United States Patent

[11] 3,581,465

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[33] **Japan**
[31] **42/77210, 41/79728, 42/34386 and 41/78803**

[54] **METHOD AND APPARATUS FOR CONCENTRATING AND TRAPPING SAMPLE COMPONENT**
5 Claims, 10 Drawing Figs.

[52] U.S. Cl. 55/67
[51] Int. Cl. B01d 15/08
[50] Field of Search 73/23.1; 55/67, 197, 386

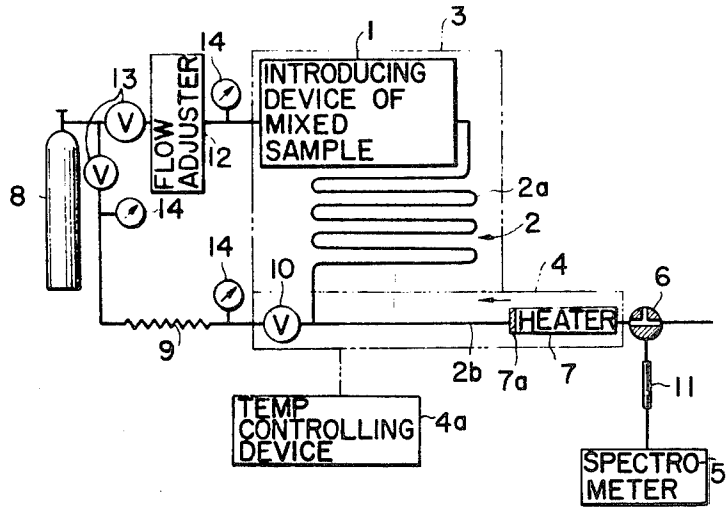
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ABSTRACT: A method and apparatus for separating a mixed sample of gas, fluid or solid into its components trapping each component in its concentrated state in a column having a temperature gradient along the length thereof and removing each component from said column by controlled heating thereof for subsequent introduction into a spectrometer.



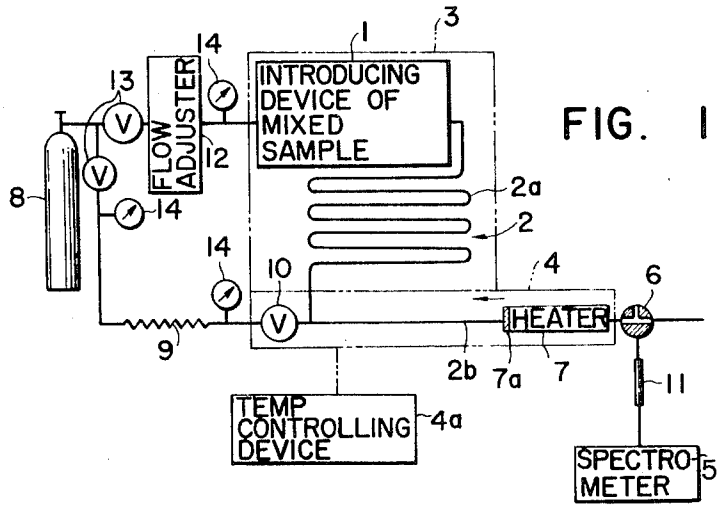


FIG. 1

FIG. 2

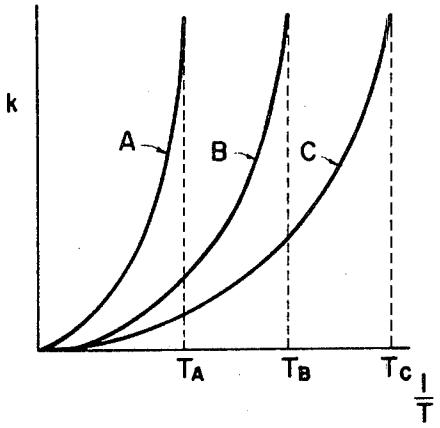


FIG. 3

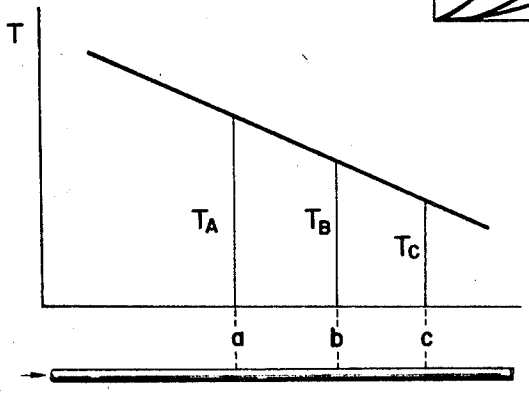


FIG. 4

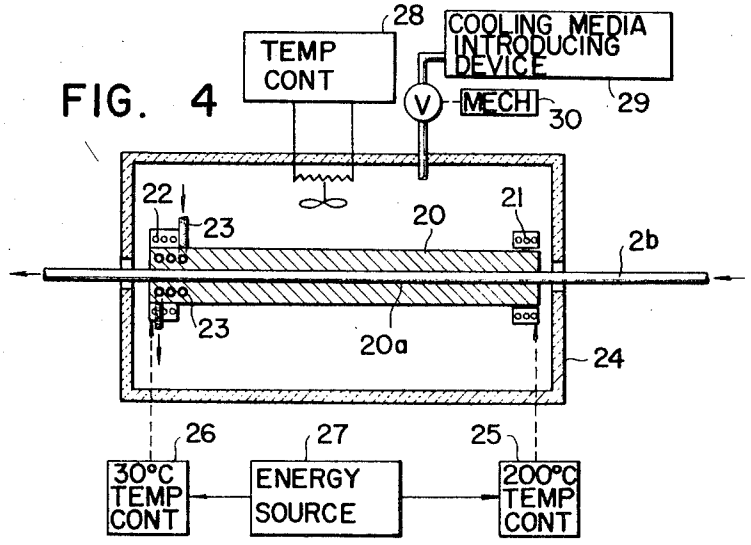
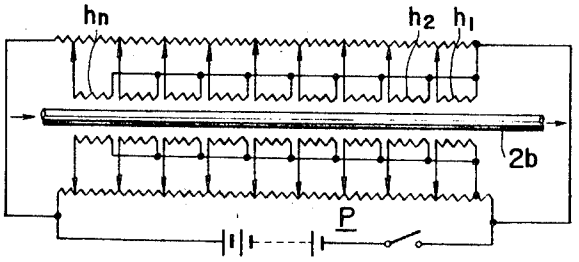


FIG. 5



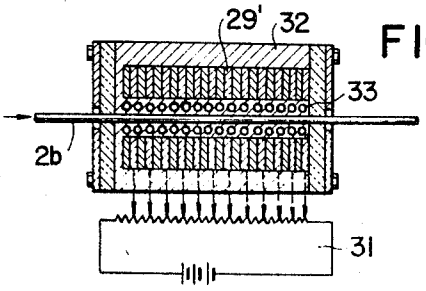


FIG. 6

FIG. 7a

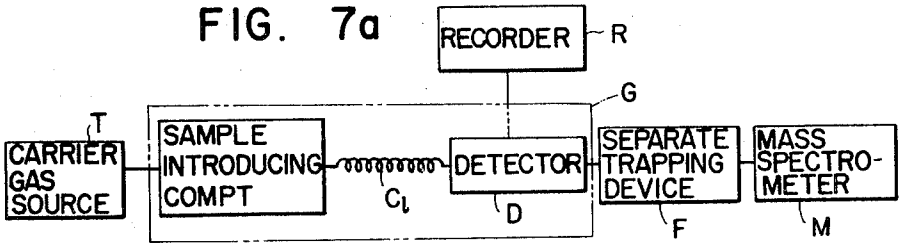


FIG. 7b

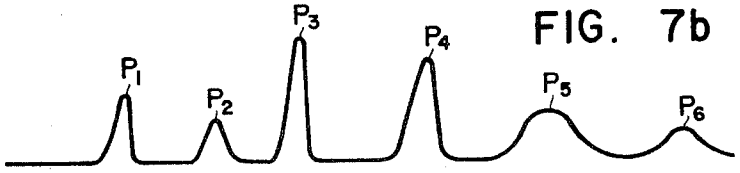


FIG. 8

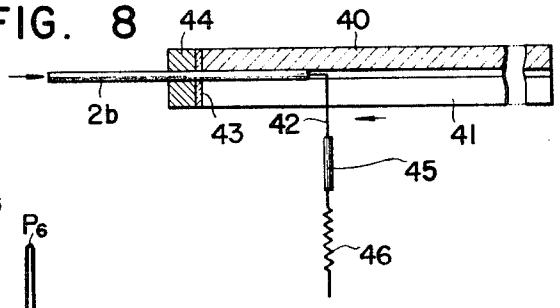
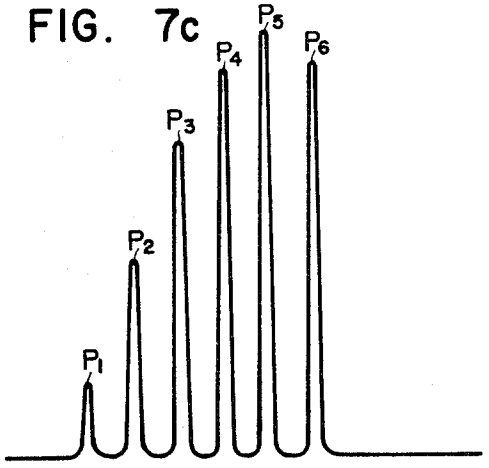


FIG. 7c



METHOD AND APPARATUS FOR CONCENTRATING AND TRAPPING SAMPLE COMPONENT

BACKGROUND OF THE INVENTION

The present invention relates to method and apparatus for separating a mixed sample of gas, vapor, fluid or solid into its components and fixing or holding said components in a concentrated condition and/or trapping the same and, in particular, to a method and device for trapping the separated components in the concentrated condition which were separated by means of a fraction device such as a chromatograph.

Generally, when analyzing a sample by means of a mass spectrometer, infrared spectrometer and the like, it is difficult to carry out the qualitative analysis as the shape of the spectrogram becomes complicated when the sample is in the mixed condition. When using a mass spectrometer, it is difficult to introduce a large amount of sample at one time into the device thereby limiting the use thereof. So, if the concentration of the sample component is thin, sufficient accuracy is not gained for the lack of sensitivity of the spectrometer. Therefore, in order to use the said mass spectrometer efficiently, it is desirable to separate the sample into the components as much as possible and to introduce the components into said spectrometer in as concentrated condition as possible. For separating a mixed sample including a plurality of components, the chromatography method is ordinarily employed. In the chromatography method, the separated components are diluted with a carrier fluid because the sample is differentially migrated in a column with a carrier fluid, and it is undesirable to introduce the components as is into the said mass spectrometer. Since the peak width of the separated component has some deviation generally in chromatography, the component can not be concentrated more than the deviation.

SUMMARY OF THE INVENTION

The primary object of the present invention is to provide a method and apparatus for separating a mixed sample containing a plurality of components into its individual components and trapping the separated components in as concentrated condition as possible to enable introduction into a spectrometer such as a mass spectrometer.

Another object of the present invention is to provide a method and apparatus for taking out a fraction of the trapped concentrated component in its highly concentrated and fluid condition for introduction as is into a high quality spectrometer.

A further object of the invention is to provide a trap for chromatography for trapping the separated components in highly concentrated condition thereby overcoming the dilution effect of the carrier.

A still further object of the present invention is to provide a fraction concentrating trapping device for the sample components utilizing a stationary phase and a mobil phase having a temperature gradient.

A still further object of the present invention is to provide a novel trapping device for controlling the temperatures at the opposite ends of the column to different fixed values and providing the temperature gradient necessary for concentration, separation and separate trapping of the components in the stationary phase.

Other objects and the advantages of the present invention will be apparent from the following description when taken in conjunction with the accompanying drawings showing the embodiments in accordance with the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a preferred embodiment in accordance with the present invention;

FIGS. 2 and 3 are explanatory graphic views showing the principle of the fixing operation of the sample component to the column;

FIGS. 4, 5 and 6 are schematic views showing three different embodiments of the device for giving a temperature gradient to the column of the separation fixing device in accordance with the present invention;

FIG. 7*a* is a schematic diagram showing the embodiment of the method and apparatus for trapping the outlet gas of the gas-chromatograph in accordance with the present invention;

FIG. 7*b* is a chromatogram of the outlet gas of the said gas-chromatograph;

FIG. 7*c* is a graph showing the concentration distribution of the trapped gas by means of the separation fixing device in accordance with the present invention; and

FIG. 8 is a partly sectionary view showing a method and device of an embodiment for trapping the fixed components at the outlet in its fluid condition.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1 showing an embodiment of the present invention, the reference character 1 represents an introducing device for a mixed sample containing a plurality of components, and 2 represents a column having a stationary phase therein like a column for gas-chromatography, the cross section of which may comprise various shapes such as a circle, a thin square or the like. As for the stationary phase, a solid phase activated adsorption agent such as alumina, carbon and silica gel, or a liquid phase such as silicone oil coated thereon or impregnated into the supporting media is employed. The reference character 3 represents a thermostat bath, 4 a temperature gradient providing device, 5 a high quality spectrometer such as a mass spectrometer, 6 a flow path changing cock, 7 a movable heater, 8 a carrier gas cylinder of He, Ne and the like, 9 a resistance pipe, 10 a flow stopping cock, 11 a stripping column, 12 a carrier gas flow adjuster, 13 stop valves and 14 represents a pressure gauge.

In this specification, hereinafter "separate trapping" is defined to include the state in which the sample components in a mobil phase are separated, by means of adsorption or partition within a stationary phase in a column, and are retained on the inner wall of the column or in the stationary phase and/or the state of the separate components being taken out in a fluid condition or gas condition through elution or flowing.

Now, the introduced sample from a sample introducing device 1, in FIG. 1, is separated into its components in a column 2, and the separated components are fixed respectively to different positions on the wall of the column 2. This fixing is carried out by giving a temperature gradient to column 2.

The linear velocity v of the sample components, is represented by the following formula

$$V=\frac{u}{1+K\frac{Vl}{VG}} \tag{1}$$

wherein u is a linear velocity of a carrier gas or developer, k is a partition coefficient, and Vl/Vg is a ratio of a stationary phase area to a mobil phase area of the separated components in the cross section. The partition coefficient k is represented with

$$k=C\ \exp.\left(\frac{-\Delta H}{RT}\right) \tag{2}$$

wherein C is a proportion coefficient, R is a gas constant, T is an absolute temperature, ΔH is a latent heat when 1 mole of the sample component is solved into the stationary phase which is ordinarily minus. The partition coefficient k increases exponentially as the the temperature decreases.

FIG. 2 is a graph showing the relation between k and T^{11} in respect to three components A, B and C, which shows that the aspect of the increasing of k as the temperature decreases is different for each component A, B and C. FIG. 2 also shows that at the temperature T_A, T_B and T_C the value of k becomes extremely large respectively in A, B and C. The linear velocity v_A, v_B and v_C of the component A, B and C is substantially zero at the temperature of T_A, T_B and T_C as apparent from the formula (1).

In the separation fixing device in accordance with the present invention, the sample is separated in the column and the separated components stops at said temperature T_A, T_B and T_C, respectively, in the temperature distribution which has a decreasing gradient on the column from the inlet to the outlet thereof. FIG. 3 is a graph showing the temperature gradient on the column. The components A, B and C are fixed at the position *a*, *b* and *c* in the column corresponding to said temperatures T_A, T_B and T_C.

The temperatures T_A, T_B, T_C in FIG. 2 indicate the temperatures at which almost all the separated sample components are absorbed in the liquid phase when the carrier gas is flowing (the so called end-point). The components are not instantaneously fixed or held at the end-point, but are continuously absorbed and fixed during the decrease in temperature. Therefore, if the flow of the carrier gas is stopped during the passage along the zones of decreasing temperature before the gas reaches the end-point, the components are separately fixed or held to such extend that corresponds to the extent the temperature has decreased.

The temperature gradient of the column **2** may be applied to the whole of the column **2**, but in the case of the device shown in FIG. **1** the portion of the column **2***a* is maintained at constant temperature and the portion of the column **2***b* connected to said portion of the column **2***a* is provided with the temperature gradient. That is, the sample is separated at the portion **2***a* of said column in the thermostat bath **3** and fixed at the portion **2***b* of said column in the temperature gradient giving device **4**. In this case, the separated components have some deviation in the mobil phase, but since the temperature zone during fixing is confined to a specific zone, it results in the concentration.

In order to introduce the fixed components for the said column portion **2***b* into the spectrometer **5** after the said separate trapping, the temperature gradient giving operation of the temperature gradient giving device is stopped by switching a temperature controlling device **4***a* and a cooling device (see FIGS. **4** and **6**) is operated thereby cooling the column portion **2***b* to a proper temperature and stabilizing the said fixing. Then the change valve **6** is rotated by 90° in the counterclockwise direction into the analysis metering position and a heater **7** (the heater-block **21** in FIG. **4** may be used) surrounding the column portion **2***b* is gradually moved in the direction of the arrow. Thus the elution of the separated components fixed to the column is gradually carried out at the lower pressure side of the outlet. In the case of the spectrometer **5** being a mass spectrometer, the load pressure is utilized for separate trapping of the components. The sample elution operation of moving the components out of the inner wall of the column portion **2***b* with the advancing of the heater **7** is also able to be carried out by introducing a small amount of carrier gas from the carrier gas cylinder **8** through the resistance pipe **9** and the change valve **10**. In the case that the stationary phase component, other than the separated components fixed to the column when the column portion **2***b* is heated with the heater **7**, may flow out and be introduced into the spectrometer, a stripping column **11** for removing the liquid phase is desired to be connected to the spectrometer. Since the higher the temperature gradient at the left edge of the moving oven is, the greater the concentration effect without a failure of separation is, it is desirable to dispose a cooling plate or an insulating member **7***a* at the front of the heater **7** in order to prevent the heat from transmitting to the moving direction. (If the heat transmits forward in the moving direction, it is feared that the component fixed forwardly thereof may be solved out therewith.)

Though in the drawing the column portion **2***b* having the separated components fixed thereto is still mounted to the device when the components are taken out, the heating device and the column to which the components are fixed with a separation fixing device may be disposed separately and take out the components with the heating device.

The separation fixing device in accordance with the present invention described hereinbefore is a device which carries out fixing of the components separated in this device as well as sample introducing as same as the ordinary chromatograph and separation through a column.

The advancing velocity of a separated component in the device becomes zero at a position on the column where the temperature thereat is peculiar to the separated components and the components are fixed to the column at the position. Even though the fixed components in this case are of an extremely small amount, it is concentrated in high density for it is fixed at an extremely narrow range, and the efficiency is close to 100 percent.

Referring to FIG. **4** showing an embodiment of a temperature gradient giving device **4** of the column in accordance with the present invention, the reference character **20** represents a heat conductor block such as aluminum having at the center thereof a groove through which a column **2***b* is inserted. A heating coil element **21** is provided for heating an end of the said conductor block **20** at regulates the higher pressure side of the column and **22** and **23** respectively designate a heating coil element and cooling coil tube for controlling the temperature at the other end of the block **20** which is the lower pressure side of the column, which temperature is a definite temperature lower than at the said high pressure side. An insulating wall **24** is provided for preventing the circumferential temperature of the block **20** from being varied with the outer temperature condition whereby the atmosphere within the wall is maintained in a constant condition. A heating current controlling device **25** for the heating coil element **21** regulates the temperature at an end of the column to a definite temperature such as 200° C and a heating current controlling device **26** for the heating coil **22** at the other end of the column regulates the temperature at the lower pressure end of the column at a definite temperature such as 30° C in cooperation with a cooling operation by a cooling media circulating pipe **23**. An electric source of current **27***a* is provided for the heating current controlling devices. Though it is not shown in the drawing, since the temperature at each end of the column is required to be strictly regulated to a definite temperature, temperature detecting elements or the like are disposed at the opposite ends of the column or block and the said controlling devices are automatically controlled by the detecting signal, whereby the temperature at each end is regulated. The reference character **28** represents a controlling device for controlling the temperature within the thermostat bath **24**, **29** is a cooling media introducing device, and **30** is a valve of said cooling media introducing device **29** to be used when uniform cooling is desired within said bath, that is said column. By heating or cooling the opposite ends of the block to different temperatures, heat is conducted from the higher side to the lower side through the aluminum block, whereby the column is provided with a linear temperature gradient.

Referring to FIG. **5** showing another embodiment of the temperature gradient giving device, a plurality of band heaters h_1, h_2, h_3....h_n are disposed around the column **2***b*. By supplying the band heaters with increasing voltages from one end to the other end by means of an electric source circuit P, a desired temperature gradient is provided on the column.

Referring to FIG. **6** showing still another embodiment of the temperature gradient giving device, a number of thermoelements **29'** are arranged around the column **2***b*. By supplying increasing current from one end to the other end to the thermoelements with a source **31**, a desired temperature gradient is provided on the column. The reference character **32** represents a mounting block for the said thermoelements and **33** represents a cooling media circulating pipe to be used during cooling of the column. Thermoelements are available for use as cooling elements by changing the current polarity thereof after being used as a heater device for providing a temperature gradient to the column and the column is able to be cooled therewith (which is of use for stabilizing the fixed components hereinafter described). Moreover, said thermoelements are available for separate flowing operation of the fixed components hereinafter described by shifting the time of heat

generating of the thermoelements by changing the switch of said circuit from one element at one end to the other element at the other end.

Other than the embodiments hereinbefore described, various types of the device may be employed such as a column with an electric heating wire wound thereon in spiral or zigzag varying the pitch thereof, and a device using a fluid heating media.

An experimental example using the said embodiments, in particular, the device of FIG. 4 is substantially as follows.

A stainless column of 3 mm. inside diameter and 4 mm. outside diameter is filled with a fire brick powder supporting media of 60-80 mesh impregnated with 15 percent SE 30 (commercial name of a methyl silicone rubber made by U.S. General Electric Co.) for use as a stationary phase. A sample of fatty acid methyl ester of C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18} is sent into the column so that the sample flows at the rate of 100 cc./min. from the inlet to the outlet with a He gas carrier, whereby a mobil phase is formed in the column making the pressure difference between the opposite ends of the column. The column is inserted into an aluminum block of 50 cm. length disposed in a thermostat bath and the temperature at the inlet of the column is made 200° C. and at the outlet 30° C., making a linear temperature gradient therebetween, and the condition is maintained for about 30 minutes. Then the valve **13** is closed to stop the flow of the carrier and the operation of the heating devices at the opposite ends of the column is stopped. When the air flow of normal temperature is sent into the bath from the cooling media introducing portion **29** (that is, the aluminum block is removed) and the column is returned to normal temperature condition, and the component having most carbons in the sample (methyl stearate C_{18}) is fixed to a portion in the column nearest from the inlet thereof, and the component having most carbons next to said component (palmitade ... C_{16}) is fixed adjacent to the said portion nearest to the inlet, and thus the components having less carbons, C_{14}, C_{12} ... are fixed to the column at equal interval along the column in the longitudinal direction and the component having C_8 is stably fixed in a concentrated condition at the nearest position from the outlet of the column.

Then, when the vale **10** was opened to let a small amount of He carrier gas of about 10 cc./min. go into the column to which said sample components are fixed separately and a pressure differential was made between the opposite ends thereof, and a heater **7** to about 250° C. was moved gradually from lower pressure side to the higher pressure side of the column, the said fixed components were eluted out and the component having C_8 was trapped out at first and the component having C_{10} was trapped out second in a concentrated gas condition and the component having C_{18} was out at the end. These components had enough density to be sent into the mass spectrometer.

Referring to FIG. 7 which shows an embodiment of the present invention in the case of being connected to a gas chromatograph, the reference character T represents a carrier gas source, and G represents a body of the gas chromatograph which comprises a sample introducing compartment S, a main column C_1, a detector D and a recorder R. The reference character F represents a separate trapping device in accordance with the present invention, and the device M is a mass spectrometer.

The components separated with a chromatography device flow out having a various peak width. The peak width, that is, the time from starting of flow out to ending thereof has a relation with its retention time. So, when it is large, the density decreases and the peak becomes lower with large deviation, and the density of the separated components is also low, but the component is fixed to the column in a concentrated condition in the said trapping device F. That is, the separated components having a distribution as shown in FIG. 7*b* at the portion of the said detector D become as FIG. 7*c* at the outlet of the said device F. The components thus fixed may be taken out by splitting or breaking the column or may be taken out by flowing out with a carrier gas raising temperature of the whole column, but it is most desirable to take out the fixed components by the following method.

Referring to FIG. **8** which shows another embodiment of a method and device for trapping sad separated fixed components in a gas or vaporized condition at the outlet of the column, a carrier gas is sent in the direction of the arrow in the column **2***b*.

A heater **40** having a slit **41** for letting the tube portion **42** pass therethrough is movable from the outlet side to the inlet side of said column **2***b*. In order to clarify the boundary of the heating portion and the nonheated portion, a cooling ring **44** is mounted to the column prior to the heater **40**. The cooling ring **44** is cooled with a thermoelement for electronic freezing or with a cooling medium. The reference character **43** represents an insulating member for insulating between the said cooling ring **44** and the said heater **40**. The thickness of the insulating member **43** is desired to be as thin as possible such as 0.2 mm. The reference character **45** represents a stripping column for removing impurities from said eluted gas.

When the heater **40** is moved in the arrow direction, the component fixed into the gas phase and is carried out of the column with a carrier gas. The heater **40** is long enough up to the end of the column for keeping the eluted component in a gas state.

It is not needed to strictly control the temperature of the heater **40** but it is desired to provide the heater with a temperature distribution which increases toward the back end thereof. The cooling ring is long enough for stably holding the fixed component at the nonheating portion.

The moving velocity of the heater **40** has a relation with the concentration of the component. For instance, in a case where it takes 1 hour to separate all the components and the components are fixed on a column of 10 cm. long in a gas chromatography, it takes 10 minutes to flow out all the components when the heater **40** is moved at the rate 1 cm./min. and this results in a six times concentration. But the value of said six times is one wherein the inner pressure and flowing quantity are operating the fixing of the components, and the magnification depends upon the inner pressure and the flowing quantity. In case of using this trapping device connected with a mass spectrometer, the linear velocity in the column is fixed against the flowing quantity to be taken into the spectrometer. As the column is set to provide the maximum efficiency, the inner pressure of the column is different from the inner pressure of the chromatography device. For instance, inner pressure of the column **3** is 7.6 mm. Hg (pressure dropping along the column is neglectable). The pressure outlet of the column of a gaschromatograph is 760 mm. Hg.

In this case, the ratio $760/7.6 = 100$ is multiplied by the six times. Said magnification can be made much larger than the one described above by choosing the resistance pipe or controlling the pressure controlling device. As is apparent from the above description, the concentration magnification is related to the moving velocity of the heater and the inner pressure.

As apparent from the above description, by mounting a device F in conjunction with the mass spectrometer, the components may be analyzed with a higher degree of accuracy in higher concentration by utilizing a plurality of chromatographs.

The method and device in accordance with the present invention makes it possible to concentrate the separated components into a fairly high density without any loss.

Though the present invention was described mainly with its connection to a gas chromatograph and with separate fixing of a gas, it is also used in a liquid chromatography. The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What I claim is:

1. A device for separately trapping components of a mixed fluid sample comprising a column having therein a stationary phase for separating the components, an introducing device for introducing a mixed sample containing a plurality of components into the column, means for giving a temperature gradient to said column and separately holding the sample components to different positions in said column, a pressure giving means for providing a pressure difference between one end and the other end of said column, and a heating means for progressively heating said column from the lower pressure side to the higher pressure side thereof along the longitudinal direction to a higher temperature than the holding temperature of said sample, whereby the fixed sample components are eluted out of the low pressure side of said column in a concentrated condition.

2. A method for separately trapping the components of a mixed fluid sample comprising the steps of guiding a mixed sample having a plurality of components into a column having therein a stationary phase for separating the sample by flowing the sample with a carrier fluid from one end of the column to the other, providing a temperature gradient along the whole effective length of said column, said temperature gradient being such that the temperature decreases in the direction of fluid flow, separately holding the component in the column without diffusion of the sample components, heating said column to a higher temperature than said holding temperature progressively from the outlet end to the inlet end of said column and providing said column with a pressure gradient decreasing in an opposite direction to the advancing direction of heating whereby the components of the sample flow out of the outlet of the column in a concentrated state.

3. A device for separately trapping components of a mixed fluid sample comprising a chromatograph having a sample separating column contained therein and a second column having temperature gradient providing means for providing a temperature gradient decreasing from the inlet end of said second column to the outlet end thereof, said second column being connected to the outlet of said chromatograph column whereby the separated sample components separated in said chromatograph are fixed separately at different positions along the length of said second column and heating means for heating said second column progressively from said outlet end to the inlet end thereof at a temperature higher than the fixing temperature of said sample components whereby the fixed components in said second column may be removed from the outlet end of said second column in a concentrated condition.

4. A method for separately trapping components of a mixed fluid sample comprising separately holding components at different positions in a column having a stationary phase along the length thereof, progressively heating said column from the outlet end toward the inlet end to a temperature higher than the highest holding temperature of the components and providing a pressure gradient decreasing from the inlet end to the outlet end of the column whereby each component will flow from the outlet end of the column in a concentrated state.

5. A device for separately trapping the components of a sample comprising a column having therein a stationary phase for separating said sample, means for holding separated components of said sample at different positions along the length of said column, means for progressively heating said column for the outlet end to the inlet side at a temperature higher than that at which the separated components are held in the column, and means for providing a pressure gradient decreasing toward the outlet end of the column whereby the sample components are separately flowed out of the outlet end of said column in a concentrated condition.