

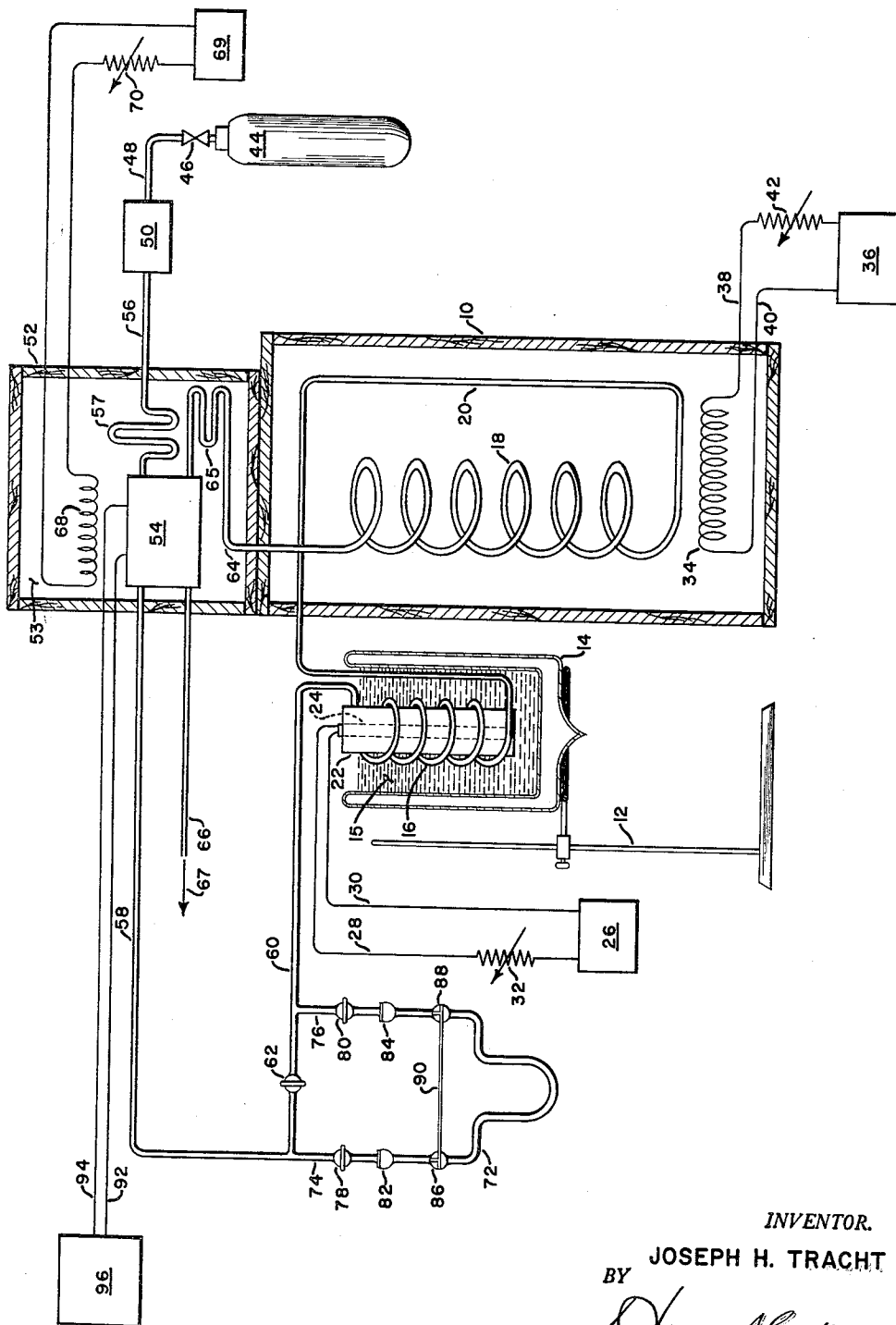
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CHROMATOGRAPHIC METHOD AND APPARATUS

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CHROMATOGRAPHIC METHOD AND APPARATUS

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The present invention relates to new and useful improvements in liquid-vapor partition chromatography, and pertains more particularly to the method of and apparatus for varying the temperature of a sample during separation in such a manner so that enhanced separations are obtained for the entire range of boiling points of the sample components.

Broadly, the present invention involves a method of and apparatus for continuously and sequentially passing a stream of carrier gas through a condensing column and a partitioning column, introducing the sample into the carrier gas stream upstream of the condensing column while maintaining the condensing column at a temperature sufficiently low to condense the sample without condensing the carrier gas, thence raising the temperature of the condensing column after the sample has condensed therein sufficiently to cause vaporization of the condensed sample, and analyzing the effluent of the partitioning column.

A preferred embodiment of the invention also involves increasing the temperature of the partitioning column after all of a predetermined component of the sample has emerged from the partitioning column. A preferred embodiment of the apparatus for controlling the temperature of the condensing column includes a heat reservoir in heat-exchange relationship with the condensing column with the optional, though preferred, additional inclusion of a heating means therefor.

The invention will be best understood upon reference to the accompanying schematic drawing of apparatus according to the invention and the following description of its use.

The numeral 10 designates a cabinet in section, access to the inside of which may be had as by the provision of a removable panel or door (not shown). Inasmuch as the interior of the cabinet 10 constitutes an air bath and is to be heated, it is preferred that the cabinet 10 be made of a material having at least moderate thermal insulating characteristics, such as wood. Outside the cabinet 10 is a ring stand 12 which adjustably supports a Dewar flask 14 containing liquid nitrogen. Mounted outside the cabinet 10 is a condensing column 16 and within cabinet 10 is mounted a partitioning column 18, such columns being connected in series by a conduit 20.

The columns 16 and 18 are preferably of helical configuration, and can be more tightly wound than as shown, with the condensing column 16 being substantially smaller than the partitioning column 18. Conveniently, the column 16 can comprise copper or stainless steel thin-walled tubing having a length of three feet and an inside diameter of one-quarter inch, the same being wound about a radius of one and one-half inches. Conveniently, the partitioning column 18 can be copper or stainless steel thin-walled tubing of seven foot length and an inside diameter of one-quarter inch and wound about a radius of ten inches. The connecting conduit 20 can be of the same character as either of the columns 16 and 18.

The partitioning column 18 is packed with a partitioning medium which can conveniently comprise a finely divided solid, such as Celite or crushed firebrick known as Silacel, each particle of which is coated with a sta-

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tionary liquid phase, such as tri-cresyl phosphate or butyl phthalate. The procedures for making and packing the partitioning column 18 for the purpose of liquid-vapor partition chromatography are well known in the art and need not be elaborated upon here, it being understood that the expression "stationary liquid phase" has reference to a substance in which components to be separated possess at least limited solubility and which does not tend excessively to migrate at temperatures of separation. The condensing column 16 can be packed in the same manner as and with the same partitioning medium as the partitioning column 18; however, it has been found that best results can usually be obtained when the condensing column 16 is filled with a solid having a large or extended inert surface area. Superior results have been obtained when the condensing column 16 is packed with fine glass beads, such as 3 M #11 glass beads.

The condensing column 16 embraces a heat reservoir comprised of a metallic core 22 preferably made of brass or copper. The heat reservoir 22 is metallic for the reason that metals generally exhibit good thermal conductivity combined with a substantial heat capacity per unit volume. Disposed axially within the heat reservoir or core member 22 is an electrical heating element 24, which is energized from a power supply 26 through leads 28 and 30. The heat output of the heater 24 is controlled by a variable rheostat 32. A further electric heater 34 is provided for heating the interior of the cabinet 10 and in particular the partitioning column 18, such heater 34 being energized from a power supply 36 through leads 38 and 40. The output of the heater 34 is controlled by a variable rheostat 42.

A source of carrier gas, such as helium, is designated by the reference numeral 44 which is connected by a valved outlet 46 and conduit 48 to a flow regulator 50. A housing 52 made of a material preferably possessing at least moderate insulating characteristics such as wood is provided to define a constant-temperature air bath 53 within which is disposed a thermal conductivity cell 54. The output of the flow regulator 50 is passed into the reference channel, not shown, of the thermal conductivity cell 54 by a conduit 56, a portion of the conduit 56 within the constant-temperature air bath 53 being coiled as shown at 57 to establish a heat-exchange relationship. The helium passes from the reference channel, not shown, of the thermal conductivity cell 54 to the condensing column 16 through conduits 58 and 60 between which a valve 62 is disposed. The outlet end of the partitioning column 18 is connected to the detector channel, not shown, in the thermal conductivity cell 54 by means of a conduit 64, it being noted that the portion of the conduit 64 disposed in the constant-temperature air bath 53 is coiled as shown at 65 to establish a heat-exchange relationship. The gases conducted by the conduit 64 and the detector channel, not shown, of the thermal conductivity cell 54 are vented through a conduit 66, as indicated by the arrow 67.

Means is provided for maintaining the air bath 53 at a constant temperature. Such means can conveniently comprise an electrical heating element 68 connected to a source of electrical energy 69, as shown, with the provision of a variable rheostat 70 for controlling the heat output of the heating element 68. With such an arrangement, the temperature within the air bath 53 can be maintained at a constant value by appropriate adjustment of the rheostat 70. It will be understood that temperature indicating means, not shown, can be provided in association with the air bath 53 and the interior of the cabinet 10 whereby to effect appropriate adjustment of the variable rheostats 42 and 70.

A sample loop 72 of known volumetric capacity, say 30 ml., is detachably coupled to the conduit 60. For this purpose, the conduit 60 is provided with a pair of parallel branch conduits 74 and 76 provided with stop-cocks 78 and 80, respectively. The free ends of the conduits 74 and 76 terminate in male ground glass fittings that are detachably and sealingly received in female counterpart fittings 82 and 84, respectively. The female fittings 82 and 84 are respectively connected to three-way valves 86 and 88 as are the opposite ends of the sample loop 72. The three-way valves 86 and 88 are ported, as illustrated schematically in the drawing, and are connected by a short conduit 90.

The thermal conductivity cell 54 is conventional in character and is for the purpose of producing an electrical potential that is a function of the difference between the thermal conductivities of the helium passed there-through and the eluant from the partitioning column 18. The electrical potential produced by the thermal conductivity cell 54 is fed by means of leads 92 and 94 to a recording potentiometer 96 for recording such electrical potential versus time. If desired, the recording potentiometer 96 can incorporate an integrating device or system, such as exemplified in United States application Serial No. 693,827, entitled "Apparatus," filed November 1, 1957, by Norman D. Coggeshall and Benjamin M. Wedner, now Patent No. 2,998,291; and United States application Serial No. 688,941, entitled "Apparatus," filed October 8, 1957, by William K. Hall, Gustave A. Sill, and Court L. Wolfe.

Of course, as is known in the prior art, carrier gas can be physically compared to the eluant from the partitioning column on a basis other than thermal conductivity as, for example, on the basis of their densities, in which case a gas density balance would be substituted for the thermal conductivity cell 54. Accordingly, for the purpose of the appended claims, the thermal conductivity cell 54 should be considered as a representative of any means for comparing a carrier gas stream and an eluant with the requisite degree of sensitivity, or of any means for detecting variation in the composition of the eluant. The basic principles of vapor-liquid partition chromatography are well known and are widely described in the literature and any detailed discussion thereof is deemed unnecessary. It is sufficient for present purposes to note that any physical or chemical difference between the carrier gas stream and the eluant stream is indicative of the presence of a substance in the eluant stream that has been eluted by the carrier gas stream. Consequently, the provision of a means 54 for sensing physical differences causes the recording potentiometer 96 to produce a record of the presence of sample components in the eluant stream versus time.

The operation of the illustrated apparatus will now be described. Initially, the fittings 82 and 84 are disconnected, the valve 62 is opened, and the valves 78 and 80 are closed so that the helium carrier gas is introduced into and passed through the columns 16 and 18 whereby the system is washed free of all elutable contaminants. The sample loop 72, which is at this time disconnected from the conduit 60, is filled with the gas to be analyzed by appropriately adjusting the valves 86 and 88 and circulating the gas to be analyzed therethrough. The gas is circulated through the sample loop 72 under standardized temperature and pressure conditions so that upon placing the valves 86 and 88 in the positions shown thereof in the drawing, a standard fixed volume of sample gas is trapped between the valves 86 and 88 in the sample loop 72. With the valves 86 and 88 in the positions shown thereof and prior to connecting the sample loop 72 to the conduit 60, carrier gas is introduced into one of the fittings 82 or 84 so as to fill the conduit 90, as well as the connections between the valves 86 and 88 and their respective fittings 82 and 84 solely with carrier gas. The sample loop 72 is then reassembled with the conduit 60

by the connections 82 and 84, after which the valves 78 and 80 are opened and the valve 62 is closed, so that the flow of helium is continued into the columns 16 and 18 through the conduit 60, with the gas sample remaining isolated in the sample loop 72.

The Dewar flask 14 is filled with liquid nitrogen and positioned, as shown, so that the condensing column 16, as well as the heat reservoir 22, is substantially entirely immersed in the liquid nitrogen. Such immersion of the column 16 and the heat reservoir 22 in the liquid nitrogen need only be for a time sufficient to lower and maintain the temperature of such elements at a temperature sufficiently low so as to condense the gas undergoing analysis, though preferably the time is extended until such elements are approximately at the temperature of the boiling point of nitrogen at atmospheric pressure. At this time, the temperature of the column 18 is preferably at about room temperature.

After the condensing column 16 and the heat reservoir 22 have been cooled to the requisite extent, the valves 86 and 88 are respectively turned 90 degrees anticlockwise and clockwise from the positions shown thereof so that the sample gas is carried into the conduit 60 and thence into the condensing column 16 by the continuing flow of the carrier gas. The gas sample condenses within the condensing column 16 due to the cold temperature thereof, though the flow of helium continues because of the latter's low boiling point relative to that of nitrogen.

As soon as the gas sample has been condensed within the condensing column 16, the Dewar flask 14 is lowered and the nitrogen contents thereof are removed, after which the empty Dewar flask is replaced in the position shown thereof in the drawing. The temperature of the condensing column 16 and its contents then begin to rise, though the rate of such temperature increase is substantially reduced by the presence of the heat reservoir 22 and the insulation afforded by the Dewar flask. Such increase in temperature of the condensing column 16 coupled with the continued flow of helium there-through tend to cause the condensed components of the gas sample to be stripped from the condensing column 16 in the order of their boiling points and introduced into the partitioning column 18 through the conduit 20 in such order. After the temperature of the condensing column 16 has been allowed to increase in the manner aforesaid for a time interval on the order of about two to about five minutes during which the temperature thereof shall have increased to a temperature of about -80° F. to about -40° F., the variable rheostat 32 is adjusted so that the temperature of the condensing column 16 increases at a rate of about 5° F. to about 10° F. per minute, with such heating being discontinued after the temperature of the condensing column 16 has reached about 350° F.

The heater 34 is not energized until after the gas sample components of the lowest boiling points have at least entered the partitioning column 18 and preferably not until such components have been eluted therefrom, after which the heater 34 is energized so as to raise the temperature of the interior of the cabinet 10. While the temperature of the interior of cabinet 10 can be raised as gradually as desired, it has been found where the sample under analysis is a natural petroleum gas, such as obtained from a condensate field, that the temperature of the interior of the cabinet 10 can be raised rapidly to 300° F. after propane has been eluted from the partitioning column 18. Delay in the use of the heater 34 until after the propane peak has passed allows effective separation of the hydrocarbons having less than four carbon atoms, while the ensuing use of the heater 34 expedites the elution of the higher molecular weight components through the partitioning column 18 while not adversely affecting the separation of such components appreciably. Also, the use of the heater 34 assures a more prompt purging of the sample from the partitioning column 18

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by the continuing flow of carrier gas so that the apparatus is readied for reuse in a shorter time interval.

While the preceding description deals specifically with analysis of natural petroleum gas such as obtained from a condensate field, it will be appreciated that the principles of the invention can be advantageously employed in connection with the analysis of widely differing types of samples, and are especially well suited for analysis of samples wherein the components of the sample have widely varying partition coefficients. It is only essential in the practice of the present invention that the condensing column 16 be cooled sufficiently to initially condense the sample without condensing the carrier gas. It will be apparent that with some sample compositions less drastic means of refrigeration than the illustrated and described liquid nitrogen bath will suffice, this being particularly true when the condensing column 16 is operated under superatmospheric pressure. In the practice of the invention, any of the gases known for use as a carrier gas in vapor-liquid chromatography, such as helium or nitrogen, can be employed, provided that the boiling point thereof be sufficiently low as to not condense in the condensing column 16 during the sample condensing step. One of the chief advantages obtained in the practice of the invention is that the partitioning column 18 can be substantially shorter than would be otherwise required in order to obtain a comparable separation of the components of the sample having the lowest boiling points. This fortuitous result arises from the fact that materials having lower boiling points usually tend to have higher partition coefficients. While the operation of the condensing column 16 during an analysis cycle does not in itself approach an efficiency of separation attainable through chromatographic procedures, the same affords a unique and highly beneficial combination with the partitioning column 18 downstream therefrom in that a significant separation of the lowest boiling components of the sample is attained, which separation can thereafter be expeditiously and efficiently sharpened by the partitioning column 18.

The advantage of the shortening of the partitioning column 18 through the use of the upstream condensing column 16 is that the overall transit time of the gas sample through the columns 16 and 18 is substantially shortened, and in addition the time required to thoroughly elute the sample from the partitioning column 18 is also substantially shortened. For example, a 50 ml. sample of natural gas can be analyzed, from methane (CH_4) through octane (C_8H_{18}), with the described apparatus and procedure and the apparatus readied for reuse in about 60 minutes.

Narrowness in scope of the invention is not to be implied from the detailed description of the method and apparatus given above, such detail having been included solely for the purpose of conveying a full and complete understanding of the principles involved, and accordingly reference should be made to the appended claims in order to ascertain the actual scope of the invention.

I claim:

1. Apparatus comprising a condensing column and a partitioning column, said columns being series connected, with the condensing column being disposed upstream of the partitioning column, conduit means for introducing a carrier gas into the upstream end of the condensing column, means for introducing a mixture to be analyzed into the upstream end of the condensing column, a heat reservoir comprised of a metal core, said condensing column being of helical configuration and embracing the core, an electrical heating element in the core, and means for selectively immersing the condensing column and the core embraced thereby in a liquefied gas.
2. The combination of claim 1, wherein the condensing column contains finely divided solid matter.
3. A method of analyzing a natural gas sample comprising continuously and sequentially passing a stream

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of helium through a condensing column and a partitioning column, introducing the natural gas sample into the helium stream upstream of the condensing column while maintaining the condensing column immersed in a liquid nitrogen bath for a time sufficient to condense the natural gas sample carried therethrough by the helium stream, thereafter removing the liquid nitrogen bath whereby the liquefied gas sample tends to vaporize and the lower boiling components thereof tend to be swept into the partitioning column by the helium, thereafter heating the said condensing column to further cause vaporization of the gas sample and to sweep into the partitioning column the higher boiling components of the condensed gas sample, and analyzing the effluent of the partitioning column.

4. The method of claim 3, wherein the temperature of the partitioning column is raised after all ethane has emerged from the partitioning column.

5. Apparatus comprising a condensing column and a chromatographic separation column, said columns being series connected with the condensing column being disposed upstream of the chromatographic separation column, conduit means for introducing carrier gas into the upstream end of the condensing column, means for introducing a mixture to be analyzed into the upstream end of the condensing column, a heat reservoir contacting said condensing column, means for cooling the heat reservoir and the condensing column, electrical heating means for heating the heat reservoir and the condensing column at a controlled rate, and means for analyzing the effluent of the chromatographic separation column.

6. A method of analyzing a gaseous mixture having a relatively wide volatility range and at least some of whose components have closely similar volatilities, said method comprising establishing flow of a carrier gas serially through a condensing column and a chromatographic separation column in the order named, introducing a sample of said gaseous mixture into the carrier gas upstream of the condensing column, condensing the gaseous sample in the condensing column without condensing the carrier gas by cooling said column, thereafter effecting a partial resolution of the condensed sample by fractional vaporization, said fractional vaporization being effected by raising the temperature of the condensing column at a controlled rate until the more volatile components are vaporized and then further raising the temperature of the condensing column at a controlled rate until the less volatile components are vaporized, further resolving the vaporized components by passing such components, together with carrier gas, into the chromatographic separation column in the order in which they are vaporized, removing the thus-resolved components from the chromatographic separation column by passage of carrier gas therethrough, and analyzing the effluent from the chromatographic separation column.

7. The method of claim 6, wherein the temperature of the chromatographic separation column is raised during removal of the less volatile components of the mixture therefrom.

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