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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

Filed May 15, 1967

5 Sheets-Sheet 1

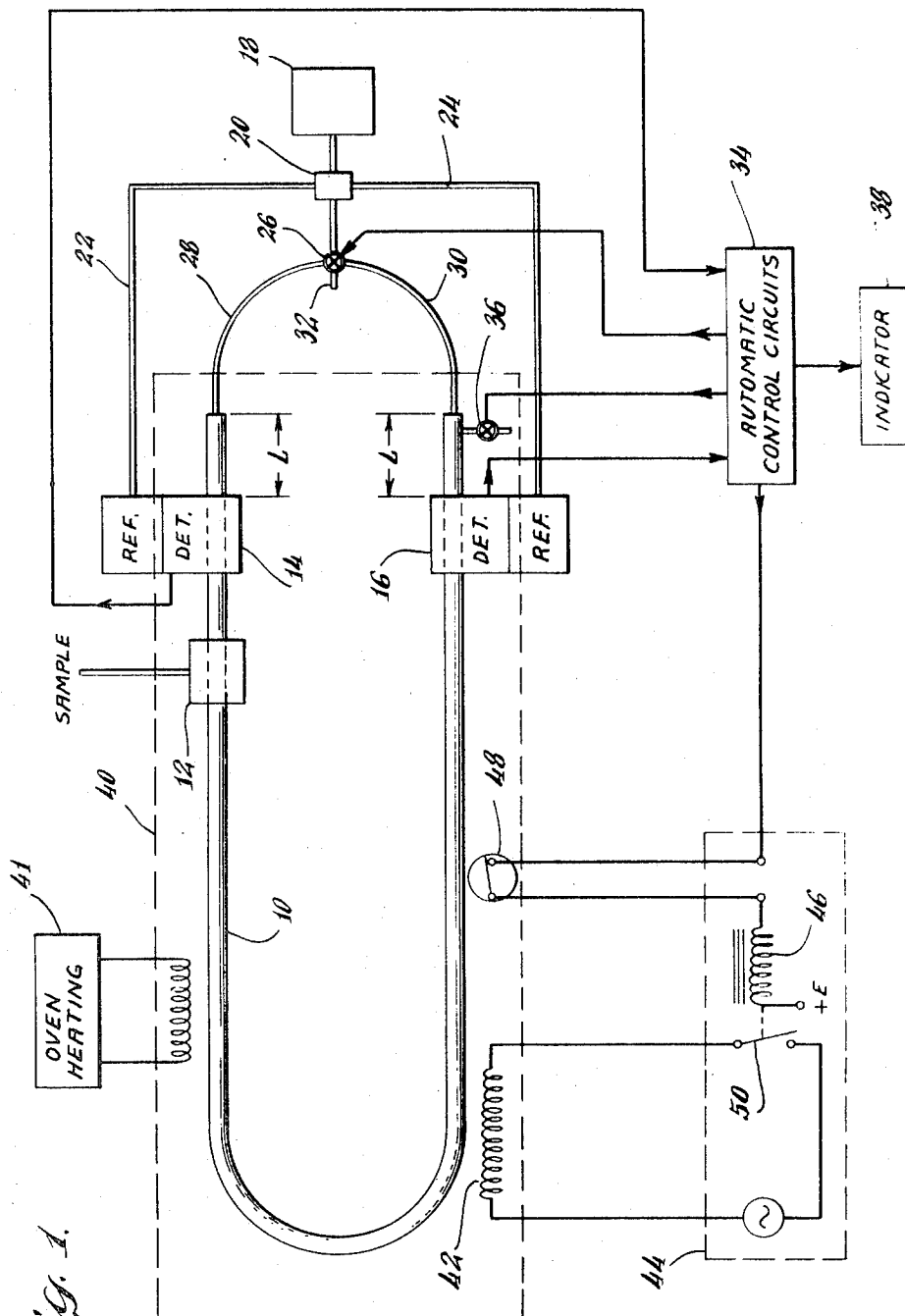


Fig. 1.

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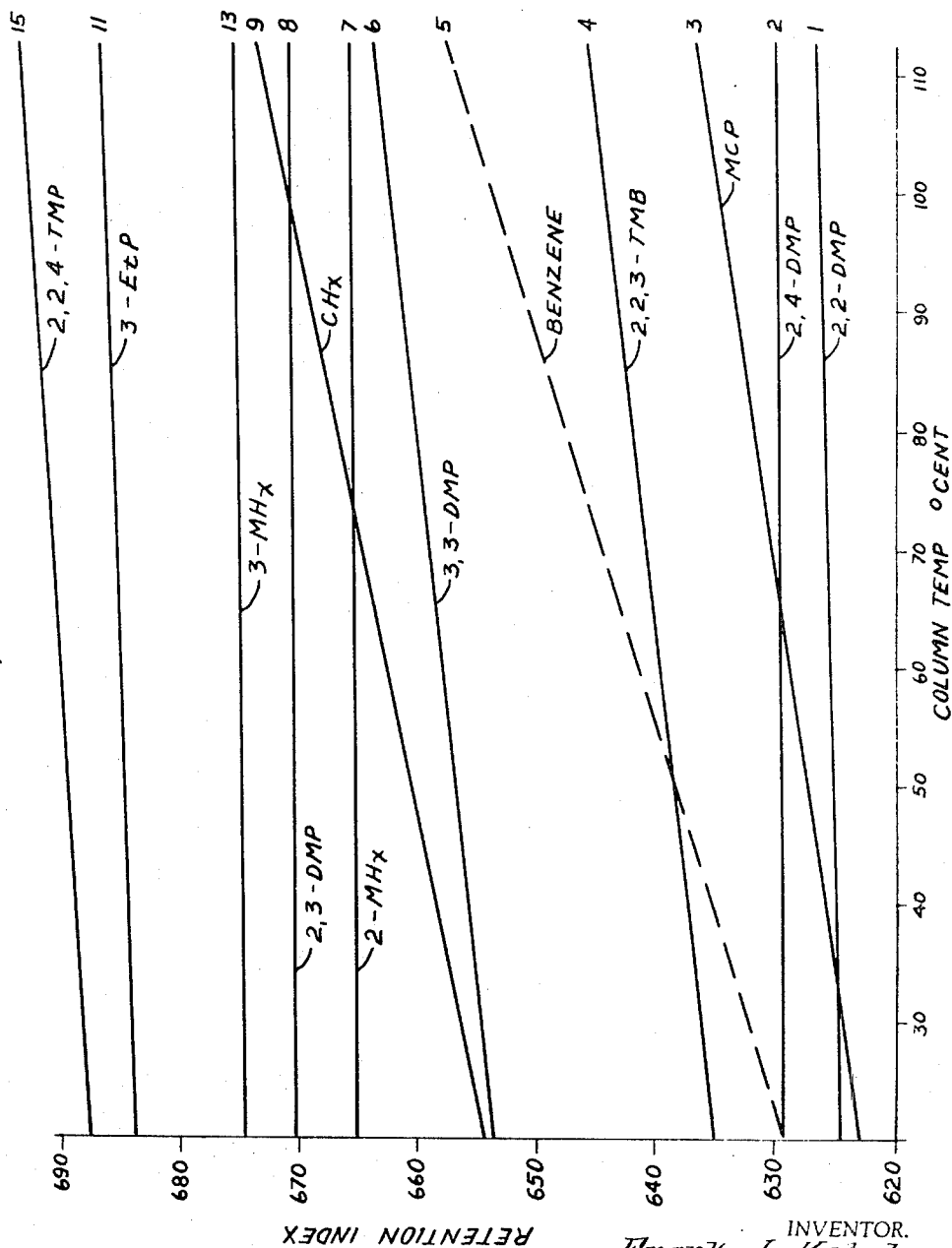
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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

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Fig. 2.



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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

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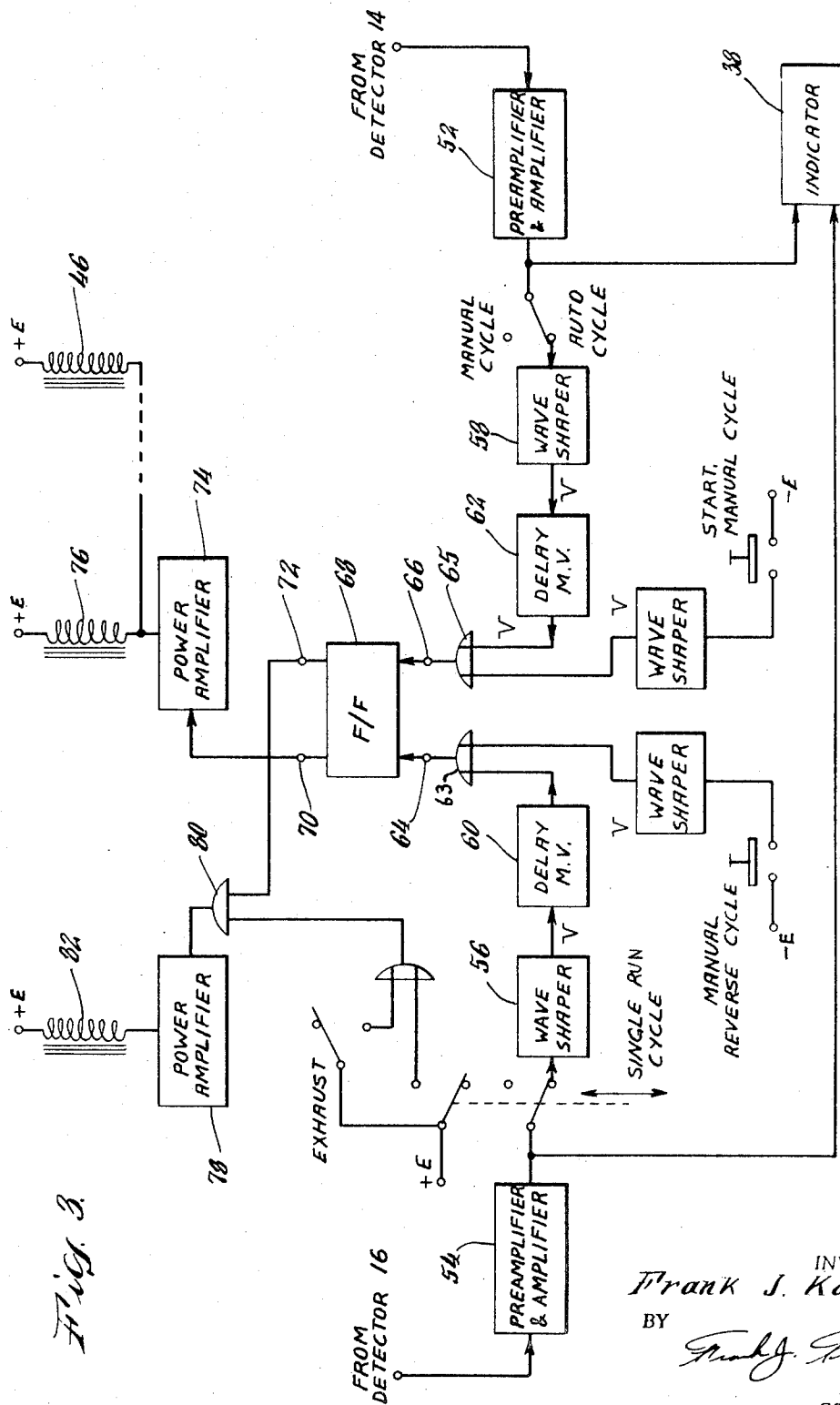


Fig. 3

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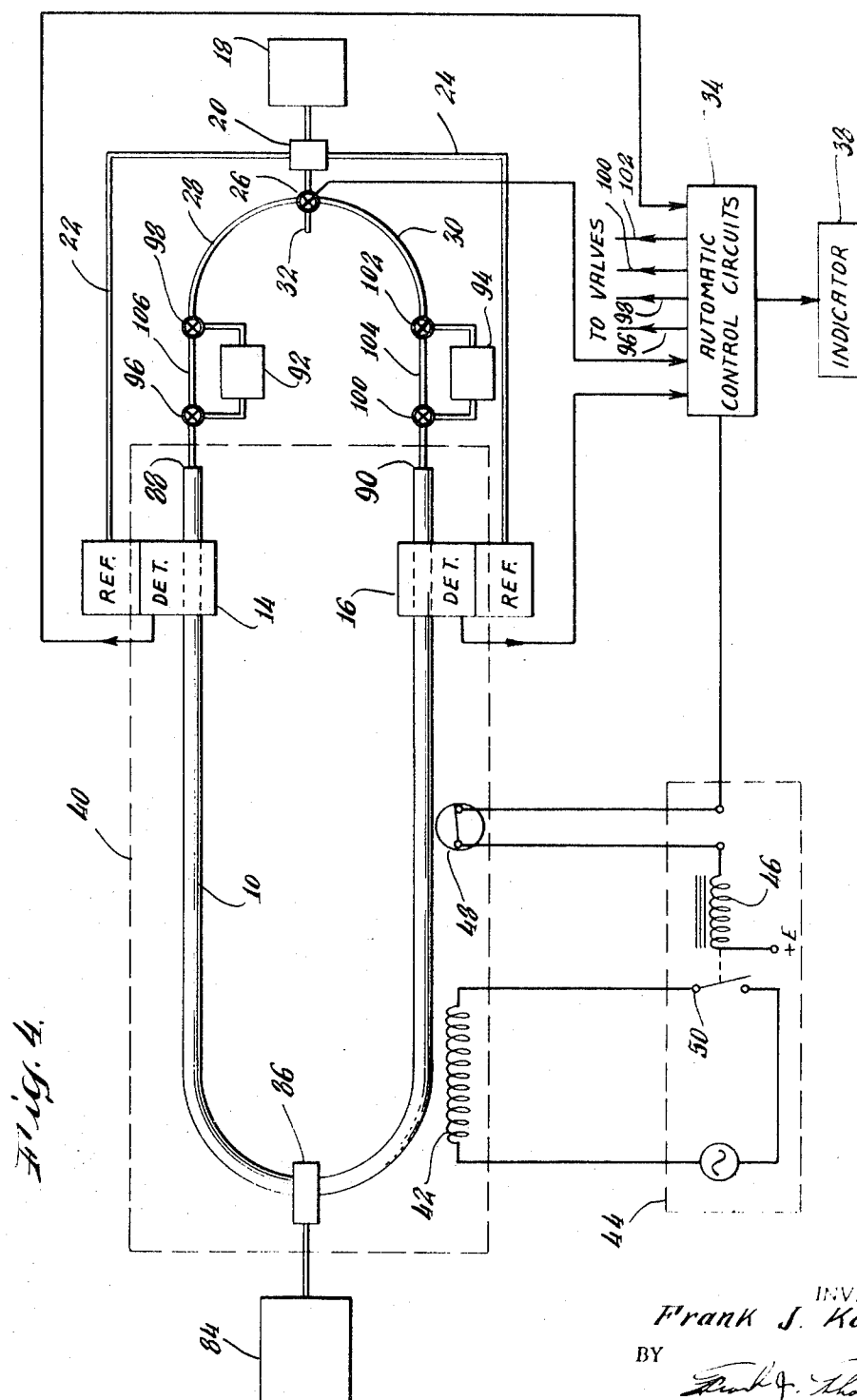
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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

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Fig. 5a.

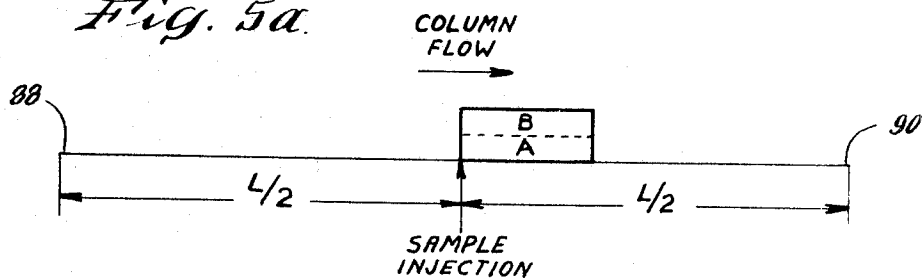


Fig. 5b.

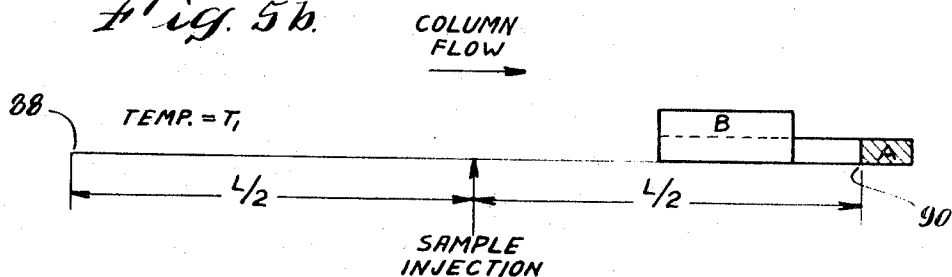


Fig. 5c.

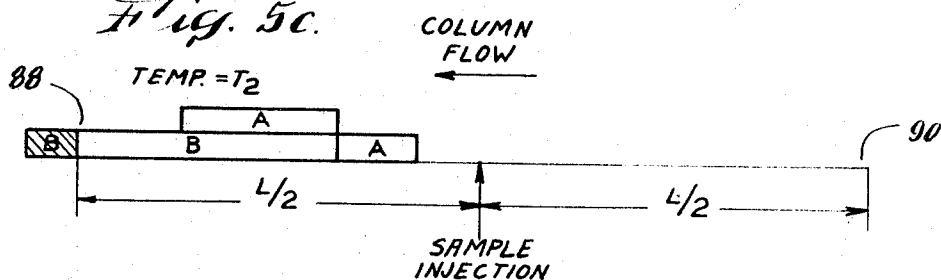
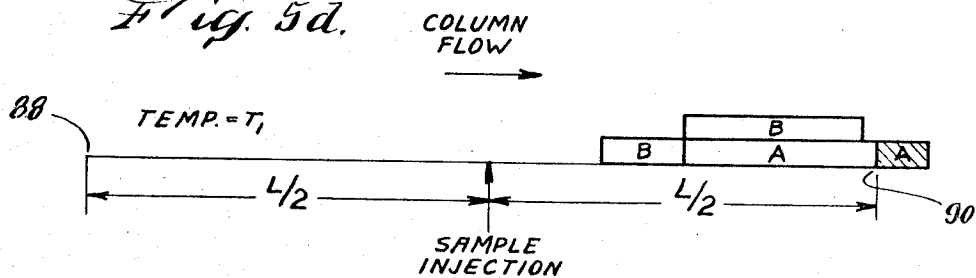


Fig. 5d.



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ELUTION CHROMATOGRAPHIC APPARATUS AND METHOD

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Int. Cl. B01d 15/08

U.S. Cl. 55—67

10 Claims

ABSTRACT OF THE DISCLOSURE

An elution chromatograph includes a separating column and means for conveying a carrier fluid through the column. Means are provided for reversing the direction of carrier fluid flow in the column and for altering the operating temperature of the column. The column is maintained at one temperature T_1 as the carrier flows in one direction through the column and at a second temperature T_2 when the direction of carrier flow is reversed. Through this arrangement, a sample having constituents exhibiting intersecting retention index curves can be held on the column and separation enhanced.

This invention relates to chromatographic apparatus and more particularly to improvements in elution gas chromatographic apparatus.

Elution gas chromatographic apparatus functions to separate the components of a sample under investigation and to provide a quantitative indication of the concentration of the sample components. A typical apparatus includes a separating column containing a component separating medium known as the stationary phase, and, a mobile phase comprising a vaporized sample and a carrier gas for transporting the sample through the column. The individual sample components of the mobile phase exhibit differing affinities for the stationary phase and thus progress through the column at differing rates and elute from the column successively in time. Means are provided for sensing the elution of components and for providing an indication of their concentration. One form of indication is a chromatogram which displays a plurality of curves extending ordinately from a time base abscissa. These curves, termed peaks, occur successively in time and are individually representative of the concentration of the known components of the sample.

The task of the analyst who interprets a chromatogram, or other indication of the separation, is at times rendered difficult if not impossible when the time differential between successive component elutions is small. Peaks displayed on the resulting chromatogram tend to bunch, or to overlap, or at times become indistinguishable. For example, it is known that a chromatogram of this type can result for some samples having components whose boiling temperatures are separated by a relatively small temperature differential. Thus, a distinguishing characteristic of any elution gas chromatographic apparatus is its resolution capability, or ability for providing adequate separation between peaks.

Various arrangements have been provided in the art for increasing the separation characteristics of the apparatus. The length of the column is a parameter which generally is varied to provide increased peak separation since the degree of separation is generally related to column length when other variables such as column temperature, stationary phase loading, mobile phase flow rate, etc. have been optimized. Increasing the column length is accompanied by various practical limitations, such as the adaptability of the column to the apparatus. This is particularly true with program heated columns because a thermostated oven for heating the column will

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be constructed of finite size. In addition, ease of handling and pressure drop in the column are further considerations which dictate a limitation on the length of the column. Other arrangements for improving peak separation provide for systematically increasing the carrier gas flow rate, the column temperature, or both. Nevertheless, relatively long columns with their attending disadvantages are required to achieve suitable separation with some substances.

Accordingly, it is an object of this invention to provide an improved form of elution gas chromatographic apparatus and method.

Another object of the invention is to provide an elution gas chromatographic apparatus having improved separation characteristics.

A further object of the invention is to provide an elution gas chromatographic apparatus which is adapted for providing improved separation characteristics while avoiding the use of unusually long columns.

Another object of the invention is the provision of an elution gas chromatographic apparatus adapted to provide continuous separation of the sample components until a desired component separation is attained.

Still another object of the invention is the provision of an elution gas chromatographic apparatus adapted for permitting an operator to control the duration of separation until a desired separation of components is attained.

It is known that for given conditions of column operation, the sample to carrier gas concentration has a value which if exceeded results in column overloading. Column overloading can result in loss of separation and render the sample analysis inaccurate and unmeaningful. The operator must therefore carefully monitor the quantity of sample injection in order to avoid overloading. When an undesirable, inadvertent column overloading does occur, the operator's labors are generally rendered useless and the analysis must be repeated.

It is another object of the present invention to provide an elution gas chromatographic apparatus which provides adequate separation of components under overloaded column conditions.

In various elution chromatographic apparatus, separation is effected primarily by virtue of boiling temperature differences, hydrogen bonding, pi bonding, permanent as well as induced dipole moment. Apparatus of this type includes preparative analytical instruments as well as large scale separating apparatus. In large scale separation apparatus, such as distillation columns, the sample which is represented by the raw product is continuously fed to the separating column and the components are continuously removed. Adequate separations in these apparatus are difficult if not impossible when the difference in boiling temperature of the components being separated is small, nonexistent or if azeotropes form.

Another object of this invention is to provide an elution preparative gas chromatographic apparatus having improved separation characteristics.

A further object of this invention is the extension of the principles of elution gas chromatography to large scale separating apparatus and the provision of an improved separating apparatus when the sample is continuously fed to the separating column.

In a column having a predetermined stationary phase, the slopes of the retention curves of sample components can differ. The retention curve is a plot of retention index or, time in the column, versus column temperature. In many cases, it is found that these retention curves intersect at a particular temperature and that the order of sample component elution in known columns will vary or reverse as the column temperature traverses the intersect temperature. In presently known apparatus this is an undesirable condition which must be guarded against

by the operator in order to provide accurate and true test results. However, the present invention advantageously utilizes this characteristic in providing improved apparatus separation characteristics.

In accordance with the general aspects of the present invention, an elution gas chromatographic apparatus includes means for maintaining the column below the retention curve intersect temperature as the mobile phase traverses the column in a first direction and for increasing the column temperature to a temperature in excess of the intersect temperature while reversing the direction of mobile phase flow in the column. By this arrangement, sample components having intersecting retention curves can be held on the column and are continuously separated as the mobile phase flows in both directions, and until a desired degree of separation is attained.

These and other objects and features of the present invention will become apparent with reference to the following specifications and drawings wherein:

FIGURE 1 is a diagram of one embodiment of an elution gas chromatographic apparatus constructed in accordance with features of the present invention;

FIGURE 2 is a graph of retention curves illustrating the intersect characteristics of curves of the components in a sample being separated;

FIGURE 3 is a diagram in block form illustrating the control circuitry of FIGURE 1 in greater detail;

FIGURE 4 is a diagram of an elution gas chromatographic apparatus adapted for continuous separation; and

FIGURES 5(a) to 5(d) are diagrams illustrating the operation of the apparatus of FIGURE 4.

Referring now to FIGURE 1, an elution gas chromatographic apparatus includes a column 10, a flow-through sample injection block 12 and flow-through nondestructive concentration detectors 14 and 16. Column 10 is a conventional packed column containing a stationary phase selected for separating the components of a particular sample under investigation. This stationary phase causes the order of elution of sample components to differ at temperatures T_1 and T_2 . The injector block 12 is conventional and the detectors may be of the hot-wire thermal conductivity type having detecting and reference filament sections. The detector sections are positioned in the mobile phase flow path.

A source 18 of a carrier gas such as helium or nitrogen is provided. This gas is conducted to the detector reference sections via a four port fitting 20 and suitable piping 22 and 24. The carrier gas is also conducted to the column through a solenoid-actuated, two position, four-port valve 26, and through alternatively a tubing 28 or tubing 30 in accordance with positioning of the valve. A carrier gas flow path is traced in order through the fitting 20, the valve 26, the tubing 28, the column 10, the tubing 30 and an exhaust port 32 of the valve 26 when the solenoid of valve 26 is deenergized. When the solenoid is energized, the valve 26 exists in a second of its two positions and a carrier gas flow path is traced in order from the fitting 20, the valve 26, the tubing 30, the column 10, the tubing 28, and the exhaust port 32. Thus, the carrier gas travels in a first direction through the column when valve 26 exists in the first of its two positions and in an opposite direction through the column when the valve exists in its second position.

A control circuit means represented by the block 34 is provided for alternating the direction of carrier gas flow in the column, for controlling the temperature of the column, and for controlling the elution of sample components from the column. This circuit, described in greater detail hereinafter, functions automatically and responsive to signals from the detectors 14 and 16 or responsive to manual operator commands to energize and de-energize a solenoid of valve 26. A solenoid energized, two-port, exhaust valve 36, also under control of circuit 34, is operated for eluting sample components from the column

after a desired separation is attained. In addition, output signals from the detectors are amplified by the circuit 34 and applied to a visual indicator 38 such as a chart recorder. The concentration of detected components is represented by the indicator as an area under peaks which are displayed by the recorder.

A heated chamber, represented by the dashed rectangle 40, is provided for varying the operating temperature of the column 10 between temperatures T_1 and T_2 . This chamber can comprise a conventional column oven which is heated and thermostatted by means indicated generally as 41 to operate at a temperature T_1 . The oven also includes additional heating means comprising a heater coil 42 and heater power supply 44 for rapidly increasing the chamber temperature and thus the column temperature to a second temperature T_2 .

This latter heating means is responsive to the control circuit 34 and the chamber is additionally thermostatted to maintain the second temperature T_2 when it is attained. A command to increase the oven temperature from T_1 to T_2 causes energization of a relay coil 46 via a thermostat contact 48 which breaks contact at or about the temperature T_2 .

As previously indicated, the present invention takes advantage of the intersecting characteristics of the separation curves of sample components for providing improved separation of the components. FIGURE 2 is a graph of the retention curves of various hydrocarbons for a particular stationary phase and illustrating the intersecting characteristics of several of the curves. The stationary phase employed in producing the curves of FIGURE 2 is squalane. The retention index is the well known Kovats index which is fully described in *Analytical Chemistry*, vol. 36, page 31A, July 1964. It can be seen that curves 2 and 3 representing the retention characteristics of 2,4-dimethylpentane and methylcyclopentane intersect at approximately 65° C. Below 65° C., the retention index of curve 2 exceeds curve 3. When a column is operated below 65° C., the order of elution of these components is methylcyclopentane and then 2,4-dimethylpentanes. When a column is operated above 65° C., then the order of elution of these components is reversed. Similar relationships exist between, curves 1 and 3, 7 and 9, and 8 and 9.

In accordance with features of the present invention, the apparatus of FIGURE 1 operates to alter both the flow direction of the mobile phase and the relative magnitude of the retention indices of components being separated by an amount sufficient to cause a reversal in the order of elution of two components. The operation of this apparatus may be explained by considering the separation of a binary mixture comprising the component of 2,4-dimethylpentane, curve 2, and methylcyclopentane, curve 3. Initially, the chamber 40 will be thermostatted to operate at a temperature T_1 , below 65° C. The solenoid of control valve 26 is de-energized and carrier gas flows counterclockwise through the column as viewed in FIGURE 1 and exhausts at port 32. A sample is introduced into the carrier gas stream, is carried through the column, and separation begins. As the mobile phase flows through detector 16, an electrical signal is generated and an indication of the degree of separation of the components is displayed by the chart recorder indicator 38. As described in more detail hereinafter, the automatic control circuit 34 senses this signal and energizes the solenoid of valve 26 before the components elute from the column 10 into the tabulation 30. Carrier gas then flows in a clockwise direction about the column as viewed in FIGURE 1 and the direction of mobile phase flow is reversed.

When only carrier gas flow is reversed, the order of elution remains unchanged and the separated components of relatively low retention would traverse the column in the opposite direction but at the same rate. The separation thus far accomplished would be reduced since com-

ponents of lower retention index overtake and at times recombine with the components of relatively higher retention index. For example, when the separated components initially reach detector 16 during counterclockwise flow, the MCP component of curve 3 (FIGURE 2) leads the 2,4-DMP component of curve 2. On reversal of carrier gas flow at the same temperature, the retention indices are unchanged and the degree of separation would decrease. In accordance with a feature of this invention, the column temperature is also changed to a temperature T_2 at which a reversal in the order of elution occurs. During clockwise flow and at a temperature T_2 , which for this example exceeds 65° , the 2,4-DMP component exhibits a lower retention index than MCP component and traverses the column at a greater rate than MCP. Thus, the degree of separation is increased during clockwise flow. As the separated components reach detector 14, a signal is generated by the detector and the control circuit responds to deenergize the solenoid of valve 26 and reverse the direction of carrier from prior to elution of the components from column 10. In addition, the heater supply 44 is also deenergized and the chamber returns to T_1 . The direction of mobile phase and order of component elution is reversed once again. During this counterclockwise progression through the column, MCP progresses at a faster rate than 2,4-DMP. Separation is therefore further increased. This separating process can continue as indicated over as many cycles as are required to provide the desired degree of separation. The degree of separation can be ascertained by the operator from the display of indicator 38. Manual control means are provided for permitting the operator to terminate the separating process and collect separated components by inhibiting reversal of gas flow, during the counterclockwise flow and by operating effluent valve 36.

FIGURE 3 illustrates in greater detail, the arrangement of the control circuit 34. Input signals from the detectors 14 and 16 are applied to preamplifier and amplifier stages 52 and 54 respectively. The applied voltages are shaped by circuits 56 and 58 which provide, responsive to the first detected peak, trigger waveforms for triggering monostable multivibrators 60 and 62. The detection of a separated component by detector 16 causes a negative trigger pulse to be generated by the MV-60 and applied via an "or" gate 63 to a trigger input terminal 64 of flip flop 68. Similarly, the detection of a separated component by detector 14 causes a negative pulse to be generated by MV62 which is applied via an "or" gate 65 to a trigger input terminal 66 of the flip flop circuit 68. A negative trigger pulse at terminal 64 causes relatively positive and negative voltages to occur at terminals 70 and 72, respectively, while a negative trigger voltage applied to input terminal 66 causes relatively positive and negative voltages to occur at terminals 72 and 70, respectively. Terminal 70 is coupled to a power amplifier 74 for energizing a solenoid coil 76 of the valve 26 and the relay coil 46. Relatively positive and negative voltages applied to the amplifier 74 causes energization and de-energization respectively of the coils 76 and 46. Terminal 72 is similarly coupled to a power amplifier 78 via an "and" gate 80 for energizing a solenoid coil 82 of effluent exhaust valve 36. The occurrence of a positive voltage at terminal 72 along with the application of either an operator command voltage to exhaust or an automatic command during a single run causes energization of the coil 82. Various arrangements as illustrated in FIGURE 3 are provided for conditioning the circuitry for start of the test, for providing manual operator control of the separation, and for adapting the apparatus to a conventional single run separation.

Delay circuit means comprising the multivibrators 60 and 62 are provided in order to inhibit a premature switching of valve 26 and reversal in the direction of mobile phase flow before all separated components have flowed

through the detector. The operator is therefore assured of a visual indication of the separation prior to reversal. The delay time may be varied in a conventional manner by adjusting a circuit time constant or magnitude of a charging potential. Additionally, MV delay circuits may be coupled in cascade when unusually long delays are required. In this regard, the detectors are positioned a sufficient distance L from associated ends of the column in order to provide adequate column length for holding on the column, separated components which are spaced over a relatively large length of the column. For a column of fixed length, L is maximum when a single detector is provided and positioned at the center of the column. In a configuration of this type, the single detector will be coupled via a delay MV to a flip flop arranged for a binary trigger input signal rather than a trigger input signal as shown in FIGURE 3.

A sample under analysis may include components having intersecting retention curves as well as components exhibiting non-intersecting retention curves. For example, a sample may include the components represented in FIGURE 2 by curves 4, 7, 9, and 15. The 2,2,3-trimethylbutane of curve 4 which exhibits a relatively lower retention index will be taken off the column first by executing a normal separation and exhaust function. This, of course, must be accomplished within the period of the delay. An operator may utilize an excessive delay and operate the exhaust and manual reverse cycle switches to effect the desired removal. Accuracy of removal of the component from the column can be increased further by positioning the exhaust valve 36 relatively close to detector 16 or by including an additional detector and associated indicator in the exhaust line itself. Cycling of the apparatus is then initiated until a desired separation of the 2-methylhexane of curve 7 and cyclohexane of curve 9 is attained. These and the 2,2,4-trimethyl-pental period of curve 15 are removed in order and at temperatures above the intersect temperature.

A sample component may include components exhibiting a plurality of intersections of their retention curves. For example, a sample may include the components designated by curves 1, 3, 7 and 9 in FIGURE 2. The apparatus of FIGURE 1 may be modified to operate at a third temperature T_3 . Operation is then provided at temperatures T_1 and T_2 for removal of the components 2,4-DMP and MCP. The apparatus then operates at temperatures T_2 and T_3 for removal of the components 2-MHx and CHx.

FIGURE 4 is a diagram of another embodiment of the invention particularly adapted for use as a preparative or relatively large scale gas chromatographic separating apparatus.

The apparatus of FIGURE 4 includes elements similar to those described with respect to FIGURE 1 and these elements bear the same reference numerals. The substance which is to be separated into components is derived from a supply source 84 and continuously supplied to the column 10 by a metering pump 86. In operation, the mobile phase is caused to flow alternately in opposite directions through the column. A quantity of one separated component of a binary mixture is removed from the column at a point 88 while another component of the binary mixture is removed from the column at point 90. The continuously sensing metering pump 86 injects a quantity of the binary mixture during one cycle which is equal to the quantity of component removed from the column.

Component removal is effected by any suitable means such as cold traps 92 and 94. Valves 96, 98, 100 and 102 comprise 3-port, 2-position valves having operating solenoids which are energized by the control circuit 34. During clockwise mobile phase flow, these valves are energized in a manner for bypassing carrier gas about trap 94 via tubing 104 and for restricting tubing 106 to cause the carrier gas and separated component to flow into trap 92. A separated component is separated from

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the carrier gas in the trap 92 and the carrier gas is exhausted via valve 98, tubing 28 and port 32 of valve 26. On counterclockwise carrier gas flow, the valves 96, 98, 100, and 102 are operated for causing carrier gas to be shunted about trap 92 while the effluent at port 90 is directed to trap 94. Carrier gas is exhausted from this trap via valve 102 tubing 30 and exhaust port 32 of valve 26.

Operation of this continuous form of elution gas chromatographic separation may be explained with reference to FIGURE 5. In FIGURE 5, binary mixture concentration profiles are illustrated which are representative of the sample components at different times during the cycling. FIGURE 5(a) illustrates the introduction of a quantity of a 50-50 binary mixture to the column. The binary mixture is comprised of the components A and B. In FIGURE 5(b), mobile phase flow is counterclockwise and the column is operating at a temperature T_1 . A quantity of the component A is separated and a quantity indicated by the darkened area is removed from the column. Flow direction is reversed and the column temperature changed to T_2 . The concentration profile of components of the column is indicated by FIGURE 5(c). A quantity of the separated component B, indicated by the darkened area, is removed at port 88 and flow direction is again reversed while the column temperature is returned to T_1 . During a cycle of operation, the metering pump 86 is continuously introducing the binary mixture in an amount equal to the quantity of the components removed from the column during a cycle. The column is thus continuously separating while overloading is avoided.

Control of the quantitative removal of the components A and B by the traps and the quantity introduced will vary with the column size, stationary phase, and particular components of the sample. Operation of the column will equilibrate and equal amounts of components, or different quantities, can be removed by operation of the valve 26. This in turn can be regulated by the operator by varying the control circuit delay multivibrators. In general, the solenoids of valves 96, 98 and the solenoids of valves 100 and 102 will be operated in accordance with switching of the valve 26. Thus, the features of the present invention are equally applicable in large scale preparative and refining processes as well as with analytical apparatus.

An improved form of gas chromatographic apparatus has thus been described which provides increased separation of difficult to separate components, while avoiding the prior disadvantageous requirement for relatively long separating columns. In addition, the features of the invention are adaptable for providing improved performance in preparative and large scale separating apparatus.

I claim:

1. An elution gas chromatographic separating apparatus comprising:

separating means, including a stationary phase, defining a flow path for a carrier gas,

a source of carrier gas coupled to said separating means,

means for introducing a vaporized substance having components to be separated into said carrier gas flow path,

means for operating said separating means at alternative different temperatures T_1 and T_2 , and

means for causing said carrier gas to flow in a first direction in said separating means at the temperature T_1 and in an opposite direction in said separating means at the temperature T_2 .

2. The chromatographic apparatus of claim 1 wherein said stationary means includes a substance adapted for providing a first relative order of elution of two components of the substance being analyzed at a first temperature T_1 and a second reverse order of elution at the temperature T_2 .

3. An elution gas chromatographic apparatus comprising:

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a elongated separating means having at least two ports and including a stationary phase defining a flow path for a carrier gas,

said stationary means adapted for providing a first relative order of elution of two components of the substance being analyzed at a first temperature T_1 and a relatively opposite order of elution at the second temperature T_2 ,

means for operating said separating means at alternatively differing temperatures T_1 and T_2 ,

a source of carrier gas,

means including a valve for alternatively coupling said carrier gas source to one of said ports of said separating means when said separating means is operating at the temperature T_1 and to the other of said ports when said separating means is operating at the temperature T_2 , and

means for introducing a vaporized substance having components to be separated into said carrier gas flow path.

4. The chromatographic apparatus of claim 3 including component concentration detection means positioned in said carrier gas flow path for detecting the concentration of the separated components and indicating means coupled to said detection means for providing a visual display of the detected concentration.

5. An elution gas chromatographic apparatus comprising:

an elongated tubular separating column including a stationary phase and defining a flow path for a carrier gas,

said stationary phase including a substance adapted for providing a first relative order of elution of two components of the substance being analyzed at a first temperature T_1 and a relatively opposite order of elution at a second temperature T_2 ,

first and second nondestructive concentration detection means coupled in said carrier gas flow path respectively near first and second end portions of said column and adapted to generate an electrical signal representative of the concentration of a separated component,

automatic control circuit means coupled to said detectors for generating a first set of electrical control functions responsive to a signal from said first detector and a second set of electrical control functions responsive to said second detector,

a source of carrier gas,

means including an electrically operated valving member for alternatively coupling said carrier gas source to opposite ends of said separating column,

means for operating said separating means at alternatively different temperatures T_1 and T_2 ,

means coupling said automatic control circuits to said temperature control means and to said valving means for causing said column to operate at a first temperature T_1 and for causing said carrier gas to flow in a first direction in said column responsive to said first control function and for causing said column to operate at a second temperature T_2 and for causing said carrier gas to flow in an opposite direction in response to said control function, and

means for introducing a vaporized substance having components to be separated into said carrier gas flow path.

6. The apparatus of claim 5 wherein said means for introducing a substance into said carrier gas flow path is adapted for introducing a predetermined batch and means are provided responsive to said control circuit for removing said separated components from said column.

7. The apparatus of claim 5 wherein said means for introducing said substance comprises a source of the substance and a substance introducing mechanism coupled near the center of said column and arranged for con-

tinuously introducing the substance into the carrier gas flow path.

8. The apparatus of claim 7 wherein the carrier gas is caused to alternatively flow in opposite directions through the column and means are provided for removing a portion of the separated components from the column and for continuously introducing an equal quantity of the substance onto the column during one cycle.

9. A method of gas chromatographic separation of sample components each having a retention index versus temperature characteristic curve which mutually intersect at a temperature T_m comprising:

maintaining a chromatographic column containing a stationary phase at a temperature T , differing from T_m ;

transporting the sample in a first direction along the column;

maintaining the column at a second temperature T_2 differing from T_1 and T_m ; and

transporting the sample in a second direction along the column.

10. A method of gas chromatographic separation of sample components each having a retention index versus temperature characteristic curve which mutually intersect at a temperature T_m comprising:

maintaining a chromatographic column containing a stationary phase at a temperature T_1 less than T_m ; transporting the sample in a carrier gas stream flowing in a first direction through the column;

maintaining the column at a temperature T_2 greater than T_m ; and varying the direction of carried stream flow thereby transporting the sample in a second opposite direction along the column.

References Cited

UNITED STATES PATENTS

3,043,127	7/1962	De Ford et al.	55—386 X
3,201,922	8/1965	Villalobos	55—67

J. L. DE CESARE, Primary Examiner