Dec. 28, 1965 F. H. BUROW 3,225,521

SERIALLY CONNECTED THERMOCHROMATOGRAPHIC COLUMNS

Filed June 4, 1962

2 Sheets-Sheet 1

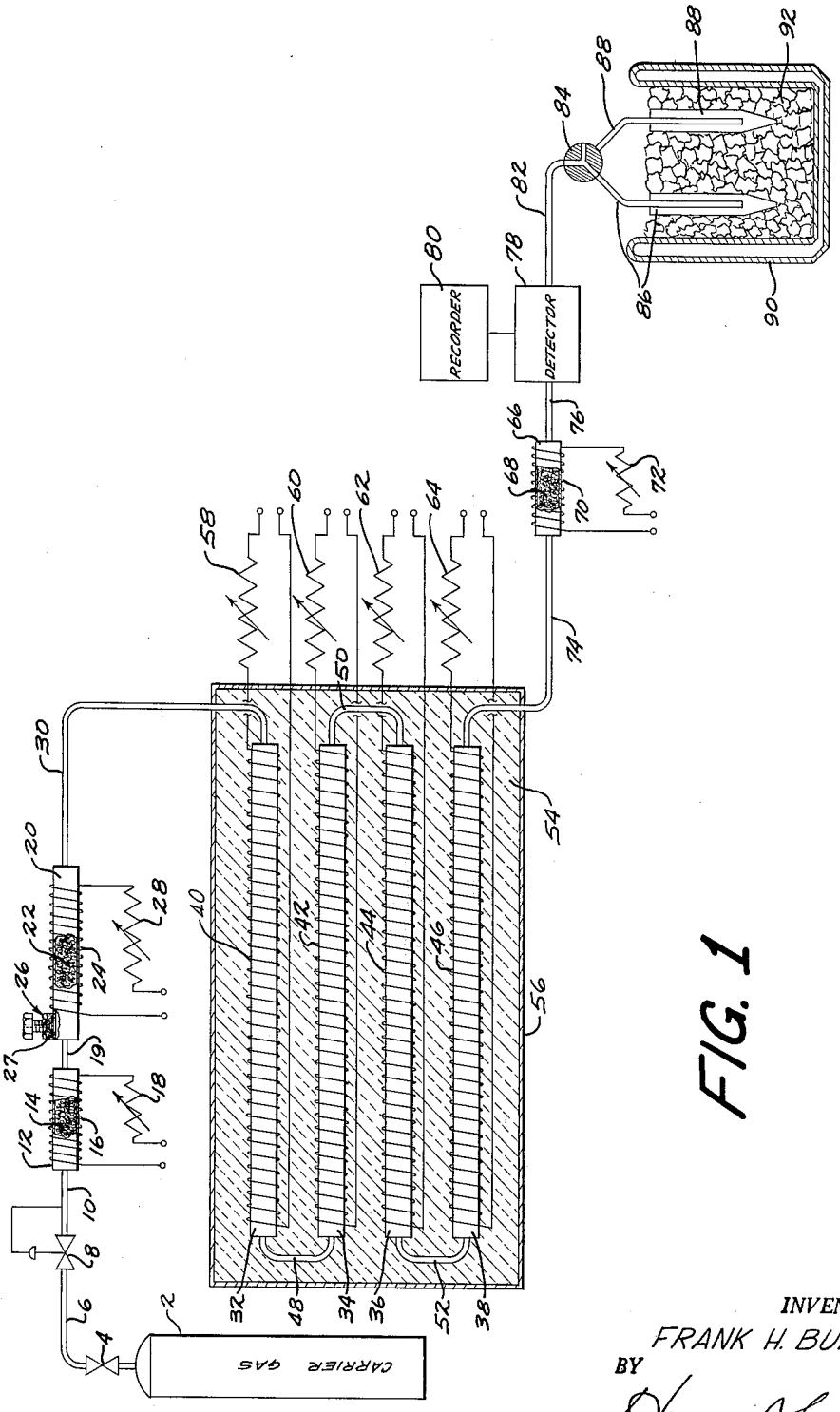

FIG. 1

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SERIALLY CONNECTED THERMOCHROMATOGRAPHIC COLUMNS

Filed June 4, 1962 2 Sheets-Sheet 2

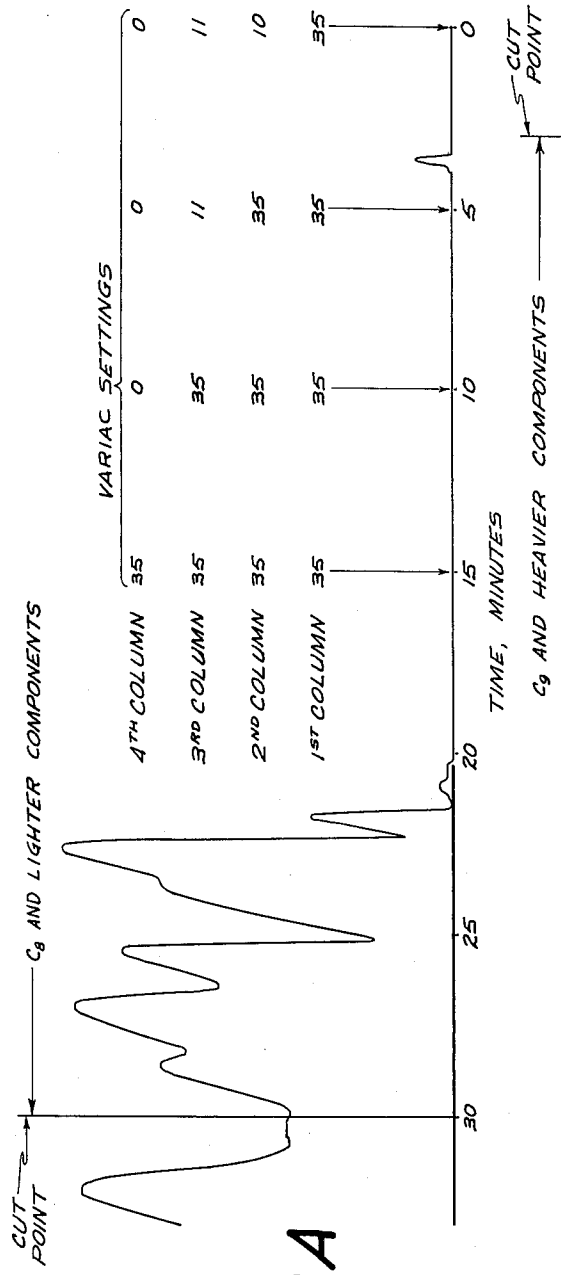

FIG. 2A

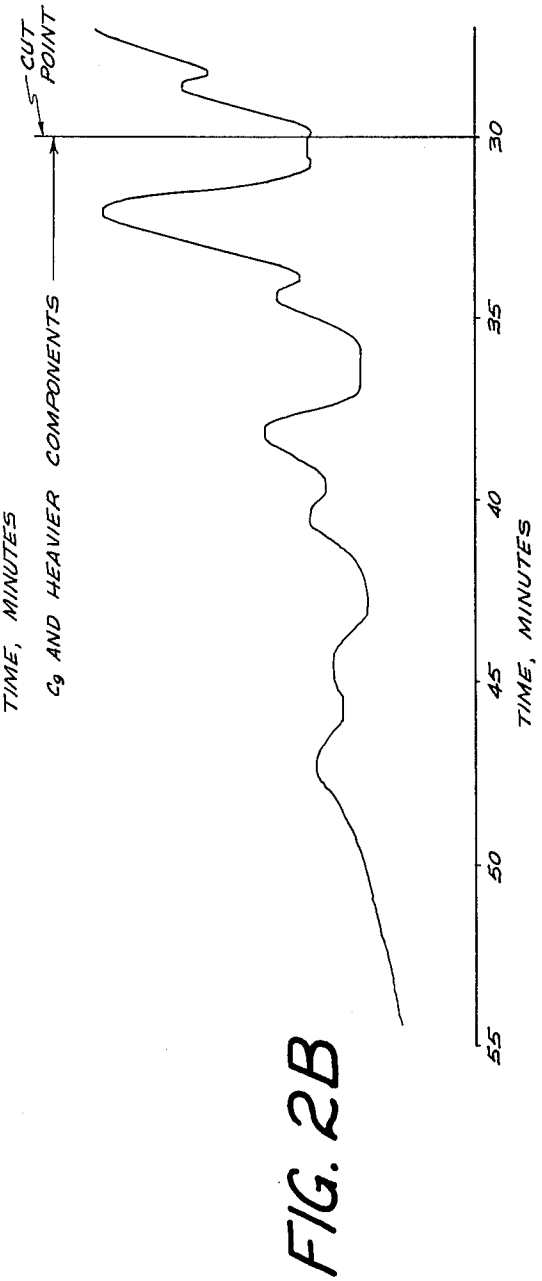

FIG. 2B

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United States Patent Office 3,225,521 Patented Dec. 28, 1965

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3,225,521

SERIALLY CONNECTED THERMOCHROMATOGRAPHIC COLUMNS

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Filed June 4, 1962, Ser. No. 199,883
4 Claims. (Cl. 55—67)

This invention relates to a chromatographic separation method and apparatus and more particularly to a method and apparatus of such kind involving separate temperature programming for a plurality of serially connected chromatographic separating zones.

In the characterization of broad boiling range mixtures, e.g., gasoline and naphtha, it is frequently desired to separate the lower boiling components., for which detailed chromatographic calibration information is available, from the higher boiling components, for which no such information is available. In this way the lower boiling components can be subjected to detailed chromatographic analysis, and the higher boiling components can be subjected to some other form of detailed analysis, for example, mass spectrometry, infrared spectrometry, chemical analysis, or the like. It is very important that the separation of lower-boiling and higher-boiling components be precise, as the detailed analysis of the separated groups of components is complicated by overlapping of components in the separated component groups. Thus, the detailed chromatographic analysis of a C_8 or lighter gasoline fraction may require several times as much operating time when a small amount of C_9 material is present than when C_8 is the highest boiling component of the fraction, and the situation is worsened still by the presence of even higher-boiling components. As only the C_8 and lighter fraction can be resolved into individual components, a complete quantitative analysis of this fraction cannot be obtained if part of a C_8 component remains in the heavier fraction where it cannot be quantitatively determined.

Fractional distillation, even in highly developed form, is impractical for sharp separations of the kind required for the purpose indicated, because of the closeness of the boiling points involved and because of the presence of reflux liquid in the fractionating column. To illustrate, the careful fractionation of a naphtha sample in a highly efficient laboratory fractional distillation column nine feet in length and one inch in diameter, and having the equivalent of 200 theoretical plates, required a period of 405 hours to complete, and more than 100 differently boiling cuts were obtained. Even so, much overlapping occurred; for example, approximately 30 of the cuts were found to to contain C_8 hydrocarbons.

While sharp separations of the kind desired can be obtained by gas chromatography using very small samples, difficulties are encountered when samples are utilized of a size sufficient for further operations (e.g., chemical analysis) which require relatively large quantities. This is because larger diameter columns and greater carrier gas flow rates ordinarily are required with larger samples in order to obtain the desired resolution. However, such greater carrier gas flow rates interfere with the collection and recovery of the separated components, as the components have to be condensed out of the hot carrier gas. The increased velocity and quantity of the hot carrier gas hinder the complete condensation and recovery of the components.

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The present invention relates to a chromatographic method and apparatus for separating a difficultly separable, wide-boiling range mixture containing a plurality of close-boiling components in an amount sufficient to permit physical recovery of separated portions of a size sufficient for further analysis, into at least two sharply defined portions containing different components, with essentially complete recovery of sample. Broadly, in accordance with the method of this invention, a partial separation of lighter components from heavier components of the mixture is effected in a first chromatographic separating zone by introducing into said zone a stream of carrier gas and a vaporous sample of said mixture of a size sufficient to permit physical recovery of separate portions in an amount sufficient for further analysis. The partly separated components are removed from the chromatographic separating zone in the order of separation by continuing the flow of carrier gas therethrough, with complete removal of the heavier components being effected by gradually increasing the temperature of the chromatographic separating zone to a temperature sufficient to insure elution of these components. A further separation of the partly separated components of the mixture is effected by introducing the effluent from the first zone into a second chromatographic separating zone, said second zone being at a lower temperature than said first zone during at least a substantial part of the time in which the temperature of the first zone is being increased. The further separated components of the mixture are removed in the order of separation from the second chromatographic separating zone by continuing the flow of carrier gas therethrough, and complete removal of the heavier components is effected by gradually increasing the temperature of the second zone to a temperature sufficient to insure elution of such components. Separated components are separately recovered as desired from the effluent carrier gas.

The apparatus of the present invention involves as its essential subcombination, a carrier gas source, a plurality of serially connected chromatographic separating zones, means defining a path of flow for said carrier gas connecting said carrier gas source and the first chromatographic separating zone in said series, said means being provided with means permitting introduction of a sample of a fluid mixture to be separated into the path of flow of said carrier gas, detecting means for sensing changes in the composition of the effluent from at least one of said zones, and separately controllable heating means for gradually raising the temperature of each of said chromatographic separating zones. The invention also includes combinations including the above-indicated apparatus wherein the means defining a path of flow for the carrier gas is also provided with means for preheating the carrier gas prior to introduction thereof into the first chromatographic separating zone, and with means for heating the fluid mixture sample within the path of flow of said carrier gas. The present invention also includes combinations of the above-indicated apparatus including means for separately recovering separated components from the effluent carrier gas.

Referring briefly to the drawings, FIGURE 1 is a diagrammatic representation of one suitable analytical instrument structure in which the method of this invention can

be carried out. FIGURES 2A and 2B together comprise a reproduction of a fragment of a recording chart of the type obtainable by the apparatus of FIGURE 1, showing a portion of a chromatogram, that is, a plot of the differential change in detector signal strength with elapsed time, for a gasoline sample separated in accordance with the present invention.

The present invention can be more readily understood with detailed reference to FIGURE 1. Thus, numeral 2 in FIGURE 1 designates a carrier gas source, which may conveniently comprise a cylinder containing liquefied helium gas. It will be understood that other suitable eluent fluids can be employed as the carrier gas. In every instance, the carrier gas should be a material that is less strongly held by the stationary phase in the chromatographic separating column than any of the components of the fluid mixture that is to be subjected to analysis. Helium is especially advantageous as a carrier gas when a detector utilizing the principal of thermal conductivity is employed, as this gas has a thermal conductivity considerably higher than any of the components of the particular fluid mixtures disclosed herein, but other gases can be employed. Examples of other carrier gases can be employed. Examples of other carrier gases are argon and nitrogen.

Numeral 4 in FIGURE 1 indicates the gas cylinder pressure regulator and valve, and numeral 8 represents a flow controller for establishing a constant rate of flow of carrier gas into and through the system. Numerals 6 and 10 comprise conduits connecting the carrier gas cylinder 2 with a carrier gas preheater 12.

Preheater 12 comprises means for preheating the carrier gas prior to admixture thereof with the sample to be analyzed, and includes a high surface area, corrosion resistant packing 14 having good thermal conductivity characteristics, resistance heating windings 16, and a variable resistance 18 for controlling the electrical current input and thus the heat output of resistance windings 16. Stainless steel turnings in the form of loose spirals and having a diameter in the range of perhaps 0.05 to 0.1 cm. are suitable packing material for purposes of this invention, but other packing materials in other forms can be used. For example, there can be used commercial wire spring distillation column packings marketed under the names of Heli-Pac, Double Spiral Podbielniak Distillation Column Packing, Fenske Spirals, and the like. Preheating of the carrier gas is desirable in order to assist in vaporization of the vaporizable components of the sample to be analyzed and also to establish a temperature gradient at least in the first chromatographic separating zone in the series. This temperature gradient is effected by transfer of heat from the carrier gas to the column packing.

The temperature at which the preheater is operated can be any temperature that will insure complete vaporization of the components of the mixture to be analyzed that are desired to be vaporized and that will not cause decomposition of the mixture components. It is preferred that the temperature employed in the preheater be somewhat greater, for example, 20 to 25° C. greater, than the temperature employed in the flash chamber 20 downstream of the carrier gas preheater. This temperature difference compensates for the temperature drop that occurs with vaporization of sample components in flash chamber 20.

The outlet of the carrier gas preheater is connected by a conduit 19 to the inlet of a tubular flash chamber 20 which constitutes means for vaporizing at least a portion of the fluid mixture samples to be subjected to analysis. Like carrier gas preheater 12, flash chamber 20 is provided with a high surface area packing 22 having good thermal conductivity characteristics, and with resistance heating windings 24 whose heat output is controlled by a variable resistance or rheostat 28. Packed flash chamber structure of a kind suitable for the purposes of this invention is described in further detail and claimed in copending patent application Serial No. 199,882, filed June 4, 1962, in the name of Frank H. Burow. Flash chamber 20 is also provided with access means 26 permitting introduction of sample at or near its inlet end. Means 26 simply comprises a housing adapted to maintain a puncturable silicone rubber diaphragm 27 in gas-tight contact with the surface of tubular flash chamber 20 in the immediate vicinity of an aperture therein providing access to the interior of chamber 20. Means 26 is provided with a vertical passageway, indicated by dotted lines, permitting access to rubber diaphragm 27 by conventional sample-introducing means, not shown.

The temperature at which the flash chamber is maintained will depend upon the nature of the mixture subjected to analysis. Any temperature can be used that is sufficient to insure full vaporization of the heaviest or highest boiling portions of the mixture that are to be vaporized, but insufficient to decompose any of the components of the mixture. For reasonably rapid vaporization, the temperature to which the flash chamber is heated will be in the range of about the 50 percent and the 90 percent distillation points for the volatilizable portion of the mixture. Thus, ASTM D910 specifications for high volatile aviation gasoline provide for a maximum 50 percent distillation point of 221° F. (105° C.) and ASTM D439 specifications for low volatile motor gasoline provide for a maximum 90 percent distillation point of 392° F. (200° C.). Accordingly, for separation of gasoline or naphtha samples, a temperature in the range of about 105° to 200° C. is suitable. A temperature that does not unduly shorten the life of the rubber disc 27 is preferred. In this respect, temperatures in the neighborhood of about 160–165° C. have been found suitable for the analysis of hydrocarbon mixtures boiling in the gasoline and naphtha range.

Numerals 32, 34, 36, and 38 comprise serially connected chromatographic separating zones or columns, the inlet of column 32, the first in the series, being connected to the outlet of flash chamber 20 by means of conduit 30. Separating columns 32, 34, 36, and 38 are serially connected by means of conduits 48, 50, and 52. Columns 32, 34, 36, and 38 are provided, respectively, with resistance heating windings 40, 42, 44, and 46 whose heat outputs are controlled, respectively, by rheostats 58, 60, 62, and 64. The maximum temperature to which columns 32, 34, 36, and 38 are heated will be governed by the same considerations controlling the selection of the temperature employed for flash chamber 20. Columns 32, 34, 36, and 38 are further provided with thermal insulation material 54, and with housing 56 therefor, to minimize heat transfer to the ambient atmosphere and between adjacent columns.

In a preferred embodiment columns 32, 34, 36, and 38 are partition columns and are packed with particles of an inert porous solid provided with a coating of a liquid or semi-liquid material suitable for the particular fluid mixture undergoing separation. Celite-type kieselguhr and insulating brick made from the same material of a particle size between about 30 and 100 mesh, preferably between about 30 and 60 mesh, are examples of suitable inert supporting materials for use in packed partition columns. Partition columns are also known in which the inner wall of the column comprises the solid support, as is the case in instances of coated capillary chromatographic columns. A wide variety of liquid materials can be used as the stationary phase material in chromatographic partition columns. When the columns are subjected to elevated temperatures, as disclosed herein, liquid materials of low volatility (high boiling point) are preferred as the stationary phase material. An example of a liquid or semi-liquid material suitable for use in partition columns useful in the present invention for separation at temperatures below about 250° C. is silicone gum or rubber. Other suitable materials are silicone oils such as General Electric Company SF–96 (1000) silicone oil,

which is useful at temperatures in the range of 0° C. to 250° C., and silicone gums such as General Electric Company SE–30 silicone gum, which is useful at temperatures as high as 300° C. Still other examples are polyethylene, squalane, and paraffin wax. Although partition columns are preferred for the separation of hydrocarbon mixtures such as gasoline, naphtha and the like, it will be understood that insofar as the principles of the invention are concerned, the chromatographic separating columns employed can be adsorption columns. In such instances, separation of mixtures occurs as a result of differential adsorption of the components of the mixture subjected to analysis on the surfaces of an inert, porous adsorptive solid employed as the column packing. Examples of suitable adsorption column packings include diatomaceous earth, silica gel, and activated charcoal, each having a bulk density less than 0.4 gram per ml. and a particle size in the range mentioned above.

Numeral **66** constitutes means for heating the effluent from the last chromatographic separating column **38** in the series so as to assure an essentially constant temperature at the inlet of the detector **78**. Means **66** should be maintained at a temperature sufficient to prevent condensation of the separated components, but not so great as to promote thermal decomposition. Heating means **66**, similarly as preheater **12** and flash heater **20** is provided with a corrosion resistant, high surface area packing **68** of good thermal conductivity characteristics, and with resistance heating windings **70** whose heat output is controlled by rheostat **72**. Numerals **74** and **76** denote, respectively, conduits connecting the outlet of column **38** with the inlet of heater **66** and the outlet of heater **66** with the inlet of detector **78**.

Detector **78** comprises means for sensing changes in the composition of the effluent from column **38**, for example, a thermal conductivity cell detector. Detecting means **78** is provided with heating means, not shown, to maintain the detector at a constant temperature, which should be sufficient to avoid condensation of the separated components. Any suitable detecting device can be used that is capable of utilizing some property of the detected component to create a signal, usually an electrical current, proportional to the concentration of that component in the effluent. Good results are obtainable by the use of conventional thermal conductivity detecting cells, as in the illustrated embodiment, but other detectors responsive to changes in the composition of the effluent gas, including gas density balances, radiological ionization detectors and flame temperature detectors can be used. Of course, if a detector that is destructive to the detected components is employed, the effluent stream of separated components should be split, with one branch being directed to the detector and the other to suitable collecting means. Numeral **80** denotes recording means associated with detector **78** for indicating the differential variation in effluent composition with time, detected by means **78**. Recorder **80** functions simply by converting the electrical output of detector **78** to mechanical motion in the form of a recording pen drive means, and by causing the recording pen to move relative to the surface of a recording chart that advances with a predetermined rate.

Numeral **82** denotes conduit means connecting the outlet of detector **78** with means for separately recovering components separated in the chromatographic separating columns. The recovery means comprises a two-way valve means **84** and condenser traps **86** and **88** (shown here in simplified form), insulating vessel **90** and a cooling source **92** such as Dry Ice.

In operation of the apparatus illustrated in FIGURE 1, rheostats **18**, **28** and **72** are set to provide the desired heat output in resistance windings **16**, **24**, and **70**, respectively, and valves **4** and **8** are set to provide a constant carrier gas flow at the desired rate through the system. After carrier gas preheater **12** and flash chamber **20** have reached the desired temperature as indicated by thermocouples, not shown, attached thereto, a sample of a fluid mixture to be separated, for example, gasoline, having a size of about 2.5 ml. is introduced into the inlet end of flash chamber **20** through means **26** by the use of a hypodermic needle, not shown. The gasoline components are vaporized by contact with pre-heated packing **22** and by contact with the preheated carrier gas. The vaporized components are swept through flash chamber **20** by means of the stream of carrier gas. A rough separation of the sample is effected at the outset in flash chamber **20** as a result of the tortuous passageways provided by the flash chamber packing **22** and as a result of the differential diffusivity of the various components of the mixture to be separated. The partially separated sample is caused to flow into chromatographic separating column **32** by means of the constant flow of carrier gas.

A downward temperature gradient in the direction of flow will exist at least in column **32** by virtue of the transfer of heat from the preheated carrier gas to the column packing during passage therethrough, and possibly in one or more subsequent columns. Establishment of a temperature gradient in the first chromatographic separating zone contacted by the sample is important. Such gradient permits the large size sample employed to be sufficiently spread out along the length of the small diameter analytical column that the column packing can still be effective to exert a partitioning effect on the components of the sample and will not become choked with the large volume of the sample. In other words, if the sample is not somewhat spread out along the length of the small diameter analytical column, there will not be enough packing surface available to contact the sample and effect a partitioning of the components, and a much greater column length will be required to effect the same degree of separation that is obtained by a shorter length of column when the sample is initially distributed over a relatively longer portion. The temperature gradient functions to distribute the sample over a relatively large portion of the column by virtue of the fact that the gradual drop in temperature encountered by the sample components as they advance through the column slows the rate of advance of the heavier components much more greatly than the lighter components. In this manner choking of the column by the relatively large sample is avoided.

Having avoided choking of the column with the sample, it might now be possible to effect the desired resolution of the sample simply by continuing to pass the carrier gas through a chromatographic separating zone until all of the products were eluted, provided that a column of sufficient length were provided in the first instance. However, in the instance of a wide boiling range mixture containing close boiling components, the column length, and consequently, the elution time, required for such resolution would be prohibitively great. In order to effect the desired degree of resolution in a relatively short length chromatographic separating column, a further downward temperature gradient in the direction of flow, in addition to that resulting from the preheated carrier gas, is set up between chromatographic separating column **32**, the first in the series, and chromatographic separating column **38**, the last in the series. This temperature gradient is brought about by switching on variable rheostats **58**, **60**, **62**, and **64** in sequential order. As a result of the sequential commencement of heating in the chromatographic separating zones, the temperature of each successive zone in the series will be lower than that of its preceding zone during a substantial part of the time in which the temperature of the preceding zone is being increased. When optimum heating rates are utilized, the temperature of each successive chromatographic separating zone in the series will be lower than that of the preceding zone when elution from such preceding zone is complete.

As the partly separated components move through the serially connected chromatographic separating zones, they progress step-wise from relatively warmer to relatively cooler zones, where the temperature reduction tends to spread out the sample still more widely by virtue of a greater slowing effect on the relatively heavier components of the sample. On the other hand, the elution time for the heaviest components is not greatly increased by the downward temperature gradient as the temperature in each of columns 32, 34, 36, and 38 gradually increases to the limit permitted by the rheostat settings employed. Thus, by the establishment of a downward temperature gradient along the lengths of the chromatographic separating zones, an unusual degree of sample resolution is obtained per unit column length, whereby large size samples can be effectively resolved in a short time, and an increase in elution time for the heaviest components of the mixture is avoided by imposing a gradually rising temperature on each of the chromatographic separating zones in sequence.

The separated components pass out of the chromatographic separating zone through line 74 into heater 66, where their temperature is raised to the degree desired prior to detection in detector 78. The variations in the effluent composition are detected in thermal conductivity cell 78 and recorded by recorder 80. The separated components are recovered from the effluent carrier gas by condensation and trapping out in refrigerated trap 86. When the desired cut point is reached as indicated by recorder 80, two-way valve 84 is switched and the subsequently eluted components are recovered from the effluent carrier gas by condensation and trapping in refrigerated trap 88. Light ends, contained in trap 86, can then be subjected to detailed analysis, for example, by chromatographic analysis in a capillary column, and the heavier ends, contained in trap 88, can be subjected to detailed analysis by infrared spectrometry, mass spectrometry, or the like.

In a specific embodiment, the carrier gas preheater and the flash chamber were constructed, respectively, of eight-inch and 14-inch lengths of ½-inch standard stainless steel pipe having an inside diameter of approximately ⅝-inch. Each of these chambers was packed loosely with stainless steel spirals of the kind described in a density corresponding to about 0.8 gram of packing per inch of pipe length. Both chambers were wound with a total of about 30 feet of 20-gauge (B and S) asbestos-covered, Nichrome wire that had been threaded into a glass fabric insulating sleeve. All variable resistances were 7.5 ampere Variac rheostats having a graduated output voltage from 0 to 140. Each of the chromatographic separating columns was formed from four feet of ¼-inch standard stainless steel pipe having an inside diameter of about 5/16-inch. Each column was wound with 30 feet of Nichrome resistance wire of the kind indicated above and insulated as described. The columns were packed with Johns Manville C–22 Silocel crushed firebrick having a size of —30, +60 mesh, and having deposited thereon a silicone rubber gum, General Electric SE–30, in the amount of 20 percent by weight. The columns were connected in series by lengths of ¼-inch stainless steel tubing, unpacked.

In starting up the apparatus the output voltage of the preheater Variac was set at 24 which corresponded to a preheater temperature of 184° C., and the output voltage of the flash chamber Variac was set at 39, which corresponded to a flash chamber temperature of about 164° C. The output voltage of the effluent heater Variac was set at 22, which corresponded to a heater temperature of about 182° C., and the output voltage of the detector heater Variac, not shown, was set at 76, which corresponded to a detector temperature of about 220° C. The thermal conductivity cell filament current was 110 milliamperes, and a 100 millivolt recorder was connected to the thermal conductivity detector. A helium carrier gas flow of 100 cc. per minute was passed through the system. After the system reached the desired starting temperatures, a 2.4 cc. sample of a 400° F. end point gasoline was introduced into the flash chamber. The temperature programs of the chromatographic separating columns, expressed in Variac output voltage settings, was as indicated in the following table:

Table

	First Column	Second Column	Third Column	Fourth Column
Start	0	0	0	0
After injection	35	10	11	0
5 Minutes	35	35	11	0
10 Minutes	35	35	35	0
15 Minutes	35	35	35	35

At the end of the separation all of the chromatographic separating columns were at a temperature of about 160° to 165° C.

When all of the C_8 components had cleared the detector as indicated on the recording chart of the recorder (see the cut point marked on FIGURE 2A and FIGURE 2B) the flow of effluent was switched to a second condenser trap, and C_9 and heavier components were recovered from the effluent carrier gas therein. The recovered fractions equalled 96.88 percent of the amount of the sample. The C_8 and lighter components and the C_9 and heavier components were then separately subjected to detailed analysis by appropriate methods.

The herein-disclosed invention is not limited to separation of the lighter and heavier components in gasoline or to any particular operating conditions, as it also can be used to separate large-size samples of other wide boiling range mixtures containing close boiling components into two or more sharply defined groups of components. For example, the herein-disclosed invention can be used to separate naphtha, jet fuel, and the like into the respective component groups contained therein for further detailed analysis by appropriate methods. Although the herein-disclosed invention is particularly adapted for separation of large-size samples, with physical recovery of separated components, the apparatus nevertheless can be used merely for analytical separation of conventional, small-size samples, with remarkably good resolution considering the relatively short column length. It will also be appreciated that while the herein-disclosed instrument has particular advantages when the rising temperature program is initiated in each succeeding chromatographic separating zone at a time later than that of the preceding zone, it will be appreciated that the instrument is nevertheless flexible, in that the temperature programs for each of the separating zones also can be simultaneously initiated, whereupon the separate zones will function as a single chromatographic separating column having a single rising temperature program. In addition, while the illustrated embodiment is adapted for manual sample introduction and manual initiation of temperature programs, it will be appreciated that the instrument can be partly or fully automated by the use of conventional automatic sample injection means, sequence controllers and the like. Although the embodiment illustrated utilizes four separate separating columns, it will be understood that the separate zones can comprise successive portions of a single column. It will also be appreciated that the invention is not limited to any particular number of separating zones beyond two. Greater resolution will be obtained, however, with increasing numbers of separately temperature-programmed separating zones.

Numerous modifications and alternative embodiments of the invention as disclosed herein will readily suggest themselves to those skilled in the art. Accordingly, the scope of the invention is not to be limited by the embodiments disclosed herein but only by the scope of the claims appended hereto.

I claim:

1. A chromatographic method for separating a wide boiling range mixture containing a plurality of close-boiling components, comprising effecting a partial separation of lighter components from heavier components of the mixture at a relatively low temperature of the temperature program in a first elongated, temperature-programmed chromatographic separating column by introducing into said column a flowing stream of preheated carrier gas and a vaporous sample of the mixture to be separated, removing partly separated components from said first chromatographic separating column in the order of separation by continuing the flow of carrier gas therethrough and effecting a further separation of the partly separated components and accelerating elution of the partly separated components from said first chromatographic separating column by gradually increasing the temperature of the entire first chromatographic separating column uniformly over its entire length, thereafter effecting complete removal of the heavier components by further gradually increasing the temperature of said first chromatographic separating column to a temperature sufficient to insure elution of said heavier components from said first chromatographic separating column, effecting a further separation of the partly separated components of the mixture by passing the entire effluent from the first column into a separate, second elongated, temperature-programmed chromatographic separating column spaced apart from and fluidly communicating with said first column, said second chromatographic column being at a lower temperature then said first chromatographic column during at least a substantial part of the time in which the temperature of said first column is being increased, removing the further separated components of the mixture in the order of separation from the second chromatographic separating column and accelerating elution of the further separated components in that form, by continuing the flow of carrier gas therethrough and effecting a still further separation of the components and accelerating elution of the thus-separated components from said second chromatographic separating column by gradually increasing the temperature of the entire second chromatographic column uniformly over its entire length, and thereafter effecting complete removal of the heavier components from said second chromatographic column by further gradually increasing the temperature of said second column to a temperature sufficient to insure elution of said heavier components.

2. A chromatographic method for separating a normally liquid, wide boiling range mixture containing a plurality of close-boiling components into at least two portions of different composition, comprising establishing a temporary temperature gradient in a first elongated, temperature-programmed chromatographic separating column by establishing a flow therethrough from a preceding sample vaporizing zone of a preheated carrier gas, introducing into said sample vaporizing zone a liquid sample of said mixture of a size sufficient to permit physical recovery of said portions, effecting a partial separation of the sample mixture by vaporizing the components of the mixture that are vaporizable at the conditions of the system by passage therethrough of said preheated carrier gas, said carrier gas being preheated to a temperature sufficient to assist in vaporizing the vaporizable components of the mixture to be separated, effecting a further partial separation of lighter components from heavier components of the mixture at a relatively low temperature of the temperature program in said first column by introducing into said column a flowing stream of the preheated carrier gas and the vaporized sample of the mixture, removing partly separated components from said first chromatographic separating column in the order of separation by continuing the flow of carrier gas therethrough and effecting a further separation of the partly separated components and accelerating elution of the partly separated components from said first chromatographic separating column by gradually increasing the temperature of the entire first chromatographic separating column uniformly over its entire length, thereafter effecting complete removal of the heavier components by further gradually increasing the temperature of said first chromatographic separating column to a temperature sufficient to insure elution of said heavier components from said first chromatographic separating column, effecting a further separation of the partly separatted components of the mixture by passing the entire effluent from the first column into a separate, second elongated, temperature-pragrammed chromatographic separating column spaced apart from and fluidly communicating with said first column, said second chromatographic column being at a lower temperature than said first chromatographic column during at least a substantial part of the time in which the temperature of said first column is being increased, removing the further separated components of the mixture in the order of separation from the second chromatographic separating column and accelerating elution of the further separated components in that form, by continuing the flow of carrier gas therethrough and effecting a still further separation of the components and accelerating elution of the thus-separated components from said second chromatographic separating column by gradually increasing the temperature of the entire second chromatographic column uniformly over its entire length, and thereafter effecting complete removal of the heavier components from said second chromatographic column by further gradually increasing the temperature of said second column to a temperature sufficient to insure elution of said heavier components.

3. A chromatographic separating apparatus comprising a carrier gas source, a plurality of serially connected, spaced-apart, separate, elongated chromatographic separating columns, each such column having an inlet and an outlet, means defining a path of carrier gas flow between the inlet of each successive chromatographic separating column in the series and the outlet of the next preceding chromatographic separating column in the series, conduit means defining a path of carrier gas flow connecting said carrier gas source and the inlet of the first chromatographic separating column of the series, means associated with said conduit means for permitting introduction of a sample of a fluid mixture to be separated into the path of flow of said carrier gas, detecting means operatively connected with said chromatographic separating apparatus for sensing changes in the composition of the effluent carrier gas from the chromatographic separating column preceding the detecting means, separately controllable heating means for successively and at intervals gradually raising the temperature of each entire chromatographic separating column uniformly along its entire length, in the order in which it appears in the series, said heating means being constructed and arranged so that a successive column never reaches any temperature above its starting temperature before the same temperature has been reached by the preceding column.

4. A chromatographic separating apparatus comprising a carrier gas source, a plurality of serially connected, spaced-apart, separate, elongated chromatographic separating columns, each such column having an inlet and an outlet, means defining a path of carrier gas flow between the inlet of each successive chromatographic separating column in the series and the outlet of the next preceding chromatographic separating column in the series, conduit means defining a path of carrier gas flow connecting said carrier gas source and the inlet of the first chromatographic separating column in the series, said conduit means being provided with means for heating the carrier gas and with means permitting introduction of a sample of the mixture to be separated into the path of flow of the heated carrier gas, detecting means operatively connected with said chromatographic separating apparatus

for sensing changes in the composition of the effluent carrier gas from the chromatographic separating column preceding the detecting means, separately controllable heating means for successively and at intervals gradually raising the temperature of each entire chromatographic separating column uniformly along its entire length, in the order in which it appears in the series, said heating means being constructed and arranged so that a successive column never reaches any temperature above its starting temperature before the same temperature has been reached by the preceding column, and means connected to the outlet of the last chromatographic separating column in the series and positioned downstream of said detecting means, for separately recovering separated components of the mixture from the effluent carrier gas obtained from the last chromatographic separating column in the series.

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