Fig. 5

AMOUNT DISTILLED, Wt. %

Fig. 6

AMOUNT DISTILLED, Wt. %
Fig. 7

RECORDER RESPONSE

INTERMEDIATE NAPHTHA
HEAVY NAPHTHA
HEATER OIL

INCREASING BOILING POINT

Fig. 8

°F

-47°F I.B.P.

WT. %

847°F E.P.

47° I.B.P.

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ANALYSIS BY GAS CHROMATOGRAPHY AND APPARATUS THEREFOR
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This invention relates to chromatographic analysis, and more particularly it relates to a method and means adapted to resolve a sample mixture into fractions of similar boiling points.

In the production of petroleum and chemical products composed of a mixture of components having different boiling points, it is desirable to determine the component distribution in boiling point order. An example is in the production of gasoline where the fuel properties are greatly affected by composition. Other examples are in processes where it is desirable to determine the boiling range of a feedstock or intermediate product in order to aid in product control and operating efficiency.

There are a number of distillation methods available to the industry by which product boiling ranges may be determined. The most widely used methods for both control and product specification tests is the ASTM distillation, as outlined by ASTM Method D—86. In brief, this method is a flask distillation which is a simple one plate distillation. In operation a sample is heated in a flask and distilled overhead at a specified rate. The vapors are condensed and collected in a measuring receiver, with vapor temperatures being determined when distillation starts, when certain percentages of condensed vapors are collected in the receiver, and when distillation ceases. Such distillations give inaccurate data on the initial and final boiling points and, in fact, approach a true picture only around the 50% point. Devices are available commercially to automatically determine the boiling range, the initial or final boiling point, or the boiling point at a pre-selected intermediate percentage. These devices are designed to give data equivalent to the ASTM method and suffer from the same limitations.

A more precise analytical distillation, commonly called true boiling point (T.B.P.) analysis, is used to more accurately determine the boiling range of petroleum fractions. In this type distillation a column having 100 theoretical plates is used, with data observations at 1% fractions. The data obtained by such a T.B.P. analysis is extensively used for process design and pilot plant studies and would be extremely useful for control of manufacturing processes. However, such an analysis typically requires at least about 100 hours, and because of the time required, it makes the method of little value for control purposes. Similar to the ASTM distillation, the T.B.P. distillation does not accurately establish the initial or final boiling points, and as the amount of the sample boiling below room temperature and above about 500° F. increases, these devices become more inaccurate.

Gas chromatography methods have also been employed to separate a sample into its various components. This subject is discussed in detail in the publication "Gas Chromatography" by A. I. M. Keulemans (Reinhold Publishing Corp., 1957). The operation of a gas chromatography system includes distributing a gaseous sample on a column packing material contained in a chromatographic column and separating the sample into its components by sweeping the column with a carrier gas so that the components are released and emerge from the column in the order of their partition coefficients. A detecting device is used to sense the composition of the column effluent as the components emerge and, thus, a quantitative and qualitative determination of the sample is obtained.

The type of separation and accuracy of determination obtained by gas chromatography will be influenced by many factors. In gas-liquid chromatography emphasis has been placed upon the use of the more highly selective stationary liquid phases which, for instance, are capable of separating a hydrocarbon mixture into its components according to structural configuration, i.e., the separation of napthenes from aromatics or the separation of isomers.

Non-selective stationary phases, effective to separate according to boiling point, have been used with a relatively narrow boiling range mixtures, but these conventional methods are not suitable for separating a wide boiling range sample into its components. The thermal stability of the stationary phase, the effects of changes in gas flow rate and temperature upon the detector, column heating, determination of retention times of components, selectivity of the stationary phase and many other factors must be considered when using chromatographic methods at high temperatures to determine boiling point distribution of broad-boiling products.

Conventional gas chromatography is not suitable for separating a wide-boiling-range sample because column temperature is optimum for only a narrow boiling range, resulting in inadequate separation of components boiling at temperatures other than column temperature. Consequently, conventional gas chromatography is not useful for resolving a wide boiling range sample into its components according to boiling point order, and conventional techniques do not provide a useful relationship between separation and boiling points which may be employed for product and operational control purposes.

The general object of the present invention is a method and means for separating a wide-boiling mixture of organic compounds having different boiling points into fractions of similar boiling points and for providing boiling point information thereon, which method and means is rapid and accurate, but inexpensive, and which is adapted to laboratory use as well as to operating plant use. Further objects of this invention will become apparent from a reading of the following description of the invention.

Briefly, this invention provides a particular chromatographic column and a particular column packing adapted to separate a mixture of organic compounds having different boiling points into fractions having similar boiling points. This is accomplished by providing a chromatographic column provided with means adapted for increasing the column temperature linearly during the analysis; which column is packed with a thermally stable packing material capable of separating a sample into its components at boiling point order, and which packing consists essentially of an inert solid support having distributed thereon a non-selective stationary liquid phase.

A detector, providing a signal output directly proportional to the weight of the sample components and linear over a wide range of gas flow rates, temperatures, and concentrations, receives the column effluent and produces a signal which is converted into usable information by correlating the retention time of the fractions to their boiling points.

It is further contemplated that the signal output from the detector may be amplified and fed to a recorder and/or may be transmitted to a printing integrator which at intervals records cumulative area of the chromatogram produced during the analysis. In this manner, the recorder tracing presents a gaseous profile of the component distribution, and integrator readings provide a printed record indicative of the weight
percent boiling at a given temperature. Thus, the profile of the product distribution may be used by operating personnel directly and the integrator readings may be used in the preparation of "true boiling point" distillation curves or to supply information to a computer controlled automatic processing plant operation.

A better understanding of our invention will be had from the following description of a particular embodiment of the invention and from the accompanying drawings wherein:

FIGURE 1 is a schematic representation of apparatus for the separation of a sample into fractions having similar boiling points; FIGURE 2 is illustrative of a preferred detector employed in the invention;

FIGURE 3 is a typical reference chromatogram where detector output is plotted as ordinate and integrator print numbers as abscissa;

FIGURE 4 is a typical reference curve where boiling point is plotted as ordinate and integrator print number as abscissa;

FIGURE 5 is a graphic representation of a chromatographic boiling point separation curve, or a similar distillation curve and a T.B.P. distillation curve;

FIGURE 6 illustrates chromatographic boiling point separation curves for a typical intermediate naphtha, heavy naphtha and a heater oil;

FIGURE 7 graphically illustrates a profile of product distribution for the products indicated in FIGURE 6; and

FIGURE 8 is illustrative of a typical boiling point separation curve for a very wide boiling range material.

Referring to FIGURE 1, a carrier gas stream from a source 11 is passed by way of the line 12 through a chromatographic column 13 from which the column effluent emerges and is passed through the detector 14. A small sample to be analyzed is introduced into the carrier gas stream through a sample introduction means 16. The sample may be vaporized by heating it to a temperature sufficient to flash vaporize the sample prior to its introduction into the column 13. The carrier gas stream then carries the vaporized sample into the column where it is distributed upon the column packing material. In this embodiment electrical means are employed for heating the column by using the column itself as a resistor. The column temperature is adjusted to a temperature at which the lowest boiling component has a suitable retention time. To begin the analysis the detector 14, the amplifier 17, recorder 18 and the integrator 19 are put into service. The column temperature is raised by supplying heat to the column while the carrier gas stream continues to flow through the system. As the column temperature increases, progressively higher boiling components in the sample mixture are eluted from the column packing material by the carrier gas stream and emerge in the column effluent in fractions according to boiling point order.

The separated fractions in the column effluent pass into the detector 14, wherein a hydrogen flame ionization detector, where they are burned in the presence of air in a hydrogen stream. An ion current is produced when ionizable molecules in the column effluent are passed through the detector, or signal output, from the detector increases or decreases according to the number of ionized particles produced, and gives a signal directly proportional to the weight of component. The signal from the recorder may be amplified upon passing through the amplifier 17 and used to drive a recorder 18 and/or integrator 19. The recorder tracing 20 develops a profile of the component distribution and the integrator readings 21 provide a printed record used to calculate weight percent removed from the column at a given temperature.

The sample mixture may be introduced into the apparatus by conventional chromatography techniques which include the use of a sample charging valve, a serum cap and syringe, a bulb and crushing apparatus, or the like. A sample heating means, such as an electrical resistance heater 22, may be employed to vaporize the sample upon introduction into the system. The sample size may vary considerably. For instance, a one ml. sample may be used, with a portion of the sample passed to the detector by the use of a vapor divider 23 positioned either between the sample introduction means 16 and the column 13 or between the column 13 and the detector 14. A micro sample ranging down to about 10^-6 ml. may also be used. The vapor divider 23 is used to pass as to pass a desired amount of sample through the detector. In the operation of the vapor divider 23 a major portion of the flow is vented from the system through an orifice sized according to the required degree of division, and the balance of the flow passed on through the system.

The sample charged to the system may be a wide boiling range mixture, e.g., hydrocarbon mixtures having a boiling range from about -260° F. to above 800° F. Hydrogen sulfide, CO₂, CO, water, nitrogen, oxygen, hydrogen, water, such materials normally contained in petroleum and chemical products will not significantly affect the sensitivity of the apparatus. Organic compounds broadly, may be separated and detected by the method and apparatus of the present invention.

The carrier gas employed in the practice of the invention may be any of the commonly used carrier gases which are not reactive with the sample mixture or the materials of the apparatus and which do not produce a response in the detector. Among the carrier gases generally suitable for this use are hydrogen, helium, nitrogen, air, carbon dioxide, argon, etc., with nitrogen being preferred. The detector employed in the invention is substantially insensitive to changes in gas flow rate, however, it is preferred to maintain a substantially constant flow rate of carrier gas through the apparatus by use of a flow regulating device such as the flow regulator 24 employed in the carrier gas line to the column 13. Gas flow rate may be varied considerably, depending upon the column and column packing. Typically, the flow rate may be as little as 0.5 ml. per minute, and as great as 100 ml. per minute, depending upon the type of column and column packing material.

The chromatograms of column 13 may be of the block type having passages drilled through a thermally conductive metal block, may be formed from a tubular member, or may be of the capillary type. Column length may vary from about 6" to 29", and may be several hundred feet in a capillary column. In any instance, it is necessary that the column be capable of being heated in order to produce a substantially linear increase in column temperatures from the beginning of the analysis to its completion. It is also important that the linearity of the heating rate be maintained over a wide temperature range within the limits of the temperatures required in the analytical determination. The range of temperatures will vary according to the sample, i.e., from a temperature providing a suitable retention time for the lowest boiling component to a temperature at which the highest boiling component is vaporized in the system. For example, with methane (B.P. -260° F.), as a component, the column may be initially chilled to about -110° F. to provide a retention time of about one-half minute. The highest temperature will depend upon the thermal stability of the liquid phase and the partial pressure of the highest boiling component in the sample.

The column may be heated by means such as an electric resistance or cartridge heater or may be immersed in a circulating heat transfer medium, with the column construction, temperature range and the rapidity of response being determinative of the specific construction. Likewise, initial chilling of the column may be accomplished by the use of a circulating refrigerant or immersion in a cold bath containing liquid nitrogen, ice, or the like.
However, it has been found advantageous to employ a column formed from a metal tube of a suitable electrical resistivity and appropriate wall thickness whereby the column itself is employed as a resistor in an electrical circuit to provide a means of increasing column temperatures. This may be accomplished by providing a linear programmed temperature controller 25 connected to the column so as to pass a flow of current through the column 13 from point 27 to point 28. A suitable linear programming temperature controller for use in this application is described in "Programmed Temperature Gas Chromatography Apparatus" by Stephen Dal Nogare and J. C. Harden, "Analytical Chemistry," volume 31, No. 11, November 1959, pages 829-32. The temperature may be increased by the programmed temperature controller when using a very thin wall stainless steel tubing for the column. Advantageously, a heavy wall tubing of about 0.030" thickness may be employed with a high unampered-current voltage current to provide sufficient mass to produce a suitable heat density which gives reproducible column heating from one run to another. For this purpose any suitable current may be used, preferably about 115 volt A.C., transformed to about 30 to 200 amps, and with 2 to 10 volts.

The packing material 31 positioned in the column 13 comprises a non-selective stationary liquid phase. When using a packed column the liquid phase is distributed on an inert solid support. When using a capillary type chromatography column only the liquid phase is used. The non-selective stationary liquid phase should be stable over the range of temperatures employed in the operation of the apparatus and not be vaporized at the highest column temperatures. Advantageously, it has a low selectivity so as to be capable of separating the components of a sample mixture into fractions having similar boiling points. This liquid phase consists of a silicone rubber gum, such as a dimethyl siloxane polymer, and preferably is a viscous, high boiling dimethyl silicone polymer, such as G.E. #SE-30 Silicone Rubber Gum, marketed by General Electric Company.

The inert solid support may be crushed firebrick or another such material provided the particle size of the support will be determined by the speed and degree of separation required, and may range from about 30 to 100 mesh. Preferably, crushed firebrick of about 40 to 50 mesh is employed for most purposes. To prevent the solid support prior to deposition of the liquid phase by caustic washing in an alkaline solution such as KOH or NaOH. The support is then washed to neutrality and dried. This treatment has been found to significantly increase the thermal stability of the liquid phase.

Subsequent to the caustic treatment the silicone polymer may be dissolved in a solvent such as chloroform, benzene, etc., and the solid support intimately mixed into the solution. The solvent is then evaporated.

In some instances it may be desirable to make a rough separation of a mixture into structural groups, e.g., separating aromatics from paraffins and napthenes in a catalytic reformat. For this purpose a selective column packing material 32, such as an anode filter on firebrick, may be employed in a prefractionation zone 34 in conjunction with the non-selective packing material 31 in the column 13. The prefractionation zone 34, herein a separate, short column, may be heated by heater 25, herein shown as a resistance heater. The selective packing, of course, will be chosen for its ability to separate according to the dictates of the particular sample on which the analysis is being conducted. In this manner boiling point data may be obtained separately for the type of compounds resolved in the prefractionation zone 34.

When the sample contains heavy components with vapor pressures lower than compounds that may be conveniently eluted in a forward direction, provision is made for re-moving these components from the column by a backflush valve 24a and line 12a. Such a device would be necessary to handle samples such as crude oil, total product from catalytic cracking, and automotive crankcase lubricants.

The hydrogen flame ionization detector 14 produces a quantitative response proportional to the number of ions formed between the electrodes 40 and 41. Further, the detector provides a linear response over wide ranges of sample concentration, gas flow rate, and temperature. Several types of flame ionization detectors are available commercially which may be employed in the invention. A detector particularly well adapted for this use is illustrated in FIGURE 2. Advantageously, the detector base 43 is heated to provide a detector operating temperature above the dew point of the gases in the detector. The detector base 43 is constructed of a block of high thermal conductivity material, such as aluminum or brass, and is provided with a column inlet 44, a hydrogen inlet 45, an air inlet 46, an electrical lead inlet 47 and a heater 48. The detector may be heated by a circulating heat medium or other means but, preferably, an electrical cartridge heater fitted into a well in the base is employed.

The flame jet 49 is comprised of a small diameter metal tube 46, preferably a platinum tube, sealed in the base 51 adapted to fit in sealing contact with the gas inlet 52. A gasket material 53 capable of withstanding the operating conditions of the detector may be employed to effect a gas tight seal. Advantageously, the flame jet 49 serves as one electrode, and a collector electrode 41, constructed of platinum gauze of about 30 mesh size, is positioned at a suitably distance above the flame jet electrode 40. The two electrodes are connected across a high impedance 56 in series with a high voltage source 57, such as a 250 volt battery. The high impedance side of the detector is then fed to the amplifier 17, recorder 18, etc. The electrical connection to the flame jet electrode 48 preferably is completed by using a spring element 58, which may be a Nichrome spring. This construction assures a positive electrical connection while permitting the flame jet to be replaced when required.

The amplifier 17 normally will be employed in the circuitry of the apparatus, but may be eliminated in certain instances, as when using a micro-volt recorder. The actual amplifications developed will vary, depending upon the type of recorder and/or integrator employed. However, some method of impedance conversion is required to transform the high output impedance of the detector to the low impedance required by most recorders. The amplifier may be of any suitable type available commercially and may comprise only an electrometer tube in a cathode follower circuit such as used in many ion gauge instruments.

Preferably, the recorder 18 is a recording potentiometer; however, a recording milliammeter may be used satisfactorily. Both instruments are commercially available. The record produced by either gives a plot of the time versus the concentration of the components of the sample mixture.

The integrator 19 is a printing electronic integrator producing at least about 6000 counts per minute. Such an integrator is marketed by Perkin-Elmer Corporation and the Perkin-Elmer Model 194-0050 Automatic Printing Integrator has been found satisfactory for this purpose when modified to record from a chromatogram at timed intervals, preferably about every 10-15 seconds. In this manner the integrator readings provide a printed record to calculate weight percent of fractions having the same boiling point separated at a given temperature. The integrator readings are in digital form and suitable for processing in a computer controller adapted for the automatic operation of a process, and these readings may also be used in the preparation of boiling point curves similar to those provided by conventional distillation techniques.
To correlate the retention times of the fractions to their boiling points, a known blend of components, preferably a blend of normal paraffins having from about 1 to 12 carbon atoms per molecule, is used as a reference standard. The prepared mixture is run through the apparatus in the same manner as an unknown sample, and a record of chromatographic presentations is obtained, showing integrator print number versus detector output, as shown in Figure 3. From the known boiling points of each component of the reference mixture and the integrator print numbers, a reference curve, as shown in Figure 4, may be obtained, with boiling point plotted versus the number of integrator readings to each peak maximum. This reference curve relating the integrator counts to the boiling point then may be used in correlating the retention times of the sample components separated by the apparatus to the boiling points of the fractions having similar boiling points.

**EXAMPLE I**

As an example of the separation obtained for a wide boiling range mixture and to illustrate a comparison with conventional distillation techniques, Figure 5 shows boiling curves for a natural gas condensate obtained by (a) T.B.P. distillation, (b) ASTM D-86 distillation and (c) the method and apparatus of the present invention. The T.B.P. curve, drawn as a solid line, was obtained from a 120 hour distillation in a 100+ theoretical plate column. The curve obtained by the ASTM D-86 method is shown as a dashed line. The curve obtained by the apparatus of the present invention is shown as a series of solid circles and was obtained in an analysis requiring about 30 minutes.

From these curves it is seen that the data obtained by the present invention differs significantly from the ASTM D-86 curve, particularly near the initial and the final boiling points. The ASTM method failed to indicate the presence of components lighter than C10's and also missed most of the C19's and higher, while the chromatographic method included a boiling range from about 30°F to 560°F. This failure may be attributed to the loss of components and to inadequate separation. Lesser differences are apparent in the first and final few percent in comparison with the T.B.P. curve. However, the T.B.P. distillation did not indicate the presence of the highest and lowest boiling components.

Separation by the chromatographic method more accurately indicates the composition lighter than pentane and also gives a better delineation of the highest boiling compounds. Compounds not observed by the ASTM or T.B.P. methods are determined, and there is no interaction or azeotrope formations as in conventional distillation.

**Utilization**

In separations made in distillation towers, the accepted monitor for product cut point is tower temperature. These cut points are usually established from extensive analysis of fractions by either ASTM D-86 or T.B.P. distillation. The efficiency of tower operation is increased by minimizing the overlap of the distillation curves for the various products. The apparatus of the invention is well adapted for this type analysis and may be used in various ways. Referring to Figure 6, chromatographic boiling point separation curves are shown for a typical intermediate naphtha, heavy naphtha and heater oil produced by a crude oil distillation unit. These curves, while indicating the true boiling range of the various products, do not indicate the amount of overlap between the products. Figure 7 illustrates the boiling point profiles, or chromatogram, from which the curves of Figure 6 were derived. From Figure 7 it is seen that there is a significant overlap between the three products which may be determined by observing the chromatogram produced by the recorder 13. These profiles are adapted to be used readily by the operating personnel.

While for most purposes it is preferred to use a recording potentiometer to plot the chromatogram, it is contemplated that an oscilloscope may be employed in the apparatus to provide an indication of component distribution. This may be desirable to incorporate a device, such as an X-Y recorder to directly plot the data in the form of the normal distillation curve.

**EXAMPLE II**

As a further example of the ability of the apparatus of the present invention to separate a wide boiling range mixture, Figure 8 illustrates a boiling point curve obtained by the present method for a gas condensate having a boiling range from 47°F to 847°F. This curve was prepared in the manner as previously described. The chromatographic column employed in this determination was a block type column heated by an electrical cartridge heater. The column packing material was 40 to 50 mesh crushed firebrick coated with a dimethyl silicone polymer, G.E. #SE-30 Silicone Rubber Gum. The detector of Figure 2 was employed, with an electrometer, recording potentiometer and electronic printing integrator as described above.

Having described our invention what we claim is:

1. Gas analysis apparatus adapted for resolving a mixture of organic compounds having different boiling points into fractions having similar boiling points and in boiling point order which apparatus comprises a gas chromatography column, means for passing a carrier gas stream through said column, means adapted for introducing a vaporized sample of said mixture into said carrier gas stream upstream of said column, a column packing material positioned in said column, which column packing material comprises a non-selective stationary liquid phase consisting essentially of a silicone rubber gum, means adapted for increasing the column temperature linearly during the course of the analysis, and flame ionization detector means adapted to receive the effluent from said column and to detect the concentration of said fractions in said column effluent, said detector being adapted to produce a signal linear over a wide range of column effluent flow rates, and temperatures, and means responsive to said signal to provide a quantitative record of each of said fractions.

2. The apparatus of claim 1 wherein said column is fabricated from an electrically conducting material of a suitable thermal and resistance requirements adapted for increasing the column temperature comprising means for passing a carrier gas stream through said column by employing said column as a resistance heater.

3. The apparatus of claim 1 wherein said column packing material is a dimethyl silicone rubber gum having a boiling point higher than the highest boiling fraction charged to said column.

4. The apparatus of claim 1 wherein said detector is electronically connected to a recorder means adapted to produce a graphic representation of the detector signal output during the course of the analysis.

5. The apparatus of claim 1 wherein an integrator is electrically connected to said detector and adapted to produce a printed record of the cumulative area of a chromatogram produced by said recorder means.

6. The apparatus of claim 1 wherein said column packing material further includes crushed firebrick.

7. The apparatus of claim 6 wherein said crushed firebrick has been pretreated with some suitable liquid phase which has been subsequently deposited thereon.

8. Gas analysis apparatus adapted for resolving a mixture of organic compounds having different boiling points into fractions having similar boiling points and in boiling point order which apparatus comprises a gas chromatography column; means for passing a carrier gas stream through said column; means adapted for introducing a vaporized sample of said mixture into said carrier gas stream.
a vaporized sample of said mixture into said carrier gas stream upstream of said column; a column packing material positioned in said column, said column packing material consisting essentially of crushed firebrick having deposited thereon a dimethyl siloxane polymer having a boiling point higher than the highest boiling fraction charged to said column; said column being made of an electrically conductive material and employed as a resistor in an electrical circuit adapted to linearly increase the column temperature during the course of an analysis; a hydrogen flame ionization detector adapted to receive the effluent from said column and to detect the concentration of said fractions in said column effluent; said detector being adapted to produce a signal linear over a wide range of sample concentration, column effluent flow rates, and temperatures; recorder means adapted to receive a signal from said detector and to produce a graphic representation of the detector signal output during the course of the analysis; and integrator means adapted to produce a printed record of the cumulative area of a chromatogram produced by said recorder means.

9. The apparatus of claim 8 wherein said crushed firebrick has been caustic treated prior to the deposition of said polymer thereon.

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