Application Note

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High Temperature Simulated Distillation Performance Using the Agilent 8890 Gas Chromatograph

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Abstract

An Agilent 8890 gas chromatograph was configured to run high temperature simulated distillation according to ASTM method D6352. Calibration was demonstrated from *n*-C_{12} to *n*-C_{102} followed by performance verified using the ASTM 5010 Reference Material. A high degree of system precision was observed by performing 10 sequential analyses of the 5010 Reference Material. Additionally, the ability to calibrate the system up to *n*-C_{102} provided improved performance for the determination of the final boiling point. Using a vacuum gas oil sample the 8890 system easily met the D6352 repeatability requirements for duplicate analysis.

Introduction

High temperature simulated distillation (SIMDIS) is a gas chromatographic technique used to characterize the boiling point distributions of mid- and heavy petroleum fractions. ASTM method D6352 is scoped for fractions with initial boiling points of 174 °C to final boiling points of 700 °C[1]. Obtaining good, precise results with this method can pose some operational challenges. First, the oven temperature must consistently program from 50 °C to 400 °C at a relatively fast rate of 35 °C/minute. At the same time, the column flow must be held at a constant 18 mL/minute during the entire run. Maintaining these conditions from run to run is crucial to obtaining the high retention time precision needed for this method. Another challenge is eliminating inlet discrimination while transferring hydrocarbons from n-C_{12} to n-C_{90} to the analytical column. Ideally, separating and detecting hydrocarbons closer to n-C_{100} improves yield temperature calculations across of the full boiling range. This Application Note describes the performance of the 8890 GC when using ASTM method D6352.

Instrument configuration and operating conditions

An 8890 GC was configured according to ASTM D6352, as shown in Table 1. A metal capillary column must be used to withstand the oven's upper operating temperature of 400 °C. The operating conditions shown in Table 2 conform to those published in the ASTM method.

Standard and sample preparation

A boiling point calibration standard was prepared by dissolving approximately 63 mg of Polywax 655 (p/n 5188-5317), 63 mg of Agilent Boiling Point Mixture #2 (p/n 5080-8768), and 3 mg of n-tetratetracontane (n-C_{44}) into 10 mL of carbon disulfide. This solution contains hydrocarbons from n-C_{12} to >n-C_{90}. The addition of the small quantity of n-C_{44} made peak assignments easier.

Table 1. 8890 GC configured for ASTM D6352.

Parameter	Value
Syringe	5 µL (p/n G4513-80206)
Inlet	Cool-on-column (COC)
Capillary column	DB-HT-SIMDIS, 5 m × 0.53 mm, 0.1 µm (p/n 145-1009)
Detector	Flame ionization (FID)

Table 2. Operating conditions for ASTM D6352.

COC Inlet	
Mode	Oven track
Initial hold time	0.1 minutes
Final temperature	400 °C
Column	
Flow rate	Helium, 18 mL/min constant flow
Initial temperature	50 °C
Initial hold time	0.1 minutes
Ramp rate	10 °C /min
Final temperature	400 °C
FID	
Temperature	450 °C
Hydrogen flow	32 mL/min
Air flow	400 mL/min
Make-up flow	N_2 at 24 mL/min

A performance test sample was prepared by dissolving 63 mg of Reference Material 5010 in 5 mL of carbon disulfide. Duplicate vacuum gas oil samples were prepared for analysis by dissolving approximately 63 mg in 5 mL of carbon disulfide. The performance test sample was run 10 times to evaluate the precision of the system performance. Each vacuum gas oil duplicate was analyzed to determine reproducibility using the 8890 GC.

Results and discussion

Figure 1 shows the D6352 calibration run. The ASTM method requires calibration up to 700 °C, as shown with the detection of *n*-C_{90}. However, boiling range results for heavy petroleum fractions can be improved with the resolution and detection of even higher carbon-numbered paraffins. The inset chromatogram in Figure 1 shows the calibration performance for normal paraffins over C_{90} achieved with the 8890 GC.

Prior to running samples, system performance was verified using the 5010 Reference Material. Ten injections of the 5010 Reference were made, and each result was compared to the consensus values published in the ASTM method. Figure 2 shows an overlay for 10 injections of the 5010 Reference Material; Figure 3 shows a typical Engineering Result Report generated by Agilent SimDis software. The 8890 GC delivered excellent retention time precision for the 10 reference runs.

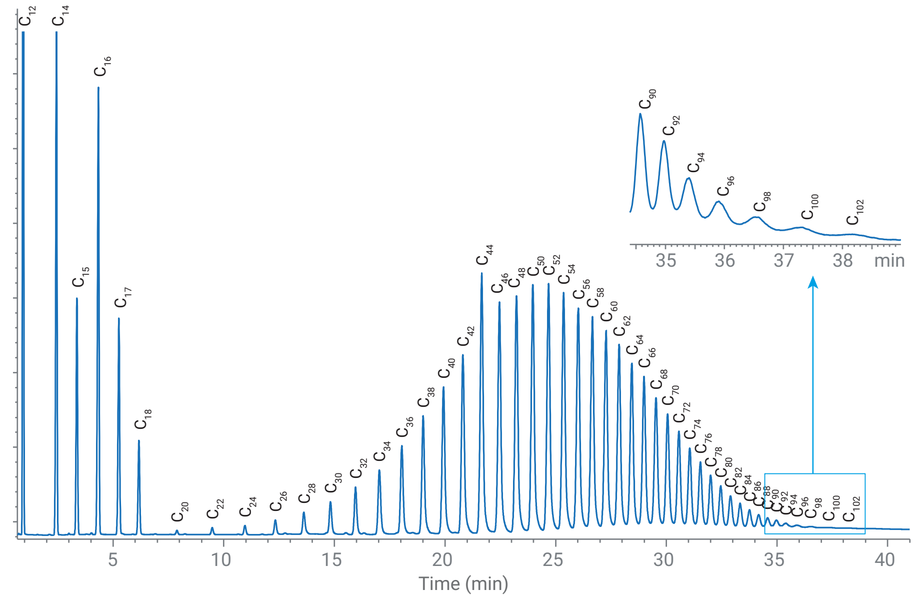

Figure 1. D6352 calibration showing elution of *n*-C_{12} to *n*-C_{102} paraffins. The inset shows details of paraffin detection greater than *n*-C_{90}.

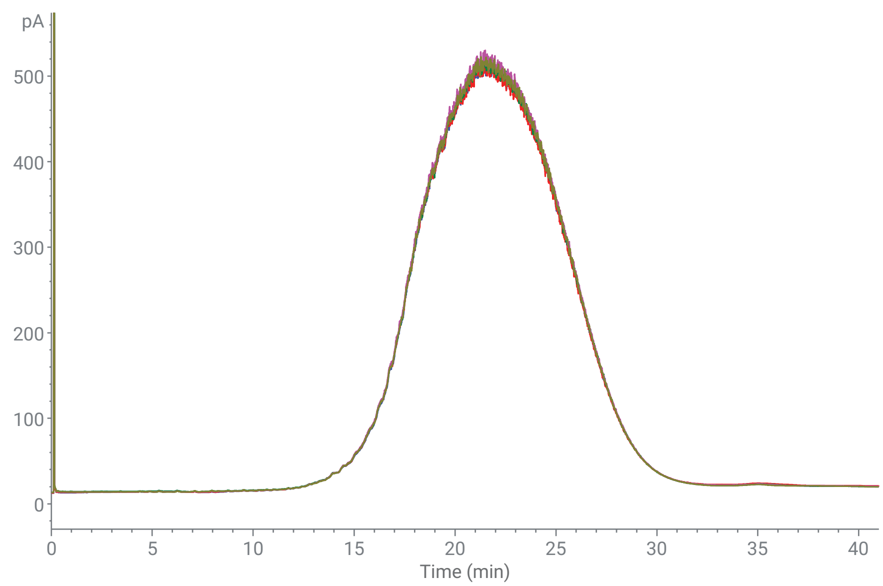

Figure 2. Overlay of 10 analyses for the 5010 Reference Material.

Table 3 shows the results for the 5010 Reference Material analyses, including precision and compliance with the ASTM requirements. The 10 runs showed extremely high precision of the temperatures calculated at each percentage yield (% Off); a direct result of the excellent retention time precision shown in Figure 1. Additionally, the temperature for each percentage yield was well matched to the ASTM consensus value, and well within the allowed temperature difference. Another impressive result was in the calculated temperature for the final boiling point cut (FBP). While the allowed difference is 18 °C, the average difference was only 4 °C for the data shown in Table 3. This result can be attributed to the ability of the 8890 to separate and detect normal paraffins with carbon numbers greater than C_{100}.

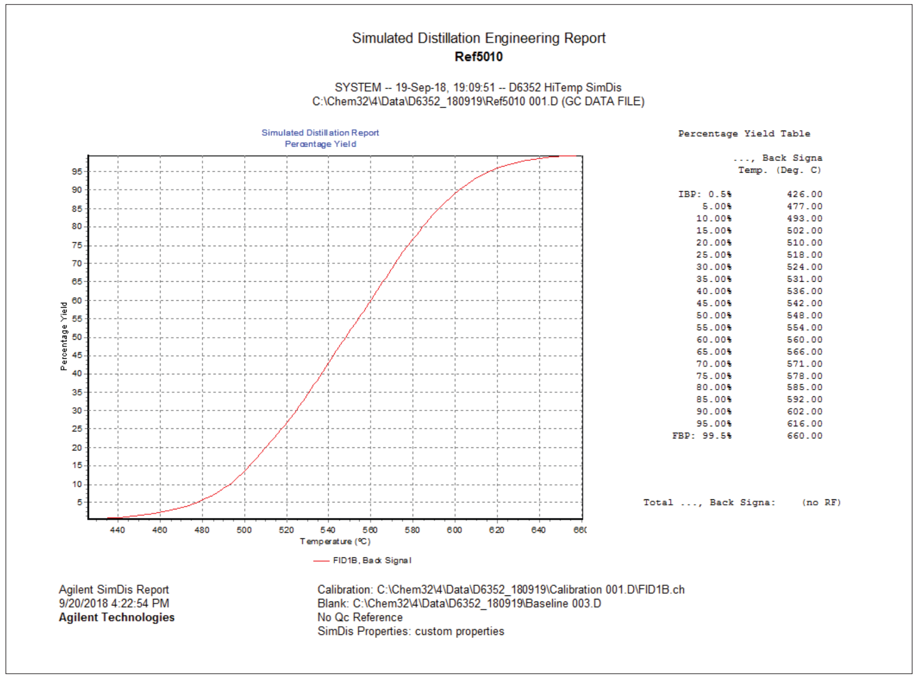

Figure 3. Engineering report for the analysis of the 5010 Reference Material. The report displays the boiling point yield curve, and lists the temperatures calculated for each yield percentage.

Table 3. Comparison of 5010 Reference Material to ASTM specifications.

	ASTM Values		Observed*		
% Off	Temp (°C)	Allowed diff. (°C)	Avg. temp. (°C)	Std. dev. (°C)	Avg. diff. (°C)
IBP (0.5)	428	9	427	1.22	1
5	477	3	478	0.45	1
10	493	3	493	0.00	0
15	502	3	503	0.45	1
20	510	3	510	0.55	0
25	518	4	518	0.00	0
30	524	4	525	0.00	1
35	531	4	531	0.00	0
40	537	4	537	0.45	0
45	543	4	542	0.00	1
50	548	5	548	0.00	0
55	554	4	554	0.00	0
60	560	4	560	0.00	0
65	566	4	566	0.00	0
70	572	4	571	0.55	1
75	578	5	578	0.00	0
80	585	4	585	0.00	0
85	593	4	592	0.45	1
90	602	4	602	0.45	0
95	616	4	616	0.45	0
FBP (99.5)	655	18	659	2.74	4

* Ten runs of Reference Material 5010

Figure 4 shows simulated distillation chromatograms for the vacuum gas oil duplicates. As with the 5010 Reference Material, the vacuum gas oil chromatograms show a high degree of retention time precision. Table 4 shows the repeatability (r) performance for this sample. At the cut point levels where ASTM has designated a temperature repeatability specification, the sample results were well within the required values.

Conclusions

The 8890 gas chromatography system was shown to be an excellent instrument for running high temperature simulated distillation analysis such as ASTM D6352. The exceptional performance for this method results from a high level of retention time precision combined with the easy separation and detection of normal paraffins with carbon numbers greater than C_{90}. The system was successfully verified using the 5010 Reference Material, and duplicate sample runs of vacuum gas oil met the ASTM repeatability specification.

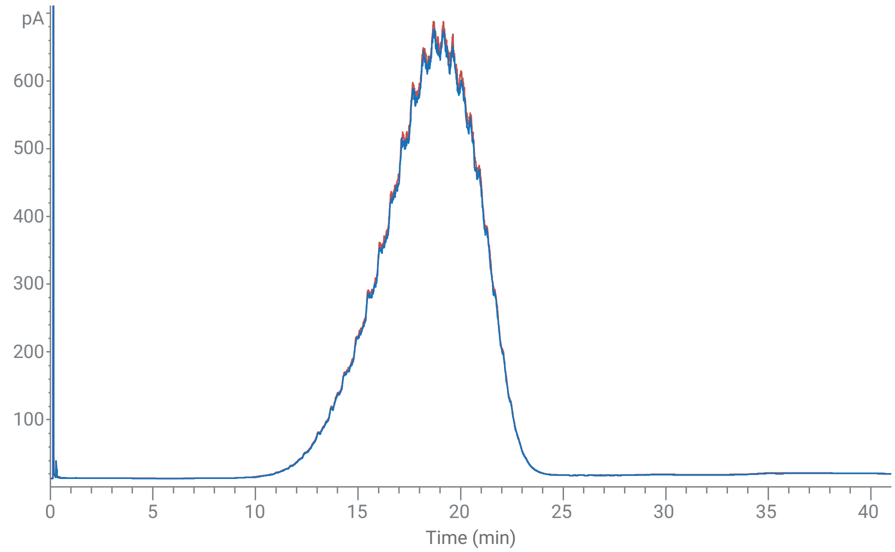

Figure 4. Overlay of duplicate analyses of a vacuum gas oil samples. Table 4 shows the results from the Agilent SimDis software engineering report along with the repeatability (r) performance compared to the ASTM D6523 repeatability limits.

Table 4. Results and precision for vacuum gas oil.

% Off	Temperature		Repeatability	
	Run 1	Run 2	Calc. r	ASTM r
IBP (0.5)	404	406	2	8.1
5	441	441	0	2.3
10	455	455	0	2.8
15	465	465	0	
20	473	473	0	2.7
25	480	480	0	
30	485	485	0	2.4
35	490	490	0	
40	495	495	0	2.6
45	499	499	0	
50	503	503	0	2.7
55	507	507	0	
60	511	511	0	2.4
65	515	515	0	
70	520	519	1	3
75	524	524	0	
80	528	528	0	3
85	533	533	0	
90	539	539	0	3.4
95	547	546	1	4.7
FBP (99.5)	570	566	4	13.9

Reference

1. ASTM D6352, Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 °C to 700 °C by Gas Chromatography, ASTM International, West Conshohocken, PA, 2015, www.astm.org

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