

May 5, 1970

L. WOOD

3,510,647

AUTOMATIC SENSITIVITY CONTROL FOR A MASS SPECTROMETER

Filed Sept. 5, 1967

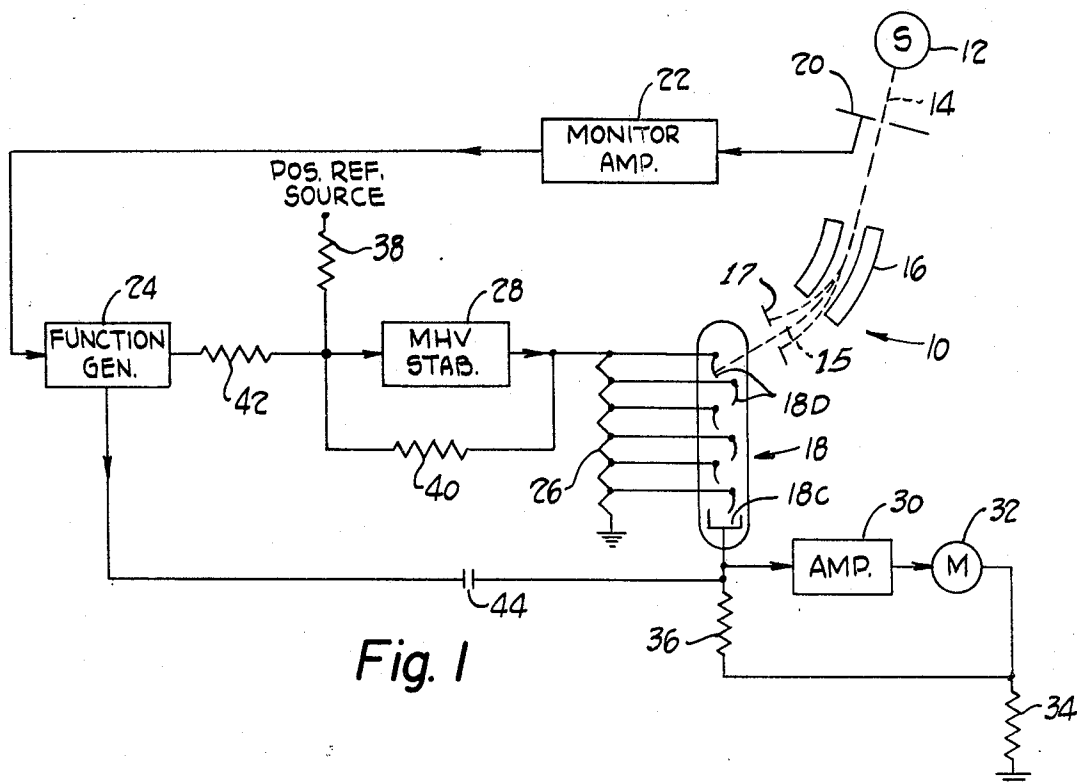


Fig. 1

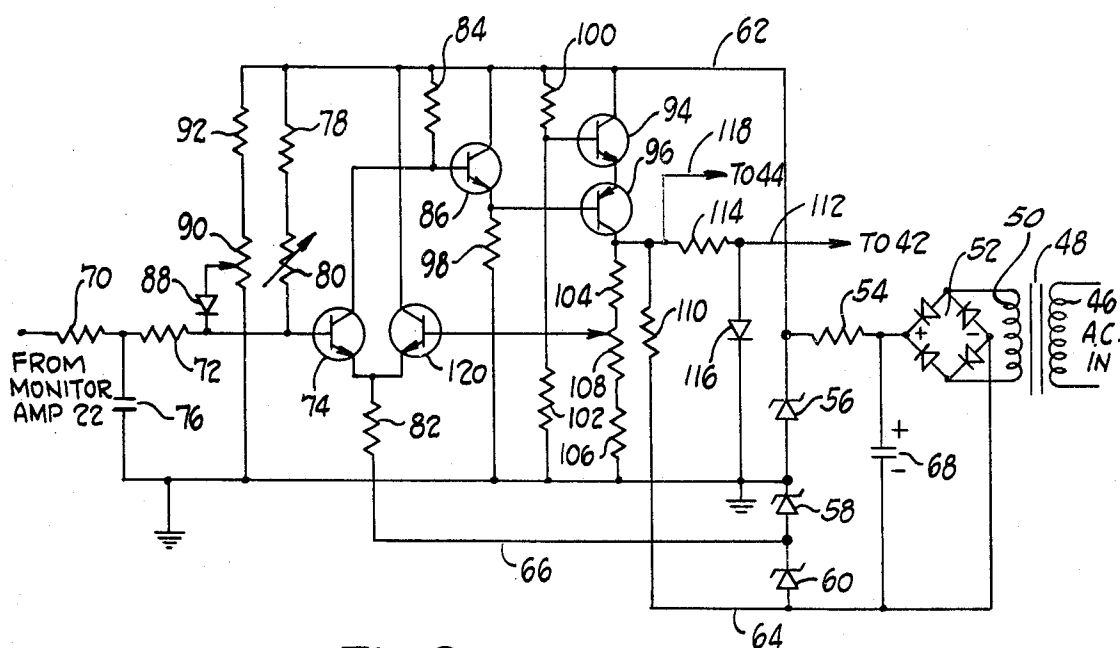


Fig. 2

INVENTOR.
LESLIE WOOD
BY *Watts, Hoffmann,
Fisher & Heinke*
ATTORNEYS.

1

2

3,510,647

AUTOMATIC SENSITIVITY CONTROL FOR A MASS SPECTROMETER

Leslie Wood, Manchester, England, assignor to Associated Electrical Industries Limited, London, England, a British company

Filed Sept. 5, 1967, Ser. No. 665,403

Claims priority, application Great Britain, Sept. 6, 1966, 39,818/66

Int. Cl. H01j 39/34

U.S. Cl. 250—41.9

17 Claims

ABSTRACT OF THE DISCLOSURE

A monitor collector positioned between a source and an analyzer of a mass spectrometer collects a constant fraction of the total ion beam from the source. The separated ion beams are amplified by an electron multiplier, whose gain is varied as a function of monitor collector current.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to mass spectrometers and, more particularly, to means for automatically controlling the overall sensitivity of a mass spectrometer to compensate for changes in source sensitivity and sample flow rate.

Description of the prior art

In mass spectrometry, a sample is ionized and then the produced ions are propelled as a beam along an evacuated ion beam tube. In a so-called "double focusing" instrument, the ions of the beam are deflected by both electrostatic and magnetic analyzers. Certain or focused ones of the ions pass through a resolving slit onto a collector. As used herein, the term "analyzer" means a magnetic analyzer as used in a "single focusing" instrument, or both an electrostatic analyzer and a magnetic analyzer, as used in a "double focusing" spectrometer.

The amount a given ion is deflected by an analyzer a function of its characteristic mass and electrical charge, its mass/charge ratio. The identity of an ion striking a collector at any given time can be determined because, with a given accelerating voltage for propelling the ion beam and known analyzer conditions, only ions of a certain mass/charge ratio are focused onto the collector.

In mass spectrometer operation it is common to "scan." Most commonly, this is accomplished by varying the energy applied to the magnetic analyzer so as to deflect differing ones of the ions comprising an ion beam onto a collector as the analyzer is scanned. This provides a spectrum of the components of the ion beam.

One of the present day methods of analyzing complex chemical mixtures is first to separate or partially separate the components by means of a vapor phase chromatograph, and then to identify the components by means of a mass spectrometer. The components emerging from the chromatograph may be collected and admitted in turn to the mass spectrometer or the two instruments may be directly coupled, so that the separate components emerging from the chromatograph pass immediately to the spectrometer inlet. The second method is preferred, because it is faster and minimizes manual handling of samples.

This preferred method presents two problems in mass spectrometry:

(a) It is necessary to scan the mass spectrum during a time when an emergent pulse of gas is emitted by the chromatograph. Since the scan may occupy an appreciable fraction of the pulse duration, the inlet pressure

to the mass spectrometer will be continually changing during the scan. This change in inlet pressure causes a distorted mass spectrum.

(b) In order to produce a spectrum in a very short time, as required for microcolumns, it is often necessary to use voltage scanning, that is, scanning of the ion accelerating voltage, instead of magnetic scanning. Voltage scanning also distorts the spectrum, because source sensitivity changes with ion accelerating voltage.

Both of these defects can be considerably reduced by the application of automatic sensitivity control to the mass spectrometer, in accordance with the present invention.

SUMMARY OF THE INVENTION

A monitor collector situated between the source and analyzer of the mass spectrometer collects a constant fraction of the total ion beam emerging from the source. The monitor collector current is thus a measure of both source sensitivity and inlet gas pressure. The separated ion beams from the analyzer or analyzers of the mass spectrometer are collected and amplified by means of an electron multiplier, the gain of which, being a function of the high voltage (HV) applied to it, is controlled by controlling the multiplier high voltage (MHV) as a function of the monitor collector current. Electron multiplier gain is not a linear function of MHV, but if the output from the monitor, or from an amplifier following it, is passed through an appropriate function generator, it can be used to control the multiplier HV in such a way that the overall sensitivity of the measuring system of the spectrometer is substantially independent of both source sensitivity and sample flow rate over a wide range.

Since there is a high capacitance between the dynodes and collector of an electron multiplier, a continuously-changing MHV will tend to create a direct current (D.C.) signal in an amplifier following the multiplier. This effect can be overcome by applying the output of the function generator to the multiplier collector through a suitable capacitor having a very high leakage resistance. This creates a D.C. signal which is equal and opposite to the unwanted signal, which is therefore neutralized.

Assuming for simplicity that multiplier gain versus multiplier high voltage is a true exponential, then $G = e^{K_1 V_m}$ where G is the gain, V_m is the MHV and K_1 is a constant.

Monitor amplifier current (I) is a measure of the combined effects of sample gas pressure and source sensitivity. For constant sensitivity the product IG must be a constant (K_2).

$$\therefore I e^{K_1 V_m} = K_2$$

or

$$\begin{aligned} K_1 V_m &= \log \frac{K_2}{I} \\ &= \log K_2 - \log I \end{aligned}$$

Hence

$$V_m = K_3 - \frac{\log I}{K_1}$$

where

$$K_3 = \frac{\log K_2}{K_1}$$

This last equation implies that the electron multiplier high voltage becomes infinite at zero monitor collector current, which is clearly impracticable. However, initial conditions can be selected such that the multiplier HV is preset to a desired maximum value for monitor currents between zero and some predetermined value, such as 1% of maximum, after which the multiplier HV falls

as monitor collector current rises according to the foregoing equation. Thus, when $I=1\%$ max.

$$\frac{\log I}{K_1} = 0$$

so V_m and hence electron multiplier gain have their maximum value. K_3 then represents the MHV which gives this multiplier gain, and the gain is reduced in the desired manner by subtracting from K_3 a voltage proportional to the log of the monitor current.

If the monitor current is passed through a high value resistor and the resultant voltage is amplified by means of an amplifier, the output of this amplifier is then a voltage which is proportional to the combined effects of both source sensitivity and inlet sample pressure. The output voltage is then fed to a function generator which, in its simplest form, gives an output voltage which is proportional to the log of the input. However, since $\log 0 = -\infty$, a log output can have no true zero. The function generator is accordingly designed so that it does not respond to the first fraction of the input—say the first 1%—but the output is proportional to the log of the input over the remainder of the input range. Thus, in the case quoted, the output would be logarithmic over 2 decades.

If the particular design of electron multiplier used has a gain versus MHV characteristic which is closely exponential over 2 or 3 decades, and if the MHV is obtained in the usual manner from a voltage stabilizer in which the MHV is proportional to a reference voltage, it follows that the multiplier gain is proportional to the exponential of the reference voltage. The output of the function generator is then caused to modify the reference voltage in such a way that the product of the monitor amplifier output and the multiplier gain is constant, which gives the desired result.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a combined schematic and block diagram of a mass spectrometer embodying the invention; and

FIG. 2 is a circuit diagram of a function generator utilized in the embodiment of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in FIG. 1, a mass spectrometer indicated generally by the numeral 10 includes an ion source 12 for providing a positive ion beam 14 to a magnetic analyzer 16 in which the ions are separated according to their mass/charge ratios into individual ion beams such as 15 which pass individually through a slit 17 to an electron multiplier indicated generally by the numeral 18. The mass spectrometer thus far described is conventional and of a type known in the art.

The mass spectrometer 10 is also provided with a monitor collector 20 located between the ion source 12 and the magnetic analyzer 16. The monitor collector 20 collects a constant fraction of the total ion beam 14 emerging from source 12. The current through the monitor collector 20 is thus a measure of both the source sensitivity or accelerating voltage and the inlet sample gas pressure. The current through the monitor collector 20 is amplified by a monitor amplifier 22 and provided as a negative-going signal to a function generator 24. The monitor amplifier 22 is conventional in design and is understood to include any dynamic electronic system for amplifying very small currents. Thus, it may be a direct-coupled amplifier using a very high value of input resistance, or it may be a vibrating reed amplifier in which the input current is converted to an alternating current by means of a vibrating reed capacitor before amplification. In either case, the active elements of the amplifier may be electron tubes or transistors. Such basic types of very small current amplifiers are well known in the art.

The function generator 24, which will be described with reference to FIG. 2, essentially converts a negative-going input signal from the monitor amplifier 22 into a negative-going output signal, which is proportional to a logarithm of the input signal.

The electron multiplier 18 includes a plurality of dynodes 18D and a collector 18C. Multiplier high voltage (MHV) is applied to the dynodes from taps on a voltage divider resistor 26 connected between the output of an MHV stabilizer 28 and ground. The dynode on which the ion beam 15 impinges is at the most negative potential of all the dynodes, which are at progressively decreasing negative potentials as they approach the collector 18C. This is necessary because the output of the electron multiplier 18 must be near ground potential to simplify feeding an amplifier 30 connected to the collector 18C. The amplifier 30, which is similar to the monitor amplifier 22 previously described has a high value input resistor 36 and output resistor 34 with negative feedback to resistor 36. The output may be read on meter 32 or on a recorder (not shown) driven from the amplifier.

The MHV stabilizer 28 is a conventional, well known device in which the output voltage is strictly proportional to a given reference input voltage. The output voltage is capable of varying over a wide range, if the reference voltage is varied. In the present case, a positive primary reference potential is provided from a source (not shown) through an adding resistor 38 to the input of the MHV stabilizer 28. A constant fraction of the MHV is compared with the reference potential by means of the resistor 38 and a second adding resistor 40 connected across the MHV stabilizer 28. The resulting error signal is amplified and used to control the MHV in such a way that it is proportional to the primary reference voltage. This technique is well known in the art. The output of the function generator 24 is also provided through a third adding resistor 42 as an input to the MHV stabilizer 28.

The function generator 24, taking its input from the monitor amplifier 22, is designed in such a way that when the monitor amplifier output is less than 1% of its maximum value, the output of the function generator is zero. When the monitor amplifier output is at its maximum value, the function generator output is equal to $\frac{1}{4}$ of the primary reference voltage, but is opposite in polarity. If the adding resistor 42 is half the value of the adding resistor 38, the effect is to make the effective reference voltage half the primary reference voltage. Under these conditions, the MHV is halved and the multiplier gain falls two decades from the previously selected maximum gain.

Since the MHV is negative, a reduction in it is a positive-going voltage. Thus, the inherent capacitance existing between the electron multiplier dynodes 18D and the collector 18C feeding the amplifier 30 places a positive voltage on the amplifier input which is proportional to the rate of change of the MHV. However, in order to produce a reduction in MHV, the output of the function generator 24 must be negative-going. If then, the output of the function generator is fed to the input of the amplifier 30 through a capacitor 44, it will produce a negative voltage at the input of the amplifier 30, which is proportional to the rate of change of the function generator output voltage and also to the capacitance of the capacitor 44. By suitable choice of the value of the capacitor 44, the two induced voltages present at the input of the amplifier 30 may be made to cancel each other.

The function generator 24, which is shown schematically in FIG. 2, is only one of a number of devices embodying various forms of logarithmic circuitry that may be utilized. Such devices are generally quite well known in the art, and the function generator shown in FIG. 2

is exemplary only. The particular device shown takes advantage of a property of many semi-conductor diodes that the voltage drop across the diode is closely proportional to the logarithm of the current flowing through the diode over a wide range of values.

As shown, power for the function generator 24 is provided from an alternating current source (not shown), which is connected to a primary winding 46 of a transformer 48. A secondary winding 50 of the transformer 48 is connected to opposing input terminals of a full wave bridge rectifier 52. A positive output terminal of the rectifier 52 is connected to a negative terminal of the rectifier through a series combination of a resistor 54 and Zener diodes 56, 58, 60. Positive potential is supplied to the elements of the generator on a line 62 connected to the juncture of the resistor 54 and the diode 56. The juncture of the diodes 56, 58 is connected to ground, a maximum negative potential is supplied on a line 64 from a negative output terminal of the rectifier 52, and an intermediate negative potential is supplied from the juncture of the diodes 58, 60 on a line 66. A capacitor 68 connected across the output terminals of the rectifier 52 serves to smooth the output voltage of the rectifier.

The negative-going input signal from the monitor amplifier 22 is provided through series-connected resistors 70, 72 to the base of an NPN transistor 74. The juncture of the resistors 70, 72 is connected to ground through a capacitor 76. Base bias is provided for the transistor 74 through a series-connected resistor 78 and a variable resistor 80 connected between the transistor base and the positive potential line 62. The emitter of the transistor 74 is connected through a resistor 82 to the intermediate potential line 66. The collector of the transistor 74 is connected to the positive potential line 62 through a resistor 84, and is also connected directly to the base of an NPN transistor 86.

The base of the transistor 74 is also connected to the cathode of a diode 88. The anode of the diode 88 is connected to the movable arm of a potentiometer 90, which is connected in series with a fixed resistor 92 between the positive potential line 62 and ground.

The diode 88 is of the logarithmic response type previously described, wherein the voltage drop across the diode is closely proportional to the logarithm to the current flowing through the diode. When a negative input signal is applied from the monitor amplifier 22, current flows from the positive potential line 62 through the resistor 92, the potentiometer 90, the diode 88 and the resistors 70, 72. The value of that current is determined almost entirely by the resistors 70, 72, so that the current through the diode is closely proportional to the input voltage from the monitor amplifier. Thus, the voltage drop across the diode 88 is closely proportional to the logarithm of the input voltage. When the input voltage has a predetermined minimum value, 1% of the maximum value as previously noted, the voltage drop across the diode is "backed off" by adjusting the movable arm of the potentiometer 90, so that there is no signal input to the base of the transistor 74. For any larger (more negative) input voltage up to the maximum value acceptable by the circuit, the voltage developed across the diode 88 is amplified by the circuit comprising the NPN transistor 74, an NPN transistor 86 and a PNP transistor 96.

The collector of the transistor 86 is connected directly to the positive potential line 62. The emitter of that transistor is connected directly to the base of the transistor 96, and through a resistor 98 to the ground. An NPN transistor 94 is connected in series with the transistor 96, with the collector of the transistor 94 being connected directly to the positive potential line 62 and its emitter being connected directly to the emitter of the transistor 96. The transistor 94, in conjunction with resistors 100, 102 connected in series between the line 62 and ground, the base of the transistor 94 being con-

nected to the juncture of those two resistors, provides the correct D.C. level for the emitter of transistor 96. The output signal of the function generator is developed across resistance 104, 106 and a potentiometer 108 connected in series between the collector of the transistor 96 and ground. The collector of the transistor 96 is also connected through a resistor 110 to the maximum negative potential line 64 and, through a resistor 114, to an output line 112. The output line 112 is connected to ground through a diode 116. Output is also provided on a line 118 connected directly to the collector of the transistor 96. The output line 112 is connected to the capacitor 44, both of which were referred to in connection with the description of FIG. 1.

The collector of the transistor 120 is connected directly to the positive potential line 62 and its emitter is connected directly to the emitter of the transistor 74 and hence to the intermediate negative potential line 66 through the resistor 82. The base of the transistor 120 is connected to the movable arm of the potentiometer 108. Thus, a fixed fraction of the output signal, selected by the position of the arm of the potentiometer 108, is fed back to the amplifier circuitry so that the overall voltage gain is substantially independent of transistor characteristics and can be set to suit the parameters of the particular electron multiplier utilized and its power supply.

In operation, the variable resistor 80 is set to provide the necessary base current to the transistor 74 so that this current does not flow through the diode 88. The diode 116 connected between the output line 112 and ground serves to hold the output of the function generator at zero when the input to the function generator is less than the predetermined minimum value previously noted. In summary, it is noted that as the voltage drop across the diode 88 varies logarithmically with respect to the current flowing through the diode, the output voltages provided on the lines 112 and 118 also vary logarithmically with respect to the input voltage from the monitor amplifier 22. It is again pointed out that the invention is in no way limited to the use of the particular function generator shown in FIG. 2, and that other devices which operate in essentially the same manner may well be utilized.

Although a preferred embodiment of the invention has been shown and described, it is apparent that many changes and modifications may be made by one skilled in the art without departing from the true spirit and scope of the invention.

I claim:

1. In a mass spectrometer having a source for emitting an ion beam and an analyzer for separating said ion beam into a plurality of separated ion beams, the improvement comprising:

- (a) a monitor collector for collecting a constant fraction of said ion beam to provide monitor collector current;
- (b) an electron multiplier for collecting and amplifying said separated ion beams and having a variable gain;
- (c) a source of high voltage for said electron multiplier; and
- (d) control means connected in circuit with said source of high voltage and said monitor collector for varying said high voltage to maintain substantially constant a product of said monitor collector current and said electron multiplier gain.

2. The improvement of claim 1, wherein said control means comprises function generator means for providing an output signal that varies as a logarithmic function of an input signal.

3. The improvement of claim 2, wherein said function generator means includes in its input circuitry semi-conductor means current through which produces a voltage drop that is substantially proportional to the logarithm of said current.

4. The improvement of claim 1, wherein said source of high voltage comprises stabilizer means for providing a high voltage output that is proportional to a reference voltage input.

5. The improvement of claim 1, wherein said source of high voltage comprises stabilizer means for providing a high voltage output that is proportional to a reference voltage input, and said control means comprises function generator means for providing an output signal that varies as a logarithmic function of an input signal, said output signal being provided to said stabilizer means to modify said reference voltage input.

6. The improvement of claim 5, wherein said function generator means includes in its input circuitry semiconductor means current through which produces a voltage drop that is substantially proportional to the logarithm of said current.

7. The improvement of claim 1, further including means in circuit with said control means and with said electron multiplier to neutralize any unwanted output signal from said electron multiplier resulting from varying said high voltage.

8. The improvement of claim 1, wherein said high voltage is negative.

9. The improvement of claim 8, wherein said electron multiplier collector is substantially at ground potential in the absence of said multiplier output signal.

10. In a mass spectrometer having a source for emitting an ion beam and an analyzer for separating said ion beam into a plurality of separated ion beams, the improvement comprising:

- (a) a monitor collector for collecting a constant fraction of said ion beam to provide monitor collector current;
- (b) an electron multiplier for collecting and amplifying said separated ion beams and having a variable gain, said multiplier having a plurality of dynodes and a collector for providing a multiplier output signal;
- (c) a source of high voltage for supplying high voltage to said dynodes;
- (d) first amplifier means connected to said electron multiplier collector for amplifying said multiplier output signal;
- (e) second amplifier means connected to receive said monitor collector current and provide a monitor output signal proportional in amplitude to said monitor collector current; and
- (f) function generator means connected to receive said monitor output signal and provide a control signal to said source of high voltage to vary said high

voltage supplied to said dynodes to maintain substantially constant a product of said monitor collector current and said electron multiplier gain.

11. The improvement of claim 10, wherein said control signal from said function generator means varies as a logarithm of said monitor output signal.

12. The improvement of claim 11, wherein said function generator means includes in its input circuitry semiconductor means current through which produces a voltage drop that is substantially proportional to the logarithm of said current.

13. The improvement of claim 10, wherein said source of high voltage comprises stabilizer means for providing a high voltage output for said dynodes that is proportional to a reference voltage input, and said control signal from said function generator means varies as a logarithmic function of said monitor output signal, said control signal being provided to said stabilizer means to modify said reference voltage input.

14. The improvement of claim 13, wherein said function generator means includes in its input circuitry semiconductor means current through which produces a voltage drop that is substantially proportional to the logarithm of said current.

15. The improvement of claim 10, wherein said source of high voltage comprises stabilizer means for providing a high voltage output for said dynodes that is proportional to a reference voltage input.

16. The improvement of claim 10, further including means in circuit with said function generator means and with said electron multiplier to neutralize any unwanted output signal from said electron multiplier resulting from varying said high voltage.

17. The improvement of claim 10, wherein said function generator means includes in its input circuitry semiconductor means current through which produces a voltage drop that is substantially proportional to the logarithm of said current.

References Cited

UNITED STATES PATENTS

2,565,265	8/1951	Peterson	-----	250—207
2,659,821	11/1953	Hipple.		
2,854,583	9/1958	Robinson.		

RALPH G. NILSON, Primary Examiner

A. L. BIRCH, Assistant Examiner

U.S. Cl. X.R.

250—207

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,510,647

Dated May 5, 1970

Inventor(s) Leslie Wood

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 18, "multiplifier" should be --multiplier--;
line 41, after "analyzer" and before "a" insert
--is--;
line 54, "thet" should be --the--;
line 55, "sepaarte" should be --separate--;
line 56, "sepaarte" should be --separate--.

Col. 2, line 21 "collectetd" should be --collected--.

SIGNED AND
SEALED
SEP 8 - 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents