

July 15, 1969

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3,455,090

CLOSED CYCLE CHROMATOGRAPHY METHOD AND APPARATUS

Filed March 6, 1967

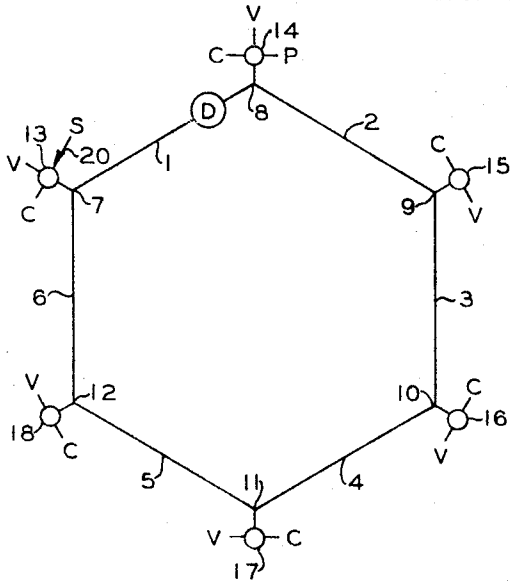


FIG. 1

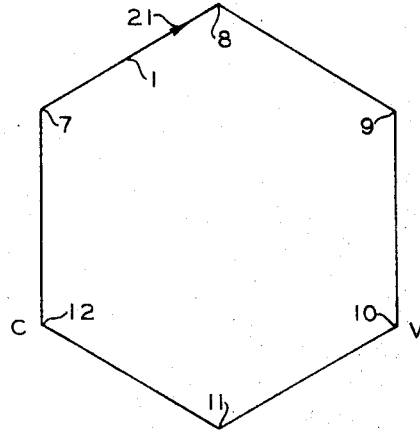


FIG. 2

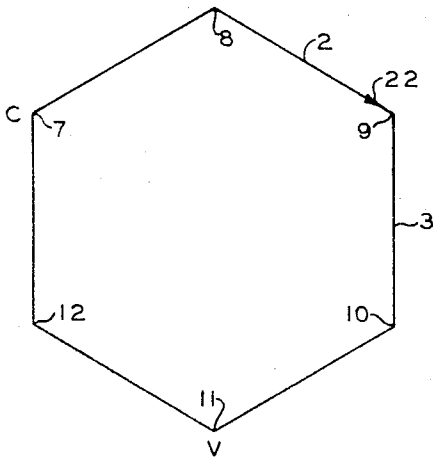


FIG. 3

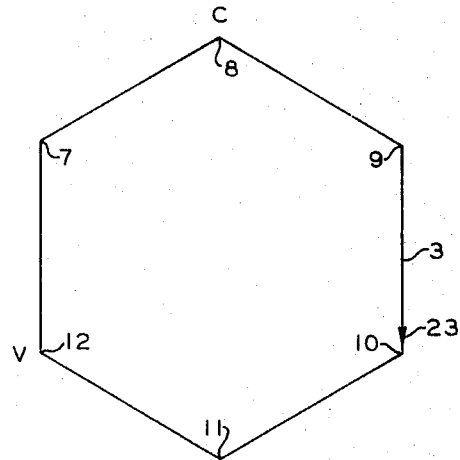


FIG. 4

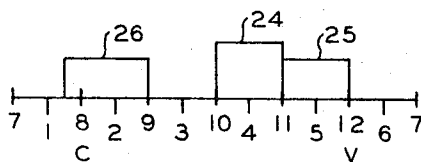


FIG. 5

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CLOSED CYCLE CHROMATOGRAPHY METHOD AND APPARATUS

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Filed Mar. 6, 1967, Ser. No. 620,980
Int. Cl. B01d 15/08

U.S. Cl. 55—67

8 Claims

ABSTRACT OF THE DISCLOSURE

Closed cycle chromatographic column having a plurality of ports for introducing and venting the sample and/or carrier fluid.

This invention relates to a method for chromatographically separating a sample into its respective components and the apparatus therefor. In one aspect this invention relates to preparative gas chromatography and the method and apparatus relating thereto.

Heretofore, conventional chromatographic procedures have encountered difficulty in coping with the isolation of large quantities of high purity components and with the component separation of a sample containing a large number, e.g. 50 or more, separate components. These difficulties have stemmed, at least in part, from the facts that both the apparatus and the time period required for such separations was exorbitantly large when conventional apparatus was employed. For example, heretofore in order to separate certain difficult separable materials or to make a clean separation of a large number of components from a single sample it was thought that chromatographic columns of lengths of hundreds of feet were necessary. Also, because of the extreme length of the columns, and because of the large pressure drops of the carrier gas in these columns, the time required for separation of a sample into its various components was very large.

According to this invention the above-mentioned long chromatographic columns are obviated without eliminating the function of those columns but with the elimination of both the need of extremely high carrier gas pressures and the long residence times in the chromatographic column by use of a chromatographic column in a closed-circuit configuration so that a sample can be circulated around the circuit as many times as is necessary, at the same time discarding various amounts of components of the sample, to get the desired separation of the components of that sample. The closed-circuit column of this invention is provided with a plurality of valve means operatively connected to the interior of the loop at spaced intervals around the circuit so that materials such as sample, carrier gas, and the like can be introduced into or withdrawn from the circuit at spaced apart points. Also, detector means for determining the position of the sample and/or various components of that sample in the circuit are carried by the circuit.

According to this invention, there is provided a method comprising passing a sample through a closed path of travel filled with a chromatographic absorbing medium until at least part of the components in said sample have separated from the original sample, the separated components traveling at least one of ahead and behind the original sample, adding carrier fluid at points along the path of travel of the original sample, venting components that are traveling ahead of the sample, and forcing any components that are traveling behind the sample in a direction reverse to the normal path of travel of the original sample to the venting zone where the components that are traveling ahead of the original sample are vented from the circuit.

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By this invention a relatively short actual length of chromatographic column is employed since that length is used over and over again depending upon the number of times the sample is passed through the circuit formed by the column. Thus, because of the shorter actual length of the column employed, lower carrier gas pressures can be used but at the same time less residence time is necessary than that required by a straight chromatographic column. The apparatus and method of this invention are particularly suitable for preparative gas chromatography where it is necessary to isolate large quantities of high purity components and/or separate a large number of components from a single sample, such as a mixture of hydrocarbons which is to be qualitatively and/or quantitatively analyzed. The invention is also suitable for purifying materials such as a mixture of hydrocarbons, e.g. gasoline.

Accordingly, it is an object of this invention to provide a new and improved method and apparatus for chromatographic separations. It is another object of this invention to provide a new and improved method and apparatus for preparative gas chromatography.

Other aspects, objects, and the several advantages of this invention will be apparent to those skilled in the art from the description, drawings, and appended claims.

FIGURE 1 shows apparatus embodying this invention.

FIGURES 2 through 4 show various stages of operation of the apparatus of FIGURE 1.

FIG. 5 shows an example of separation of three components in the apparatus of FIGURE 1.

FIGURE 1 shows six straight chromatographic columns 1 through 6 joined in an end-to-end fashion to form a closed circuit in the form of a hexagon, the hexagon having six end-to-end junctures 7 through 12.

Six valves 13 through 18 are operatively connected to the interior of the circuit formed by the six columns so that materials such as carrier gas, sample, separated components, and the like can be introduced into and removed from the closed circuit at any of the six valves. In FIGURE 1 valves 13 and 14 are shown as four-way valves and valves 15 through 18 are shown as three-way valves. The use of two four-way valves and four three-way valves is a preferred embodiment of the invention but is not necessary to effect the advantages of the invention. Valve 13 shows one position denoted S for introducing sample into the circuit, another position V for venting material from the interior of the circuit, and another position C for introducing carrier gas into the circuit. Valve 14 has similar carrier gas and vent ports but its third port denoted by P is for removing product from the circuit for further chromatographic or other analysis for other treatment as desired. Valves 15 through 18 have positions denoted by V for venting materials from the interior of the circuit and still other positions denoted by C for introducing carrier gas into the circuit. Generally, any suitable valve means for allowing the introduction of material into and the withdrawal of material from the interior of the circuit is suitable for use in this invention.

A conventional chromatographic detector such as a thermistor is mounted in column 1 so that the position of the sample or various components inside the circuit can be determined from time to time and also so that the time for passage of the sample or any particular components around the circuit one time can be determined. Any suitable chromatographic detector can be employed, such detectors being well known in the art. Also, more than one detector can be employed in one or more of columns 1 through 6; for example, a detector can be employed in each of the six columns.

FIGURE 1 shows by arrow 20 the introduction of a sample which is to be separated into its various com-

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ponents by conventional chromatographic techniques being introduced through valve 13 into column 1. At this time carrier gas is being introduced through valve 18 into the interior of column 6 toward column 1 thereby picking up the sample and starting it in a clockwise path of travel through the circuit. Some of the carrier gas introduced through valve 18 also passes into column 5 and thereby starts a flow of carrier gas in a counterclockwise direction through the circuit. Further, at the same time the sample and carrier gas are being introduced, the vent port on valve 16 is open so that carrier gas passing in a counterclockwise path of travel passes out valve 16 and does not run into the clockwise traveling sample.

FIGURE 2 shows the sample represented by arrow 21 as it passes to the end of column 1 with carrier gas being continued to be introduced at juncture 12 and the vent port of the valve at juncture 10 continuing to be open.

FIGURE 3 shows the sample as it continues in its first circuit around the circuit and as it reaches the end of column 2, arrow 22, at which time the valve at juncture 10 is closed and the vent port of the valve at juncture 11 is opened while the valve at juncture 12 is closed and carrier gas is introduced into the interior of the circuit through the valve at juncture 7. The changing of the valves can be done either manually or by conventional automatic switching machines well known in the art.

FIGURE 4 shows the sample as it continues to travel to the end of column 3, arrow 23, at which time the valve at juncture 7 is closed and the vent port of the valve at juncture 12 is opened and carrier gas is introduced into the circuit through the valve at juncture 8.

This changing of position of valves around the circuit as the sample passes through the circuit continues in the same fashion as already described, i.e. vent two columns ahead of the original sample and introduce carrier gas one column behind the original sample, until the separation operation is discontinued and the desired material is removed from the circuit through the product port of valve 14.

As the sample passes around the circuit a number of times the various components separate from one another, some components traveling ahead of other components and yet other components traveling behind some components. If, for example, the desired component has other components both in front and behind it, the component traveling in front of it will be vented from the circuit when it travels far enough ahead of the desired component to run into the valve whose vent port is open. Similarly, components which are traveling behind the desired component will fall further and further behind until they are traveling in a column in which the carrier gas is passing through in a counterclockwise direction. When a component encounters counterclockwise moving carrier gas it is backflushed counterclockwise to the valve which has its vent port open. Thus, by letting the undesired components move forward and/or fall behind the desired component as all the components travel through the circuit, the components that travel ahead ultimately vent themselves whereas the components traveling behind are backflushed with counterclockwise flowing carrier gas to the same vent. Thus, after a finite residue time in the circuit what is left is the desired component and it is removed as the product of the separation.

FIGURE 5 shows the relative position of three components of a single sample after these components have separated to a point where some venting of the undesired components can take place. For clarity's sake, the circuit of FIGURE 1 is then straightened out into a straight line so that reference numbers 1 through 12 of FIGURE 5 represent the columns and junctures as described in FIGURE 1.

The block represented by numeral 24 is the desirable component of the sample and blocks 25 and 26 are the undesirable components, component 25 traveling faster

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than component 24 and component 26 traveling slower than component 24. After a suitable residence time in the circuit, component 25 will be one full column ahead of component 24 and thereby approaching juncture 12 whose valve has its vent port open. Thus, component 25 is about to be vented from the circuit at juncture 12 and thereby separated from component 24. Similarly, component 26 has fallen one full column behind component 24 and has spread out to cover more than one length of column so that it covers all of column 2 and part of column 1. The carrier gas being introduced through the valve at juncture 8 thereby in part passes in a counterclockwise direction into column 1 and will force that portion of component 26 which is in column 1 counterclockwise through columns 1 and 6 to the vent valve at juncture 12, thereby separating at least part of component 26 from component 24.

At the next switching of valves when component 24 has moved into column 5 more of component 25 will be vented from the circuit and more of component 26 will be backflushed and then vented from the circuit. Thus, after a repetition of these steps for a sufficient number of times substantially all that is left in the column is the desired component 24 which can then be vented from the circuit at any juncture desired.

This invention is applicable to samples wherein the undesired components thereof all move faster than the desired component or all move slower than the desired component. Also, this invention applies to samples wherein the desired product moves faster or slower than the undesired components. Further, this invention is applicable to the separation of two or more desired components, more than one desired component being separable from the circuit through any of the valves associated with the circuit, e.g. valve 14 of FIGURE 1.

Generally, any known chromatographic column can be employed. Further, any known chromatographic absorbing medium such as squalane, squalene, octadecane, benzol celosolve, paraffin wax, silicone fluids, dioctyl phthalate, and the like can be employed in a conventional manner known in the art. Any conventional carrier gas such as hydrogen, argon, nitrogen, and the like can be employed. Any inert or active absorbing support for the chromatographic absorbing medium can be used, e.g. Chromasorb, kieselguhr, fire brick, diatomaceous earth, silica gel, activated carbon, alumina, glass beads, granular polytetrafluoroethylene, molecular sieves, charcoal, silica gel, eutectic salts, and the like. This invention can be used for separating components of any material whose components are separable by conventional chromatographic analysis. This invention is particularly applicable to organic, preferably hydrocarbon, samples. The invention is applicable to the separation of samples formed from hydrocarbons and/or inorganic compounds containing from 1 to 100 carbon atoms per molecule, inclusive.

EXAMPLE

The apparatus of FIGURE 1 is employed using six three-foot lengths of 1/4 inch diameter chromatographic columns filled with Chromasorb support material carrying 3 weight percent, based on the total weight of the support, of squalane uniformly dispersed throughout all six columns. A sample composed of 15 weight percent 2,3-dimethylbutane, 70 weight percent 2-methylpentane, and 15 weight percent 3-methylpentane is injected into the column through valve 20 while hydrogen carrier gas under a pressure of 20 p.s.i.g. is introduced through valve 18 and valve 16 has its vent port open. The hexahedron circuit and chromatographic process is carried out substantially at room temperature.

The sample is cycled six times through the circuit in a manner set forth with respect to the discussion of FIGURES 2 through 4 at which point the samples are spread out through the circuit in the manner shown in FIGURE 5, block 25 representing the 2,3-dimethylbutane compo-

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nent, block 26 representing the 3-methylpentane component, and block 24 representing the desired 2-methylpentane component. Thus, at the end of six cycles around the circuit of FIGURE 1 the 2,3-dimethylbutane is starting to be vented through valve 18 while the 3-methylpentane component is starting to be backflushed by hydrogen carrier gas introduced through valve 14. After a few more cycles of the sample through the circuit substantially all of the 2,3-dimethylbutane and 3-methylpentane has been vented from the circuit thereby leaving substantially only the 2-methylpentane which is removed from the circuit through the product port of valve 14 for further analysis or other treatment.

If the process of this example was carried out in a straight chromatographic column, a column 60 feet long would be required and a hydrogen carrier gas under a pressure of at least 60 p.s.i.g. would also be required in order to carry the sample through the 60 feet of column. However, in spite of the substantially higher carrier gas pressure used with this straight column, triple the amount of time would be required for the separation of the 2-methylpentane from the 2,3-dimethylbutane and 3-methylpentane than is necessary for the process of this invention because of the large pressure drops encountered in the 60-foot straight column that are not present in the circuit apparatus of this invention.

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope thereof.

I claim:

1. A chromatographic method comprising passing a sample containing a plurality of components through a closed path of travel filled with chromatographic absorbing medium until at least part of the components in said sample have separated into positions of at least one of ahead and behind the original sample as the sample travels through said closed path, adding carrier fluid to said path of travel at points along said path so that said carrier fluid passes in both a clockwise and counterclockwise direction around said path, venting from said path any component that travels ahead of said original sample, forcing with carrier fluid any components that travel behind said original sample in a direction reverse to the normal path of travel direction of said sample and to the venting zone where said components that travel ahead of said original sample are being vented, and separately recovering from said path the remaining components of said sample.

2. The method according to claim 1 wherein said sample is formed of organic components.

3. The method according to claim 2 wherein said components are hydrocarbons.

4. The method according to claim 3 wherein said hydrocarbons are a mixture of 2-methylpentane, 2,3-dimethylbutane, and 3-methylpentane, the carrier gas is hydrogen, and the chromatographic absorbing medium is squalane.

5. Chromatographic apparatus comprising a chromatography column in a closed-circuit configuration so that a sample can be circulated around the circuit any desired number of times, a plurality of valve means operatively connected to said column at spaced intervals around said circuit so that the circuit is split into a plurality of segments, each segment having both end points terminated by valve means, a plurality of conduits connected to each of said valve means to allow materials to pass into or pass out of the circuit selectively through said valve means, and at least one detector means operably connected to said circuit for determining the position of material within said circuit.

6. The apparatus according to claim 5 wherein said circuit is formed from a plurality of straight chromatographic columns joined in an end-to-end fashion, and one of said valve means is operatively connected to the interior of said circuit at each end-to-end juncture of said circuit.

7. The apparatus according to claim 6 comprising six straight chromatographic columns joined in an end-to-end fashion to form a hexahedron, one of said valve means being operatively connected to the interior of said circuit at each of the six end-to-end junctures in said hexahedron circuit.

8. The apparatus according to claim 7 wherein four of said valve means are three-way valves and two of said valve means are four-way valves.

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