United States Patent

[11] **3,633,404**

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[73] Assignee **Phillips Petroleum Company**

[54] **PROGRAMMER FOR CHROMATOGRAPHIC ANALYZER**
7 Claims, 2 Drawing Figs.

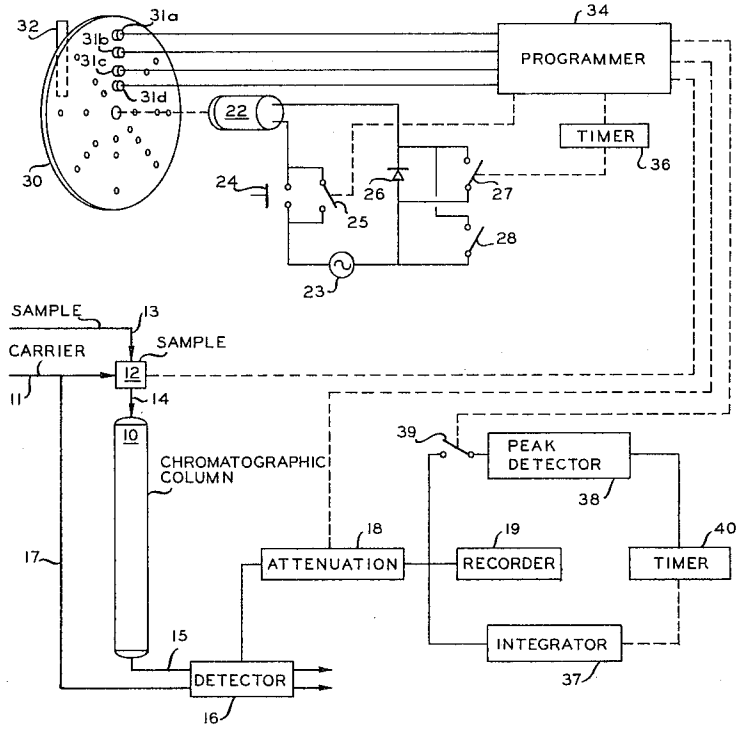
[52] **U.S. Cl.** **73/23.1,** 55/197, 235/151.35
[51] **Int. Cl.** **G01n 31/08,** G01d 15/08, G06f 15/46
[50] **Field of Search** 73/23.1; 235/151.12, 151.13, 151.35; 55/67, 160, 197, 271, 386, 387

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ABSTRACT: The timing motor which controls a programmer of a chromatographic analyzer is stopped during intervals of the analysis cycle when control operations are not being performed. This permits higher speeds of rotation during the remainder of the cycle, and thereby results in more accurate switching.



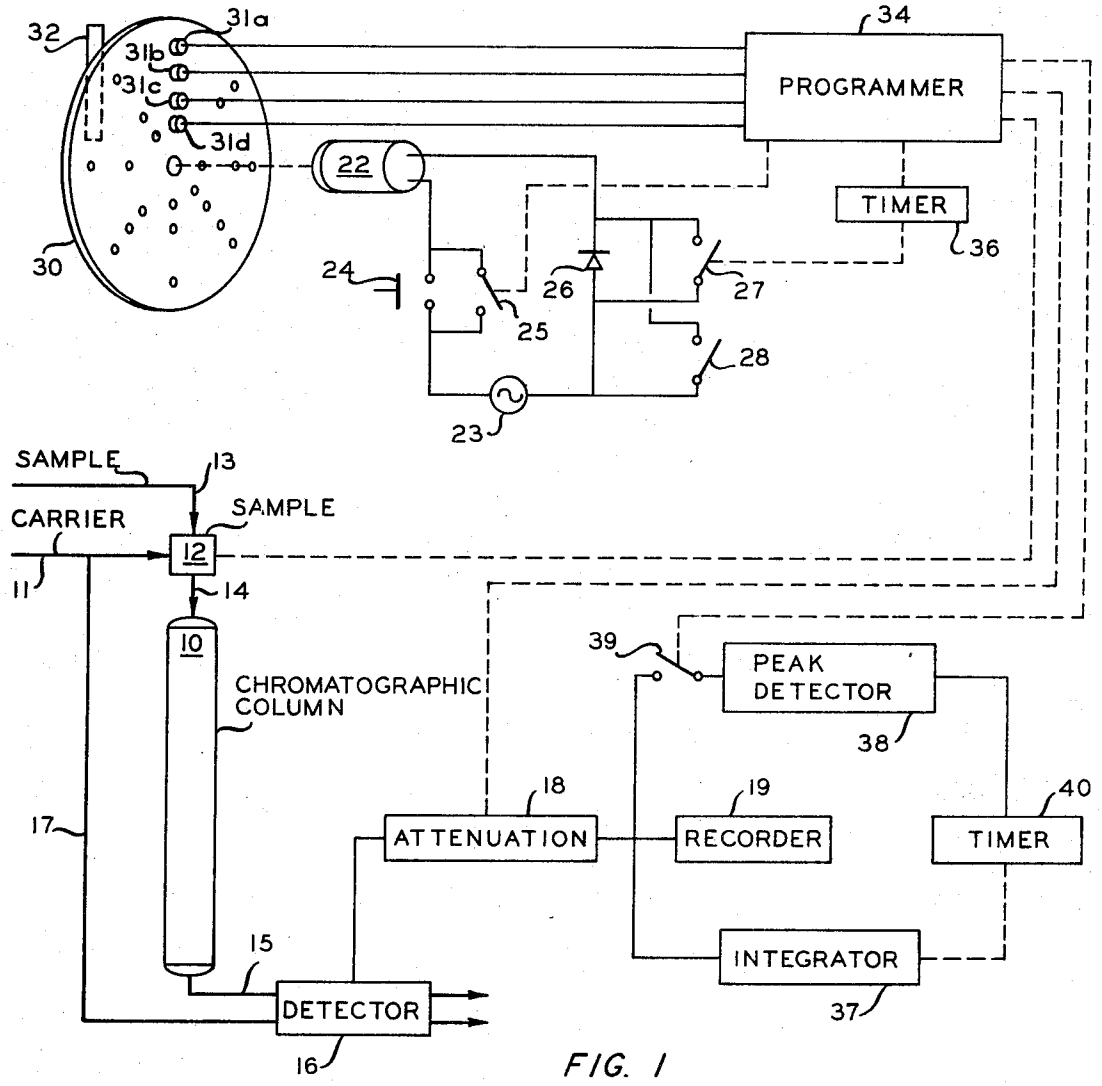


FIG. 1

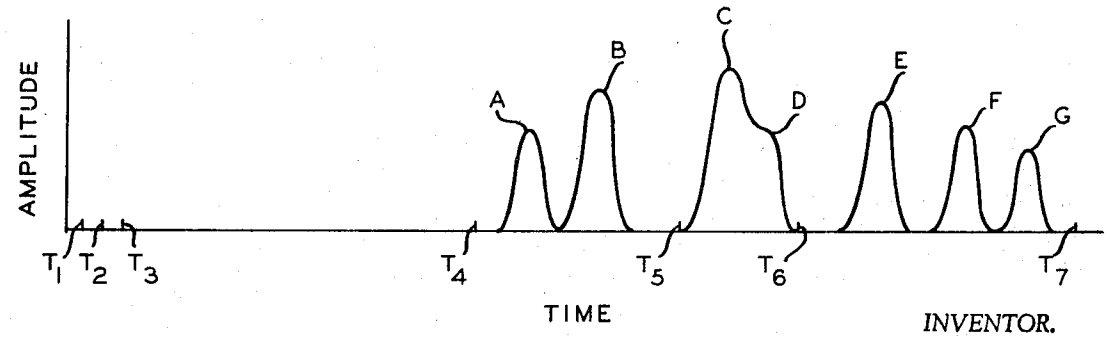


FIG. 2

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PROGRAMMER FOR CHROMATOGRAPHIC ANALYZER

In recent years widespread use of chromatographic analyzers has been made in various analytical and process control operations. These analyzers are particularly useful when analyses are to be made of relatively complex fluid mixtures. Most chromatographic analyzers are provided with automatic programming devices so that repeated analyses can be made with a minimum amount of adjustment and supervision. These programming devices usually comprise a timing motor which drives a series of cams or a perforated disk which is disposed between a light source and a series of photocells. The cams or photocells actuate circuits which can be employed to control the operation of sample valves, to adjust signal-attenuating networks, and to control detectors and other output circuits.

In the analysis of complex mixtures by the use of programmers of the type described, it is often difficult to control all of the switching operations at precisely the correct times. This is due to the fact that the disks or cams must make only a single revolution during the analysis period. The timing motor must be geared to drive the disk or cams at a very low speed if the analysis period required any appreciable length of time. The resulting slow movement prevents precise actuation of the control circuit because the perforations or cams must have some minimum size and thus may actuate switching elements over somewhat longer periods of time than is desired.

In accordance with this invention, an improved programmer is provided for use with chromatographic analyzers. Provision is made for stopping the timing motor during periods that switching operations are not required. For example, a substantial period of time often elapses between the introduction of a sample into the column and the appearance of the first peak in the column effluent. In accordance with this invention, the timing motor is turned off during this period. The timing motor can be operated at a higher rate of speed during the remainder of the analysis cycle so that more precise switching operations are obtained.

In the accompanying drawing,

FIG. **1** is a schematic representation of a chromatographic analyzer having an embodiment of the programmer of this invention incorporated therein.

FIG. **2** is a graphical representation of a typical output signal obtained by the analyzer of FIG. **1**.

Referring now to the drawing in detail and to FIG. **1** in particular, there is shown a chromatographic column **10** which contains any suitable packing material that selectively retards passage of the constituents of a fluid sample. A carrier fluid is introduced through a conduit **11** which communicates with an inlet of a sample valve **12**. A conduit **13** introduces a sample to be analyzed. The effluent from valve **12** is directed through a conduit **14** to the inlet of column **10**. The effluent from column **10** is directed through a conduit **15** to the first channel of a differential detector **16**. A portion of the carrier fluid is transmitted from conduit **11** through a conduit **17** to the second channel of detector **16**. Detector **16** thus provides an output signal which is representative of the difference between the compositions of the two streams passed therethrough. The signal is transmitted through an attenuation network **18** to a recorder **19**.

The apparatus thus far described constitutes a conventional chromatographic analyzer. Carrier fluid initially passes through sample valve **12** and column **10** so that carrier fluid alone passes through both channels of detector **16**. At this time, the output signal from the detector is zero when the detector circuit is properly balanced. At the beginning of an analysis cycle, valve **12** is actuated to introduce a predetermined volume of sample into conduit **14**. Thereafter, the valve is returned to its initial position so that the carrier fluid passes through the column to elute the constituents of the sample in sequence. Various known types of rotary and pneumatically operated sample valves can be employed for this purpose. Because the constituents of the sample are often present in substantially different concentrations and have different physical properties, it is desirable to provide an attenuation network **18** so that the amplitude of the output signal from detector **16** can be adjusted as the different constituents appear in the column effluent. This permits the output signals applied to recorder **19** to be of more nearly uniform magnitude for the different peaks.

The chromatographic analyzer thus far described can be operated automatically by a programming device which is controlled by a timing motor **22**. Motor **22** is energized by an alternating current source **23**. One terminal of current source **23** is connected to the first terminal of motor **22** by means of a starting switch **24** which has a switch **25** connected in parallel therewith. A rectifier **26** is connected between the second terminal of current source **23** and the second terminal of motor **22**. Switches **27** and **28** are connected in parallel with rectifier **26**. The drive shaft of motor **22** is connected by suitable gearing to rotate a perforated disk **30** at a preselected speed. A plurality of photocells **31***a*, **31***b*, **31***c* and **31***d* are positioned along a radial line adjacent one side of disk **30**, and a lamp **32** is positioned on the other side of the disk adjacent the photocells. In this manner, the photocells receive light when selected perforations in the disk are positioned between the lamp and the photocells. The lamps are connected to a programmer **34** which provides output control signals that are representative of the cells illuminated at any given time.

Programmer **34** can be of the type described in U.S. Pat. No. 2,982,123 or in U.S. Pat. No. 3,119,995. Perforations are formed in disk **30** in a pattern so that the sequence of events described hereinafter are performed by the programmer as disk **30** is rotated by timing motor **22**. Switching means within the programmer provide signals to perform these events.

FIG. **2** represents a typical chromatogram of the type obtained when a sample containing seven constituents is introduced into column **10**. These seven constituents provide peaks A to G in spaced relationship on the record. In the particular embodiment illustrated, the peaks are reasonable well spaced except that peaks C and D overlap. The analysis illustrated in FIG. **2** requires approximately 7 minutes, for example. The first peak A does not appear in the column effluent until approximately 3 minutes have elapsed following introduction of sample into the column.

At the beginning of the analysis cycle, switch **24** is closed momentarily to apply current to timing motor **22**. Switch **27** is in a closed position initially so that there is a direct circuit path between current source **23** and motor **22**. This effectively eliminates rectifier **26** from the circuit. The perforations in disk **30** are positioned so that programmer **34** provides a first output signal almost immediately after rotation of disk **32** is started. This signal is applied to close switch **25**. Switch **25** remains closed until a complete cycle of rotation of disk **30** has been completed so that motor **22** remains connected to current source **23** after the starting switch has opened. Within a very short time interval after rotation of disk **32** has begun, time T_1 in FIG. **2**, programmer **34**, transmits an output signal to sample valve **12**. This signal serves to actuate the sample valve to introduce a predetermined volume of sample into the column. Shortly thereafter, at time T_2, the valve is switched back to its initial position to pass carrier fluid into the column once again. A few seconds later, at time T_3, programmer **34** provides an output signal to start a timer **36**. Timer **36** immediately opens switch **27** and keeps this switch open until a time T_4. The opening of switch **27** eliminates the direct circuit path between current source **23** and motor **22** since switch **28** is open at this time. Thus, the only circuit path is through rectifier **26**. The insertion of rectifier **26** in circuit with synchronous motor **22** immediately stops the motor,

The rectifier provides positive stopping action. Switch **27** is closed by timer **36** at time T_4 and remains closed during the remainder of the cycle so that disk **30** is rotated until time T_7, which is the end of the analysis period. At this point, programmer **34** opens switch **25** to stop the cycle.

Programmer **34** provides a series of control signals to attenuation network **18** during the times that the individual peaks appear in the column effluent. These signals adjust the

attenuating network so that all of the peaks remain on the scale of the recorder and are of sufficient amplitude to be identified. The adjustment of the attenuating network in this manner can be carried out as described in the above-mentioned patents. In view of the fact that disk **30** is stopped during a substantial period of the analysis cycle, from time T_3 to time T_4, the disk can be rotated at a higher speed during the remainder of the cycle and thereby provide more precise programming of the attenuating network.

In accordance with another embodiment of this invention, the detector output signal is applied to an integrator **37** which is employed to provide a more complete analysis of a selected peak or peaks. In the illustrated example, the integrator is operated between timing intervals T_5 and T_6 to integrate combined peaks C and D. This integration is timed by means of a peak detector **38** which is connected to the output of attenuation network **18** when a switch **39** is closed. Switch **39** is manipulated by programmer **34** so as to be closed before a preselected peak in the curve of FIG. **2** is detected. If peaks C and D are to be analyzed by integrator **37**, peak detector **38** can be connected into the circuit by closing switch **39** immediately prior to the appearance of either peak A or peak B. When the top of the selected peak is detected, an output signal is applied from detector **38** to a timer **40** which controls integrator **37**. Timer **40** is set so that the integrator is turned on at time T_5, which occurs at a predetermined time interval following the top of peak B. Integrator **37** is turned off at a time T_6 which represents the end of combined peaks C and D. The use of programmer **34** and peak detector **38** to control integrator **37** results in a more precise integration than is normally obtained if the integrator is controlled directly from timing disk **30**. In most analyses, the times between the appearance of the individual peaks in the chromatogram remain substantially constant, whereas the times that the peaks appear with respect to the initial operation of the sample valve may vary from time to time.

Programmer **34**, disk **30**, and timers **36** and **40** can be adjusted initially by manually operating the analyzer to determine the approximate times of appearance and amplitudes of the peaks of the chromatogram. Thereafter, the analyzer can be operated automatically as long as the sample composition does not change substantially. If repeated analyses are desired, switch **25** can remain closed.

In some analyses, a substantial period of time may elapse between the presence of individual peaks in the output of the detector. If this occurs, timer **36** can be adjusted to stop rotation of motor **22** more than once during an analysis cycle. Timers **36** and **40** can be represented by motors which rotate cams to control switch **27** and integrator **37**. If desired, a second switch **28** can be provided in parallel with switch **37** to permit rotation of motor **23** to be started manually by closure of switch **28**.

While this invention has been described in conjunction with presently preferred embodiments, it should be apparent that it is not limited thereto.

What is claimed is:

1. In an analyzer which includes a chromatographic column, a sample valve connected to the inlet of said column to control the introduction of carrier fluid and sample mixtures into the column, a detector connected to the outlet of said column, a recorder, and an attenuation network connected between said detector and said recorder; means to control the sample valve and attenuation network comprising:

a motor;

a source of current;

means connecting said motor to said source of current to energize said motor;

a programmer including a rotatable element, said programmer providing a series of output signals in response to rotation of said element, said rotatable element being connected to said motor so as to be rotated thereby;

means responsive to an output signal of said programmer to actuate said sample valve;

means responsive to output signals of said programmer to control said attenuation network at predetermined times after said sample valve is actuated; and

means responsive to an output signal of said programmer to terminate rotation of said rotatable element for a predetermined time interval at least once after said sample valve has been actuated but prior to completion of an analysis cycle.

2. The apparatus of claim **1** wherein said motor is an alternating current synchronous motor, said current source provides alternating current, said means connecting said motor to said current source includes a rectifier and a switch connected in parallel with one another, and said means to terminate rotation comprises means to open said switch for said time interval.

3. The apparatus of claim **1** wherein said programmer includes a plurality of photocells, said rotatable element comprises a disk having perforations therein, and wherein a light source is positioned on one side of said disk and said photocells are positioned on the other side so that the photocells are illuminated when perforations appear between said light source and said photocells.

4. The apparatus of claim **1**, further comprising an integrator, means connecting the output of said detector to said integrator, a peak detector, means connecting the output of said detector to said peak detector, and means responsive to the output signal of said peak detector to control said integrator.

5. The apparatus of claim **1** wherein said programmer actuates said means to terminate rotation so that said time interval occurs prior to the time that said means to control said attenuation network is actuated.

6. The apparatus of claim **4** wherein said means connecting said detector to said peak detector includes a switch actuated by an output signal of said programmer, and wherein said means responsive to said peak detector includes a timer which establishes at least first and second output signals at predetermined spaced time intervals after said timer is actuated.

7. The apparatus of claim **2** wherein said means to open said switch comprises a timer which is actuated by an output signal of said programmer, said timer being connected to said switch to open said switch at the beginning of said time interval and thereafter to close said switch at the end of said time interval.

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