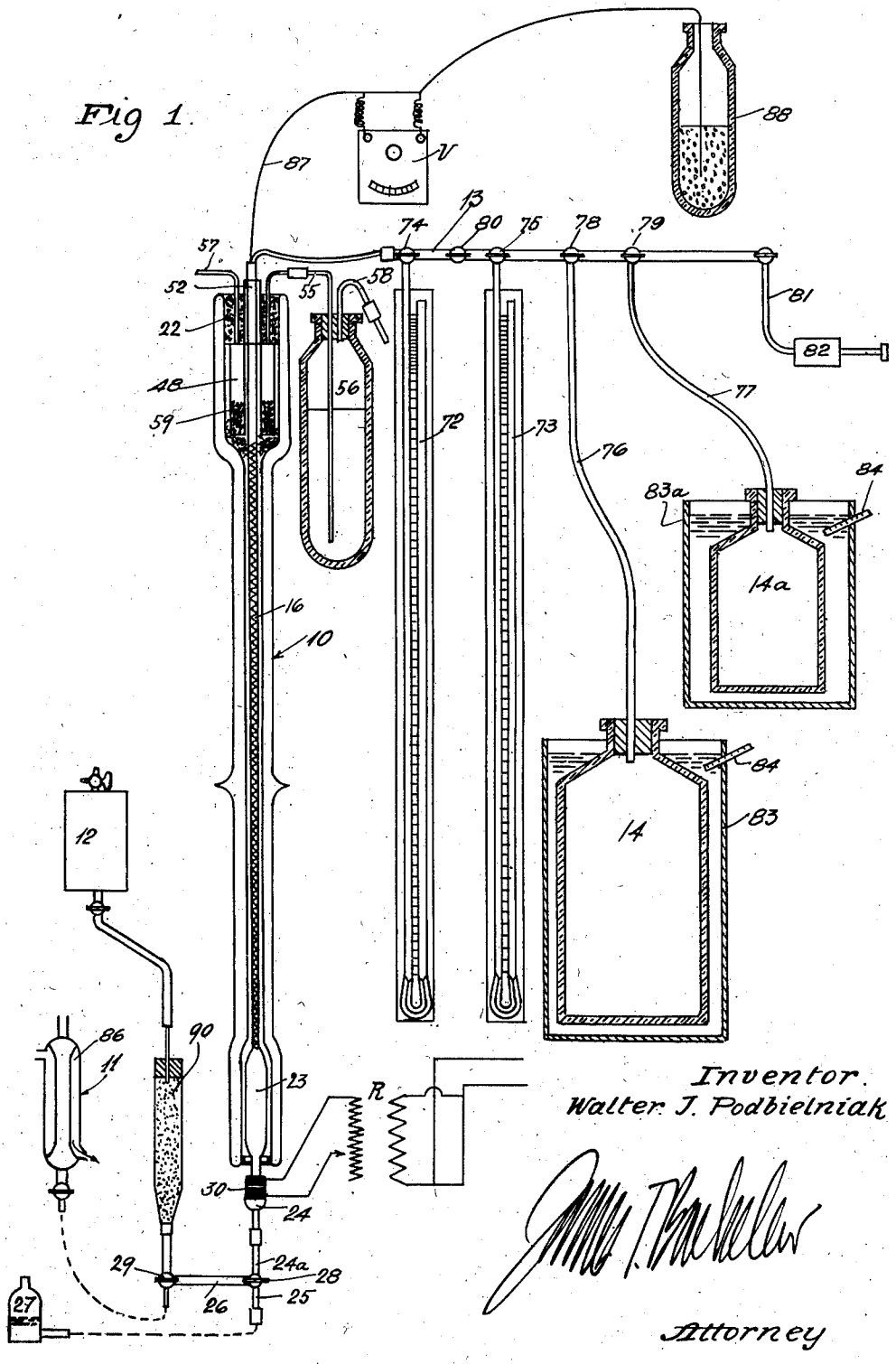
July 11, 1933. W. J. PODBIELNIAK 1,917,272

ANALYTICAL FRACTIONATING COLUMN

Filed Aug. 15, 1930 3 Sheets-Sheet 1

Fig 1.



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ANALYTICAL FRACTIONATING COLUMN

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Fig. 2.

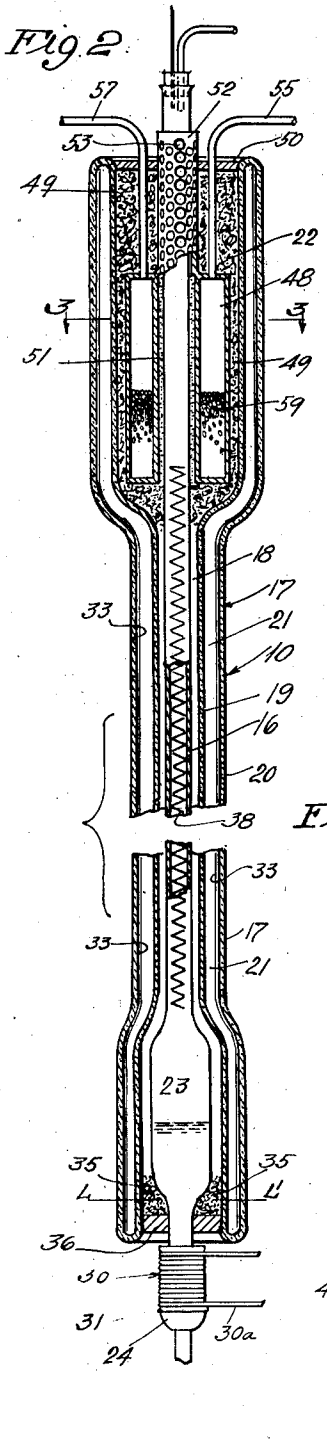


Fig. 10.

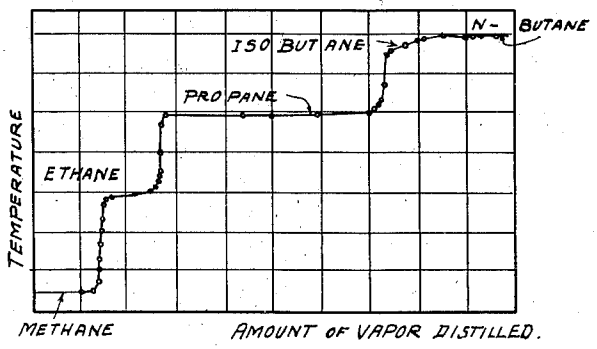


Fig. 6.

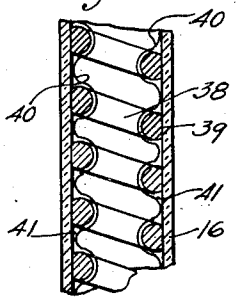


Fig. 7.

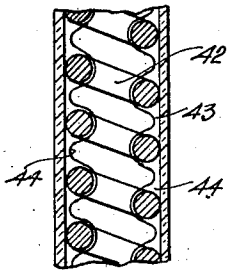


Fig. 4.

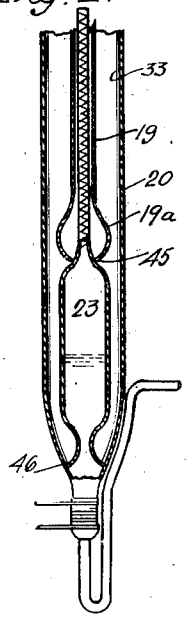


Fig. 5.

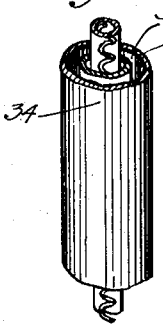
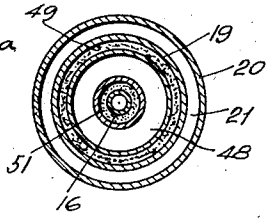


Fig. 3.



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Fig. 8.

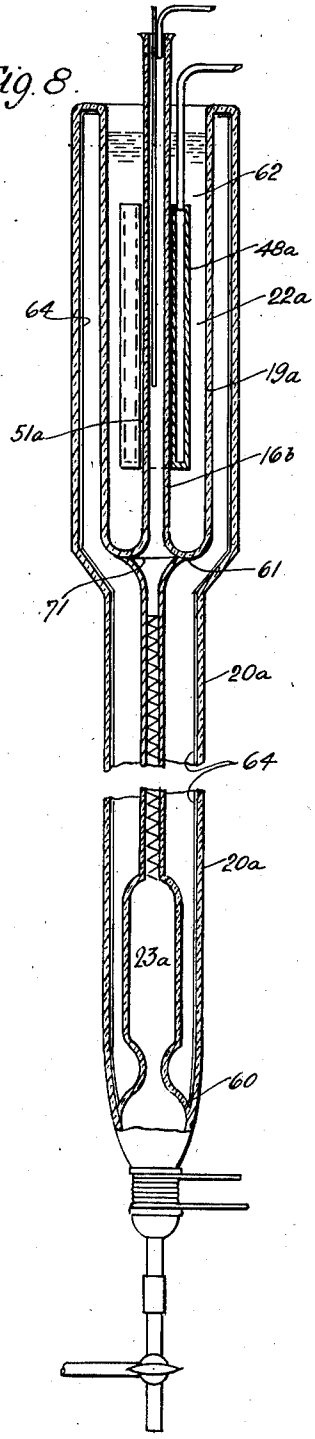
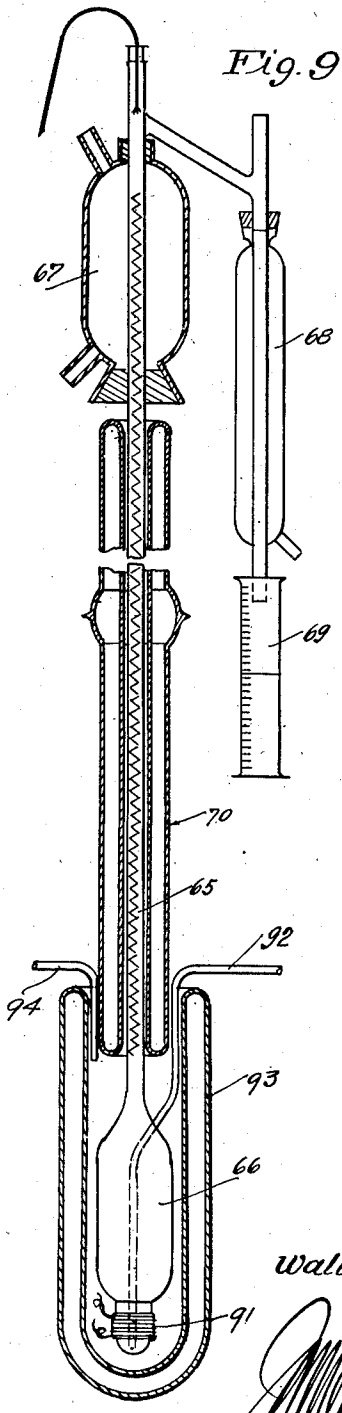


Fig. 9.



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UNITED STATES PATENT OFFICE

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ANALYTICAL FRACTIONATING COLUMN

Application filed August 15, 1930. Serial No. 475,585.

This invention has reference to laboratory apparatus for the fractional analysis of volatile liquids and gases or vapors containing condensible liquid fractions, and has to do particularly with analytical fractionating columns of the character described in my copending application on Method for analyzing liquid and gas, Serial No. 351,726, filed April 1st, 1929, of which the present application is in part a division.

It is a general purpose of the invention to provide a fractionating column whereby the fluid being analyzed may be subjected in a single operation to such sharp fractionation or separation that the constituents of the fluid may be obtained in the order of their higher boiling temperatures, substantially in the pure state; and in the broader aspects of the invention, either in liquid or vapor phase. This general object of the invention is accomplished by providing a fractionating column which is so constructed and proportioned as to obviate the commonly encountered difficulty in preventing "overlapping" of the fractionated constituents or cuts, or in other words preventing any one of the fractionated constituents from being contaminated with constituents of higher or lower boiling point.

My improved form of fractionating column may be characterized as comprising a distilling or fractionating tube surrounded by an evacuated jacket which provides an effective thermal insulation for the fractionating tube. The insulation afforded the latter is further increased by plating the jacket with suitable heat reflecting and insulating metal. I may state at this point that one feature of the invention resides in the plating of the jacket in a manner such that the distilling tube will be visible to the analyst through the insulating jacket. According to my preferred construction the distilling tube and jacket are made separate, thereby rendering the apparatus less subject to breakage than would be likely in case these parts were made integral, with joints that might easily become fractured. Building the column with the distilling tube and jacket as separate parts has the additional advantage of providing a more simple and economical construction, and rendering one or the other of the parts replaceable in case of breakage, without necessitating replacement of the entire column.

By proper dimensioning of the distilling tube, the vapors therein are allowed an extended path of flow in intimate exposure to the reflux liquid, such as is required for efficient fractionation, yet, however, without necessitating other than a small volume of vapors to be contained within the column at any one time. I have also provided an improved form of packing within the distilling tube whereby the reflux liquid is caused to have extended and thorough surface exposure to the vapors, without causing but a small amount of the reflux to be held in the column by the packing. Thus by reducing both the quantities of vapor and reflux within the distilling tube, conditions are such as to bring the degree of fractionation of the constituents of the fluid being analyzed, to a nicety, and to prevent lagging or overlapping of the constituents due to there being an excessive quantity of reflux held up in the column.

The invention embodies numerous additional features and advantages which however will require no preliminary description and will best be taken up at later points hereinafter.

I describe my invention hereinafter as embodied in a complete apparatus for analyzing fluids, suitably of the type comprising the subject matter of my copending application on Apparatus for analyzing liquids and gases, Ser. No. 475,584, filed of even date herewith, primarily for the purpose of showing one use of the fractionating column under conditions where close fractionation is essential, and where the efficiency of the column in effecting such separation will be appreciated. The invention is also described in this connection since it has at present its most general use in analytical apparatus of the character described in my co-pending application. It is to be understood, however, that my improved fractionating column is in no way limited to use in the particular apparatus hereinafter described, and that it is to be considered as independent and capable of general

use, either alone or in combination with other apparatus, for the fractional analysis of fluids.

The invention will now be explained more fully and in detail in the following detailed description, wherein reference is had to the accompanying drawings, in which:

Figure 1 is a general illustration, diagrammatic in parts, of the entire apparatus utilized in the analysis of fluids, and embodying my preferred form of fractionating column;

Fig. 2 is a broken longitudinal section through the fractionating column on an enlarged scale;

Fig. 3 is a section on line 3—3 of Fig. 2;

Fig. 4 illustrates a modified form of construction for the lower end of the fractionating column shown in Fig. 2;

Fig. 5 is a fragmentary view showing a modified method of plating the insulating jacket;

Fig. 6 is an enlarged fragmentary view showing a section of the distilling tube containing a preferred form of packing;

Fig. 7 is a view similar to Fig. 6; and is included for purposes of illustrating the advantage of the packing shown in Fig. 6 over an ordinary wire coil;

Fig. 8 is a view similar to Fig. 2 showing a modified form of fractionating column in which the distilling tube is formed integral with the insulating jacket;

Fig. 9 illustrates another modified form of fractionating column wherein the insulating jacket is formed separate from the distilling tube; and

Fig. 10 illustrates a typical distillation curve plotted from the results obtained during an analysis of a sample of natural gas.

In Fig. 1, illustrating the entire apparatus in connection with which my improved fractionating column is herein described, numeral 10 refers generally to the fractionating column which may be supplied with liquid or gaseous samples to be analyzed, from suitable containers 11 and 12, respectively. For purposes of general description it will suffice to state at this point that the sample taken into the column is subjected to rectification and fractionation therein, and vaporized and uncondensed constituents of the sample are conducted from the fractionating column through the manifold 13 to suitable containers 14, 14*a* of known volume. As will later appear, fractionated constituents of the sample being analyzed are maintained in vapor phase within the containers, and are quantitatively determined by measuring vapor pressures therein.

As shown most clearly in Fig. 2, my preferred form of fractionating column comprises an elongated distilling tube 16 which may be of any suitable dimensions, typically of about 1 to 6 feet in length and preferably not greatly exceeding about 5 mm. internal diameter. Careful observation and experimentation have indicated that maximum fractionating efficiency is had with a column having an internal diameter of from about 3.4 to 4.0 mm., these limits representing the range in which the capillary action is most suitable for bringing about the most extended and intimate contacting of vapor and refluxed liquid and yet prevent flooding or priming of the column. The distilling tube 16 is surrounded and thermally insulated by an evacuated jacket 17 spaced at 18 from the tube and comprising spaced inner and outer walls 19 and 20 closed at their upper and lower ends. The space 21 between the walls is evacuated as completely as possible to provide an effective thermal insulation throughout substantially the entire length of the distilling tube. The jacket is enlarged at its upper end to provide a reflux or cooling chamber 22 about the upper end of the distilling tube, the cooling chamber being of sufficient size to accommodate a cooling vessel for effecting condensation of the vapors within the distilling tube to provide reflux, as will be more fully described hereinafter. The distilling tube and its surrounding jacket will be preferably formed of pyrex glass.

The lower end of the distilling tube is enlarged so as to form a distilling bulb 23, there being a portion 24, which may or may not be enlarged, directly below the distilling bulb, and which forms what may be termed the displacement bulb. The latter is communicable through tube 24*a* with tubes 25 and 26, leading to the mercury bottle 27, and the liquid and gas sample containers 11 and 12, respectively. Three-way cocks 28 and 29 are provided for controlling the introduction of mercury and the samples to be analyzed, to the base of the fractionating column in a manner which will hereinafter appear. I may state that any suitable means may be employed for introducing the samples to the column, the illustrated apparatus, however, being preferred on account of the convenience of manipulation.

Heat is supplied to the contents of bulbs 23 and 24 by means of heating element 30 comprising a high resistance coil of wire 30*a* wound around a suitable mat 31, for instance a layer of asbestos, placed about the displacement bulb. The current supply wires 30*a* of the heating element lead from the heating element to the conventionally illustrated rheostat R which may be controlled to accurately regulate the temperature to which the liquid portion of the sample in the distilling bulb is heated. I prefer to utilize an external heating element of the character described instead of an internal heating element contained within the displacement or distilling bulb, due to the fact that an internal heating element may readily be short circuited and corroded. An internal heating

element has the additional disadvantage of necessitating substantial enlargement of the distilling bulb and correspondingly greater exposure to the atmosphere, which is undesirable for the most efficient operation of the column.

It is preferred that jacket 17 be silver plated, with the result that the insulation afforded thereby is greatly increased over that due alone to the evacuated space 21. Any suitable heat reflecting material such as silver, platinum, etc., may be utilized for plating the column, silver being preferred. It is desirable that during the course of an analysis the operator be enabled to observe at all times the conditions within the distilling tube, and therefore it is desirable that the insulating jacket be transparent at least to a certain degree. In order to permit visibility of the distilling tube and yet provide additional thermal insulation, there may be deposited a semi-transparent silver film 33 on the inside of the outer wall 20 of the evacuated jacket, the film serving to greatly increase the insulation, and yet being sufficiently thin that visibility of the distilling tube through the jacket is permitted, a flash-light usually being used to observe conditions in the interior of the tube. Due to the thorough thermal insulation of the distilling tube afforded by the plated jacket, highly volatile liquefied or condensed vapors may be retained in the distilling bulb and in the distilling tube without excessive boiling or priming. In case a gas sample is being analyzed, a comparatively large quantity of gas may be passed into or through the column in a given period of time, inasmuch as adequate cooling of the gas stream is effected to condense and retain in the column the desired condensible constituents thereof. Since the silver column is practically adiabatic in operation, the efficiency of fractionation within the column is considerably improved over that possible using a non-silvered column.

In Fig. 5, I have illustrated a method of plating the jacket with a comparatively heavy and opaque silver-plate, yet rendering the entire length of the distilling tube below the reflux cooling chamber visible to the operator. According to this variational method, an opaque silver plate 33*a* may be deposited on the inside of the jacket, leaving narrow unplated strips 34 at opposite sides of the jacket and extending longitudinally of the column, through which the distilling tube may be viewed. Inasmuch as the distilling tube is of small diameter, the unplated strips 34 may be correspondingly narrowed to such an extent that the effectiveness of the insulation will not be appreciably reduced.

By constructing the jacket separate from the distilling tube, additional insulation is provided by the air space 18 between the distilling tube and the inner wall of the jacket. Space 18 is closed off below the distilling bulb by asbestos packing 35, and ring 36 fitted within the lower end of the jacket to support the distilling tube. Space 18 is closed at its upper end by packing within the reflux cooling chamber, thus providing about the distilling tube a dead air chamber which is particularly effective in adding to its thermal insulation. It may be mentioned that should the fractionating column be mounted or constructed in a manner such that the distilling tube is stationarily held at both ends, longitudinal expansion of the tube upon being heated may be taken care of by forming the tube with such thin walls that it may be permitted to bend within space 18 in accordance with the degree of expansion. The column shown in Fig. 2 may also be constructed with the distilling bulb outside the vacuum jacket and separately contained in a suitable thermos bottle as shown in Fig. 9, hereinafter described.

Within the distilling tube is placed a suitable form of packing for the purpose of bringing about extended and intimate surface exposure of the downwardly flowing reflux liquid to the rising vapors. Any suitable type of packing may be used which will aid in bringing about thorough exposure of the reflux liquid to the vapors, but preferably the packing will be of the form shown in Fig. 6, for reasons that will presently appear. One of the advantages of this type of packing is that it brings about the desired intimacy of exposure and contacting between the reflux liquid and vapors, and yet retains only a minimum amount of liquid in the distilling tube at any one time. The result is that sharp fractionation between the constituents of the sample is brought about by preventing lagging and overlapping in the fractionation of the various constituents due to liquid being held up in the column.

The packing 38 comprises a coil of small wire, the normal external diameter of the coil being greater than the internal diameter of the distilling tube, and the exterior surface of the coil being ground down as at 39 to the diameter of the distilling tube and to the point at which the coil will fit snugly therein. Preferably the cross section of the coil wire will be substantially semi-circular, to the end that the tendency for the reflux liquid 40 flowing downward over the packing to collect in the crevices 41 between the wires and the wall of the tube will be minimized in comparison with the amount of liquid that would be held up by wires of circular cross-section, due to the greater depth of the crevices formed by the latter. This is clearly illustrated by comparing Fig. 6 with Fig. 7 wherein the coil 42 is comprised of wire of circular cross section which forms comparatively deep crevices 43 with the wall of the tube which results in a much greater quan-

tity of the reflux liquid being retained by the packing, as illustrated by the liquid films 44. Thus by providing a distilling tube of such small volume that only a small quantity of vapor will be subjected to fractionation at any one time, and by reducing the quantity of reflux liquid present in the column to the least possible amount, consistent with bringing about the proper intimate surface exposure of the liquid to the vapors, conditions are established whereby the vapors may be subjected to extremely close fractionation.

In Fig. 4 I show a form of construction for the lower portion of the fractionating column whereby the distilling tube may be formed integral with the jacket, the upper portion of the column, however, being substantially as shown in Fig. 2. In Fig. 4, the inner wall 19 of the jacket is shown to be joined at 45 to the tube immediately above the bulb 23, there being a bulge 19*a* in the inner jacket wall at the point of juncture with the distilling tube in order to avoid sharp angles between the joined parts which would likely cause the joint to be fractured under comparatively slight shock or strain. The distilling tube is joined to the outer wall 20 of the jacket immediately below the bulb 23 as at 46, the wall of the tube being curved sharply toward the jacket to increase the angularity therebetween and thereby strengthen the joint as mentioned with reference to the upper joint 45.

Condensation of the vapors in the upper portion of the distilling tube within the cooling chamber 22 is accomplished by passing a suitable refrigerant through a cooling vessel 48, of cross sectional shape as illustrated in Fig. 3 and extending around the distilling tube. The cooling vessel will preferably be made of high thermal conductivity metal. A suitable insulating material 49 may be placed between the cooling vessel and the evacuated jacket, and also above the cooling vessel to the top of the jacket. The cooling chamber may be sealed against the admission of moisture by depositing a suitable moisture proof material 50 on top of the asbestos packing 49. The cooling vessel is spaced, for example, as at 51 from the distilling tube, and the space filled with a material of high heat conductivity, for example finely divided or powdered copper. The upper end of the distilling tube projecting above the cooling vessel may be protected against breakage by a sleeve 52 joined to the top of the cooling vessel and extending more or less closely about the tube. In order to insure ample protection for the distilling tube, sleeve 52 will preferably be of metal, and in order to reduce its heat conductivity to a minimum, the sleeve will be provided with closely spaced perforations 53 throughout its length.

Vessel 48 is cooled, for example, by circulating or blowing a suitable refrigerant therethrough, and for this purpose I have shown typically an inlet tube 55 communicating with a thermos bottle 56 containing a refrigerant such as liquid air. The desired amount of the refrigerant is discharged in vessel 48 by applying pressure to the surface of the liquid in the bottle through tube 58. The refrigerant expands in the cooling vessel 44 to secure the desired cooling effect. In order to obviate the necessity for having to introduce the refrigerant to the cooling vessel with undue frequency to compensate for heating of the vessel as the vapors are condensed in the distilling tube, there is placed within the cooling vessel suitable material, such as glass beads 59, having a high specific heat, and which when once cooled to low temperature, will remain near such temperature for a considerable length of time because of their high degree of heat conductivity. The analyst is thereby enabled to admit comparatively larger quantities of refrigerant to the cooling vessel at longer intervals than would otherwise be permissible in the absence of the material, so that a fairly constant reflux temperature is maintained. And of course the quantity of the beads 59 in the vessel may be increased or decreased in accordance with the operating conditions desired.

In Fig. 8 I show a form of fractionating column similar in certain respects to the type shown in Fig. 2, but differing mainly in that the distilling tube, throughout the greater portion of its length, forms the inner wall of the jacket, the tube being spaced from the jacket only within the reflux chamber. In this form the lower section 16*a* of the distilling tube is joined at its lower end below the bulb 23*a* to the wall 20*a* of the jacket as at 60, and is joined at its upper end at 61 to the lower end of the inner wall 19*a* of the jacket surrounding the cooling chamber 22*a*. The upper section 16*b* of the distilling tube extends upward from the joint 61 through the reflux chamber as in the previously described form. Cooling vessel 48*a* may be similar to that shown in Fig. 2, and is immersed in a suitable low freezing point liquid 62 contained within the cooling chamber, the cooling vessel being spaced from the tube as at 51*a* to allow the latter to be in contact with the liquid throughout its length. I may state that the use of a volatile liquid within the cooling chamber, instead of the provision of the insulating packing such as shown in Fig. 2, may be preferable in certain instances. The liquid used in the cooling chamber may conveniently be comprised of, for example, certain of the more volatile low freezing point fractions of casing head gasoline, or other liquids of similar volatility. As in the previously described design, the column will be insulated by a silver plating 64 deposited on the inner surface of the wall 20*a* of the jacket.

In Fig. 9 I show another form of column

of somewhat simpler construction, and illustrating another situation in which an evacuated jacket, separate from the distilling tube, may be used to advantage. This particular form of column, I may state, may be utilized in the analysis of liquids of comparatively less volatility, such as the usual petroleum oils, and for this reason it does not become necessary to insulate the distilling vessel or bulb and the reflux chamber, since the liquids being analyzed would undergo no vaporization at atmospheric temperatures, and the vapors would be readily condensible at atmospheric temperature or at temperatures not greatly below atmospheric.

The apparatus shown in Fig. 9 comprises a distilling tube 65 having on its lower end an enlarged distilling bulb 66, around the lower end of which is wrapped the heating element 91. Fluid to be distilled is introduced to the distilling bulb through tube 92 extending through the wall of the bulb and terminating at a point spaced slightly above the bottom thereof. After the sample has been completely passed into the distilling bulb, mercury may be introduced through tube 91 for the purpose heretofore described of sealing the sample within the column. At the end of the distillation, the mercury may be drawn out of the distilling bulb through tube 92, substantially all the mercury being removable since the tube terminates at the bottom of the bulb. The vapors at the upper end of the tube are subjected to partial condensation to provide the reflux, by a suitable condenser 67 through which a cooling fluid is passed. The vapors are finally liquefied in condenser 68 and the liquid fractions measured in graduate 69. The distilling tube is thermally insulated between the distilling bulb and the reflux condenser by means of a separate evacuated jacket 70 of the general character described with reference to Fig. 2, excepting its difference in shape.

The distilling bulb 66 may be lowered into a wide mouth evacuated thermos jacket or bottle 93 plated either transparently or opaquely with a transparent area through which the distilling bulb is visible, the plating of the vessel 93 being similar to the plating of the distilling tube insulating jacket. The insulating vessel 93 has a dual purpose in that it provides a means for precooling the sample in the distilling bulb and within tube 92 as the sample is passed thereinto, and also in that it provides an effective thermal insulation to the atmosphere for the distilling bulb during the distillation. For purposes of precooling the sample in the distilling bulb prior to starting of the distillation, liquid air or other suitable refrigerant may be passed into the thermos vessel through tube 94. After the distillation is started the refrigerant will of course be removed. It may be stated that the advantage of this design resides in its simplicity and elimination of the use of special clamps for supporting the apparatus, and also in that the thermos vessel serves both for the purpose of providing a precooling bath, and an effective thermal insulation from the atmosphere.

The form of fractionating column shown in Fig. 2 may be considered as preferred mainly for two reasons. In the first place by constructing the distilling tube and jacket separately, replacement of either one of these parts, should one become broken, may be made without the necessity for rebuilding or replacing the entire column, and in this regard it may be stated that the probability of breakage is gradually reduced by the elimination of such joints as shown at 60 and 61 in the integral design of Fig. 8, which may become fractured when subjected to severe strains or shocks. Again by providing a separate, single and continuous distilling tube, the possibility of liquid becoming held up within the column at the joints, with the resultant introduction of error in the results due to lagging, as heretofore explained, is prevented. For instance, in Fig. 8 it will be noted that the joint 61 forms a pocket at 71 within which the reflux liquid would have a tendency to collect, with resultant lowering of reduction in the closeness of fractionation of the sample, as will be readily apparent.

I shall now describe briefly the remainder of the apparatus, and the operation of the system in conducting analysis of liquid and gaseous samples. Manometers 72 and 73 are provided for measuring the pressures within the fractionating column and receiving bottles respectively, three-way cocks 74 and 75 being provided at the junctures of the manometer tubes with the manifold. Receivers 14 and 14*a* communicate with the manifold through tubes 76 and 77, three-way cocks 78 and 79 being provided at the junctures of said tubes with the manifold. A regulating cock 80 is placed in the manifold between cocks 74 and 75, cock 80 being adjustable to controlling the rate of distillation from the fractionating column, as will hereinafter appear. Beyond cock 78 is an exhaust line 81 leading to the vacuum pump 82 by means of which the distilling tube, manifold connections and the receiving vessels may be evacuated before starting the analysis. As will later be explained, the amount of vapor collected in the receivers is calculated from the known capacity of the receiver and from the pressure and temperatures of the vapors therein, and in order that the temperatures in the receivers may remain as nearly constant as possible, to prevent errors or necessitate troublesome corrections in the calculations, the receivers are immersed in liquid contained in tanks 83, 83*a*, the liquid temperature being measured by thermometers 84.

Accurate reading of the temperature of va-

por flowing from the reflux tube to the manifold 13 is indicated by milli-voltmeter V in the circuit of thermocouple 87, a refrigerant in thermos bottle 88 providing a cold junction for the thermocouple.

I shall describe first the procedure followed in the analysis of a sample of natural gasoline. The latter usually being highly volatile at ordinary temperatures, it may be desirable to cool the sample before introduction to the fractionating column, and for this purpose I have shown the sample container 11 to be surrounded by a jacket 86 through which a suitable cooling agent, such as carbon dioxide, may be expanded. Before introducing the sample to the column, the apparatus is evacuated and the reflux chamber cooled by blowing liquid air through the cooling vessel. Stop-cock 80 being then closed, stop-cocks 28 and 29 are turned to admit the desired quantity of liquid to the distilling bulb 23, both cocks being closed when a sample of the desired size has been put into the column. Stop-cock 28 is then turned to admit mercury from bottle 27 to tube 24, and by elevating bottle 27, mercury is caused to rise within the column and into bulb 24, thereby displacing the sample into the distilling bulb 23. The mercury may be considered as standing at a level L—L', although it may be maintained at other levels, and the entire sample trapped within bulb 23, by the mercury seal. The heat supplied to the sample for distillation from the heating element 30 is conducted through the body of mercury in the displacement chamber 24. Since the bulb 23 is thoroughly insulated by the evacuated jacket so as to insure the sample against atmospheric heating by cooling of the reflux to a low temperature, as previously described, the distillation may be started at a temperature below atmospheric. It may be stated at this point that the amount of sample is calculated from the determined amount of vapor distilled during the run and from the amount of residue removed from the column at the end of the distillation.

After introducing the sample to the column, the pressure therein is somewhat below atmospheric, and, in starting the distillation, the column pressure is preferably brought to approximately atmospheric by applying heat to the mercury in the displacement bulb by means of the rheostat controlled heating element. In building up the pressure in the fractionating column to the desired amount, stop-cock 80 is closed at first and the vapors rising within the distilling tube are condensed in the upper part of the distilling tube. If the sample is of such volatility as to vaporize or boil excessively at room temperature or to such an extent that it becomes difficult to avoid flooding the column, the pressure may be allowed to rise somewhat above atmospheric. Again, should the vapor temperature rise above room temperature before the pressure in the column builds up to the amount desired, it may be necessary to start the distillation at a lower pressure, since otherwise the vapor delivered from the column would condense in the manifold connections.

When conditions are satisfactory within the column, distillation is started by cracking the regulating cock 80 to allow the fractionated vapors to pass slowly into receiver 14, cocks 74 and 75 being open and cock 79 closed. Frequent simultaneous readings of the milli-volmeter V, indicating the fractionated vapor temperatures at the point of outlet from the column, and of the manometers 72 and 73, indicating the pressures in the column and receiving bottle, respectively, are recorded, from which data the analyst later constructs a graph plotting vapor temperatures (corrected to a standard pressure) against the amount of vapor distilled.

As the distillation proceeds, it will be noted that the vapor temperature remains almost constant for a relatively long period, assuming of course that the pressure is maintained constant. This indicates that one of the volatile hydrocarbon constituents is being fractionated from the sample with but slight contamination. After most of this particular hydrocarbon has been distilled, the vapor temperature tends to rise, and this rise in temperature should be prevented by adjusting cock 80 to retard the rate of distillation, thereby increasing the reflux ratio to improve the fractionation at the end point of that particular fraction. In controlling the operation of the system, it may be stated that the rate of distillation is controlled by the regulating cock, and that the pressure and degree of fractionation in the column are controlled by the regulating cock, amount of heat input, and cooling of the reflux. The same general procedure is followed as described, during the fraction of each of the individual constituents of the fluid being analyzed.

The fractions are thus distilled off one by one until the volatility of the residue left in the distilling bulb is such as to render further distillation tedious and impractical, due to the frequent evacuation of the receiving bottle necessary to maintain a pressure sufficiently low to prevent condensation of the distillate in the manifold connections and in the receiver. At this point the distillation is stopped, cock 80 being closed and heating and cooling in the fractionating columns discontinued. After the column packing is completely drained, the column is vented to the air and the liquid residue discharged to a suitable measuring container. By calculating the amount of vapor in the receiver and connections, that amount added to the meas-

ured quantity of residue from the column indicates the size of sample originally distilled. It will be understood that at no time during the analysis does the vapor pressure in the container 14 exceed what may be termed the "condensation pressure" of the gas at the temperature in the container, that is, the pressure above which condensation of any of the vapor fractions could take place.

In the analysis of a natural gas sample receiver 14ª is used. The apparatus is first evacuated, preliminary to the introduction of the sample. In order to gain accuracy in the analysis of a gas sample, it is desirable that the sample be of considerable volume, and especially in case the gas is dry. In the testing of samples containing comparatively small amounts of heavier hydrocarbons such as pentane and hexane in natural gas, it may be necessary to handle a fairly large sample in order to retain in the column a sufficient volume of condensate for distillation. The gas sample may be taken from any desired source, for instance, a measured sample of gas is held in the container 12, the latter being of smaller capacity than the receiver 14*a*, and the gas pressure preferably being at or above atmospheric. After purging line 26, having opened cock 28, evacuation of the apparatus is discontinued, cock 75 is turned to connect the receiver with manometer 71, and regulating cock 50 is turned to cut off the fractionating column from the remainder of the apparatus. A mercury seal is then formed in the column immediately below the heating element by permitting mercury to rise from the leveling bottle.

Cock 29 is then cracked to allow gas from the sample vessel 12 to flow into the apparatus through tube 90 containing a suitable drying reagent, the gas thence passing through the mercury seal into the fractionating tube. During the introduction of gas to the column, the pressure therein may build up to atmospheric or greater, and the heavier fractions are condensed as reflux in the upper part of the column, the reflux bath being kept at the lowest temperature possible, in case the gas sample contains highly volatile fractions such as methane. Condensation in the reflux section of the distilling tube is continued throughout the period of feeding gas into the column, and the condensible fractions of the gas are continuously condensed so that the column pressure does not build up to an excessive degree. In case the pressure should tend to build up abnormally, fixed gases may be taken off to the receiver until the entire gas sample is put into the column. After feeding the gas sample to the column, cock 29 is closed and the condensed fractions of the gas contained in the distilling bulb 23 are subjected to fractional distillation according to the previously described procedure followed in the analysis of gasoline.

In case the gas sample contains but a low percentage of condensible vapors, it may be necessary to put through the column a large sample of the gas and to analyze the heavy hydrocarbon liquid condensate. To avoid filling the distilling bulb and fractionating tube with condensate, most of the methane and lighter gases may be allowed to pass from the top of the column while only the comparatively heavy fractions are condensed as reflux. However, it is readily possible to condense the methane and other liquid fractions at the top of the column, and to distill and fractionate them in the same manner as the heavier fractions. It may be added that should a large gas sample be available, and after the column is once primed with reflux, it is possible thereafter to conduct the distillation in a manner such that not only the heavier fractions but also a considerable proportion of the lighter fractions present in the sample may be retained in the column, while the non-condensible portions of the gas are distilled off during the entry of the sample. Calculations for the conversion of vapor in the receiver to liquid volume are based upon the ideal gas laws. The vapor fractions are collected in the receivers at such low pressure below the condensing pressures of the hydrocarbons at normal atmospheric temperatures, that deviations from the ideal gas laws are made negligible.

In the analysis of extremely volatile gases containing relatively large amounts of fractions such as methane which require an extremely low temperature refrigerant, such as liquid air, for their condensation, a refrigerant of this nature may not be available. It is possible, however, to modify the analytical procedure somewhat in order to analyze these gases when having available a refrigerant not capable of condensing the more volatile fractions by themselves. Thus, before entering the gas sample to the fractionating column, the latter may first be primed with a liquid, the vapors from which at the temperature of the particular refrigerant being used in the reflux chamber are capable of condensing. It may be assumed, for instance, that the distillation tube is first primed with a suitable quantity of propane, carbon dioxide being used as a refrigerant in the cooling vessel. Then upon introducing the sample to the column, volatile fractions in the gas are dissolved in the priming liquid. After being dissolved in the propane, the partial pressures of the volatile fractions are lowered to such an extent that the vapors will condense at the temperature in the reflux chamber. The heavier fractions in the gas samples, such as propane, hexane, etc., of course are readily condensible in the reflux tube. In this manner the volatile constituents in this sample may be condensed as the latter is fed into the column; and either dur-

ing the entry of sample, or after the entire sample has been condensed and retained in the column, separation of the successive constituents for delivery to the receivers may take place in the manner heretofore described. When the fractions of higher volatility than propane have been separated, a propane constituent containing that utilized as the priming liquid and also the propane contained in the gas sample, is separated, and having previously noted the amount of propane used as priming liquid, the propane content of the gas may be calculated from a distillation curve as shown in Figure 10.

In Fig. 10 there is shown a typical graph of results plotted from a distillation in which the fractionated compounds range from methane to n-butane, the amount of vapor distilled, as measured in the receiver, being plotted against the temperature at the fractionating column outlet. The irregular curve illustrated in the graph serves not only to identify and determine the amount of the various fractionated compounds, but also to show the sharpness with which these products were fractionated and their state of purity as produced. Thus when substantially all of a particular fraction, for instance methane, has been distilled off, the curve rises almost vertically to the vaporizing temperature of the next heavier compound ethane, in the series, the rise of the curve between the methane and the ethane plateaus indicating sharp fractionation between these compounds. Also the fact that the various plateaus extend substantially horizontally, indicating constant temperature during their respective vaporization, serves to show that these fractions are produced in substantially a pure state.

I claim:

1. Apparatus for precise analytical fractionation comprising an elongated distilling column, means for supplying vapors to the lower portion thereof, means for cooling the upper portion thereof, and an evacuated insulating jacket surrounding the column and having its inner wall spaced therefrom to provide an air space between the column and the jacket.

2. Apparatus as described in claim 1, wherein the space between the insulating jacket and the distilling column is closed at a point near the lower portion of the column and at a point near the upper portion of the column, to provide a relatively stagnant air space between the column and the jacket.

3. Apparatus for precise analytical fractionation comprising an elongated distilling tube, means for supplying vapors to the lower portion thereof, means for cooling the vapors at the upper portion thereof, and heat insulating means surrounding said tube, the tube being of a diameter to secure capillary action on reflux fluid to bring about extended contacting of vapor and reflux fluid therein without flooding the column and not substantially exceeding 5 mm., said column having an open core.

4. Apparatus as described in claim 2, wherein the heat insulating means is an evacuated jacket surrounding said distilling tube.

5. Apparatus as described in claim 2, wherein said heat insulating means is an evacuated jacket surrounding the distilling tube, said jacket having therein means providing a reflecting surface and extending longitudinally of the tube for substantially the length thereof.

6. Apparatus for precise analytical fractionation comprising an elongated distilling tube, means for supplying vapors to the lower portion thereof, means for cooling the vapors at the upper portion thereof, heat insulating means surrounding said tube, the tube being of a diameter to secure capillary action on reflux fluid to bring about extended contacting of vapor and reflex fluid therein without flooding the column, and a helical wire coil within the tube and having its turns in contact with the wall thereof, there being an open core within said column and coil.

7. Apparatus as described in claim 6, wherein the exterior surface of the turns of said coil are formed flat to contact with the wall of the tube.

8. Apparatus for precise analytical fractionation comprising an elongated distilling tube, a distilling bulb formed in the lower portion of said tube, means for applying dry, radiant cooling to an upper portion of said tube and insulating means surrounding said tube, bulb and cooling means.

9. Apparatus for precise analytical distillation comprising an elongated distilling tube, means for supplying vapors to the lower portion thereof, heat insulating means surrounding the tube for substantially the entire length thereof, said insulating means being spaced from the tube at the upper portion thereof to provide a reflux chamber, and means within said reflux chamber for applying dry radiant cooling to the tube to form reflux therein.

10. Apparatus for precise analytical distillation comprising an elongated distilling tube, means for supplying vapors to the lower portion thereof, heat insulating means surrounding the tube for substantially the entire length thereof, said insulating means being spaced from the tube at the upper portion thereof to provide a reflux chamber, a cooling vessel within said chamber embracing the upper portion of the tube and spaced therefrom, and means for supplying a refrigerant fluid in said cooling vessel whereby dry, radiant cooling is applied to the tube to form reflux therein.

11. Apparatus as described in claim 10,

wherein a dry, heat conductive material in finely divided form is interposed between said cooling chamber and said column.

12. Apparatus for precise analytical distillation comprising an elongated distilling tube, means for supplying vapors to the lower portion thereof, an evacuated jacket surrounding the tube for substantially the entire length thereof, said jacket being spaced from the tube at the upper portion thereof to provide a reflux chamber, a cooling vessel having heat-conductive walls within said chamber embracing the tube and spaced therefrom, means for supplying a refrigerant fluid in said cooling vessel, and dry, finely-divided heat conductive material interposed between the inner wall of the cooling vessel and the tube whereby dry radiant cooling is applied to the tube to form reflux therein.

13. Apparatus as described in claim 12, wherein the cooling vessel is partly filled with small particles of high heat capacity, such as glass beads.

14. Apparatus for precise analytical distillation, an elongated distilling tube, means for supplying vapors to the lower portion thereof, and cooling means at the upper portion thereof, said cooling means comprising a vessel having heat-conductive walls embracing said tube and spaced therefrom, means for supplying a cooling fluid to said vessel and dry, finely divided heat conductive material interposed between the cooling vessel and the tube.

15. Apparatus for precise analytical fractionation comprising an elongated distilling tube, a distilling bulb at the lower end of said tube and communicating therewith, said bulb having a downwardly projecting extension for applying heat to said extension, and a heat conductive fluid within said extension to seal a fluid to be distilled in the bulb and convey heat thereto.

16. Apparatus for precise analytical fractionation comprising an elongated distilling tube, a distilling bulb at the lower end of said tube and communicating therewith, said bulb having a downwardly projecting extension, an electrical heating coil surrounding said extension and a heat conductive fluid within said extension to seal a fluid to be distilled in the bulb and convey heat thereto.

17. Apparatus for precise analytical fractionation comprising an elongated distilling tube, a distilling bulb formed at the lower end of said tube and an evacuated jacket surrounding the tube and bulb, said bulb having a portion extending downwardly beyond said jacket, and means for applying heat to said extending portion.

In witness that I claim the foregoing I have hereunto subscribed my name this 31st day of May 1930.

WALTER J. PODBIELNIAK.