

## SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY: A COMPUTER PROGRAM

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### INTRODUCTION

A distillation curve is an important physical characteristic of a hydrocarbon mixture. Physical distillation test methods are generally employed to obtain this property.

A number of investigators have also reported the use of gas chromatography to obtain distillation curves<sup>1-6</sup>. Varying accuracies are reported, depending on the system used and the type of distillation simulated. More recently, an improved and automated system to yield boiling point distribution curves equivalent to that obtained from a 100 theoretical plate distillation column, was reported<sup>2,4</sup>. Whereas instrumentation in the gas chromatographic system proper has already reached a high level of sophistication, simulated distillation by gas chromatography still suffers from the necessity of having to make a large number of reiterative calculations before the raw data can be transformed into conventional true boiling point (TBP) curves. To process the data from a single sample, several hours of manual computations are necessary. A computer program is, therefore, an essential first step to reduce the amount of work connected to handling the raw data, especially if large numbers of samples have to be analyzed routinely.

### GAS CHROMATOGRAPH, COMPUTER AND PLOTTER

The gas chromatographic system used in these investigations is the Varian Aerograph Simulated Distillation Apparatus Model 900. The principle and operating procedures have already been described elsewhere<sup>2,4,7</sup>.

The output of the system is in the form of a tape with two columns of data. The numbers in the first column are consecutive from zero up and are called the print numbers. The zero term corresponds to the time of injection. Printout time is once every ten seconds. The four digits in the second column are proportional to the total area on the chromatogram up to that point. Data from this tape have to be key-punched manually to obtain the data cards for the computer program.

The computer used to process the data is an IBM 7094. A Calcomp 570 plotting system, to which a Model 563 Calcomp digital and incremental plotter is attached, is used to present the output of the computer in the form of completely annotated graphs, complete with scale markings, legends, and curve identification symbols.

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## COMPUTER PROGRAM

The program is written in FORTRAN. It consists of a main program, a calibration subprogram, a plotter subprogram, each having approximately 120 FORTRAN statements, and several smaller function subprograms. The plotter subprogram uses existing subroutines to make the Calcomp tape, and the calibration subprogram uses several curve-fitting routines, as different correlations between print number and boiling point are tested. The separate subroutines will be discussed under the appropriate headings.

Fig. 1 shows the simplified flow diagram of the program. From the data furnished, the IBM 7094 prepares a magnetic tape which monitors the output of the plotter. This magnetic tape contains all the necessary instructions on how to plot the

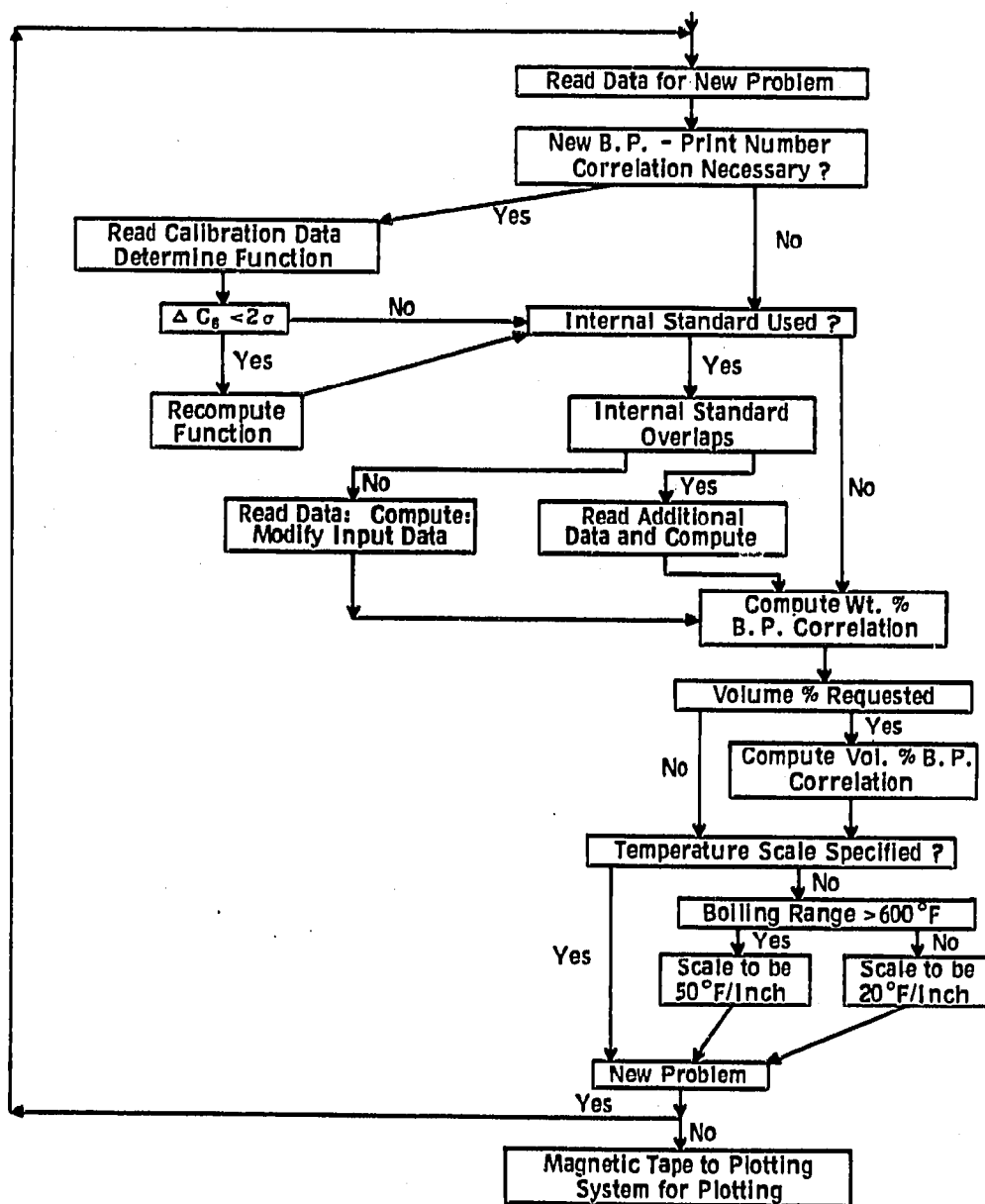


Fig. 1. Simulated distillation computer flow diagram.

calibration curve, the choice of scales, and whether the derived volume percent boiling curve has to be drawn.

#### PRINT NUMBER-BOILING POINT CORRELATION

The relationship between print number and boiling point is obtained by processing a synthetic mixture of *n*-hydrocarbons under defined conditions through the chromatograph and plotting the print number, *R*, of each hydrocarbon against its boiling point,  $\beta$ . Boiling point data were obtained from API Project 44<sup>8</sup>. By connecting these points, a curve is obtained which, on a linear scale for both axes, becomes a straight line for  $C_7$  and higher hydrocarbons.

A least square fit is first carried out on these higher boiling components. If  $C_6$  is within two standard deviations of this computed line, this line is redetermined with  $C_6$  included in the fit. The standard deviation of the correlation is usually a fraction of a print number. The remaining points,  $C_3$ ,  $C_4$ ,  $C_5$ , and, if necessary,  $C_6$ , are correlated by the function:

$$\beta = a_1R + a_2 + a_3/(R + a_4) \quad (1)$$

where the  $a_i$ 's are determined so that the function has the same value and slope as the linear function at  $C_6$  (or  $C_7$ ) and the best approximation is obtained (least squares) for the observed values. A nonlinear regression routine from a program library is used for this. The differences between observed and computed values in this curved region are slightly larger than in the linear range. Several more complicated functions gave better fits but were too difficult to work with in a situation where fits were to be made routinely by machine.

#### INTERNAL STANDARDS AND HIGH BOILING PRODUCTS

For practical reasons, the time corresponding to a boiling point of 1000°F of the product is equated to an arbitrary limit. Most high resolution TBP's do not exceed this point except for the very few instances where the end point would be just slightly above 1000°F. ASTM D 1160 distillations have a wider range and can go deeper into heavier stocks; for a high resolution TBP, however, the limit of 1000°F is more than adequate. In addition, the print number-boiling point correlation will begin to deviate from linearity some time above 1000°F because the retention time of dotetracontane (boiling point ~ 1000°F) is near the end of the temperature programmed section of the heating curve. In the final isothermal portion of the run, the retention time-boiling point relation is, of course, not linear anymore.

For higher boiling products not completely eluted at that time, an internal standard is used to compute the fraction of sample eluted at the 1000°F point. The internal standard used can be either a simple hydrocarbon or a mixture of hydrocarbons. The mathematical treatment of this case has already been given by WORMAN AND GREEN<sup>9</sup>.

We have to distinguish between two cases; *viz.*, the peak(s) from the internal standard either overlap(s) or it (they) do(es) not overlap the chromatogram of the sample proper.

Overlap will be the most general situation. Two runs are now carried out; one of the sample proper and another of the sample to which the internal standard has been added.

No overlap takes place in those cases where the internal standard can be placed in an area of the chromatogram where no components of the sample are present. The procedure is then simplified because only one run has to be carried out. In the usual case the internal standard will elute before the sample proper and a minimum initial boiling point of the sample is necessary because the internal standard used should not be too volatile. For products with an initial boiling point of around 350°F or higher<sup>9</sup>, 5-10% *n*-octane is weighed in as internal standard.

#### WEIGHT PERCENT-VOLUME PERCENT CORRELATIONS

Data obtained by physical distillation are generally of the volume percent boiling point type. ASTM D 86, ASTM D 1160, ASTM D 1078, and other distillation test methods all yield relationships between boiling point and volume percent distillate. Even with high resolution TBP's obtained on efficient distillation columns, it is common practice to correlate the volume distillate to the boiling point. To obtain weight percent data, fractions would have to be taken during the distillation and weighed. This is more complicated than direct volume readings.

There is a description of an instrument to yield weight percent boiling curves by physical distillation<sup>10</sup> but it is little known and not extensively used.

Data obtained from simulated distillations are based on weight percents. To convert to volume percent, the density-boiling curve should be known. This relationship is obviously dependent on the composition of the sample; and short of analyzing small fractions for its density, the exact correlation cannot be determined.

For any product boiling in a certain range, densities will vary with structure. In the case of hydrocarbons, a survey shows that on the average the *n*-hydrocarbons have densities which lie between the extreme densities observed for other hydrocarbons boiling in that particular region. The general relation which is used in this program is derived from the density boiling point correlation of the *n*-hydrocarbons. Prime data have been obtained from API Research Project 44<sup>8</sup>. The following equation has been used

$$d = T^{C_2} 10 \{C_1 + C_3 (\log T)^2\} \quad (2)$$

where  $d$  is the density and  $T$  is the atmospheric boiling point in °R. Equation 2 is obtained by plotting the density-boiling point data on a log-log graph and fitting a quadratic curve through these points. The three constants,  $C_1$ ,  $C_2$ , and  $C_3$ , have been computed by the method of least squares to yield

$$C_1 = -4.46344$$

$$C_2 = 2.66225$$

$$C_3 = -0.40425$$

The largest deviations occur at the very low values of  $T$ . For *n*-propane, the observed deviation is slightly more than 1%. A very much improved correlation is observed for the higher boiling hydrocarbons. Considering the possible error by using

the *n*-hydrocarbon density instead of the true density, the error introduced by this correlation is negligibly small.

#### VOLUME PERCENT BOILING CURVE

To compute the volume percent curve from the weight percent curve, the weight fraction between each two consecutive print numbers is divided by a density obtained from the density-boiling point correlation for a temperature corresponding to the average of the two print numbers. To obtain the volume fraction at any given temperature, the sum of the quotients of the above computation up to the relative print number is divided by the total sum of these quotients for all the print numbers.

#### OUTPUT

The final output from the program consists of the plots and the printed output. The printed output from the IBM 7094 is seldom used because information is more easily gained from the plots.

#### TIME

In a recent test run, three boiling point-retention time calibration curves and five simulated distillations were processed to produce both volume and weight percent curves. The total IBM 7094 computing time was less than one minute; the Calcomp plotting system needed 27 minutes to draw the 13 graphs.

#### PLOTS

Fig. 2 shows the weight percent TBP curve of a heavy gasoline. This graph is completely machine drawn by the plotter. The original graph is 10 in. wide and drawn

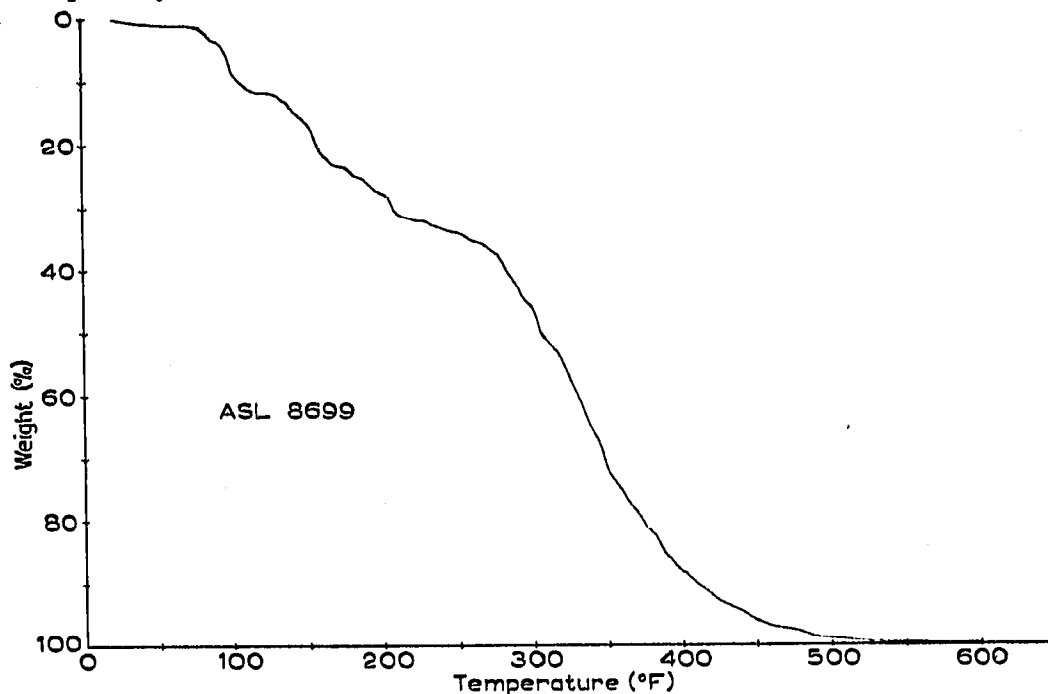


Fig. 2. Weight per cent TBP curve of a heavy gasoline.

on coordinate paper to facilitate interpretation. The crosshatch lines have been screened out in the photographic reduction process.

Details of the FORTRAN code and computer program are available on request.

#### ACKNOWLEDGMENT

Gas chromatography data for Fig. 2 obtained on a Varian Aerograph Simulated Distillation Chromatograph Model 900, were kindly put at our disposal by Varian Aerograph, Walnut Creek.

#### SUMMARY

A computer program to process the data from a simulated distillation gas chromatograph is described. Part of the final output is in the form of weight and volume percent true boiling point (TBP) curves which are traced by a Calcomp 570 plotting system from a magnetic tape prepared on an IBM 7094 computer.

#### REFERENCES

- 1 R. C. BARRAS AND J. F. BOYLE, *Oil Gas J.*, 70, No. 31 (1962) 167.
  - 2 R. DICK, C. H. HARTMANN AND K. P. DIMICK, *Conf. Anal. Chem. Appl. Spectroscopy*, 16th, Pittsburgh, March, 1965, Abstr. No. 157.
  - 3 F. T. EGGERSTEN, S. GROENNINGS AND J. J. HOLST, *Anal. Chem.*, 32 (1960) 904.
  - 4 L. E. GREEN, L. J. SCHMAUCH AND J. C. WORMAN, *Anal. Chem.*, 36 (1964) 1513.
  - 5 H. J. MAIER, C. J. BOSSART AND H. HELLER, *Instr. Control Systems*, 8 (1964) 75.
  - 6 J. A. PETROCELLI, T. J. PUZNIAK AND R. O. CLARK, *Anal. Chem.*, 36 (1964) 1008.
  - 7 *Aerograph Research Notes*, Walnut Creek, Calif., Spring 1965.
  - 8 F. D. ROSSINI, *API Project 44, Selected Values of Physical Constants and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, April, 1956.
  - 9 J. C. WORMAN AND L. E. GREEN, *Anal. Chem.*, 37 (1965) 1621.
  - 10 I. M. ALEKSANDROVA AND D. D. ZYKOV, *Khim. Tekhnol. Topliv. i Masel*, 9, No. 12 (1964) 39.
- J. Chromatog.*, 28 (1967) 219-224