Jan. 31, 1967 E. L. LEVY ETAL 3,301,040

AUTOMATIC FRACTION COLLECTING SYSTEM FOR VAPOR PHASE CHROMATOGRAPHY

Original Filed March 24, 1958 4 Sheets-Sheet 1

Fig. 8.

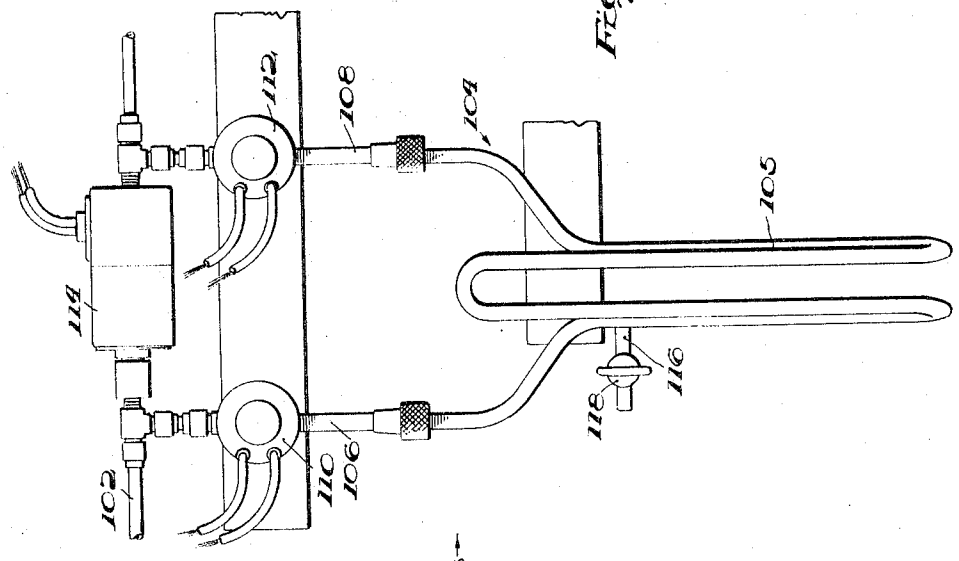
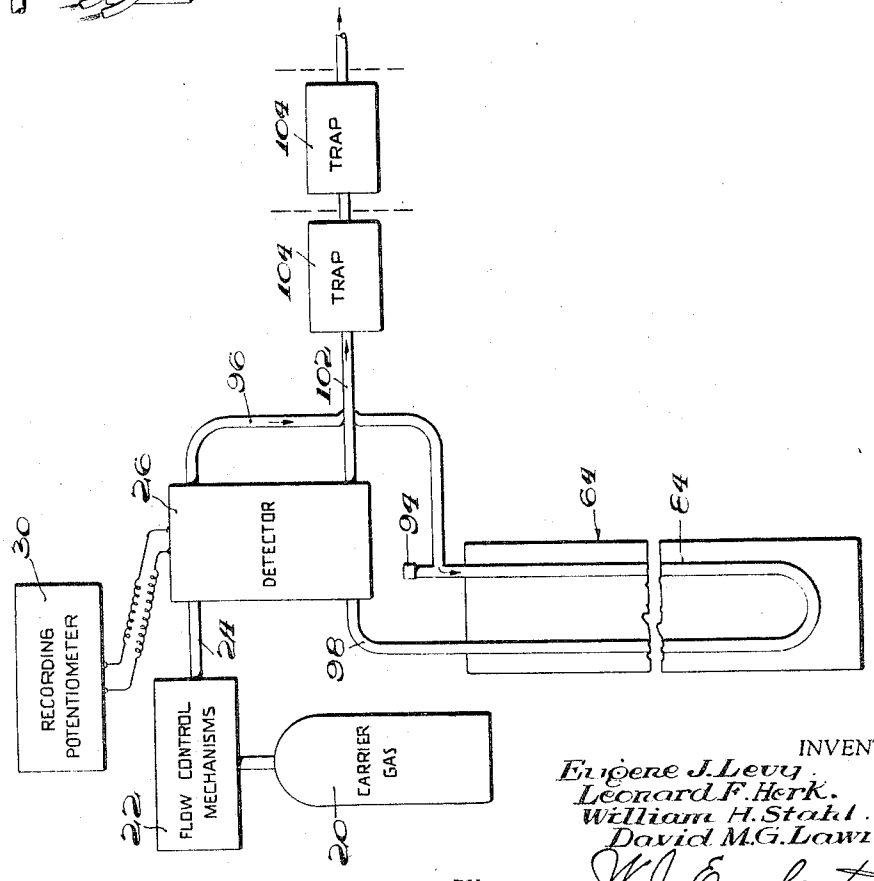


Fig. 1



INVENTORS
Eugene J. Levy.
Leonard F. Herk.
William H. Stahl.
David M. G. Lawrey.

BY W. J. Eudeston

ATTORNEY

Jan. 31, 1967 E. L. LEVY ETAL 3,301,040

AUTOMATIC FRACTION COLLECTING SYSTEM FOR VAPOR PHASE CHROMATOGRAPHY

Original Filed March 24, 1958 4 Sheets-Sheet 2

Fig. 2.

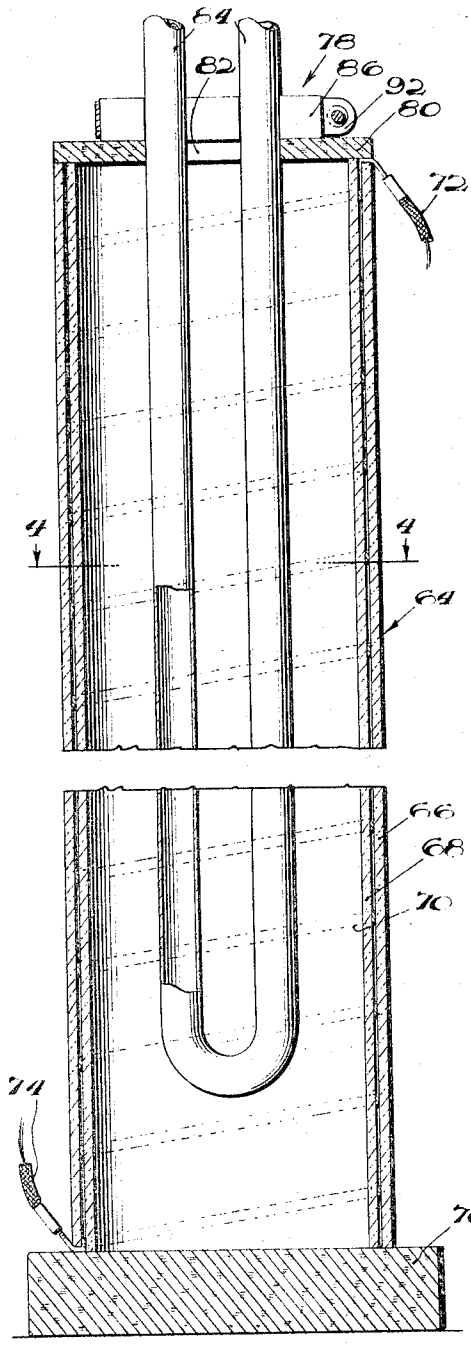


Fig. 3.

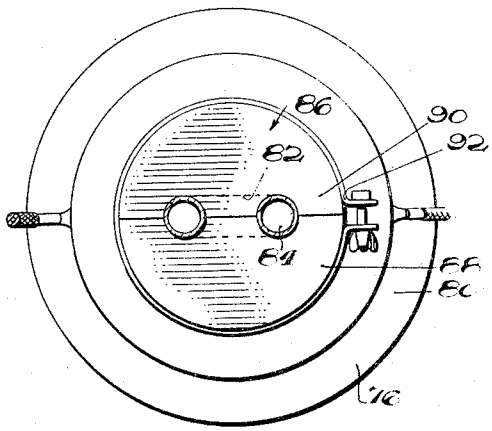
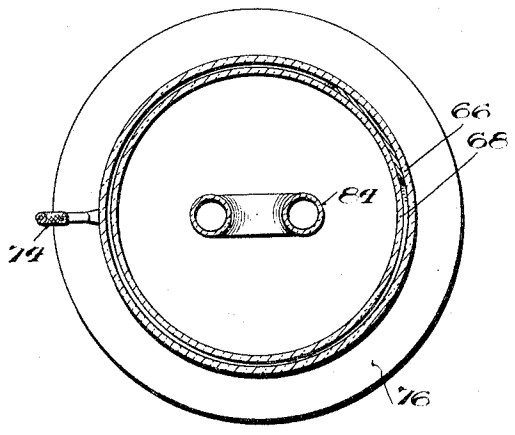


Fig. 4.



INVENTORS
Eugene J. Levy
Leonard F. Herk.
William H. Stahl
David M.G. Lawrey

BY W. J. Eccleston

ATTORNEY

Jan. 31, 1967 E. L. LEVY ETAL 3,301,040

AUTOMATIC FRACTION COLLECTING SYSTEM FOR VAPOR PHASE CHROMATOGRAPHY

Original Filed March 24, 1958 4 Sheets-Sheet 3

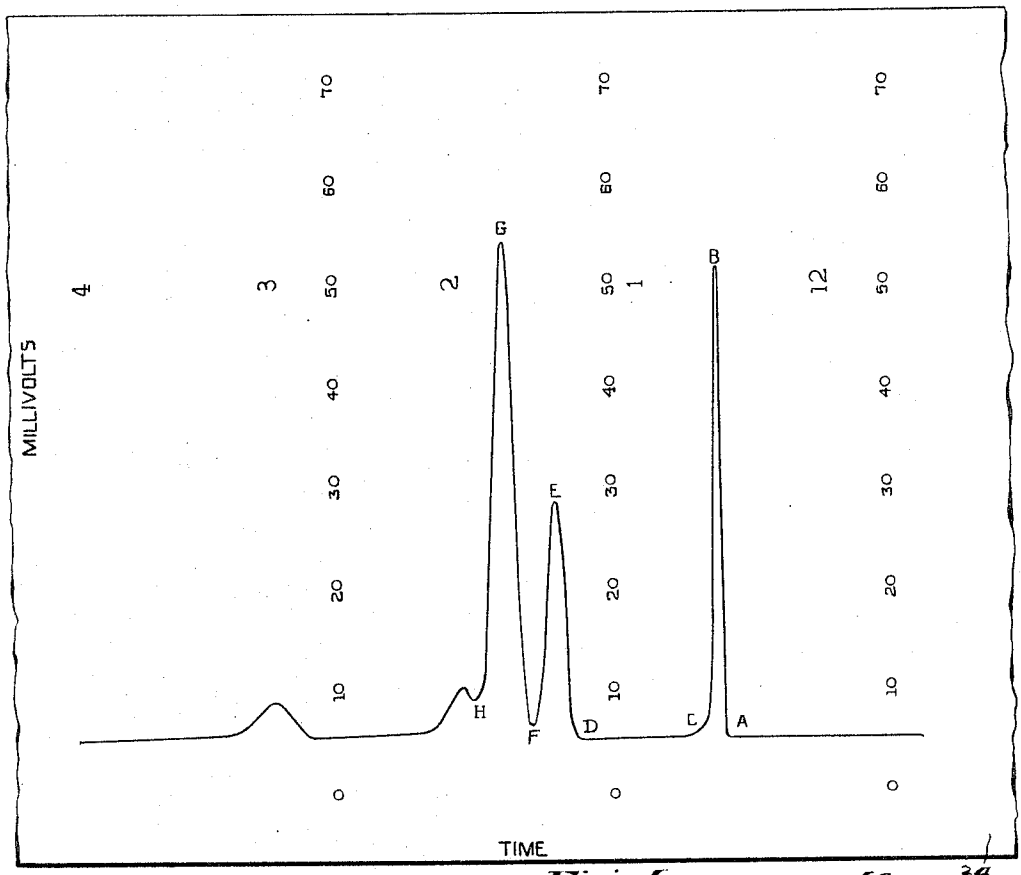


Fig. 5.

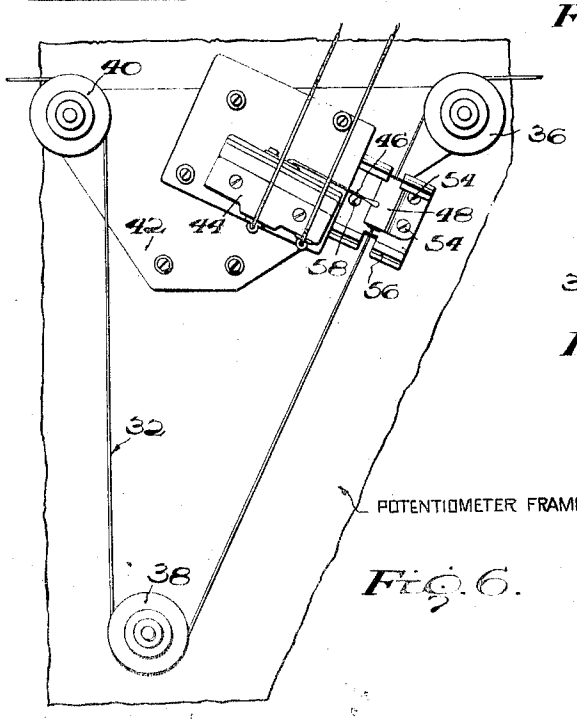


Fig. 6.

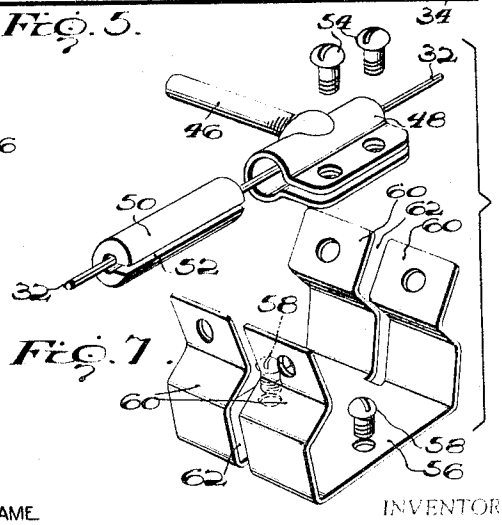


Fig. 7.

INVENTORS
Eugene J. Levy
Leonard F. Herk,
William H. Stahl
David M.G. Lawrey
By W. J. Eccleston
ATTORNEY

Jan. 31, 1967 E. L. LEVY ETAL 3,301,040

AUTOMATIC FRACTION COLLECTING SYSTEM FOR VAPOR PHASE CHROMATOGRAPHY

Original Filed March 24, 1958 4 Sheets-Sheet 4

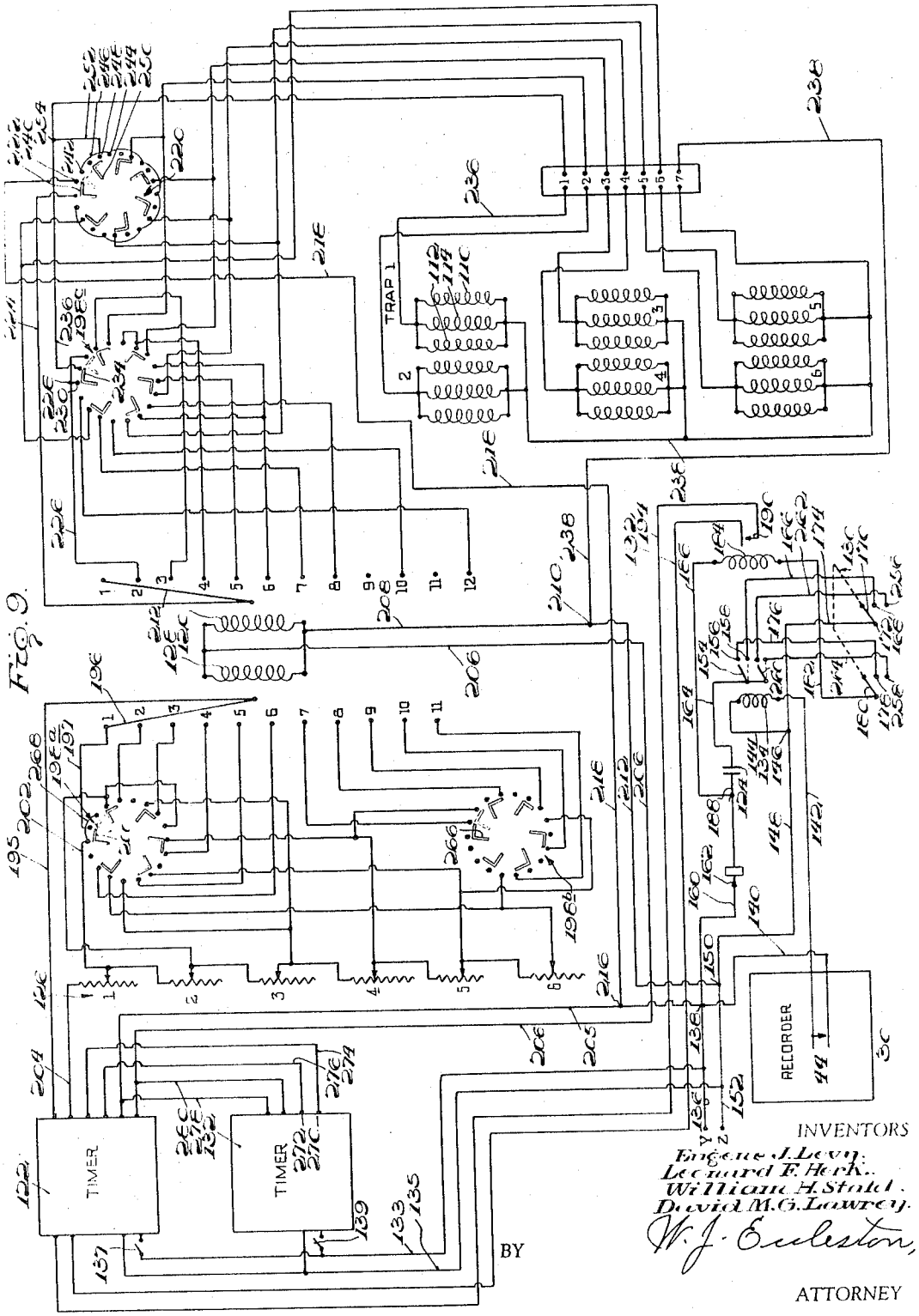


Fig. 9.

INVENTORS
Eugene J. Levy,
Leonard E. Herk,
William H. Stahl,
David M. G. Lawrey.
W. J. Eudeston,
ATTORNEY

BY

United States Patent Office 3,301,040 Patented Jan. 31, 1967

3,301,040

AUTOMATIC FRACTION COLLECTING SYSTEM FOR VAPOR PHASE CHROMATOGRAPHY

Eugene L. Levy, R.D. 1, Box 2913, Oxford, Pa. 19363; Leonard F. Herk, 156 Otis Ave., St. Paul, Minn. 55104; William H. Stahl, 15 Murray Hill Circle, Baltimore, Md. 21212; and David M. G. Lawrey, 224 Valley Green Drive, Chester, Pa. 19014

Continuation of application Ser. No. 723,614, Mar. 24, 1958. This application Oct. 20, 1965, Ser. No. 528,660
17 Claims. (Cl. 73—23.1)

This application is a continuation of our copending application Ser. No. 723,614, filed March 24, 1958.

The invention described herein, if patented, may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

The present invention relates to chromatography, and more particularly to mechanism for automatically separately trapping the different components or fractions of a mixture separated out by a chromatographic apparatus.

Chromatographic apparatus has heretofore been used to separate fluid mixtures into their several components or fractions, which apparatus included a plurality of traps separately to trap individual fractions and manually operated valves to control communication between the chromatographic column in this apparatus and the separate traps. An operator or attendant was required manually to open the valves establishing communication to a particular trap as a fraction from the column arrived at the trap and subsequently to close the valves on the trap. In view of the small volume of the individual fractions, precise opening and closing of the traps was required to insure collection of pure fractions. Insofar as is known, the only chromatographic apparatus which even remotely approached automatic operation had a trap, the opening and closing of which was controlled by a clock or timer. If the retention time of a fraction was unknown, one or more trial runs was required to determine this time in order properly to set the apparatus for collecting a particular fraction. A new trial run was required each time a change was made in the fraction which it was desired to trap, and this apparatus had only one trap. Obviously, manual control of the traps, or the necessity for trial runs, add complications to the operation of chromatographic apparatus which detract from its usefulness and accuracy, particularly in those installations where skilled attendants are not readily available to operate the apparatus.

The apparatus of the present invention corresponds generally to known chromatographic apparatus, but includes, in addition, mechanism automatically to open and close communication to the traps in the apparatus in response to detection of the separation of fractions by the chromatographic column and in timed relation to detection so that the individual fractions may be trapped in separate traps without the intervention of an operator, the successive fractions being automatically directed to successive traps and thus being automatically separately trapped.

Accordingly, an object of the invention is to provide a new and improved chromatographic apparatus.

Another object of the invention is to provide a new and improved mechanism for automatically trapping the fractions separated by a chromatographic column in separate traps.

A further object of the invention is to provide a new and improved chromatographic apparatus, including electromagnetically operated mechanism to open and close fraction collecting traps in this apparatus in response to the separation of fractions in the chromatographic column of the apparatus and in a sequence assuring collection of the individual fractions in separate traps.

A still further object of the invention is to provide a new and improved mechanism for automatically trapping the fractions separated by a chromatographic column in separate traps which is equally effective for trapping by what is known as the total trapping method and by what is known as the center cutting method, and which may collect by either method at the option of the operator.

Another object of the invention is to provide a new and improved automatically operable chromatographic apparatus, including a series of traps for separately trapping the fractions separated from a fractionizable mixture, which series of traps may be readily flushed between trapping operations.

A more general object of the invention is to provide a new and improved apparatus of the type mentioned in the foregoing objects which is inexpensive to construct and maintain, reliable in operation, and easy to adjust and to operate.

Another general object of the invention is to provide a new and improved automatically operable fraction collecting system for a chromatographic apparatus which requires a minimum of alteration of existing chromatographic apparatus to be utilized therewith so that existing apparatus may be readily converted to automatic operation.

These and other objects, advantages, and capabilities of the invention will be apparent from the following description wherein reference is made to the accompanying drawings in which:

FIG. 1 is a schematic diagram of a chromatographic fraction separating and collecting apparatus;

FIG. 2 is an axial section of a temperature-regulated chromatographic column partly broken away;

FIG. 3 is a top plan view of the column;

FIG. 4 is a diametrical section on the line 4—4 of FIG. 2;

FIG. 5 is a portion of a chromatogram produced in the apparatus of the present invention;

FIG. 6 is an elevation of part of an automatically operable sensing device forming a part of one embodiment of the present invention;

FIG. 7 is an enlarged exploded view of parts of the sensing device;

FIG. 8 is an elevation of a single fraction trapping or collecting unit; and

FIG. 9 is a schematic wiring diagram for the automatically operable fraction trapping system of one embodiment of the present invention.

Referring to FIG. 1, the chromatographic apparatus there shown, all of which may be of conventional construction, includes a tank **20** from which carrier gas under pressure is supplied to the system to induce flow of a sample of the mixture to be analyzed into the fractionating chromatographic column and flow of the components or fractions separated out by the column into the traps provided for collecting these fractions. Helium is preferred as a carrier gas because of its low condensation temperature, the noninterference of its mass spectrum with other mass spectra and because its high thermal conductivity increases the sensitivity of the thermal conductivity cell or detector which is used to detect the separation of fractions by the chromatographic column. However, in a locality where helium is not available, hydrogen or nitrogen may be used. Suitable conventional equipment, such as valves, gauges, flowmeters, and the like indicated collectively at **22**, may be provided for obtaining a uniform flow of carrier gas through the system at a controlled rate. A line or conduit **24** connects the outlet side of this flow-regulation equipment to the reference side of a detector **26**, suitable absorbent traps (not shown) of conventional construction being provided to dehydrate the carrier gas and remove other impurities from the same before it reaches the detector. A heating coil or other mechanism (not shown)

may also be provided in the line 24 for heating the carrier gas to any desired operating temperature. Since all of the equipment thus far mentioned may be conventional, it has not been shown or described in detail.

Any device operating on the principle of detecting a difference between two gases by differences in such of their properties as thermal conductivity, density, chemical structure, or radioactivity may be used as a detector. These devices include such well-known laboratory equipment as thermal conductivity cells, gas density balances, infra-red gas analyzers, hydrogen flame detectors, surface potential detectors, radioactivity detectors, and ionization gauges as well as other detectors. Specifically, a thermal conductivity cell has been used as a detector in the apparatus described herein. This cell may be either of the filament type or of the thermistor type, the latter being preferred. These detectors include normally balanced circuits which are unbalanced by changes in the conditions in a measuring or test cell with which these detectors are equipped, such as a change in the thermal conductivity of the gas in the test cell which occurs when a gas under test differing from the gas in the reference cell of the detector is admitted to the test cell. In the embodiment of the present invention described herein, any change or unbalance in the test cell of detector 26 causes a change in the voltage coordinates of the detector and actuates a recording potentiometer 30.

Recording potentiometer 30 is of conventional construction, preferably of the type described in U.S. patents to John A. Caldwell, No. 2,423,480, dated July 8, 1947, and No. 2,526,196, dated October 17, 1950. As described in the Caldwell patent, the potentiometer 30 includes a pen (not shown) for making a continuous record of the changes sensed by the potentiometer upon chart paper which is moved through the potentiometer at a uniform rate. This pen is driven by a pen drive cable, which, in turn, is actuated by the driving motor of the potentiometer. A portion of the pen drive cable is shown at 32 in FIG. 6, which shows a portion of the back of the potentiometer. This cable is driven in opposite directions by a reversible motor in the potentiometer which is caused to turn in one direction or the other as the result of changes in the balance or voltage coordinates of the circuits of the detector 26 in a known manner. An example of the record made by the recording pen is shown in FIG. 5 where a fragment of the moving chart paper is shown at 34. Projections ABC, DEF, and FGH extending upwardly from the horizontal, as viewed in FIG. 5, are made by the recording pen of the potentiometer each time the separation of a fraction is detected. These projections are commonly called peaks, and they are a measure of the fraction which has separated out, both quantitatively and qualitatively. Since the potentiometer forms no part of the invention, and the above-mentioned elements and their manner of operation are described in detail in the aforesaid patent, a further disclosure of the same is believed to be unnecessary.

In addition to driving the recording pen previously mentioned, the pen drive cable 32 (FIGS. 6 and 7) which extends around grooved pulley wheels 36, 38, and 40 rotatably mounted on the back side of the potentiometer 30 also opens and closes a microswitch 44 for a purpose to be described. Microswitch 44 is fixed to a plate 42 secured to the back side of the potentiometer. It has an outwardly projecting arm or blade 46 which may be rocked in opposite directions to open and close the switch. The end of arm 46 remote from the body of the switch 44 is soldered, or otherwise fixedly anchored to a generally cylindrical hose type clamp 48, which surrounds a generally cylindrical friction sleeve 50. A material suitable for this sleeve because of its temperature resistance, lubricity, and toughness is the Du Pont resinous plastic sold under the trademark "Teflon."

When relaxed, the friction sleeve 50 is loosely receivable upon pen drive cable 32. It has a radial slot 52 extending from end to end thereof, so that it may be forced into gripping engagement with the pen drive cable 32 by tightening a pair of adjusting screws 54 in the clamp 48. The pitch of the threads on those screws preferably is small, and they are accurately machined so that the frictional drag between the cable 32 and the clamp and sleeve assembly may be accurately adjusted as desired. In practice, the clamp 48 is tightened enough to cause sufficient frictional drag to be generated between the sleeve 50 and cable 32 to cause the sleeve and clamp assembly to move with the cable in the absence of an arresting force and to open or close switch 44 during this movement depending upon the direction it takes.

The extent of movement of the sleeve 50 and clamp 48 is limited by a generally U-shaped stop 56 anchored to the plate 42 on the back of the potentiometer by screws 58. This stop has duplicate opposed upstanding arms 60 spaced from each other a distance somewhat greater than the end to end length of the sleeve 50 and provided with opposed slots 62 as shown in FIG. 7. Stop 56 is so mounted on the back plate 42 that the pen drive cable 32 is aligned with and freely receivable in the opposed slots 62, while the sleeve 50 and clamp 48 are captive between the opposed arms 60. The arms are so spaced that the switch 44 is open when the clamp and sleeve assembly abut against one of the arms and closed when the clamp and sleeve assembly abut against the other arm. In either event, the pen drive cable 32 is free to continue movement in either direction, after movement of the clamp and sleeve assembly have been arrested, unimpeded except by the friction between it and the sleeve 50. Microswitch 44 is connected in circuits which control operation of the mechanism for automatically trapping separated fractions all of which will be described in detail hereinafter.

Separation of fractions from the fractionizable mixture under analysis occurs in a known manner in an elongated chromatographic column or separator indicated in its entirety by the number 64 and in detail in FIGS. 2, 3, and 4. This column or separator includes a cylindrical casing or housing approximately 3 inches in diameter and 3 or more feet in length comprising a pair of coaxially arranged cylindrical Pyrex glass tubes 66 and 68 dimensioned to provide an annular space therebetween in which a heating element 70, preferably in the form of Nichrome wire or ribbon is spirally sandwiched. This heating element is connected to a suitable source of current by conductors 72 and 74 connected to its opposite ends. The housing above described rests upon a base 76 which may comprise an asbestos block, while the upper end of the housing is closed by a cap or closure 78, including an asbestos disc 80 which has a diametrical slot 82 for a purpose to be described.

The chromatographic column per se comprises an elongated generally U-shaped glass tube 84, approximately one fourth inch in diameter, depending through the slot 82 in the closure disc 80 lengthwise of the housing tubes 66 and 68 to a point adjacent the base 76. The column 84 is supported in this depending position by a stop 86 adjacent its upper end which seats upon the top side of top closure disc 80.

Stop 86 comprises a pair of hemi-discs 88 and 90 preferably made of cork and having recesses along their diametrical edges which are disposed in opposed relation to receive the opposite ends of the U-tube or column 84 when the parts are disposed in assembled relation as shown in FIGS. 2 and 3. The hemi-discs 88 and 90 are held in tight clamping engagement with the opposite ends of the column 84 by a cylindrical hose-type clamp 92, so that the gripping force of the stop may readily be relaxed and the stop removed from or adjusted along the column 84 by loosening this clamp. When the parts are in assembled relation as shown in FIG. 2, the stop 86 closes the slot 82 in top closure disc 80. By virtue of this construction, a fractionating

column 84 may be readily removed so that one column may be readily substituted for another, if this is desired, without dismantling the entire apparatus.

Contained within the column 84 is the material which actually effects separation of the fractions from the sample of the mixture which is being analyzed. Since the fractionating material to be used will vary because of differences in the composition of the different mixtures which it may be necessary or desirable to fractionate, easy substitution of one column for another is a decided advantage. By way of example, for certain purposes, the column 84 may be packed with an inert material in finely granulated form so as to provide an extremely large adsorbing surface area such as a material sold under the trademark "Colite 545." This inert packing is coated with a high-boiling organic liquid, such as trimetacresyl phosphate, dioctylphthalate or dinonylphthalate to provide an adsorbing film. It is to be understood that these materials are merely exemplary, the packing of the column being determined by the supposed composition of the sample which is to be fractionated.

It is also to be understood that materials other than glass may be used for the column and its housing. For example, metals, such as copper or stainless steel, can be used, but the material used must be non-reactive with the chemicals being separated under the normal operating conditions of the system. Furthermore, the chromatographic column 84 need not necessarily be a U-tube but may be a straight tube or a coiled tube. Nor need temperature regulation of the column be carried out as described herein. It may be achieved by any one of a number of conventional laboratory means for regulating temperature on such a column, tube, or coil.

Referring again to FIG. 1, it will be observed that one end of the column 84 terminates in a sample inlet 94 through which the material to be analyzed may be admitted to the column. Any conventional structures designed for this purpose may be used in the present apparatus. This inlet end of the column 84 is also connected to the outlet side of the reference cell of the detector 26 by a suitable connection 96 communicating with the column on the downstream side of the inlet 94 so that carrier gas from the detector entering the column at this point carries forwardly into the packed portion of the column the material or sample admitted at the inlet 94.

At its opposite or outlet end, the column 84 communicates with the measuring or test cell of the detector 26 through a connection 98. After passing through the test cell of the detector, the carrier gas and separated fraction pass into a line or manifold 102 to which is connected a series of traps 104 of the type now to be described.

While the apparatus of the present invention is designed primarily for use with a plurality of traps, for example 10 or more traps, only one trap will be described because they may be of duplicate construction. Referring to FIG. 8, it will be observed that this trap comprises a glass tube formed into elongated convolutions 105. The traps 104 normally are disposed in a vertical plane, and each trap has separate inlet and outlet connections 106 and 108, respectively, connected to the previously-mentioned fraction conveying manifold 102. Communication between this manifold and the trap through the inlet and outlet connections is controlled by normally closed solenoid valves 110 and 112 of duplicate construction in the inlet and outlet connections 106 and 108, respectively, and a normally open solenoid valve 114 in the manifold 102 between the points at which the trap inlet and outlet connections 106 and 108 communicate with the manifold. Thus, when valve 114 is in its normal position, i.e., open, and valves 110 and 112 are in their normal position, i.e., closed, a fraction flowing in the manifold 102 will bypass the trap 104, but when these valves are in the reverse position, a fraction flowing in manifold 102 will be directed into the trap 104. The valves 110, 112, and 114 may be of conventional construction, preferably of the all-metal type. One type of valve found suitable for this purpose is made by the Skinner Electric Valve Division, of the Skinner Chuck Company, New Britain, Connecticut (Catalog No. D1, 1955). These valves should include adjustable flow devices which may be of conventional construction to avoid surges in the system, and the valves 110, 112 preferably are located as close to the manifold 102 as possible.

In addition to the inlet and outlet connections 106 and 108, each trap 104 is provided with a by-pass connection 116 through which a fraction collected in the trap may be removed for further analysis or for any other purpose. Communications through this by-pass is controlled by suitable conventional valves, one of which is shown more or less diagrammatically at 118. Since the procedure for removing a fraction from a trap is conventional, and forms no part of the present invention, it will not be described.

A brief review of the operation of the apparatus is set forth below followed by a more detailed description of one series of electric circuits which might be used to control operation of the apparatus and the manner in which this series of circuits is energized and de-energized. In the operation of the apparatus of the present invention, automatic trapping of the successive fractions emerging from the chromatographic column 84 in successive traps 104 is accomplished by opening and closing the solenoid valves 110, 112 and 114 in timed relation to the opening and closing of microswitch 44 by the pen drive cable 32 of the potentiometer 30 as previously described. The selection of succeeding traps for collecting the successively emerging fractions is accomplished by a stepping relay 120 (FIG. 9) which is energized by a time delay circuit that delays the energizing of the valves for a particular trap until the fraction to be trapped therein is carried by the carrier gas from the detector 26 through manifold 102 to or close to the entrance of the particular trap. The time delay is controlled by a cyclically operable first precision timer 122 which is brought into operation by the discharge of a capacitor 124, this discharge being controlled by the opening and closing of microswitch 44. After an appropriate time delay, finish relays in the timer 122 close thereby energizing stepping relay 120 which completes a circuit to the solenoid valves 110, 112 and 114 of the trap in which the particular fraction is to be collected.

A cyclically operable timer suitable for use in this embodiment of the present invention is disclosed in Electronics, volume 21, No. 12, December 1948, pp. 88 and 89 by Sidney Wold of the RCA Victor Division, Camden, New Jersey. Timers of this type have timing intervals ranging from .01 to 100 seconds and may be obtained from the Hunter Manufacturing Company, Iowa City, Iowa. The time constant of these timers is obtained by discharging a fixed capacitor in the timer through a selected resistance to a voltage source of reversed polarity all in a known manner. These timers normally include manually variable resistors for selecting a time constant within the aforementioned range. However, in the present embodiment of this invention, timer 122 is modified by substituting a group of series-connected variable resistors designated as a group by the number 126 for the manually variable resistors normally included in the timer circuit. The value of the resistance to be included in the discharge circuit of the capacitor in the timer 122 for each cycle is controlled by a stepping relay 128 which is energized by the finished relay of timer 122 to include predetermined additional resistance from the series of resistors 126 in the capacitor discharge circuit of the timer for each successive cycle. This progressively increasing time delay compensates for the progressively in-

creasing distance the successive traps **104** are spaced from the detector **26** in this embodiment of the invention.

Two different methods of trapping may be practiced with the apparatus disclosed herein. In what is known as total trapping, the entire fraction emerging from the column **84** is collected. In the method known as center cutting, only that portion of the fraction emerging from column **84** is collected which separates during an interval of time approximately midway between the beginning and the end of the full period during which the particular fraction is emerging. To trap by those two methods automatically obviously requires somewhat different sequences of operation of the elements of the system. With reference to FIGURE 5, in the operation of the system by the so-called total trapping method, the timing cycle of timer **122**, and hence the time delay, is initiated at the time the fraction is first detected by detector **26** as represented by point D in FIG. 5, for example, whereas, in the center cutting method of trapping, the time delay is initiated at the point where the highest concentration of the fraction is emerging from the column **84** as represented by point E on the same peak in FIG. 5. This change is sequence is accomplished by a triple pole, triple throw function switch **130** (FIG. 9) in the timer starting circuit.

A second cyclically operable timer **132** is utilized in the center cutting operation to return the valves **110**, **112** and **114** of the collecting traps to their normal position a predetermined period of time after they are actuated by the first timer **122**, in order that only the most concentrated portion of the fraction is collected. In view of this fact, only one predetermined interval of time delay is required of the second timer regardless of the number of traps used. The two timers are supplied with current through leads **133** and **135**, which are controlled by switches **137** and **139**.

A multi-point stepping relay which has been found suitable for use as relays **120** and **128** in the apparatus of this invention is manufactured by Guardian Electronic Manufacturing Company, Chicago, Illinois, Model 056563, 123 ohms and 450 ohms. These relays may be provided with conventional reset means (not shown) for returning them to their initial position prior to the starting of a new trapping operation.

A further distinction between the total trapping and center cutting methods of trapping involves the use of a Dewar flask (not shown) containing liquid nitrogen or other refrigerating medium surrounding the traps in the trapping operation. This technique, which is conventional in this art, is required to condense the fraction flowing into a trap during total trapping while permitting the carrier gas to continue to flow through the trap until the trap is closed coincident with the opening of the succeeding trap. This technique is not required in center cutting because the volume of the traps is sufficient to contain the limited portion of the entire fraction which is trapped in center cutting.

OPERATION

A total trapping operation will first be described to explain the operation of the improved chromatographic apparatus of the present invention, reference being had to FIG. 9 for this purpose. The apparatus is set to total trap by shifting the function switch **130**, which has off, center cut and total trap positions one step clockwise from the off position shown in full lines in FIG. 9 to its total trap position and also closing switch **137** which supplies power to the first timer **122**. Assuming the desired rate of carrier gas flow has been obtained by means of the control mechanisms **22** (FIG. 1) for example, 50 cc. per minute, and a sample fo the substance or mixture to be analyzed has been introduced into the system at sample inlet **94**, this sample is carried into the chromatographic column **84** which is maintained at an elevated temperature, for example 75–100° C., by the carrier gas where the fractions separate out at intervals so that they are separately carried into the test or measuring cell of the detector **26** through the connection **98**, and from the detector the fractions pass into the manifold **102**. The passage of a fraction through the test cell of the detector **26** causes a signal to be sent to the potentiometer **30** in a known manner, the first signal being caused by an air fraction which may be admitted with the sample and normally is not collected but serves to trigger the collecting system for collecting automatically by the total trap method.

As long as the apparatus is inoperative, the microswitch **44** remains open so that no current will flow in the system shown in FIG. 9. This condition continues to prevail during the first phase of the detection by the detector **26** of the initial air fraction previously mentioned because the signal sent to the potentiometer **30** by the detector during a period of increasing concentration of the gaseous fraction passing through the test call of the detector causes the pen drive cable **32** and the pen carried thereby to be driven in a direction to trace a line exemplified by the line AB (FIG. 5) on the moving chart **34** in the potentiometer. The friction generated in the friction sleeve **50** holds the microswitch **44** in open position during movement of the cable in the above-described direction, and thus no current flows to the automatic trapping mechanism.

As will be obvious from FIG. 5, at the point B motion of the pen drive cable **32** reverses. Consequently, the frictional drag upon friction sleeve **50** is reversed and causes the switch blade **46** to be shifted in a direction to close microswitch **44**. This closes a circuit from a suitable source of alternating current YZ (FIG. 9) to a relay field coil **134** from the side Y of the source through a conductor **136**, a junction **138**, a conductor **140**, microswitch **44**, a conductor **142**, relay coil **134**, a conductor **144**, a junction **146**, a conductor **148**, a junction **150**, and a conductor **152** to the side Z of the source. Energization of field coil **134** causes a switch blade **154** to open a normally closed contact **156** and close a normally open contact **158** as indicated in dotted lines in FIG. 9. This closes a circuit for charging the capacitor **124** from the source YZ through conductor **136**, junction **138**, a conductor **160**, a rectifier indicated generally by the number **162**, capacitor **124**, a conductor **164**, switch blade **154**, contact **158**, a conductor **166**, a contact **168**, a switch blade **170**, a contact **172**, a conductor **174**, junction **146**, conductor **148** and junction **150** back to the side Z of the source.

Since the microswitch **44** will remain closed until the direction of movement of pen drive cable **32** again reverses and this does not occur until the next component or fraction is detected by the detector **26**, the only effect of the peak caused by the air component is to charge the capacitor **124**, and thus trigger the system for automatic collection of the fractions subsequently emerging from the column **84**. Thus, when detector **26** detects the first of these fractions, potentiometer **30** responds by again moving the pen drive cable **32** in a direction to open microswitch **44** as indicated by the line DE traced by the recording pen on the chromatogram illustrated in FIG. 5. This opens the previously described energizing circuit for the relay field coil **134** causing the movable switch blade **154** again to close contact with fixed contact **156**. A capacitor discharge circuit is thus completed, which extends from one side of capacitor **124** through conductor **164**, switch blade **154**, fixed contact **156**, a conductor **176**, a fixed contact **178**, a movable switch blade **180**, and a conductor **182** to one side of a relay field coil **184**. The other side of this coil is connected to the other side of capacitor **124** through conductors **185** and **188**.

Energization of a field coil **184** momentarily closes a normally open relay contact **190** between conductors **192**

and 194, thereby closing a starter circuit for the first timer 122. This starts a cycle of this timer which includes conventional mechanism for closing and opening the circuits necessary to effect the automatic collection of the different fractions emerging from the column 84 in separate traps as described hereinafter.

The wiring diagram (FIG. 9) shows the position of the parts when the device is inoperative in full lines. Since the time at which a fraction will arrive at a particular trap in the series of traps 104 will vary with the rate of flow of carrier gas and the distance between the detector 26 and the traps, the interval of delay between detection of a fraction by the detector 26 and the opening of the trap which is to receive this fraction must be increased progressively with increasing distances between the detector and the trap which is to receive the fraction in question. By way of illustration, in one embodiment of the invention the distance from the detector 26 and the first trap 104 is 90 cm. which requires a 14 second time delay at a flow rate of 50 cc. per minute. This time delay increases by from three to six seconds for each succeeding trap. To accommodate for this difference, the series of resistances 126 heretofore mentioned is provided in the starting circuit of the first timer 122. As will be later described, the resistance selecting relay 128 automatically provides an appropriate increased resistance in this starting circuit of the first timer 122 for each succeeding cycle of this timer which results in an appropriate increase in the time delay between detection of a fraction by detector 26 and the energizing of the valve circuit of the trap in which the particular fraction is to be collected.

At the commencement of the first time cycle of the timer 122, a circuit is completed through a conductor 195, a movable contact or blade 196, and a conductor 197 to the first section of a multi-pole, two position three section gang switch. The first section of this switch has been designated 198*a*, while the second and third sections are designated 198*b* and 198*c*, respectively. This switch may be moved between the total trap position shown in full lines in FIG. 9 and a center cut position at which it is rotated one step clockwise from the position shown in FIG. 9. Switch section 198*a* includes a jumper 200 closing a circuit from conductor 197 to a conductor 202 and resistance No. 1 in the series of resistances 126 back to conventional first finish relay (not shown) in the timer 122 through a conductor 204. Thereupon, the timer 122 operates to close circuits to actuate the previously mentioned stepping relays 120, 128 through one step. It will be understood that closing of this finish relay circuit will be delayed after discharge of the capacitor 124 for an interval the length of which is determined by the value of resistance No. 1 in the series of time delay resistances 126. The energizing circuit for actuating the stepping relays 120, 128 is closed from the side Y of the source through conductor 136, junction 138 and a conductor 205 to one side of the aforementioned finish relay in the timer 122. A conductor 206 connects the other side of this finish relay to one side of the stepping relays 128, 120 which are connected to the other side Z of the source by a conductor 208, a junction 210, a conductor 212, junction 150, and conductor 152. Thereupon, movable blade 196 is stepped from position 1 to position 2, but this has no effect on the present cycle of the system. It merely closes a circuit which includes resistance No. 2 in the series of time delay determining resistances through which the finish relay of timer 122 will be energized in the second cycle of the system. A movable blade 212 in the trap selecting portion of the circuit represented by the portion of the wiring diagram to the right of the stepping relays 128, 120 in FIG. 9 also is stepped from position one which is blank to position 2 which is connected in the circuit of the solenoid valves 110, 112, and 114 on the first trap 104. A circuit from the source of current is thus completed through conductor 136, junction 138, a portion of conductor 205, a junction 216, a conductor 218 to a multi-pole two position switch 220 which may be set at an operating or collecting position when fractions are to be collected, or at a flushing position when it is desired to flush the traps, it being shown at collecting position in full lines in FIG. 9. The operation of flushing will be described hereinafter.

Switch 220 has a series of jumpers, one of which is indicated by the number 222. This jumper provides a connection between the conductor 218 and a conductor 224 connected to the movable blade 212 of the trap selecting relay 120. From the contact at position No. 2 to which this blade has been stepped as previously explained, the circuit leads through a conductor 226, a junction 228 a conductor 230 to switch section 198*c*. A jumper 234 in switch section 198*c* provides a connection to a conductor 236 connected to the solenoids in the valves 110, 112, and 114 on the first trap 104. These solenoids are also connected to the opposite side of the source of current through a conductor 238, junction 210, conductor 212, junction 150, and conductor 152. Energization of this circuit causes manifold valve 114 on the first trap to close and the valves 110 and 112 in the inlet and outlet 106 and 108, respectively, of this trap to open so that the first fraction will be directed from the manifold into the first trap. This circuit remains closed until that phase in the trapping of the second fraction is reached, at which the stepping relays 128, 120 advance movable blades 196 and 212 from position 2 to position 3. This opens the energizing circuit for solenoid valves 110, 112 and 114 of the first trap allowing them to gravitate to their normal positions and energizes the circuit for the solenoid valves of the second trap.

However, at the time the concentration of the first fraction begins to decrease, the direction of movement of the pen drive cable 32 (FIG. 6) reverses as indicated at E in FIG. 5. This closes microswitch 44 and thus again closes the previously described circuit for charging capacitor 124. The capacitor will remain charged throughout the period EF (FIG. 5), thus triggering the control system for the second cycle of operation. This second cycle will not begin until the detector 26 begins to detect the second fraction represented by FGH on FIG. 5. As a result, the direction of movement of the pen drive cable 32 will reverse and the microswitch 44 will open causing the capacitor 124 is discharge through the previously described capacitor discharge circuit, thus causing time delay circuits to be energized through the first timer 122 like those previously described except that these circuits include time delay resistance 2 in the series of time delay resistances 126 as well as 1 because the movable blade 196 was brought into engagement with fixed contact 2 of the resistance selecting relay 128 in the first cycle of the timer 122. This increases the delay between detection of the second fraction and opening of the second trap by an amount sufficient to compensate for the additional time it takes the second fraction to travel from trap 1 to trap 2.

After a trapping operation, it may be desirable to flush all of the traps 104 with carrier or other gas. This can readily be accomplished by closing all of the normally open manifold valves 114 and opening all of the normally closed trap inlet and outlet valves 110 and 112 respectively. Circuits to accomplish this will be closed by the multipole switch 220 when the latter is shifted clockwise one step from the position shown in FIG. 9. A circuit is then completed from conductor 218, which is connected to one side of the source of current, to a contact 240 in the switch 220. At the same time contact 240 is connected to a second contact 242 in this switch by the jumper 222 then in the position shown in dotted line in FIG. 9. Contact 242 is connected to a contact 244 in switch 220 by a lead 246, and this latter contact is connected to a contact 248 by a second jumper 250. A conductor 252 connects contact 248 to the conductor 236 at a junction 254, the conductor 236 being connected to the solenoids in the

valves 110, 112, and 114 on trap 1. These solenoids are connected back to the other side of the source through conductor 238 as previously described. A similar circuit is established for each of the valves in each of the traps 104 in the system through a series of jumpers and leads in switch 220 similar to the jumpers 222 or 250, and the lead 246 and conductors similar to conductors 236 extending from the switch 220 to the solenoid valves in the successive traps 104. The traps will all remain open until the switch 220 is shifted from flushing position to operating position.

To trap fractions by the center cutting method, the switches 137 and 139 controlling flow of current to the two timers are both closed and both the function switch 130 and the three-section gang switch 198*a*, *b*, *c*, are shifted to center cutting position. This swings movable blades 170 and 180 into contact with fixed contacts 256 and 258 and advances the jumpers in the three sections of the switch 198 clockwise one step from the position shown in full lines in FIG. 9. A capacitor charging circuit it thereby closed from fixed contact 256, switch blade 170, conductor 174, junction 146, conductor 148, junction 150, and conductor 152 to one side of the source YZ. The other side of the source is connected by conductor 136, junction 138, and conductor 160 to one side of the rectifier 162 which is connected on its other side to one side of capacitor 124 by conductor 188. The other side of the capacitor is connected back to contact 256 by conductor 164, a movable switch blade 260, and a conductor 262. It will thus be seen that mere shifting of the function switch 130 to center cutting position automatically results in the capacitor 124 being charged and thus triggers the system for immediate trapping, in contrast to the total trapping method of operation which requires the emergence of an initial fraction or peak to trigger the system for trapping.

When the gang switch 198*a*, *b*, *c*, is shifted to center cutting position, the several jumpers therein like the jumper 200 in section 198*a*, a jumper 266 in section 198*b*, and jumper 234 in section 198*c* connect the contacts in the switch as shown in dotted lines in FIG. 9. The other jumpers in this switch likewise make connections advanced one step clockwise from the positions at which they are shown in full lines in FIG. 9. As a result, contact 1 of resistance selecting relay 128 is connected through conductor 197, jumper 200, a connection 268, and conductor 202 to time delay resistance No. 1 in the group of time delay resistances 126. It will be observed that contact 2 of relay 128 is blank, contact 3 is connected to time delay resistance No. 2, contact 4 is blank, and so on to the last of the series of time delay resistances 126. However, the circuit to time delay resistances 126–4, 5, and 6 is made through switch sections 198*b*, as will be obvious from an inspection of FIG. 9. Similarly, section *c* of gang switch 198 in advancing one step clockwise will connect contact 2 of the trap selecting relay 120 to the solenoid valve circuits of the first trap 104 through conductor 226, jumper 234, and conductor 236. Contact 3 of relay 120 will become blank, contact 4 of relay 120 will be connected to the valve circuit of the second trap 104, contact 5 will become blank and so on through the series of contacts in the trap selecting relay 120 so that the valve circuits of the successive traps 104 are connected to alternate contacts of the trap selecting relay 120.

The center cutting operations utilizes a second timer designated generally by the number 132. This timer may comprise a Model 111A timer as manufactured by Hunter Manufacturing Company, Inc., Iowa City, Iowa, and is used as furnished by the manufacturer. The starting relay of the second timer 132 has contacts 270 and 272 thereon connected to a second conventional finish relay in the first timer 122 by conductors 274 and 276. A pair of conductors 278 and 280 connect the finish relay of the second timer 132 to conductors 205 and 206, respectively, in parallel with the first-mentioned finish relay in the first timer 122.

In center cutting, the carrier gas flow is established and the sample introduced in the same manner as previously described for a total trapping operation. The chromatographic column 84, detector 26, and potentiometer 30 function in the same manner as previously described. The individual fractions of the sample are detected and recorded by the pontentiometer on the moving chart 34 creating a record similar to that shown in FIG. 5. In contrast to total trapping, in center cutting all of the traps 104 remain closed throughout the period of operation of the system except for an interval sufficient only to receive the center portion of a fraction. Bearing in mind that the capacitor 124 is charged and the microswitch 44 open in that phase of separation of a fraction represented by the line DE (FIG. 5), as the peak begins to recede from point E, microswitch 44 closes thus completing a circuit which energizes relay field coil 134. As a result, the movable contact or blade 260 is shifted to a position to close a discharge circuit for the capacitor 124 like that previously described, except for the fact that it is completed through fixed contact 258 in the function switch 130 instead of contact 178. This momentarily closes normally open relay contact 190 and thus starts the timing cycle of the first timer 122 which, after the time interval determined by the time delay resistance 126–1, causes the stepper relays 120, 128 to advance the movable blades 212, 196 to position 2. Position 2 in the resistance selecting relay 128 is blank, but position 2 in the trap selecting relay 120 is connected to the source of current and the solenoid valves in the first trap 104 in the manner described for total trapping except for the slight but obvious difference in connection in switch section 198*c* caused by the advance of jumper 234 one step to the position shown in dotted lines in FIG. 9. As a result, the solenoid valves in the first trap 104 are actuated in a direction to cause the first fraction to be directed from the manifold 102 into the first trap.

The closing of the first finish relay of the first timer 122, which results in opening the first trap, also initiates the timing cycle of the second timer 132. This latter timer has been pre set for a fixed time constant appropriate to the flow rate of the carrier gas, for example, five seconds when the carrier rate is 50 cc. per minute. Closing of the finish relay of this second timer 132 causes stepping relays 120 and 128 to advance the movable blades 212, 196 associated therewith to position 3. This de-energizes the solenoids on the valves in the first trap 104 because position 3 in the trap selecting relay 120 is blank so that the manifold valve 114 returns to open position and inlet valves 110, 112 close. It will be apparent that, once the appropriate resistance settings have been established for the flow rate being used, it is possible to trap the center portion only of the fraction which is represented in its entirety by the peak DEF (FIG. 5), and to trap the center portions of successive fractions in successive traps.

It can be seen therefore that the essential difference between the total trapping and center cutting operations of the apparatus resides in the initiation of the first timer 122 at the peak of fraction discharge iin center cutting, rather than at the beginning thereof, as in total trapping and the use of a second timing cycle to close the trap at a predetermined time in advance of the time separation of a fraction is completed. This difference in the functioning of the apparatus of the present invention is produced by the function switch 130 and the different circuits controlled by it, the microswitch 44 operating in the same manner during center cutting as total trapping, i.e., it opens upon detection of a fraction and closes as a peak begins to recede. When the function switch 130 is set at center cutting, circuits are closed for charging the capacitor 124 when the microswitch 44 is open and discharging it when this microswitch closes, whereas the reverse is true when the function switch is set at total trap. As a result, traps open at the high point of a peak, such as the point E in peak DEF (FIG. 5) in center cutting and at the beginning of this peak in total trapping. In addition, the

second timer 132 causes the traps to close at a predetermined time after they open in center cutting, whereas, in total trapping, a trap remains open until the next fraction is detected and the succeeding trap thus opened.

Since the second timer 132 actuates the time delay and trap selecting stepping relays 128, 120, respectively, twice for each emerging fraction, only alternate contacts in these relays 128 and 120 are connected to close circuits to the time delay resistance 126 and successive traps 104, so that successive fractions separating out during center cutting are trapped in successive traps 104 as in total trapping.

It is to be observed that the use of the circuits shown in FIG. 9 will result in the trapping of the center portion of the air peak on the first actuation of the control system, if in fact, air is admitted with the sample. This is due to the fact that operation of the apparatus to center cut does not require a triggering peak as in total trapping, as previously explained. Instead, a portion of each fraction emerging from the column, including the first, will be trapped. If it is desired to avoid trapping the air fraction in center cutting, the arrangement of conductors in section 198c of the gang switch could be varied to blank out the first three contacts of trap selecting relay 120 and to connect the first trap valve circuit to contact 4 of relay 120. Successive trap valve circuits could then be connected to alternate contacts of relay 120, as previously described.

It should be apparent from FIGURE 9 that additional traps may be added to the apparatus by adding correspondingly to the number of resistance in the group of resistance 126, by adding additional sections to three section switch 198*a*, *b*, *c*, and the switch 220 and by providing additional contacts on stepping relays 120 and 128.

From the foregoing description of the present embodiment of this invention, it will be apparent to those skilled in the art that a number of other methods of arranging a multiplicity of traps may be utilized other than that shown herein. A "spokes in a wheel" arrangement with a rotary valve at the hub thereof could, for example, be utilized to provide a uniform time delay in the passage of a fraction from the detector to the individual traps. Similarly, a number of other mechanical and/or electrical means of sensing a change in the direction of the voltage cordinates of the detector 26 may be employed in lieu of the microswitch 44 described herein.

While a preferred embodiment of the invention has been shown and described in connection with the chromatographic separation or fractionation of a gaseous mixture, it is to be understood that the principles of the invention may be used in other fractionating systems. It will also be apparent that variations and modifications of the invention other than those mentioned herein may be made without departing from the underlying principles thereof. It is desired, therefore, by the following claims, to include within the scope of the invention, all such variations and modifications by which substantially the results of the invention may be obtained through the use of substantially the same or equivalent means.

We claim:

1. Apparatus for automatically separately collecting fractions separated from a fractionizable mixture comprising fraction-detecting means, a series of fraction collecting traps, means for conveying fractions to said traps, the distance over which fractions must be conveyed to reach successive traps in said series increasing progressively as the number of traps increases, valve means to open and close said traps to the admission of the fractions, means including cyclically operable timing mechanism to time actuation of said valve means and detector responsive means for starting a cycle of said timing mechanism at a predetermined phase in the detection of each fraction detected by said detecting means, said timing mechanism including means to increase progressively the time interval between detection of a fraction and the actuation of said valve means upon successive cycles thereof by an interval corresponding substantially to the time of transport of a fraction from one trap to the next succeeding trap.

2. Apparatus for automatically separately collecting the successive fractions separated from a fractionizable mixture by a fractionating column comprising a plurality of fraction collecting traps connected to said column through a common connection at distances therefrom along said connection which increase progressively as the number of traps increases, means to supply fluid carrier for transporting fractions through said connection at a controlled rate, valve means for controlling the admission of fluid carrier and fractions from said connection to said traps, and cyclically operable timing mechanism for selectively actuating said valve means to admit fractions to said traps in response to the separation of successive fractions including mechanism to delay actuation of said valve means in response to the separation of successive fractions by an interval of time proportional to the flow rate of said carrier and the distance between successive traps to insure trapping of the successive fractions separated from said mixture in successive traps.

3. Apparatus for automatically separately collecting fractions separated from a fractionizable mixture by a fractionating column comprising fraction detecting means, a plurality of fraction collecting traps, means for establishing communication between the output side of said column and said traps including valve means to open and close communication to said traps, a series of electrical circuits to control operation of said valve means, a source of electrical energy and mechanism for selectively connecting circuits in said series to said source and disconnecting the same therefrom in response to detection of the commencement of separation of successive fractions from said mixture individually to open and close said traps in timed relation to the detection of fractions and in a predetermined sequence, said mechanism for selectively connecting circuits being adjustable to vary the interval a trap remains open.

4. Apparatus for automatically separately collecting the fractions separated from a fractionizable mixture comprising fraction detecting means, a plurality of fraction collecting traps, means for conveying separated fractions to said traps, means including valve means to control the admission of fractions to said traps, a series of circuits to control operation of said valve means, means including cyclically operable timing mechanism to control the time of energization of said valve control circuits, circuits to control actuation of said timing mechanism, a switch in the control circuits of said timing mechanism responsive to detection by said detector of the commencement of separation of successive fractions from said mixture, said timing mechanism including means to increase the time period of said timing mechanism progressively on the successive cycles resulting from the separation of successive fractions from a single mixture, and means for resetting said timing mechanism at any time after the first cycle thereof to start a new series of cycles.

5. Apparatus for automatically separately collecting fractions separated from a fractionizable mixture by a fractionating column comprising fraction detecting means, a plurality of fraction collecting traps, means for establishing communication between the output side of said column and said traps including valve means to open and close communication to said traps, a series of electrical circuits to control operation of said valve means, a source of electrical energy, detector responsive mechanism for selectively connecting circuits in said series to said source and disconnecting the same therefrom individually to open and close said traps in a predetermined sequence, and a manual switch simultaneously to connect or disconnect said source and all of the valve opening circuits in said series simultaneously to open communication to all of said traps for a time interval controlled by the operator.

6. Apparatus for automatically collecting fractions separated from a fractionizable mixture comprising fraction detecting means, at least one fraction collecting trap, means for conveying separated fractions to said trap, means including valve means to control the admission of separated fractions to said trap, a series of circuits to control operation of said valve means, cyclically operable timing mechanism to control energization and de-energization of said valve control circuits, circuits to effect actuation of said timing mechanism through sequences effective to collect in said trap either the entirety or predetermined portions only of successive fractions separated from a mixture, a manual switch for selecting the sequence through which said timing mechanism is to operate and a switch responding to detection of the separation of a fraction from said mixture to start a cycle of said timing mechanism at a predetermined phase in the separation of each of the successive fractions separated from a mixture.

7. Apparatus for automatically separately collecting fractions separated from a fractionizable mixture by a fractionating column comprising at least one fraction collecting trap connected to said column, means including valve means to control the admission of separated fractions to said trap, a series of circuits for controlling operation of said valve means, cyclically operable timing mechanism to control energization of said valve control circuits, fraction detecting means having driven mechanism changing in direction of operation at the beginning and the high point in the separation of each fraction separated from a mixture, a switch operated by each change in the direction of operation of said driven mechanism, means including circuits to start said timing mechanism alternately in response to opening of said detector operated switch or in response to closing thereof and a manual switch to select the starting circuit of said timing mechanism.

8. Apparatus for automatically collecting fractions separated from a fractionizable mixture comprising fraction detector means, at least one fraction collecting trap, means for conveying separated fractions to said trap, means including valve means to control the admission of fractions to said trap, a series of circuits to control operation of said valve means, cyclically operable first timing mechanism to control the energization of said valve control circuits, circuits to control the operation of said first timing mechanism, means including detector responsive means for effecting energization of the said control circuits for said first timing mechanism alternately upon initial detection of a fraction or at a predetermined interval of time subsequent to initial detection of a fraction and a second timing mechanism to control de-energization of said valve control circuits when the control circuits for said first timing mechanism are energized subsequent to initial detection of a fraction.

9. Apparatus as defined in claim 8 wherein the said second timing mechanism de-energizes said valve control circuits after a predetermined period of time less than sufficient for separation of the said fraction to have been completed.

10. Apparatus for automatically collecting fractions separated from a fractionizable mixture comprising fraction detecting means, at least one fraction collecting trap, means for conveying separated fractions to said trap, means including valve means to control the admission of fractions to said trap, a series of circuits to control operation of said valve means, cyclically operable first timing mechanism to control the energization of said valve control circuits, a switch operable by said detector upon either the initial or the high point in detection of the separation of a fraction, circuits controlled by said detector operated switch to start said first timing mechanism upon either response of said detector operated switch, a manual switch to select the timer starting circuit to be energized by said detector operated switch and a second timing mechanism to control de-energization of said valve control circuits when energization of the starting circuit for said first timing mechanism occurs upon detection of the high point in the separation of a fraction.

11. Apparatus for automatically separately collecting fractions separated from a fractionizable mixture by a fractionating column comprising fraction detecting means, a plurality of traps connected to said column at progressively greater distances therefrom, means including valve means to control the admission of fractions to said traps, a series of circuits to control operation of said valve means, cyclically operable timing mechanism to control energization of the said valve control circuits, means including circuits to control operation of said timing mechanism, a series of resistors, means operated by said timing mechanism to interpose progressively increasing numbers of said resistors in said valve control circuits upon successive actuations of said timing mechanism to compensate for the additional time it takes fractions to travel between successive traps, and a detector controlled switch in the control circuits of said timing mechanism.

12. Apparatus as defined in claim 11 wherein the said resistors are adjustable so that the value of the resistance in the said valve control circuits may be varied by an operator.

13. In apparatus which includes a gas chromatograph column, a plurality of fraction-collection means coupled to said column for receiving the separated gas fractions present at the output thereof, and also includes means coupled to sai doutput for producing a graphic record which comprises a plurality of successive signals in response to the detection of different ones of said separated fractions, the improvement which comprises: means coupled to said record-producing means for controlling the application of predetermined ones of said separated fractions to respectively different ones of said collecting means in response to the production by said record-producing means of the respective signals which correspond to said predetermined ones of said separated fractions.

14. In apparatus according to claim 13 wherein said controlling means applies said predetermined ones of said separated fractions to respectively different ones of said collecting means at predetermined times after the beginning of the production of said respective signals.

15. Gas chromatograph apparatus which comprises:

(a) a chromatograph column having an output,

(b) a plurality of means for receiving said output,

(c) means coupled to said output and to said receiving means for conveying the separated fractions at said output to said receiving means,

(d) means coupled to said output for producing a plurality of successive recorded signal peaks in response to the detection of successive separated fractions at said output, and

(e) means coupled to said (d) means and to said plurality of receiving means for controlling the application of predetermined ones of said separated fractions to respectively different ones of said receiving means at predetermined times after the beginning of the production of said signal peaks corresponding to said predetermined ones of said separated fraction.

16. Apparatus for automatically collecting successive fractions separated from a fractionizable mixture by a gas chromatographic column and which includes a detector which produces signals respectively representative of said fractions, comprising a plurality of fraction collecting traps, means responsive to the beginning of the respective signals corresponding to detection of separation of successive fractions by said column for automatically bringing corresponding ones of the traps in

said series successively into communication with the output side of said column and means responsive to the termination of the respective signals corresponding to the detection of said respective fractions for automatically bringing said corresponding ones of said traps out of communication with the said output side.

17. Apparatus for automatically collecting fractions separated from a mixture by chromatographic apparatus comprising:

(a) means for detecting a plurality of fractions which were separated from said mixture by said chromatographic apparatus and producing a plurality of signal peaks corresponding respectively to said fractions,

(b) a plurality of collecting means for collecting predetermined ones of said fractions,

(c) means for conducting said separated fractions to said collecting means, and

(d) means responsive to the maxima of the respective ones of said signal peaks for initiating the application of said predetermined fractions corresponding to said signals via said conducting means to predetermined ones of said collecting means, and

(e) means responsive to predetermined subsequent portions of said respective ones of said signals for terminating the application of said corresponding predetermined fractions to said predetermined ones of said collecting means.

References Cited by the Examiner

UNITED STATES PATENTS

2,692,820 10/1954 Alway et al. _____ 73—23.1 X

OTHER REFERENCES

Article: Ambrose et al. in Nature, Jan. 14, 1956, vol. 177, page 84.

RICHARD C. QUEISSER, *Primary Examiner.*