FRACTIONAL DISTILLATION: ANALYSIS OF ORGANIC LIQUIDS.

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ABSTRACT.

Apparatus is described for the accurate fractional distillation of organic liquids. The course of the distillation is followed by determining the weight and refractive index of each fraction. From these values the percentage of each constituent in the mixture is calculated.

The analysis of organic liquids by means of careful fractional distillation has proven so useful and accurate that a more extended description of the apparatus and method, than has previously been given[1], seems advisable.

Figure I gives a diagrammatic representation of the distillation apparatus. The 1-liter distilling flask *A* rests in a metal bath which is heated electrically. The temperature is controlled by a variable resistance. A weighed amount of the liquid to be analyzed is put into the flask and one glass bead *B* is added to prevent bumping. During the distillation the bead dances up and down, giving off a stream of bubbles each time it touches the bottom of the flask. The vapour passes into the fractionating column of 8 mm. internal diameter. The jacketed part of this column is 110 cm. long. A distinctive feature is that an even spiral, 4 turns in 15 cm., is pressed into this column. This spiral brings about a more efficient interchange between the descending liquid and the ascending vapour without holding up too much liquid. The rather fragile column is strengthened by being enclosed in a slightly larger tube. The space between is filled with magnesia packing which equalizes the heat generated by a coil wound on the whole length of the tube. The amount of heating is controlled by a variable resistance. About the column is an asbestos heat insulator. Above the heating unit the fraction-

[1] King and Beazley, *Proc. N. S. Inst. Sci.*, 18, 204 (1934).

ating column passes into a cooling device *D*, 12 cm. long. The cooling is regulated by a constant level syphon device (not shown in cut) which may be raised or lowered. Above the cooler the column is bent in a semi-circle and is wrapped with asbestos to avoid irregularities due to drafts. At the top of the bend a glass diaphragm *E* prevents the sweeping over of liquid along the sides of the glass tube. No thermometer is used, since this holds back sufficient liquid to decrease the accuracy of the analysis. The downward portion of the column is cooled by a condenser *F*, 15 cm. long, and passed into a receiver *G*, from which the condensate may be withdrawn at intervals into small weighed containers *H* without destroying the vacuum. The apparatus is evacuated to the desired pressure through *J*, which leads to a manometer and an oil pump. Before reaching the pump the vacuum line includes a tube about 100 cm. long and 5 cm. wide packed with broken sticks of potassium hydroxide in order to protect the pump from any acid fumes. To minimize the effect of any small leakages in the apparatus several empty Winchester bottles are included in the line. The containers *H* are made by cutting down 1.8 cm. test tubes to 6 cm. length. 50 cc. pyrex flasks may be substituted when it is desired to collect larger fractions.

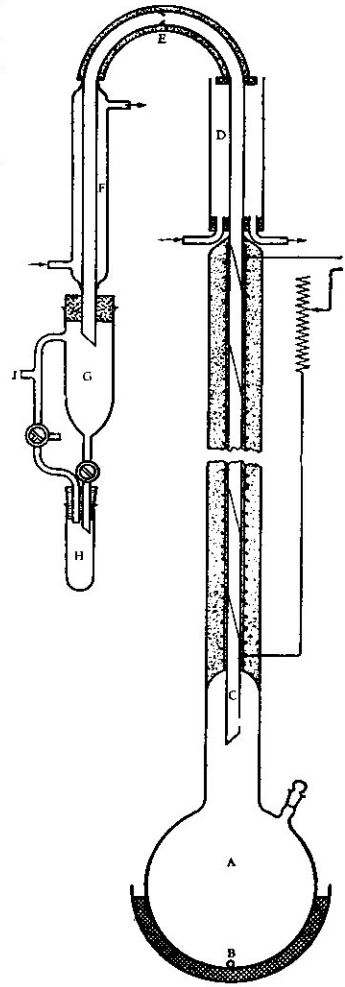

Fig. I.

Three hundred grams of the sample are heated in the distilling flask under reduced pressure until the reflux from the fractioning column drips at just a countable rate. The fractionating column is heated until refluxing takes place in the water-filled cooler. The level of the water is lowered until the ratio of the drops in the reflux to those delivered into the receiver is about 10 to 1. In early experiments with this apparatus the vacuum was held constant automatically, but it was noticed that, whenever the pump started, a flood of vapour passed over, so in later experiments the pressure was brought to the desired point before collecting a sample. During the collection of the sample the pressure remains practically constant. If there is any material change in pressure it is adjusted between the taking of samples, the cooler being filled with water to prevent distillation during the operation.

Each sample is received into a weighed container, weighed, and its refractive index determined by an Abbé refractometer.

This method of analysis does not require complete separation of the constituents. For accuracy it does require that certain samples only be pure, and that the intermediate fractions be mixtures of only two constituents. Let us assume that in a distillation a series of samples have constant refractive indices. Then these samples are composed of a single component A (either a pure substance or a constant boiling mixture). If succeeding samples have rising refractive indices followed by another series with constant refractive indices of component B, it is assumed that the intermediate samples are composed of mixtures of A and B. By making up known samples of various mixtures of A and B and determining their refractive indices, a curve relating refractive index and percentage composition is obtained, and the composition of any unknown mixture may be easily determined. If a linear relation holds, then the weight of one constituent X may be calculated from the formula.

$$x = \frac{ab}{c}$$

where a = wt. of the fraction.
b = n_D of sample − n_D of A.
c = n_D of B − n_D of A.

The summation of the analyses of each fraction gives the composition of the original sample.

Two errors are introduced in this method of analysis. It is impossible to distil all the liquid, so a small part is left as residue. Also a few grams are lost by volatilization during the distillation.

Examples of analyses made by this method are given in a previous paper[1] and in that following[2].

We wish to acknowledge the assistance of Mr. W. B. Beazley in setting up the distillation apparatus.

[2] King and Merriam, *Proc. N. S. Inst. Sci.*, 18, 276, (1935).