OPTIMISED FOR SPEED AND ACCURACY: ASTM D2887 OPTION B

Simulated distillation determines the boiling point distribution of a petroleum product by gas chromatography rather than physical distillation. It is a well-established method for several matrices including crude and finished products.

One of the main advantages of simulated distillation is speed; the ability to automate the process; and to provide a quick finished report. Laboratory throughput requirements have increased in a very high demand industry for fast results.

Study Objectives

In keeping with this need and the desire to use conventional instruments and columns to achieve greater efficiency and higher throughput, ASTM has supported development of an accelerated method as part b in D2887 (1).

An advantage to this solution is that detailed separation is not required as it is in a detailed hydrocarbon analysis which allows for fast chromatography.

The data presented here demonstrates pairing the accelerated chromatography with a gas chromatograph designed to provide maximum throughput and accuracy.

Instrumentation

The Clarus® 690 Gas Chromatograph (GC) with wide range flame ionization detector (FID) was used in these experiments. TotalChrom® chromatography data system (CDS) was used for instrument control and data collection (Shelton, CT). Dragon® simulated distillation software from Envantage® (Cleveland, OH/ Houston,TX) was used to calculate and report the boiling point distribution from the TotalChrom result file.

Developing a fast method with a conventional GC

A GC method has been developed with a focus on speed for both rapid heating to enhance chromatography (GC) runtime, and rapid cooling to minimise delay for the analysis of the next sample. In this development, ASTM D2887 requirements have been maintained.

The Clarus 690 GC has the ability for rapid heating while maintaining stringent retention time repeatability. An additional criterion of the new oven design was ensuring temperature uniformity to eliminate hot or cool zones. This aids in retention time stability which is critical for accuracy in this solution. Oven temperature uniformity eliminates what is known in the industry as "Christmas tree" effects on chromatographic peaks. Narrow Gaussian peak shapes are achieved even for the most volatile compounds.

In addition to fast GC runtimes sample throughput is optimised by fast temperature oven ramp profiles including the unique ability to rapidly cool and re-establish the oven initial temperature. The GC oven cools from 350 to 40 degrees in less than 1.5 minutes. During this time, the syringe is prepared for the next injection further enhancing sample throughput.

Experiment

In addition to an optimised GC, hydrogen was used as the carrier gas in this experiment. According to Van Deemter equation (2), hydrogen is the best carrier gas to use when fast column carrier flows are desired. Hydrogen has the highest efficiency at these flow rates; therefore, optimizing resolution while attaining faster chromatography.

A narrow bore capillary column was investigated to determine if this column could provide faster results while improving the rigorous accuracy required by this solution. The phase and dimensions of this test column was an Elite 1ms: 14 m x 0.18 mm x 0.18 µm which will be compared to an Elite 1: 10 m x 0.53 mm x 1.5 µm (PerkinElmer). They will be referred to as the narrow bore and wider bore columns, respectively. The wide bore, 0.53 mm id, is one of the columns suggested in the method.

Table 1: GC oven conditions used on the narrow bore column

Steps	Ramp (°C/min)	Temp (°C)	Hold (min)
Initial		40	1
1	140	70	0
2	105	115	0
3	85	175	0
4	55	300	0
5	35	340	0.9

Boiling point time assignments were made using ASTM D2887-12 Calibration Standard containing 20 n-paraffins (Restek). The concentration of this stock solution is 1% of the paraffins in carbon disulfide (CS2) that was diluted 1 to 10.

Three reference fluids were included in this study to qualify the boiling point assignments. Reference Gas Oil (RGO) #2 (Spectrum Quality Solutions) and two Canadian Proficiency (cross check or CC) Samples D282 and D283 (InnoTech Alberta, Edmonton, AB).

Reference samples were not diluted and a 0.1 µL injection was made. Blanks were made without a solvent injection for subtraction.

Discussion and results

Table 1 displays the oven profile used on the 14 m x 0.18 mm x 0.18 µm. Figure 1a and 1b are the chromatograms collected on the narrow bore, 0.18 mm id (run time 6.2 min) and megabore, 0.53 mm id (run time 6.6 min) columns, respectively. The peak shapes and separations are acceptable in both chromatograms; however, the peak efficiency is much improved on the narrow bore column. Because of enhanced resolution, the run time of 6.2 minutes on the narrow bore column can be improved.

The results of skewness, resolution and retention time repeatability for the calibration standard are presented in Table 2. For the narrow bore column, precision was accomplished over eight consecutive runs. For the wide bore column, the calibration standard for precision was acquired at five-point intervals during a nine-hour batch of samples. Even though both are acceptable, the narrow bore column demonstrate improvement in efficiency.

The peak resolution of both narrow and wide bore columns is acceptable (meet the criteria in ASTM D2887 of greater than 3 for C16 and C18 resolution); however, the peak shape (skewness) of the narrow bore column is much improved. ASTM D 2887 recognises that peak skewness results in a distortion of the peak apex, therefore distorting the retention time, and hence creating an error in the boiling point calibration. The sharper and narrower the peaks, the more accurate the retention time calibration. Skewness in section B is listed as between 0.8 and 1.3 section 18.3

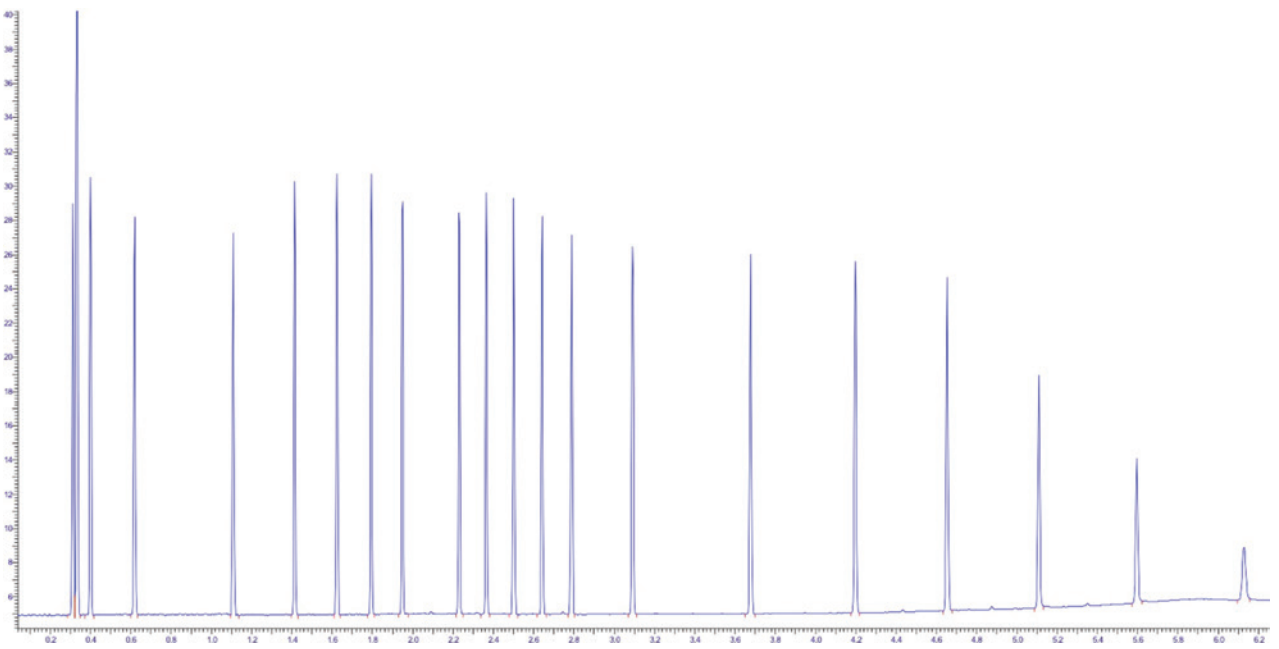

Figure 1a. Chromatography from the narrow bore column

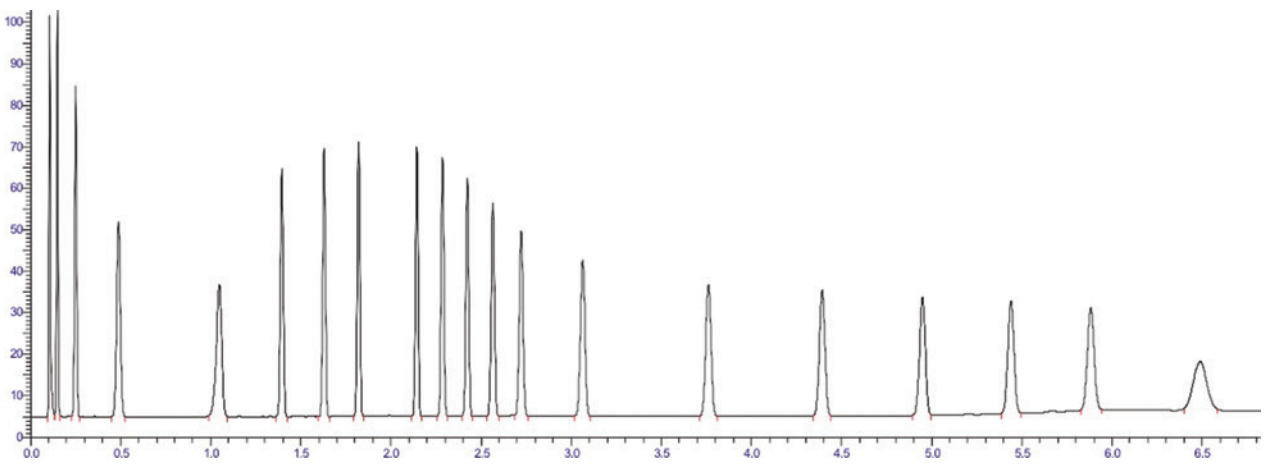

Figure 1b. Chromatography from the wide bore column

Table 2. Results for skewness, resolution and retention time repeatability (precision %RSD) from the narrow and wide bore columns

n-Paraffin	Narrow bore			Wide Bore		
	Skewness	Resolution	RT Prec (n=8)	Skewness	Resolution	RT Prec
C5	1.025	n/a	0.056	1.010	n/a	0.084
C6	1.009	4.7	0.061	1.004	3.0	0.083
C7	1.020	19.6	0.060	1.008	5.5	0.079
C8	0.998	29.1	0.063	1.001	8.0	0.081
C9	0.990	20.2	0.065	0.862	11.9	0.084
C10	0.984	15.5	0.064	0.984	8.1	0.086
C11	0.986	13.2	0.061	0.980	8.0	0.074
C12	0.987	12.0	0.058	0.993	6.9	0.068
C14	0.981	21.9	0.052	0.972	11.9	0.068
C15	0.971	10.3	0.049	0.988	5.2	0.056
C16	0.970	10.0	0.049	0.991	4.6	0.064
C17	0.969	10.0	0.053	0.995	4.4	0.066
C18	0.968	10.0	0.068	0.983	4.3	0.066
C20	0.958	19.6	0.069	0.989	8.0	0.074
C24	0.951	35.9	0.063	0.961	13.7	0.073
C28	0.956	30.4	0.059	0.981	11.3	0.073
C32	0.927	26.0	0.052	0.979	9.5	0.078
C36	0.929	24.6	0.044	0.999	7.9	0.052
C40	0.909	21.3	0.024	0.992	6.7	0.073
C44	0.893	21.6	0.023	1.007	5.8	0.085

Table 3. Results of RGO #2 from both columns. Temperatures are listed in Celsius

% off	RGO #2 Certificate of Analysis		Narrow Bore column results		Wide Bore Column Results	
	BP Temp	Valid Window	Actual Temp	Variance	Actual Temp	Variance
IBP	106.111	7.000	104.640	-1.471	104.326	-1.785
10	195.556	4.444	195.390	-0.166	194.853	-0.703
20	233.333	5.000	233.930	0.597	233.104	-0.229
30	266.667	4.778	267.390	0.723	265.903	-0.764
40	297.778	4.278	297.890	0.112	295.029	-2.749
50	321.111	4.278	322.100	0.989	320.457	-0.654
60	341.667	4.278	343.060	1.393	341.600	-0.067
70	358.333	4.278	359.270	0.937	357.853	-0.480
80	377.778	4.278	378.530	0.752	377.186	-0.592
90	406.111	4.278	407.140	1.029	406.136	0.025
95	431.111	5.000	432.420	1.309	431.519	0.408
FBP	496.111	11.778	499.740	3.629	501.809	5.698

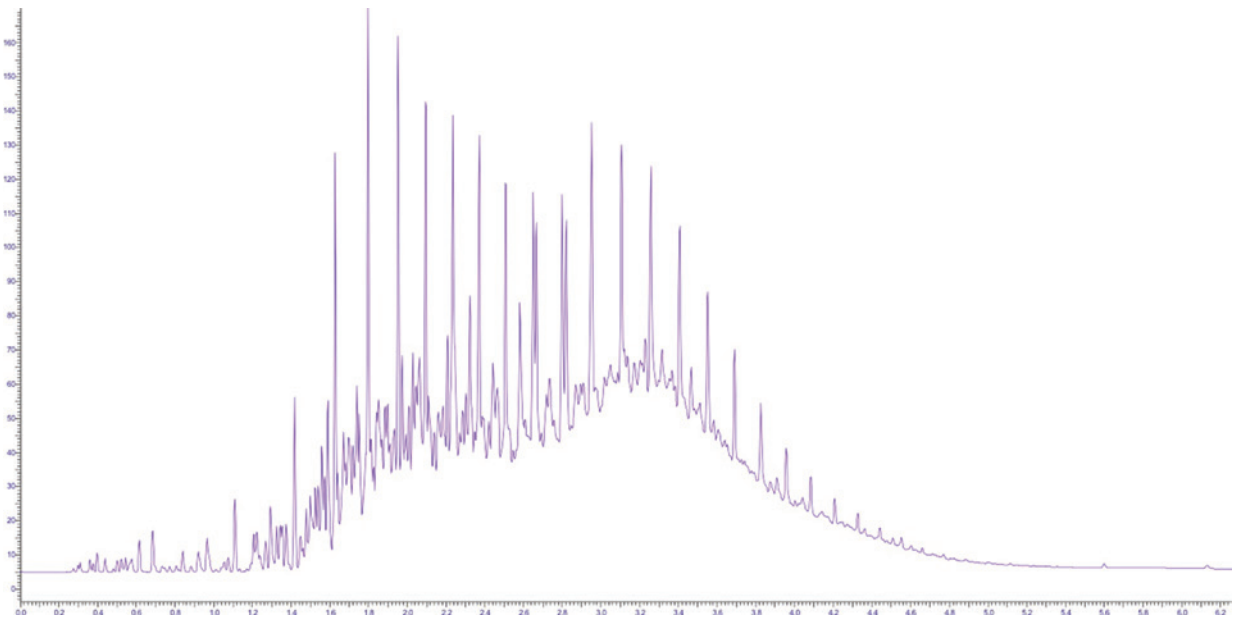

Figure 2: Chromatogram of RGO #2 on the narrow bore column without baseline subtraction

Figure 2 represents a chromatogram from RGO #2 on the narrow bore column. This chromatogram is presented without baseline subtraction to demonstrate raw data on this thin film column.

Table 3 demonstrates excellent performance for boiling point accuracy using the RGO #2 for both columns with all boiling points passing criteria. The narrow bore column did out perform on initial boiling point (IBP) and final boiling point (FBP). Five injections of the RGO #2 was performed over a three-day period using the same retention time calibration file with very similar results to those listed in Table 2. One example is provided.

Table 4 tabulates the results from two Canadian cross check samples analysed in this research. The average temperature and the standard deviation from the proficiency data are presented.

The temperatures from the PerkinElmer Clarus 690 GC using the narrow bore column are documented. The % deviation from the average temperature from the CC samples compared to the temperatures from the narrow bore column are recorded. The temperature is in degrees Celsius.

Table 4: Results from proficiency (cross check) program compared to the narrow bore

% OFF	Proficiency (CC) Report Sample D282			
	CC Avg Temp (n=14)	CC Std Dev	Narrow Bore Column Temp	%Dev from CC Avg
IBP	110.44	3.552	110.43	-0.01
5	177.83	1.474	176.91	-0.52
10	200.54	1.412	200.40	-0.07
20	229.61	1.682	229.97	0.16
30	252.44	2.772	253.59	0.46
40	271.13	2.981	271.16	0.01
50	288.90	3.018	289.48	0.20
60	305.02	3.066	304.97	-0.02
70	322.93	3.437	323.45	0.16
80	344.83	3.600	345.34	0.15
90	364.06	3.969	363.98	-0.02
95	385.19	4.892	384.97	-0.06
FBP	437.22	4.881	438.01	0.18
% OFF	Proficiency (CC) Report Sample D283			
	CC Avg Temp (n=13)	CC Std Dev	Narrow Bore Column Temp	%Dev from CC Avg
IBP	97.78	2.641	96.91	-0.89
5	140.18	2.218	139.99	-0.13
10	154.03	2.158	150.64	-2.20
20	171.05	3.466	169.18	-1.09
30	183.35	2.431	180.89	-1.34
40	196.65	0.840	195.95	-0.36
50	209.68	2.231	208.04	-0.78
60	220.05	1.970	218.62	-0.65
70	234.42	2.153	233.26	-0.50
80	247.01	1.078	246.72	-0.12
90	261.07	1.042	261.09	0.01
95	270.37	0.776	270.29	-0.03
FBP	287.40	1.935	286.79	-0.21

Future work

Additional work has been performed on enhancing analysis time on the narrow bore column. A solution with an analysis time under 5.5 minutes and an inject to inject time of under 7.5 minutes using conventional columns and a conventional GC has been achieved. This research continues with validation on these new parameters including reference standards and cross check samples. Also, Interlaboratory Study (ILS) sample results will be submitted.

Conclusion

The narrow bore column demonstrates excellent performance for skewness, retention time precision and resolution. These results outperform the requirements in ASTM D2887 with multiple injections over a period of months. The results of the three reference standards is further testament to the accuracy of this fast method.

The ability for fast cooldown and fast heating rates enhances sample throughput for the need of this industry for quick results.

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