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Martin

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[54] APPARATUS FOR STABILIZING COMPONENT ELUTION TIMES IN GAS CHROMATOGRAPHS

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[52] **U.S. Cl.** **73/23.1**

[51] **Int. Cl.** **G01n 31/08**

[58] **Field of Search** ..... 73/23.1; 23/232 C

[56] **References Cited**

UNITED STATES PATENTS

3,245,269	4/1966	Ivie	73/23.1 X
3,267,264	8/1966	Burk et al.	73/23.1 X
3,069,895	12/1962	Burk	73/23.1

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[57] **ABSTRACT**

A peak stabilizer in accordance with this invention controls the peak retention time during an analysis, by gas chromatograph, for example, so that this time will be the same for all determinations. This allows a peak to be gated or picked for process control or read-out without the undesirable possibility that it would drift beyond the time limits of the gate. If a peak in the chromatogram, for example, is sampled on the leading and trailing slopes at predetermined times, a comparison of these voltages will indicate if the peak is early, late or at its right time. The carrier gas flow or other rate control parameter may be automatically changed to bring the peak back to the proper retention time.

3 Claims, 2 Drawing Figures

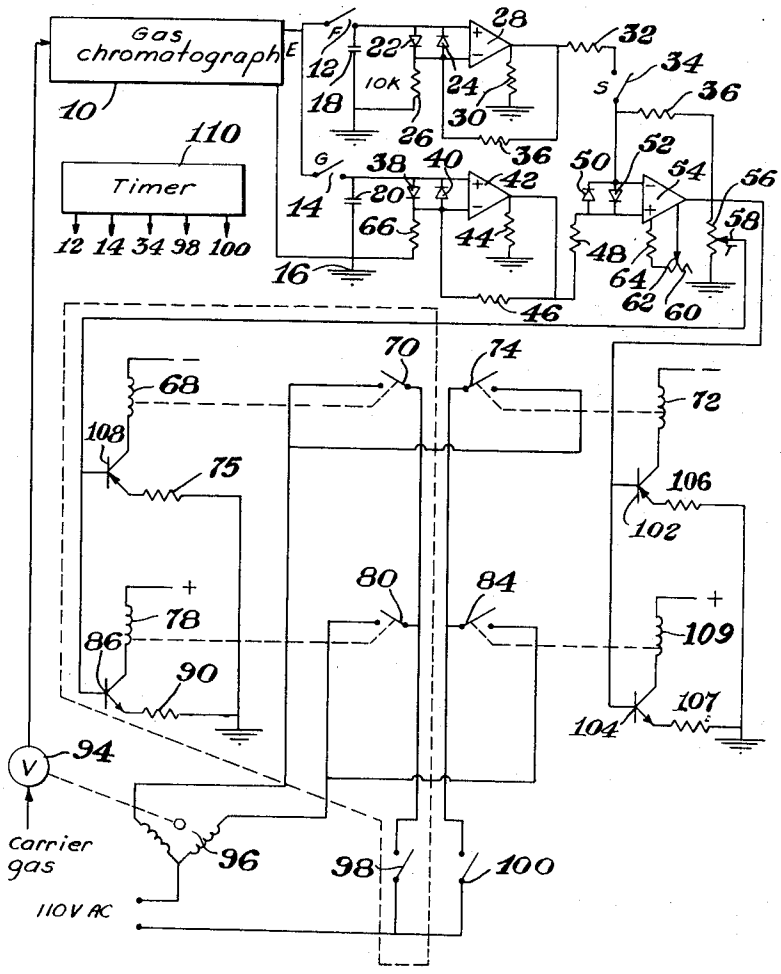

Fig. 2

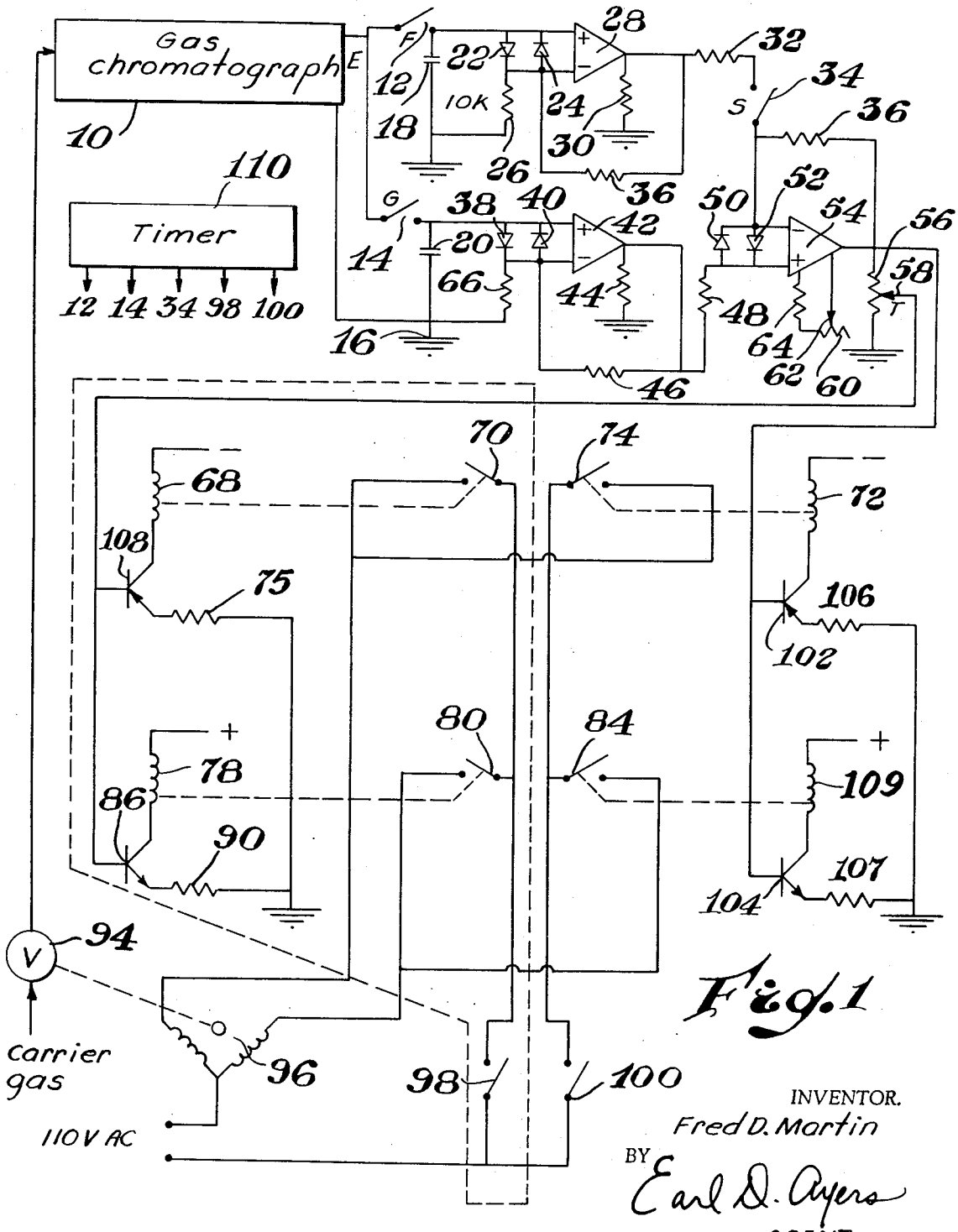

Fig. 1

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APPARATUS FOR STABILIZING COMPONENT ELUTION TIMES IN GAS CHROMATOGRAPHS

BACKGROUND OF THE INVENTION

This invention relates to peak stabilizer apparatus, and particularly to apparatus for controlling the retention of a peak during an analysis, as by gas chromatography, for example.

Small changes in carrier gas flow or column temperature in a gas chromatograph analyzer will cause the time the resolved sample component peaks emerge from the separating column to vary. Normal temperature control and gas flow control provide acceptable retention time reproducibility for most applications, however more elaborate controls may not be adequate where peak information is automatically selected for special readout or process control. In these cases, the peak time gate must be set to identify the peak or peaks of interest and it is apparent that if the peak retention time varies, it may drift beyond the time limits of the gate.

Another problem exists if the peak retention time changes between analyses. It becomes necessary to measure peak area rather than peak height to obtain accurate quantitative determinations. When a given amount of sample is retained in the separating column a longer period of time, the emerging peak will be broader and shorter.

Accordingly, a principal object of this invention is to provide improved apparatus for stabilizing peak retention times in the output signal of an analytical instrument.

Another object of this invention is to provide improved apparatus for use with a gas chromatograph to stabilize peak retention time.

In accordance with this invention a peak in the chromatogram is sampled on the leading and trailing slopes at predetermined times, these voltages, when compared, will provide an output which is neutral, negative or positive and thus indicate if the peak is at its right time, is early or is late. The carrier gas flow may be automatically changed to bring the peak back to the proper retention time in accordance with the polarity and magnitude of the output of the apparatus.

The invention, as well as other objects and advantages thereof, will best be understood when the following detailed description is read in connection with the accompanying drawing, in which:

FIG. 1 is a diagrammatic view of apparatus in accordance with this invention, and

FIG. 2 is a representation of output peaks of an analytical instrument which is used to illustrate the operation of the apparatus of FIG. 1.

Referring to FIG. 2, there is shown a typical chromatogram composed of peaks A, B, C and D. A major peak that is always present and emerges late is selected as the control peak for correcting the flow rate through the chromatography device for the next analysis. Peak D meets these requirements.

Operation may be understood by following the circuit in FIG. 1. The sequence is controlled by a timer **110** that operates switches **12, 14, 98,** and **100** and is initiated by a master timer (not shown). The output voltage E of gas chromatograph **10** is sampled at time X (FIG. 2) by closing contact F on switch **12** for a short period of time. This value is stored by the hold amplifier **28** which has inverted polarity diodes **22, 24** coupled across its input positive and negative inputs. The input value from contact F is applied to the positive input of amplifier **28**. Capacitor **18** and resistor **26** are coupled between ground and the positive and negative inputs, respectively, of amplifier **28**. Then the output voltage E is sampled at time Y (see FIG. 2) by closing contact G of switch **14**. The value is stored by amplifier **42** which is similar to amplifier **28**. The two values of E at times X and Y are compared by amplifier **54**. Amplifiers **42** and **54** each have inverted diodes **38,40** and **50,52** respectively, connected in parallel across their positive and negative inputs.

Amplifier **42** has a capacitor **20** and resistor **66** connected across its inputs and to ground **16** the same as capacitor **18** and resistor **26** are connected to amplifier **28**. Amplifiers **28** and **42** each have a resistor **30,44** respectively coupled between its output and ground and a feed back resistor **36,46** respectively coupled between its output and negative input.

The output of amplifier **28** is coupled through resistor **32** and contact **34** of switch S to the negative input of amplifier **54**, while the output of amplifier **42** is coupled through resistor **48** to the positive input of amplifier **54**. Feed back from the output of amplifier **54** to its negative input is accomplished through resistor **36**.

An internal trim adjustment composed of resistor **64** and variable resistor **60** having a movable contact **62** is shown coupled to the amplifier **54**. Similar trim adjustments, not shown, may be provided for amplifiers **28** and **42**.

The output of amplifier **54** is coupled to the base of transistors **102, 104** whose emitters are coupled through resistors **106, 107**, respectively, to ground.

The collector of transistor **102** is coupled to a negative voltage through relay coil **72** which controls the opening and closing of switch **74**.

The collector of transistor **104** is coupled to a positive voltage source through relay coil **109** which controls the opening and closing of switch **84**.

A part of the output of amplifier **54** is coupled from the movable contact **58** of variable resistor **56** to the bases of transistors **108, 86** whose emitters are coupled to ground through resistors **75,90**, respectively.

The collectors of transistors **108,86** are coupled respectively to negative and positive voltage sources through relay coils **68,78** which control the opening and closing of switches **70,80** respectively. Switches **70,80** are connected in parallel with switches **74,84**, respectively.

A reversible electric motor **96** has the junction of its two windings coupled to one side of a suitable A.C. power source. The other side of the A.C. power source is coupled, respectively, through switches **98, 100, 80, 84** or **98, 100, 70, 74** to an end of one of the windings of the motor **96** which is mechanically coupled to the valve **94** in the carrier fluid line feeding the gas chromatograph **10**.

For the sake of simplicity, a timer **110** is shown which controls switches **12, 14, 34, 98, 100** in suitable operating sequence.

In operation, the timer **110** first closes switch **12** at F to couple the output of the chromatograph **10** to the amplifier to store the value of point X (FIG. 2) on peak D. The timer **110** then couples the output of the chro-

matograph **10** across switch **14** to amplifier **42** to store the value of point Y of peak D.

Then, with switch S (**34**), and switches **98** and **100** usually closed, the values of X and Y are compared in amplifier **54** and the resultant output of that amplifier is coupled to the transistors **102, 104, 108, 86** controlling switches **74, 84, 70** and **80**, respectively.

The switch **100** is closed for a shorter time than is switch **98**, used for making so-called large timing corrections in carrier fluid flow through the chromatograph **10**.

The output of amplifier **54** is either positive, negative or zero.

If the output is at or near zero, none of the switches **74, 84, 70** or **80** will be operated.

If the output of the amplifier **54** is positive or negative, the appropriate relay switch **74** or **84** will be closed and, during the time the switch **100** is energized, the motor **96** will be energized to correct the flow of carrier fluid to the chromatograph **10** by a specific amount.

If the amplitude of the output signal from the amplifier **54** exceeds a predetermined amount (as selected from the movable contact **58**), the switch **70** or **80** closes, allowing a larger correction to be made, since the switch **98** is closed for a longer time than is the switch **100**.

The switch **34**, when open, leaves one input to the amplifier **54** floating, effectively preventing any output from the amplifier **54** and possible energization of relays until the actual comparison of X and Y signals are to be made. The switch S (**34**) could be eliminated if power economy were not desired.

In view of the time delay between successive cycles of operation, values of previous X and Y signals dissipate so that the "new" signals are the result only of the "new" X and Y values.

What is claimed is:

1. A system for stabilizing the peak retention time in fluid chromatographs, comprising means including a capacitor and an amplifier for sequentially measuring and storing amplitude values at points along opposite slopes of a selected peak signal, signal comparison amplifier means for providing an output signal which is a function in amplitude and polarity of the difference between said stored values, means for applying said output signal to polarity and amplitude sensitive switching means, said switching means coupling a power source to reversible motor drive means, said drive means being coupled to a valve for controlling the flow of carrier fluid to said chromatograph as a function of the polarity and amplitude of said signal.

2. A system in accordance with claim **1**, wherein timer means controls the time interval during which said drive means may be actuated.

3. A system in accordance with claim **1**, wherein said output signal is split and is coupled to separate polarity sensitive switching means, each of said switching means being coupled to a separate electrical winding of said reversible motor drive means, said power source being coupled to said switching means at predetermined times.

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