

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

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### THE APPLICATION OF THE METHOD OF CONSTANT BOILING-POINT MIXTURES TO THE QUALITATIVE ANALYSIS OF CERTAIN MIXED ORGANIC LIQUIDS.

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THE present paper is an attempt to illustrate the usefulness of distillation methods for qualitative analysis. In certain cases it is also a most reliable means of quantitative analysis, as may be seen by reference to Young's "Fractional Distillation."

In the course of some recent work it was necessary to make analyses of rather complex mixtures of organic liquids—commercial solvents and so forth. A preliminary qualitative analysis was made on the following lines: In organic analysis it is customary to determine the boiling-point of a liquid after purification as a means of identification. But such purification is frequently difficult, or impossible in the case of certain mixtures when the quantities are small. It is often possible, however, to add another liquid with which the unknown liquid will form a mixture of constant boiling-point, and so to identify a small amount of it in a mixture. A list of such mixtures, their boiling-points and compositions, may be found in "Fractional Distillation." Data concerning more recently discovered mixtures may be found in the "Tables Annuelles de Constantes et Données Numériques."

To carry out the analysis a small round bottomed flask is fitted below a Young's "evaporator" still head. One of eight-sections was used, but a five-section head would suffice for most purposes. The contents of the flask are heated with a small naked flame. If the amount of liquid in the flask is to be reduced to a small volume towards the end of the distillation it is advisable to have a thin wisp of cotton wool wound round the bulb of the thermometer. The thread of the mercury should be in the vapour as far as possible. In some of the recently manufactured English made still-heads of this type the length above the top section and below the side tube is too short, and not in accord with the original design.

The following examples of the application of this method may be given :

It was desired to ascertain the composition of a liquid smelling of alcohol. A small quantity of benzene, free from thiophene and redistilled till pure, was added to the mixture and the whole carefully distilled at a rate not exceeding sixty drops a minute, usually at about forty per minute. The thermometer rose rapidly to the neighbourhood of the boiling-point of the binary mixture of methyl alcohol and benzene ( $58.35^{\circ}\text{C.}$ ), and halted at about that point for some time. Thus the presence of methyl alcohol was established. There was another slight halt at about  $64.8^{\circ}\text{C.}$ , a slight turbidity appearing in the column, followed by a rise to the region of

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68.25° C., at which a good quantity came over. The thermometer then rose to about 78.3° C. Thus, there is no doubt that the other constituent of the mixture was ethyl alcohol with a trace of water, for the halts were at the boiling-points of the mixtures, ethyl alcohol, water, benzene, and ethyl alcohol, benzene, and finally at that of ethyl alcohol.

Another sample already contained some benzene, so the points of arrests were obtained without its addition.

The presence and approximate amount (about 2 per cent.) of water in commercial methyl ethyl ketone were also ascertained by distillation. There was a halt at the boiling-point of its binary mixture with water, and the fraction up to the middle point between this and that of the pure liquid was collected and weighed. Since the composition of the mixture was known, the amount of water could be calculated.

Again, the presence of a small amount of methyl ethyl ketone in a mixture of acetone and benzene was shown by distilling off most of the acetone, and adding a little water. A small fraction was collected at about 73° C., the boiling-point of the constant boiling mixture of the ketone and water, and thus its presence was demonstrated. It may be mentioned that the ketone forms another constant boiling mixture, of as yet unknown composition, with benzene. This, however, boils at a temperature so close to the boiling-point of the pure ketone that it could not be used to detect the presence of a small quantity with any degree of certainty. Since the qualitative reactions of acetone and its next higher homologue are so much alike, I am not aware of any other method by which the presence of the trace of the higher ketone could be detected.

Thus, by the addition of water, benzene, or both of them, the presence of many alcohols in mixtures can be ascertained. No doubt other liquids may be added also, as the range of substances investigated increases. An additional advantage of the method is that when only a small quantity—*e.g.*, 1 or 2 c.c.—of liquid is available, a distillation can be made by diluting largely with water, benzene, alcohol, or other suitable liquid. Also where a ternary mixture distils over the percentage of alcohol is usually small, and so in quantitative work errors, due to evaporation and drainage losses, are minimised. In qualitative work the increased volume of the distillate prolongs the arrest in the thermometer readings during distillation at a uniform rate, and so renders the test more delicate. These references illustrate the usefulness of the method; applications in individual cases will easily suggest themselves. Its special utility lies in the study of mixtures of homologous series, in which the ordinary qualitative reactions frequently offer but little help.

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