsive to the variations in output of the high current amplifier to vary the setting of a compensating resistor in the null balance network or by means of an electronic amplifier connected to feed an auxiliary current through a fixed resistance located in the null balance network, the magnitude of this auxiliary current being proportional to the difference between the high current amplifier output voltage and a reference voltage.

The invention will be more clearly understood by reference to the following detailed description thereof taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a diagrammatic illustration of one type of mass spectrometer;

Fig. 2 is a circuit diagram of one embodiment of the invention, and

Fig. 3 is a circuit diagram of a second embodiment of the invention.

The conventional 180° magnetic analyzer mass spectrometer shown diagrammatically in Fig. 1 has an ion source 11, an analyzer tube 12 and a pair of ion collectors 13, 13A, all disposed within an envelope 14. Analyzer tube 12 is provided at the end adjacent the ion collectors 13, 13A with so-called resolving or exit slits 15, 15A, respectively, through which the ion beams are focused on the respective collectors. An electron gun (not shown) develops an electron beam 16 which is projected through the ion source between a pusher electrode 17 or a pair of pusher or re-

peller electrodes and a first accelerator electrode 18. The first accelerator electrode 18 and a second accelerator 20 spaced therefrom are provided respectively with a first slit 18A and a second slit 20A through which ions formed by the beam 16 are collimated and propelled into the analyzer tube 12.

The spectrometer is provided with an envelope exhaust line 24 which may be connected to a mercury diffusion pump, molecular pump or any appropriate evacuating system (not shown). The analyzer tube may be provided with ports 25 by means of which the ion source and the analyzer tube are evacuated through the envelope. Alternatively, the envelope may be omitted by making the analyzer tube 12 gas-tight and attaching the evacuating system to it by means which are well known in the art.

An inlet line 26 provides means for introducing the sample to be analyzed either continuously or intermittently into the ion source 11. The ions formed in the source are propelled therefrom as a heterogeneous beam into the analyzer tube 12. In the analyzer tube the heterogeneous beam is segregated into diverging ion beams, each beam being composed of ions of a given specific mass, the ion segregation being brought about by means of an electrical or magnetic field established across the tube transverse to the direction of ion travel. Means for obtaining such a transverse field are well known and form no part of the present invention and may comprise magnet pole pieces (not shown) disposed adjacent opposite walls of the tube. The diverging ion beams are focused on the ion collectors 13, 13A through the exit slits 15, 15A by adjusting the potential applied to the accelerating electrodes 17, 18. In the specific example considered, HDO ions as well as any isobaric ions formed in the system will be focused through the exit slit 15A to fall on collector 13A, and H_2O ions will be focused through exit slit 15 to strike the collector 13. The ions of the heaviest mass assume paths of travel of the greatest radii. The collector electrodes 13, 13A are connected to an amplification and recording system (not shown in Fig. 1), by leads 28, 28A, respectively, sealed through the tube 14.

The mass spectrometer illustrated in Fig. 1 is only one of many conventional types. The invention is directed to improvements in mass spectrometers of any type capable of measuring the relative abundance of isotopes in a sample. In accordance with the invention, the leads 28, 28A are connected to an amplification and recording system of the type shown in Figs. 2 or 3.

Referring to Fig. 2, the high current collector 13, this being the collector on which the more abundant H_2O ions are discharged, is connected to a feed-back type D. C. amplifier 30. The feedback system of the amplifier is shown diagrammatically only and includes a lead 31 connecting output lead 32 with the input lead 28 through an input grid resistor 33. The low current collector 13A is connected by lead 28A to a D. C. amplifier 36 provided with a zero set adjustment 37. The output lead 32 of the high current amplifier 30 is connected to one end of a voltage dividing network 40 including resistors 41, 42 and a tapped-off resistor 43 serially connected between the lead 32 and ground. A slidewire potentiometer 44 is connected to the voltage dividing network 40 across the resistor 42. The tap 44A of the potentiometer 44 is connected by a lead 48 to the input lead 28A of amplifier 36 through an input grid resistor 46. The output side of the amplifier 36 is connected to drive a servo system

50 which in turn is connected to control the position of the tap 44A along the slidewire potentiometer 44. A recorder 52 is ganged to the system to record the excursions of the potentiometer tap 44A. To this extent, and with the exception of the arrangement of the voltage dividing network 40, the system is substantially the same as that described in the prior art for this purpose.

Before the ion current is turned on, i. e. before the current is being delivered from the collector electrodes to the amplifiers, amplifier 36 is adjusted for zero output by means of the zero set control 37. In the circuit as illustrated, it should be pointed out that zero balance results in the pen moving at zero rate regardless of position.

With amplifier 36 balanced, the ion current is turned on and the circuit automatically adjusts itself to indicate the correct isotope ratio. The signal applied to amplifier 30 from collector 13 is applied to the voltage divider network 40 without voltage amplification, since amplifier 30 is a feed-back amplifier having a unity gain. After the magnitude of the output signal from amplifier 30 is adjusted in the voltage divider 40 it is applied across the potentiometer 44. A portion of this signal is tapped-off by tap 44A and applied through grid resistor 46 to the input of amplifier 36. When the signal tapped off the potentiometer 44 and applied to the input of the amplifier 36 exactly balances the signal from the low current collector 13A, the output of the amplifier 36 will be at zero level. There will then be no signal applied to the servo system 50, and the tap 44A will remain at a fixed position. When the ion current at 13A varies, the resultant unbalance output of amplifier 36 will actuate the servo system to vary the settling of tap 44A to rebalance the network.

In accordance with one embodiment of the present invention, as shown in Fig. 2, a servo system is connected to the output lead 32 of the high current amplifier 30 to adjust the position of the tap 43A on the resistor 43 in the voltage dividing circuit 40 in proportion to the variations in the amplifier output. This system includes a servo amplifier 54 into which the output of amplifier 30 and a reference voltage signal are fed. The reference voltage is derived from a voltage source 55 connected across a slidewire potentiometer 56, a fraction of the voltage across the potentiometer 56 being tapped therefrom and fed to the servo amplifier 54. The amplifier is so constructed as to amplify only the difference between the output voltage of the high current amplifier and the reference voltage, the amplified difference being applied to drive a servo motor 58, which is connected to adjust the positions of tap 43A, along resistance 43 and tap 56A of the poteniometer 56. The effect of the variation of resistance between resistor 42 and ground in the voltage divider network 40, such variation being brought about by variation in the portion of the resistor 43 tapped-off by the tap 43A, is to shift the potential of the X-end of the potentiometer 44 with respect to ground, i. e. to vary the potentiometer to ground potential. If the error factor was of any appreciable magnitude, a second variable or compensating resistor would have to be located between the resistor 41 and the potentiometer 44 to avoid a change in voltage across the potentiometer. Since the error factor is small as compared to the voltage across the potentiometer 44, the additional compensating resistor can be eliminated and for all practical purposes the effect of the adjustment of resistor 43 is to shift the potentiometer to ground potential without

varying the voltage across the potentiometer. In other words, the voltage change across the slidewire 44 is negligible, the important result of the compensating network being to vary the voltage at the X-end of the potentiometer with respect to ground.

As fully described above, the effect of introducing this compensating function into the ratio-measuring network is to balance out any spurious variation in ratios brought about by fluctuation in the partial pressure of water vapor in the ion source, which fluctuation causes a proportional variation in the presence of objectionable isobaric ions.

Another means for accomplishing the same end result is shown in Fig. 3. The circuit shown in Fig. 3 is, in many respects, identical to that shown in Fig. 2, including the amplifiers 30, 36, feed-back loop 31 through grid resistor 33 to the amplifier 30 and the feed-back loop 46 from potentiometer tap 44A and through grid resistor 43 to the input of the amplifier 36. The output 32 of the amplifier is again connected to one end of a voltage dividing network 40 including resistances 41, 42 and 43 serially connected between the output lead 32 of the amplifier 30 and ground and a slidewire potentiometer 44 connected across the resistor 42. In this embodiment, a compensating function is applied to the ratio-measuring system by means of a direct current electronic amplifier network including a comparator tube 60 and a cathode follower 62. In the comparator tube 60 a signal is developed in the plate circuit proportional to the difference between a reference signal derived from a voltage source 64 and a fraction of the output signal of the amplifier 30 as tapped-off a slidewire 66. The two signals are applied to the grids of the comparator tube 60 and the unbalance signal, if any, is applied to the grid of the cathode follower 62. With this system, when the output of the high current amplifier varies so that there is an unbalance in the signals applied to the grid 60, a current is introduced to the voltage divider network 40 at the point Y between the resistors 42 and 43 so as to vary the voltage drop across the network and shift the potential across the potentiometer 44 with respect to ground. As in the system of Fig. 2, this shift is accomplished without significant change in the voltage across the potentiometer, the current flow upwardly in the voltage divider from the point of introduction at Y being negligible in comparison with that flowing through resistor 43 to ground.

The functioning of the system of Fig. 3 is substantially identical with that of the system of Fig. 2, the net result being to cancel out any error introduced by fluctuations in partial pressure of water vapor in the ion source.

The invention has been described particularly with reference to the analysis of HDO–H_2O ratios but is equally applicable to any isotopic ratio-measurement in which the problem of isobaric ions is encountered. As an additional example of the existence of this problem is the analysis of the ratio of H_2–HD isotopes, wherein H_3 is present as an isobaric ion to an extent sensible to variations in partial pressure of H_2 in the ion source.

We claim:

1. In an isotope ratio mass spectrometer having dual ion collectors and electrical means for determining the ratio of the discharge currents developed at the collectors, the combination comprising means operable responsive to variation in the discharge current at one of said collectors to vary the indicated ratio in proportion to said variation.

2. In an isotope ratio mass spectrometer having dual ion collectors and electrical means for determining the ratio of the discharge currents developed at the collectors, the combination comprising means operable responsive to variation in the discharge current at the one of said collectors on which the more abundant isotope is discharged to vary the indicated ratio in proportion to said variation.

3. In a mass spectrometer comprising two collector electrodes, a first amplifier connected to one of the electrodes, a second amplifier connected to the other of the electrodes, a potentiometer connected between the first amplifier and ground, the tap of the potentiometer being connected to the input resistor of the second amplifier, and means operable responsive to output of the second amplifier to adjust the position of the potentiometer tap to drive the second amplifier to a null output, the improvement comprising means operable responsive to variation in the output of the first amplifier to apply a signal between the potentiometer and ground proportional to such variation.

4. In a mass spectrometer comprising two collector electrodes, a first amplifier connected to one of the electrodes, a second amplifier connected to the other of the electrodes, a potentiometer connected between the first amplifier and ground, the tap of the potentiometer being connected to the input resistor of the second amplifier and means operable responsive to the output of the second amplifier to adjust the position of the potentiometer tap, the improvement comprising means operable responsive to variation in the output of the first amplifier to vary the potentiometer to ground potential and proportional to said variation in the first amplifier output.

5. Apparatus according to claim 4 wherein said means for varying the potentiometer to ground potential comprises a variable resistor connected between the potentiometer and ground and means for varying the value of the resistor in proportion to variation in the output of the first amplifier.

6. Apparatus according to claim 4 wherein said means for varying the potentiometer to ground potential comprises a variable resistor connected between the potentiometer and ground, a servo amplifier connected to the output of said first amplifier in parallel with the potentiometer, a source of reference voltage connected to said servo amplifier whereby the output of the servo amplifier is proportional to the algebraic sum of said reference voltage and first amplifier output, and a servo motor operable responsive to output of said servo amplifier to vary said variable resistance and the reference voltage.

7. Apparatus according to claim 4 wherein said means for varying the potentiometer to ground potential comprises a fixed resistance connected serially between the potentiometer and ground and a direct current amplifier connected to the output of the first amplifier in parallel with said potentiometer, a source of reference voltage connected to the direct current amplifier so that the output thereof is proportional to the algebraic sum of the reference voltage and the output of the first amplifier, and means for feeding an additional current through the fixed resistor and proportional to the output of the direct current amplifier.

8. In a mass spectrometer having two ion col-

lector electrodes, a first amplifier having its input circuit connected to one of the electrodes, a second amplifier having its input circuit connected to the other electrode, and means coupled to the output circuits of the two amplifiers for providing a comparison of the relative magnitudes of the discharge currents developed at the two collectors, the improvement which comprises means in addition to the comparison means coupled to the output circuit of the first amplifier and responsive to variations in its output signal for varying the amplification of the second amplifier.

9. In a mass spectrometer having two ion collector electrodes, a first amplifier having its input circuit connected to one of the electrodes, a second amplifier having its input circuit connected to the other electrode, a voltage divider connected across the output circuit of the first amplifier, an adjustable tap on the voltage divider coupled to the second amplifier for controlling its amplification, and means coupled to the output of the second amplifier for controlling the position of said adjustable tap to cause the output of the second amplifier to be substantially zero, the improvement which comprises means coupled between the output circuit of the first amplifier and the voltage divider for varying the potential at the tap on the voltage divider in accordance with variations in the output signal of the first amplifier.

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