

Determination of the Boiling-Point Distribution by Simulated Distillation from *n*-Pentane through *n*-Tetratetracontane in 70 to 80 Seconds

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Abstract

This work presents the carrying out of boiling-point distributions by simulated distillation with direct-column heating rather than oven-column heating. Column-heating rates of 300°C/min are obtained yielding retention times of 73 s for *n*-tetratetracontane. The calibration curves of the retention time versus the boiling point, in the range of *n*-pentane to *n*-tetratetracontane, are identical to those obtained by slower oven-heating rates. The boiling-point distribution of the reference gas oil is compared with that obtained with column oven heating at rates of 15 to 40°C/min. The results show boiling-point distribution values nearly the same (1–2°F) as those obtained with oven column heating from the initial boiling point to 80% distilled off. Slightly higher differences are obtained (3–4°F) for the 80% distillation to final boiling-point interval. Nonetheless, allowed consensus differences are never exceeded. Precision of the boiling-point distributions (expressed as standard deviations) are 0.1–0.3% for the data obtained in the direct column-heating mode.

Introduction

One of the most widely used characterizations of complex hydrocarbon mixtures is the determination of the boiling-point distribution. The measurement of this distribution is carried out by guidelines established in methods of the American Society of Testing Materials (ASTM). There are two types of methods used, glassware distillation and simulated distillation (SIM DIST), which is carried out by gas chromatographic (GC) techniques. The method discussed in this work is ASTM D2887 (1). The procedure is used for characterizing petroleum products and distillates that have initial boiling points (IBP) of 30°C and final boiling points (FBP) of 538°C, covering the range of the elution of *n*-pentane (*n*-C5) through *n*-tetratetracontane (*n*-C44).

The most widely used columns for this analysis are wide-bore columns (0.53-mm i.d.), which have a film thickness ranging from 0.8 to 3.0 µm of dimethylpolysiloxanes. These columns are favored over the traditional packed columns because of their relatively low bleed, comparatively high packed column flow rates,

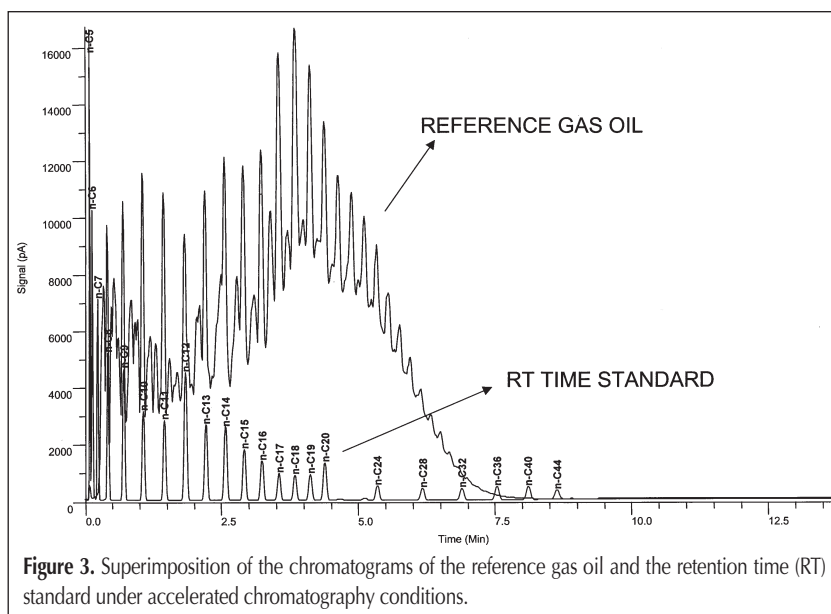
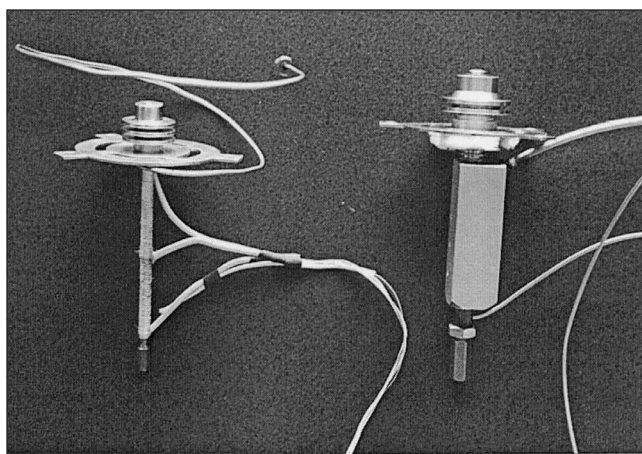
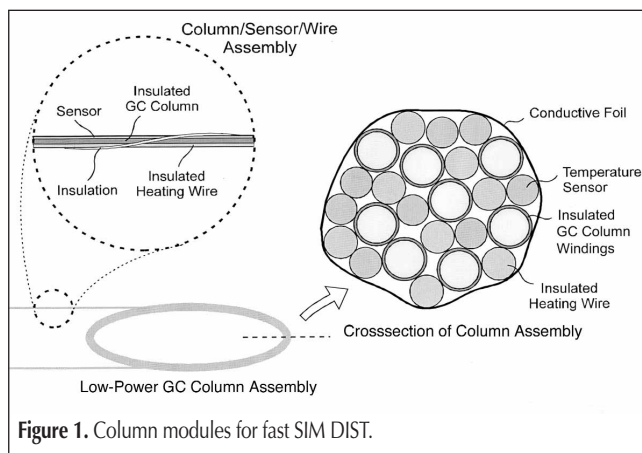
and reduced analysis time. All of these columns can be used without sample dilution. Another characteristic of the methodology is that a highly resolving column is not required. Thus, short columns of 5 to 10 m are used. With flow rates ranging from 10 to 20 mL/min, the time required for the elution of *n*-C5 through *n*-C44 is usually 14 to 20 min. Constant flow throughout the analysis is required by the method during the temperature-programmed analysis. Method D2887 recommends the use of either an isothermally heated inlet or a programmed temperature vaporizer (PTV) inlet without a sample split point. The latter has the advantage that the sample is delivered to the column or the inlet as a liquid plug rather than a vaporized cloud emerging from a heated needle. The temperature-programmable inlets usually have a glass liner, permitting the injection of the sample either on-column or near-column.

In the last four years several efforts have been made to reduce the time for this analysis. Giarroco (2) carried out a D2887 analysis in 7 min by using a fast oven program at 40°C/min and a column with characteristics of 1-m × 0.1-mm i.d. and 0.5-µm film thickness of dimethylpolysiloxane. The analysis included flow programming from 1 to 3 mL/min at 90 mL/min while using a split/splitless inlet.

Lubkowitz (3), using a 3-m × 0.32-mm-i.d., 0.5-µm film thickness dimethylpolysiloxane column with a temperature-programmable inlet and programming the inlet and the column oven at 40°C/min, eluted *n*-C44 in 7 min using a rather large constant flow of 30 mL/min. Thus, the limiting factor in reducing the analysis time lies in the rather large mass of the oven, which cannot be heated faster than 40°C/min. Additional equipment is required such as using oven filler material to reduce the volume and special oven-heating elements operated at 240 V ac (4). In addition, because the column must be programmed from 40°C to up to temperatures of 350°C, a waiting period ranging from 8 to 12 min must also be added to the analysis time to allow the column to cool back to the initial oven temperature for the next analysis time.

Fast chromatography is a technique in which short columns with a narrow diameter, high flows, and narrow sample introduction bands are used in order to carry out chromatography in sec-

onds. One variation of this technique for quantitative analysis has been reported that uses direct column heating (5). Chromatograms showing the elution of *n*-octane (*n*-C8) through *n*-eicosane (*n*-C20) were obtained in 40 s. Commercial instrumentation has been available with direct column heating (6). This



instrumentation has been applied to the analysis of the C1–C15 fraction in crude oils (7).

This study explores the feasibility and the results obtained from programming the column directly to obtain boiling-point distributions. A study of the boiling-point distribution of hydrocarbons under direct column heating has not been previously reported. By heating the column (4-m \times 0.32-mm i.d., 0.5- μ m film thickness) directly using the modules described by Mustacich (8,9), the elution of the hydrocarbons *n*-C5 and *n*-C44 have been carried out in 72 s. The technique was also used to analyze a reference material (reference gas oil), and the precision obtained has shown relative standard deviations of 0.1% to 0.3% for boiling points ranging from 238°F to 888°F. The values obtained for the boiling point distribution are in good agreement with the consensus values reported in the ASTM D-2887–99 method (1).

Experimental

Retention time standards

In order to calibrate the retention time as a function of boiling points, solutions were prepared containing the following hydrocarbons: *n*-C5, *n*-hexane (*n*-C6), *n*-heptane (*n*-C7), *n*-C8, *n*-nonane (*n*-C9), *n*-decane (*n*-C10), *n*-undecane (*n*-C11), *n*-dodecane (*n*-C12), *n*-tridecane (*n*-C13), *n*-tetradecane (*n*-C14), *n*-pentadecane (*n*-C15), *n*-hexadecane (*n*-C16), *n*-heptadecane (*n*-C17), *n*-octadecane (*n*-C18), *n*-nonadecane (*n*-C19), *n*-C20, *n*-tetracosane (*n*-C24), *n*-octacosane (*n*-C28), *n*-dotriacontane (*n*-C32), *n*-hexatriacontane (*n*-C36), *n*-tetracontane (*n*-C40), and *n*-C44. These hydrocarbons were obtained from Aldrich Chemical Co. (Milwaukee, WI). All hydrocarbons used were subject to purity analysis by differential thermal analysis (10) and chromatographic analysis. These steps were necessary because the purity of the hydrocarbons as labeled by the manufacturer is inadequate to calculate the final purity of the mixture. The purity determination must be stressed because the assessment of equal response of the chromatographic system must rely on the individual hydro-

carbon weights corrected for the purity of the hydrocarbons. A primary mixture of these hydrocarbons was made containing *n*-C5 through *n*-C20 in equal weights (approximately 1 g), and the remaining hydrocarbons were added at approximately 0.3 g. This mixture was then diluted gravimetrically in carbon disulfide (Spectrum Scientific, Gardena, CA) in order to achieve a total hydrocarbon weight fraction of 2%. The reference gas oil (labeled as Reference Gas Oil, No.1 Lot 2, supplied by Phillips Chemical Co., Bartlesville, OK) was used to compare the boiling-point distribution measured with the consensus values obtained for this gas oil, which are published in ASTM Method D2887-99. A solution of 200 mg/10 mL of CS₂ was used for all injections.

Column modules

The column used had a 4-m \times 0.32-mm i.d. and a 0.5- μ m film thickness of dimethylpolysiloxane

(J&W Scientific, Sacramento, CA). This column was used for fast analysis. The column was assembled into a module as shown in Figure 1, which was obtained from RVM Scientific (Santa Barbara,

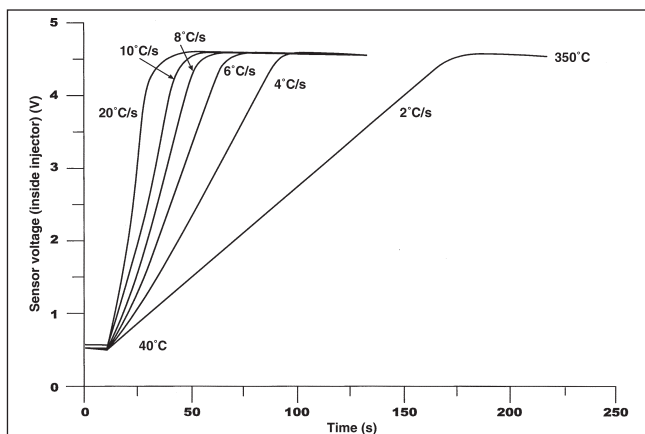


Figure 4. Fast programmable inlet temperatures versus time.

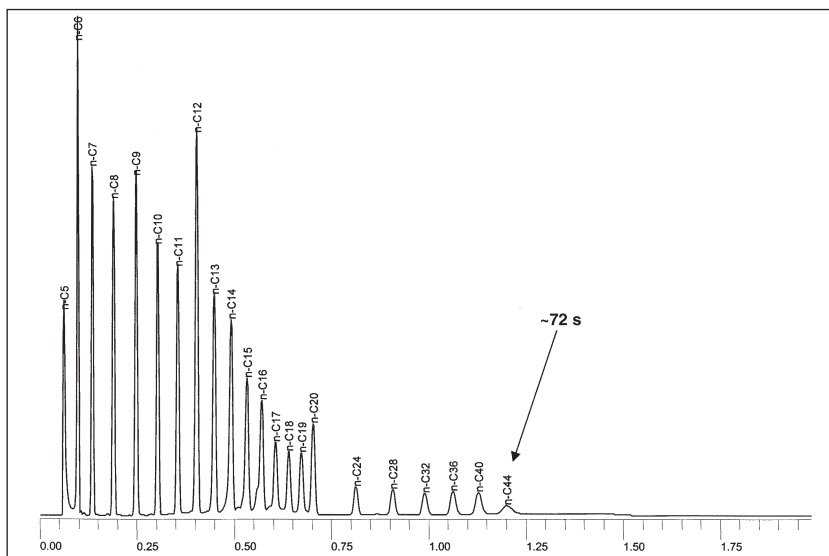


Figure 5. A 72-s retention time calibration chromatogram. The column ramp was 300°C/min.

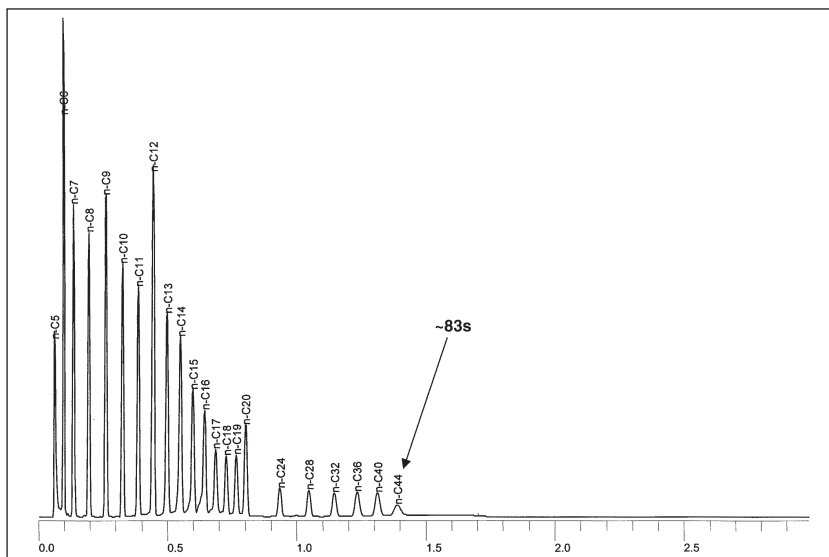


Figure 6. An 83-s retention time calibration chromatogram. The column ramp was 250°C/min.

CA). The column was interwoven with the heating wire and the platinum sensor wire, and then the entire package was covered with aluminum foil as previously described (8,9). The column was mounted in a metal screen to which a 24-V dc fan was mounted in order to cool the column. Two additional 1/16-inch tubes were used to heat the two parallel legs of the finished column module, which terminate in 1/16-inch miniunions (Valco, Houston, TX). These miniunions were used to connect the column module to the inlet port and the flame ionization detector (FID). The entire column module was then suspended in the GC oven.

GC

The GC used was an Agilent (Wilmington, DE) 6890. It was provided with an electronic pneumatic control module for maintaining constant flow during the analysis (30 mL/min). An FID was the detector used. It was operated at 360°C. The flow rates of the auxiliary gases were 40 mL/min for hydrogen and 450 mL/min for air. No make up gas was used. The door of the GC was removed, and a magnet was used in order to close the switch thus deceiving the electronics of the GC. The platinum oven sensor was removed and replaced with a precision 110- Ω resistor. Under these conditions the GC achieved the condition of ready without a door and without turning on the GC oven. The GC was also provided with an Agilent 7683 autosampler with a 10- μ L syringe. The injection volume was kept constant at 0.2 μ L.

Temperature-programmable inlets

The inlet was similar to a conventional temperature-programmable inlet (Separation Systems, Gulf Breeze, FL) Model SS-46001. The difference was in the fact that the thickness of the stem body was reduced in order to facilitate rapid heating. The stem body was directly wrapped with the heating wire instead of using a cartridge heater that heats an aluminum block. A comparison of the two inlets is shown in Figure 2. The conventional inlet was used for the 7-min SIM DIST as well as for the wide-bore SIM DIST comparisons. A dimethylpolysiloxane column with dimensions of 4-m \times 0.53-mm -i.d. and 3.0- μ m film thickness (J&W Scientific) was programmed from 40°C to 350°C at 35°C/min at a flow rate of 30 mL/min. This column was used for all accelerated SIM DIST experiments. A 10-m \times 0.53-mm-i.d., 3.0- μ m film thickness column (J&W Scientific) was used for the conventional D-2887 analysis by programming the oven at 15°C/min.

Electronic control module

This module was built by RVM Scientific (Santa Barbara, CA). It had four constant temperature zones that are required to heat the column to the inlet transfer line and the column exit transfer line to the detector entrance port. These were kept constant at 360°C. In addition, the controller had a microprocessor that allowed for the setting of

the initial temperature, final temperature, and heating ramp of the column as well as that of the inlet. When all zones were equilibrated at the set temperatures, a signal was sent to the GC so that the injection was carried out. The controller also turned the

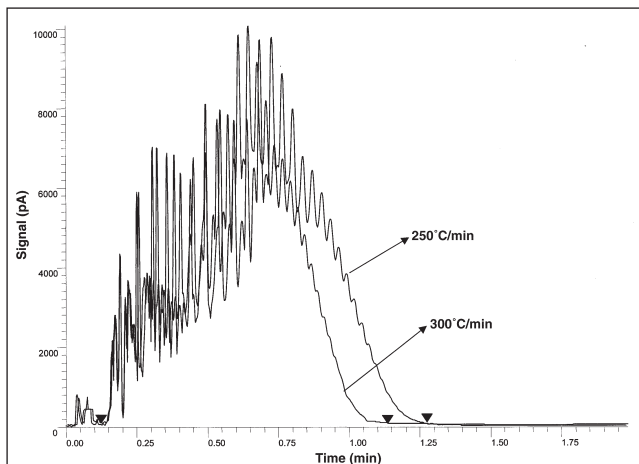


Figure 7. Comparison of the reference gas oil chromatogram obtained with column ramps of 250°C/min and 300°C/min.

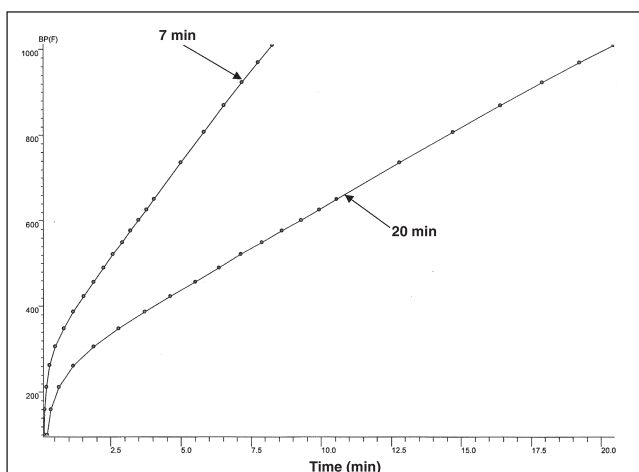


Figure 8. Retention time versus boiling point calibration for the accelerated (7 min) and conventional (20 min) SIM DIST.

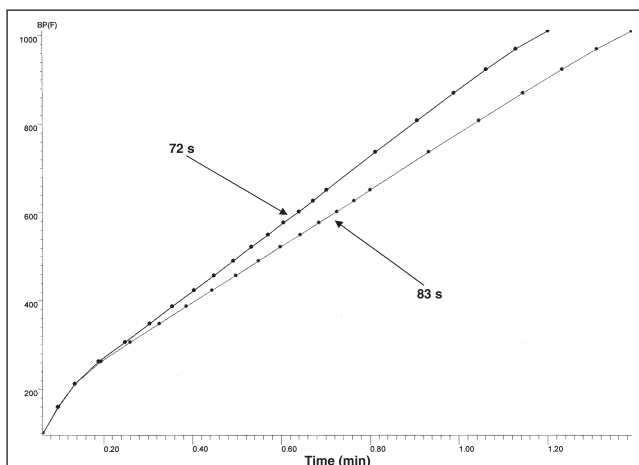


Figure 9. Retention time versus boiling point calibration for the fast modes of 72 and 83 s, respectively.

fan at the end of the run and cooled the column from 350°C to 40°C in approximately 20 s. Two heating ramps (300°C/min and 250°C/min) were used during this study. The typical ramp used was 40°C for 2 s, and then either ramp was executed to 350°C with a hold time of 2 s. Thus, the total chromatography time was carried out in 72 and 83 s, respectively.

Data-acquisition system

Data-acquisition software, Chemstation Software Version 8.04 (Agilent), was used to acquire the data at 20 Hz. The software was used to control the autosampler variables as well as the detector operational variables. All remaining functions of the GC were not used.

SIM DIST calculations

All boiling-point distributions were carried out using SimDis Expert software (Separation Systems). Baselines were acquired with the injection of the solvent and used to subtract it from every sample chromatogram. The calibration of the time axis was carried out by injecting the solution of the retention time standard. The algorithm for the detection of the start of elution and end of sample elution were enabled as described in the ASTM D2887 appendix.

Results and Discussion

Figure 3 shows both the chromatogram of the reference gas oil and the chromatogram of the retention time standard obtained under the conditions of accelerated SIM DIST. This experiment was carried out with the conventional PTV and programming the oven at 40°C/min. The sample eluted completely at approximately 7.6 min. In addition, approximately 10 min was required to cool the oven in order to begin the next injection. This analysis represented the limit in time of what can be obtained with heating the oven. We have termed this type of SIM DIST as accelerated SIM DIST in order to differentiate it from true fast chromatography.

The inlet for the fast SIM DIST experiments was evaluated in order to determine the heating ramps that can be achieved. Figure 4 shows the results of measuring the sensor voltage as a function of time. The sensor voltage was proportional to the temperature, thus the curves represent the different heating rates that can be achieved with this inlet. It can be observed that the inlet can be programmed linearly at fast rates ranging from 2 to 20°C/s. A ramp of 6°C/s was chosen for all sample injections (300°C/min).

Figure 5 shows the chromatogram of the retention time standard obtained by programming the column at a rate of 300°C/min. One can observe that good peak shape was obtained and impurities of *n*-C15 and *n*-C16 were partially resolved. The retention time of *n*-C44 was approximately 72 s. We slowed the heating ramp to 250°C/min and obtained a chromatogram of the retention time standard, which is shown in Figure 6. There was very little difference in the two chromatograms of Figures 5 and 6 except that the retention times of the hydrocarbon standard in the latter were slower than in the chromatogram of the 300°C/min ramp. The time of elution of *n*-C44 was then 84 s. A similar effect can be observed in Figure 7, which shows the chro-

matogram of the reference gas oil obtained with both ramps of 300°C/min and 250°C/min, respectively. The slower heating ramp (250°C/min) caused a complete sample elution at 1.2 min, and the faster ramp yielded complete sample elution at 1.10 min.

In order to calculate the boiling-point distribution for the reference gas oil, it was necessary to evaluate the calibration curves of the retention time versus boiling point. These curves are plotted in Figures 8 and 9. Figure 8 shows the calibration curves for the conventional SIM DIST (20 min) as well as the accelerated 7-min SIM DIST. Figure 9 shows the calibration curves for the fast SIM DIST (column heating rates of 250°C/min and 300°C/min, respectively). It is important to note that the curves were nearly identical in shape for all modes in SIM DIST (i.e., the curves were composed of two segments). The first segment was a convex curve, which usually covers the retention time of *n*-C5 through *n*-C8. This segment had a relative steep curve that can be linearized by lowering the initial column temperature to subambient temperatures. This steep curve was a result of the fact that these rapidly eluting components were partially partitioned in the liquid phase. The second segment was a straight line. The importance that all types of SIM DIST have a similar type of calibration function lies in the fact that the algorithm for the determination of the temperature of each slice depends on the shape of these curves. This algorithm was based on the time extrapolation of the retention time of the slice in the time interval of two successively eluting hydrocarbons. Once the time of the slice was known, its equivalent temperature was determined by linear extrapolation.

Thus, no further modification of the algorithm was required for the fast SIM DIST obtained in seconds.

A further confirmation of the equivalence of the retention time versus boiling point function lies in the comparison of the calculated boiling points for the reference gas oil. The reference gas oil has a well-characterized boiling-point distribution. The comparison of the boiling-point distributions obtained for the four modes of SIM DIST discussed in this work are shown in Table I. Table I also shows the consensus values obtained for the reference material from 19 participating laboratories whose statistically analyzed values are shown in the last column of Table I. In addition, the last column also shows the allowed deviations (Δ) from the consensus values that were derived from the statistical analysis of the results of the participating laboratories in the round robin. Table I shows the individual Δ for each type of SIM DIST carried out, which is the difference between the boiling-point distribution obtained for each SIM DIST mode and the consensus values. The consensus values reported did not cover all of the distillation points that can be observed in Table I. For example, the 45%, 55%, and 65% off did not have corresponding consensus values. However, several of these points were reported in order to obtain a thorough comparison of the results of the boiling-point distribution of all four modes. It can be observed that the results for the fast SIM DIST did not exceed the allowed Δ values. The results of the 83-s SIM DIST for the 80%, 90%, and 95% off, respectively, were slightly higher than for the remaining SIM DIST modes. We attribute this to the difficulty in avoiding col

Table I. Comparison of the Boiling-Point Distribution of the Reference Gas Oil Carried Out Under Different SIM DIST Modes and Heating Rates*

%Off	Wide bore		Accelerated		Fast (83 s)		Fast (72 s)		Consensus	
	BP [†] (°F)	Δ	BP (°F)	Δ	BP (°F)	Δ	BP (°F)	Δ	BP (°F)	Δ Allowed
IBP [‡]	237.3	2.7	236.2	3.8	239.9	0.1	239.3	0.7	240.0	13.7
5	304.4	0.4	303.6	0.4	304.6	0.6	304.2	0.2	304.0	6.8
10	348.1	0.1	347.1	0.9	348.8	0.8	350.2	2.2	348.0	7.4
15	394.6	1.6	393.7	0.7	395.1	2.1	396.1	3.1	393.0	8.1
20	437.1	2.1	436.2	1.2	437.2	2.2	438.0	3.0	435.0	8.7
25	471.7		470.4		471.3		471.8			
30	501.1	2.1	499.5	0.5	500.3	1.3	499.6	0.6	499.0	8.4
35	528.5		526.3		528.2		526.6			
40	554.5	2.5	552.0	0.0	554.5	2.5	552.4	0.4	552.0	7.7
45	577.4		575.8		577.6		575.2			
50	595.6	1.6	592.7	1.3	595.4	1.4	592.7	1.3	594.0	7.7
55	611.3		608.0		611.8		609.9			
60	629.6	0.6	626.9	2.1	630.5	1.5	628.7	0.3	629.0	7.7
65	649.8		646.5		650.6		648.8			
70	669.5	1.5	666.3	1.7	670.7	2.7	669.3	1.3	668.0	7.7
75	691.0	1.0	688.0	2.0	692.8	2.8	691.6	1.6	690.0	
80	713.1	1.1	710.3	1.7	715.7	3.7	714.7	2.7	712.0	7.7
85	737.1	1.1	735.2	0.8	740.2	4.2	739.5	3.5	736.0	
90	764.8	0.8	762.8	1.2	768.7	4.7	767.9	3.9	764.0	7.7
95	803.6	0.6	802.2	0.8	807.7	4.7	806.7	3.7	803.0	9.0
FBP [§]	885.2	2.8	887.7	0.3	888.9	0.9	887.9	0.1	888.0	21.2

* $n = 5$.

[†] BP, boiling point.

[‡] IBP = 0.5% off.

[§] FBP = 99.5% off.

spots in the transfer lines. However, these values were still one-half better than the allowable Δ .

Table II compares the precision obtained in all four modes of SIM DIST. It is evident that the standard deviations of the temperature for the fast SIM DIST modes were slightly larger than those obtained for the accelerated and conventional SIM DIST, respectively. The probable reason for this difference lies in the fact that the repetitive heating of the column should be considered as a pulse column-heating chromatography experiment, in which a heat pulse of a certain duration (70–80 s) is applied every 140 s (considering that it takes 20 s to cool the column). It is more dif-

ficult to control the heat transfer of this pulse because there are several thermal variables such as insulation, heat losses, and heat transfers that are difficult to reproduce from one heat pulse to the next. Nonetheless, the precision obtained is within the limits of what is determined in the ASTM method (1).

Figure 10 shows the time comparison of the different operations required in order to obtain a SIM DIST result in the accelerated and the 72-s modes of operation, respectively. It is interesting to note that the autosampler required approximately 41 s in order to deliver an injection. This time was approximately half of the chromatography time (column ramp time). Rather large time decreases were obtained by directly cooling the column. The fact that a total analysis can be made in 143 s renders a 100-position autosampler to be refilled in approximately 4 h, which is a considerably shorter time than the 10 h we normally expect to clear up a complete sample tray.

Conclusion

This work has shown the applicability of fast chromatographic techniques for the determination of boiling-point distributions. It is possible to obtain 70–80-s SIM DIST boiling-point distributions yielding similar results to those obtained with either conventional column oven heating or accelerated oven techniques.

There are several handicaps at present required to facilitate the use of this technique. The column modules used in this work were approximately 5 cm in diameter. Most GCs are designed with

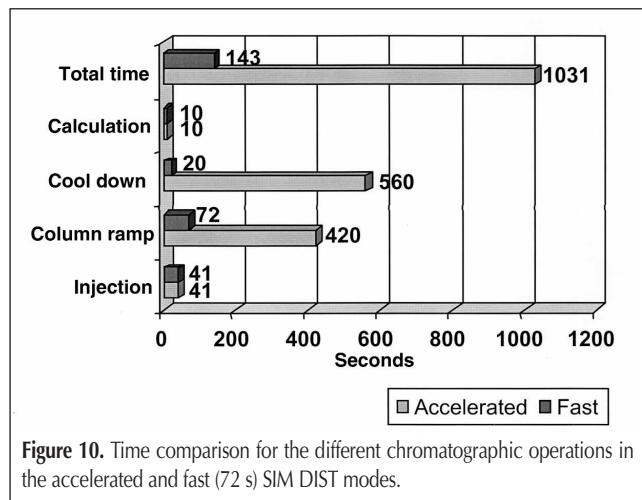


Figure 10. Time comparison for the different chromatographic operations in the accelerated and fast (72 s) SIM DIST modes.

%Off	Wide bore		Accelerated		Fast (83 s)		Fast (72 s)	
	Avg BP [†] (°F)	%SD [‡]	Avg BP (°F)	%SD	Avg BP (°F)	%SD	Avg BP (°F)	%SD
IBP [§]	237.8	0.4	237.5	0.2	239.9	0.3	239.3	0.1
5	304.2	0.1	304.7	0.1	304.6	0.2	304.2	0.1
10	347.5	0.1	348.7	0.1	348.8	0.2	350.2	0.7
15	394.4	0.1	395.3	0.1	395.1	0.4	396.1	0.6
20	437.0	0.1	438.1	0.1	437.2	0.4	438.0	0.6
25	471.6	0.1	472.6	0.1	471.3	0.4	471.8	0.5
30	500.9	0.1	501.9	0.1	500.3	0.5	499.6	0.4
35	528.4	0.1	529.3	0.1	528.2	0.4	526.6	0.4
40	553.9	0.1	555.2	0.1	554.5	0.3	552.4	0.3
45	577.2	0.1	578.0	0.1	577.6	0.2	575.2	0.4
50	594.2	0.1	596.0	0.1	595.4	0.3	592.7	0.5
55	610.8	0.1	611.8	0.1	611.8	0.3	609.9	0.3
60	628.4	0.1	630.2	0.1	630.5	0.2	628.7	0.3
65	649.6	0.1	650.5	0.1	650.6	0.3	648.8	0.3
70	669.0	0.1	670.2	0.1	670.7	0.3	669.3	0.3
75	690.6	0.1	691.7	0.1	692.8	0.2	691.6	0.3
80	712.9	0.1	713.9	0.1	715.7	0.2	714.7	0.2
85	736.8	0.1	737.9	0.1	740.2	0.1	739.5	0.1
90	765.1	0.1	765.8	0.1	768.7	0.1	767.9	0.1
95	804.4	0.2	804.7	0.1	807.7	0.1	806.7	0.1
FBP**	886.0	0.4	888.4	0.3	888.9	0.1	887.9	0.3

* $n = 5$.
[†] Avg BP, average boiling point.
[‡] SD, standard deviation.
[§] IBP = 0.5% off.
** FBP = 99.5% off.

inlet to detector distances for cages of 17 to 20 cm. This places a large burden on adapting transfer lines that must meticulously be heated in order to avoid cold spots, which is at present one of the weaknesses of this technique.

Also, column modules are not yet readily available. Although small footprint GCs are already available for gas analysis, this is not the case for this application requiring an FID and a fast liquid sample injection for samples having wide boiling-point ranges.

Additional studies are required in order to evaluate the life of the column modules.

Acknowledgments

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