Application Note

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Ultrafast Simulated Distillation of Middle Distillates Using ASTM Method D7798 on the Agilent Intuvo Gas Chromatograph

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Abstract

ASTM method D7798 is designed to provide middle-distillate boiling range distribution data in less than three minutes using techniques of ultrafast gas chromatography. This method was implemented on the Agilent Intuvo 9000 GC with its unique direct heating column oven and precise column flows. These attributes provided the high degree of retention time precision needed for this method without the need for postrun manipulation of the data. Instrument performance was demonstrated in three ways:

- Multiple calibration runs were shown to have near-perfect retention time precision and no inlet discrimination.
- The Intuvo was easily validated according to the ASTM protocols.
- The boiling range distribution results for three different samples matched those in the ASTM D7798 research report as well as a separate study using the D2887 referee method.

Introduction

Simulated distillation (Simdis) provides reliable and fast boiling point distribution data for petroleum feedstocks and finished products. ASTM D2887 is a widely used Simdis method specifically designed for middle distillate fuels such as kerosene, jet fuel, diesel fuel, and heating oil.[1] This method can provide quality results in as little as eight minutes, and is also the referee method for middle distillates. Recently, ASTM introduced method D7798, a middle-distillate Simdis method using shorter columns, higher carrier flow rates, and fast oven heating to reduce run time to approximately three minutes.[2]

The Intuvo 9000 GC is specifically designed to run ultrafast GC methods such as D7798 using conventional GC capillary columns. The unique direct column heating element combined with the sixth-generation electronic pneumatics control (EPC) are combined to precisely control both fast column heating and high column flow rates. The result is extraordinarily consistent retention times needed for ultrafast simulated distillation. Additionally, Intuvo's easy system maintenance and smart, automated diagnostics are ideal for laboratories seeking to maximize productivity.

Experimental

Instrument configuration and operating conditions

An Agilent Intuvo 9000 GC was configured to run ASTM D7798 as shown in Table 1.

Table 2 shows the operating parameters used with the Intuvo to run ASTM D7798. Under these conditions, the maximum analysis time will be less than three minutes.

A boiling point calibration standard containing normal hydrocarbons from C5 to C44 was prepared by dissolving the Agilent D2887 calibration mixture (p/n G3440-85037) in 15 mL of carbon disulfide. The calibration standard was run five times on the Intuvo GC using the instrument conditions listed in Table 2. After calibration, the system performance was validated by analyzing reference gas oil sample 1, batch 2 (RGO, p/n 5060-9086). Three middle-distillate samples, representing boiling ranges across the D2887 scope, were then run. The RGO sample and the three middle-distillate samples were analyzed without any solvent dilution or preheating.

Table 1. Agilent Intuvo 9000 GC configured for ASTM D7798.

Automatic Liquid Sampler	Agilent 7650A automatic liquid sampler
Syringe	Autosampler syringe 10 µL (p/n G4513-80203)
Inlet	Multimode (MMI)
Inlet Liner	Low pressure drop, Ultra Inert with glass wool (p/n 5190-2295)
Intuvo Flow Path	Agilent Intuvo Guard Chip (p/n G4587-60565) Agilent Intuvo Flow Chip (p/n G4581-60031) Agilent D1 Intuvo Flow Chip (p/n G4581-60032)
Analytical Column	Agilent J&W DB-Sim-Dist, 4 m × 0.25 mm id, 0.25 mm (p/n 122-4002-INT)
Detector	Flame ionization detection (FID)

Table 2. Agilent Intuvo 9000 GC operating conditions for ASTM D7798.

ALS Setpoints	
Sample Injection Volume	0.2 µL
Pre-Injection Solvent Washes	5 × 0.5 µL carbon disulfide
Pre-Injection Sample Washes	None
Sample Pumps	5
Post-Injection Solvent Washes	5 × 0.5 µL carbon disulfide
Inlet Setpoints	
Mode	Split ratio 30:1
Temperature	360 °C
Analytical Column Setpoints	
Carrier Gas	Helium
Column Flow	4 mL/min, constant flow
Intuvo Flow Path Setpoints	
Guard Chip	350 °C
Bus	350 °C
Column Oven Setpoints	
Initial Temperature	40 °C
Ramp Rate	160 °C/min
Final Temperature	360 °C
Final Hold Time	1 minute
FID Setpoints	
Temperature	400 °C
Hydrogen Flow	30 mL/min
Air Flow	400 mL/min
Make-Up Flow	N_2 at 25 mL/min

Results and discussion

Figure 1 shows an overlay of the five calibration runs made on the Intuvo 9000 GC system. Retention time precision was extremely high, with the largest retention time range of 0.002 minutes observed for the *n*-C44 peak. This level of precision is inherent in the raw data without the need for any postacquisition manipulation to artificially line up the peaks. No significant inlet discrimination was observed, with near complete transfer of all alkanes to the column. The average *n*-C44 recovery was 94%.

Before running samples, the system performance was validated by analyzing an RGO sample, and comparing the experimental cut point temperatures to the published reference values. Figure 2 shows an overlay of five RGO chromatograms obtained on the Intuvo system. RGO analysis was completed in less than 2.5 minutes. The inset chromatogram confirms the same high retention time precision seen with the calibration standard. Additionally, the consistent response profile demonstrates complete transfer of the sample from the inlet through the Intuvo flowpath.

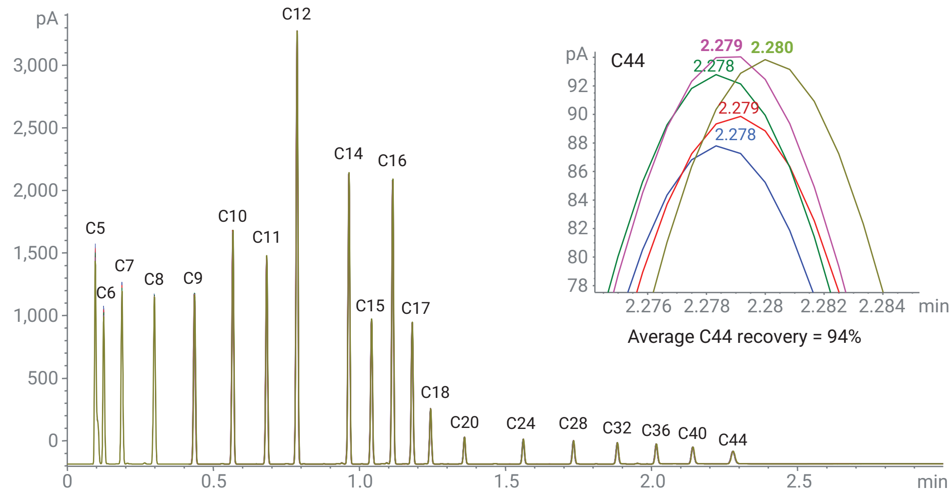


Figure 1. Overlay of five calibrations runs on an Agilent Intuvo 9000 GC. The inset shows the retention time precision and average recovery for the n-C44 peak.

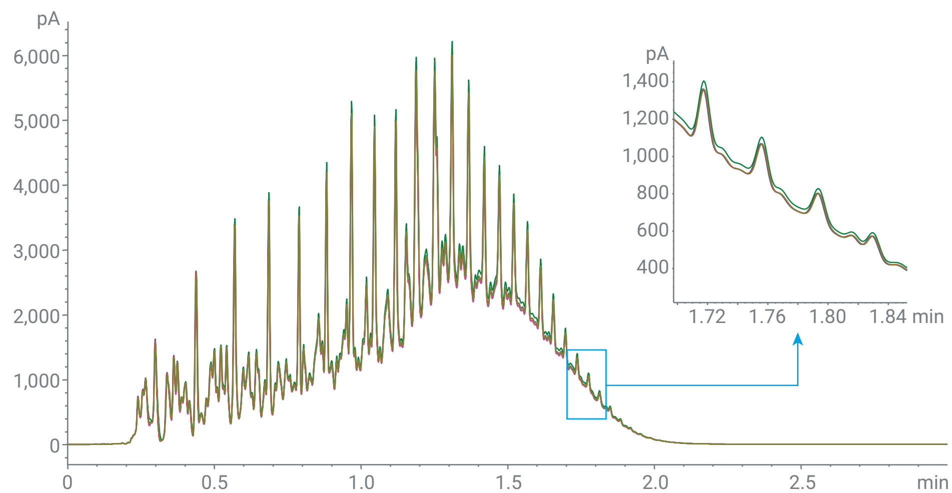


Figure 2. Overlay of five RGO analyses on an Agilent Intuvo 9000 GC. The inset illustrates the same high retention time precision seen with the calibration runs.

Table 3 lists the experimental RGO performance results compared to the ASTM reference values. The overall precision at each cut point temperature was exceptional, with RSDs well below 0.5%. The experimental temperatures at each cut point were almost perfectly matched to the ASTM reference values, all well within the allowed difference.

With the Intuvo system validated for D7798, three samples were analyzed. The samples chosen were a jet fuel, a diesel fuel, and a waxy distillate, each obtained from the D7798 ASTM Interlaboratory Study (ILS).[3] Figure 3 shows the chromatograms obtained for all three samples from Intuvo running D7798. The analysis times were very fast, between 1.5 and 2.5 minutes.

Table 3. RGO validation performance on the Agilent Intuvo 9000 GC.

	ASTM Reference		Experimental Results*			
% Off	°C	Allowed Difference (°C)	Average (°C)	Std. Dev. (°C)	RSD (%)	Average Difference (°C)
IPB 0.5%	115	7.5	114	0.00	0.000	1.0
5	151	3.8	151	0.00	0.000	0.0
10	176	4.1	175	0.00	0.000	1.0
15	201	4.5	202	0.55	0.272	0.6
20	224	4.9	225	0.45	0.199	1.2
25	243		244	0.55	0.224	
30	259	4.7	261	0.45	0.171	1.8
35	275		276	0.00	0.000	
40	289	4.3	290	0.45	0.154	1.2
45	302		304	0.55	0.180	
50	312	4.3	314	0.00	0.000	2.0
55	321	4.3	323	0.00	0.000	2.0
60	332	4.3	333	0.00	0.000	1.0
65	343	4.3	344	0.45	0.130	1.2
70	354	4.3	355	0.00	0.000	1.0
75	365	4.3	367	0.00	0.000	2.0
80	378	4.3	380	0.45	0.118	1.8
85	391	4.3	393	0.45	0.114	1.8
90	407	4.3	409	0.45	0.109	1.8
95	428	5	431	0.45	0.104	2.8
FBP 99.5%	475	11.8	477	2.24	0.469	2.8

*Average, Std. Dev., RSD, and average difference were calculated from five RGO analyses.

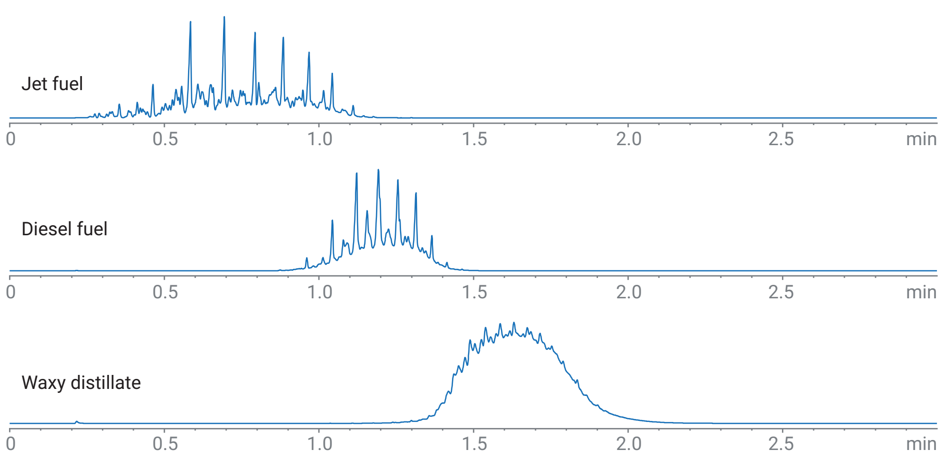
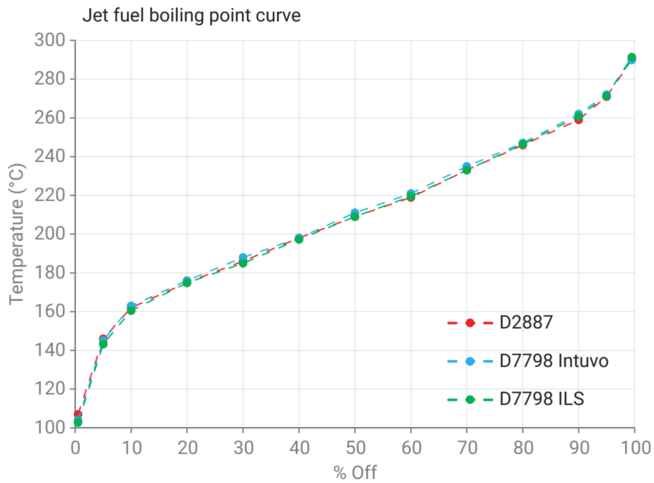


Figure 3. Chromatograms of three middle-distillate samples analyzed on an Agilent Intuvo 9000 GC using the ASTM D7798 ultrafast GC method for simulated distillation.

Boiling range distribution results were obtained for these data with the Agilent Simdis software for ChemStation. Using these ILS samples allowed comparison of the Intuvo D7798 results with those reported in the ILS. Since ASTM D2887 is the referee Simdis method for middle distillates, the Intuvo D7798 sample results were also compared to those obtained with a D2887 study. Figures 4, 5, and 6 tabulate the boiling range distribution results for the three samples. Graphic representations of each sample's data are shown in the boiling point curves. For each sample, the Intuvo results are nearly identical to those obtained with D2887 as well as the D7798 ILS. These results ensure accurate and precise boiling range distribution calculations when using Intuvo with ASTM D7798. Additionally, the Intuvo results combined with the reported D7798 ILS results show that this ultrafast GC method compares favorably with D2887.

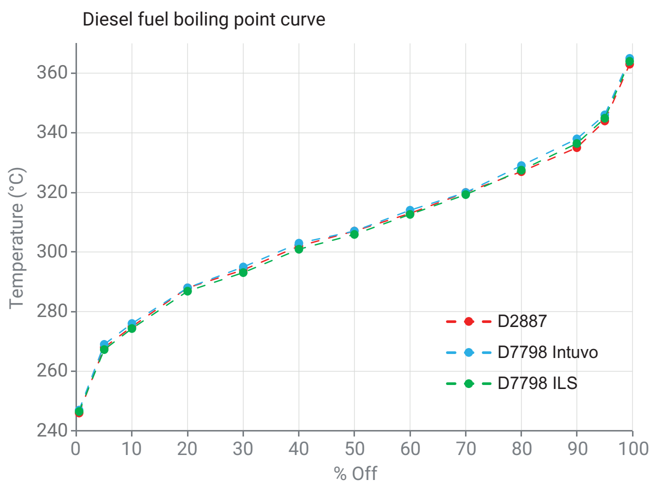
Conclusion

ASTM method D7798 was designed to provide ultrafast boiling range distribution data for a wide range of middle-distillate fuels and hydrocarbons. The Agilent Intuvo 9000 GC was shown to be an excellent instrument for running this method. The precise retention times needed for simulated distribution were obtained using the combination of Intuvo's fast direct column oven and precise column flow controls. Unlike other systems, there was no need to use postacquisition software to artificially line up peak retention times. D7798 method validation was easily met using the Intuvo 9000 GC, and sample results were nearly identical to those reported in the ASTM D7798 research report as well as a separate D2887 study.



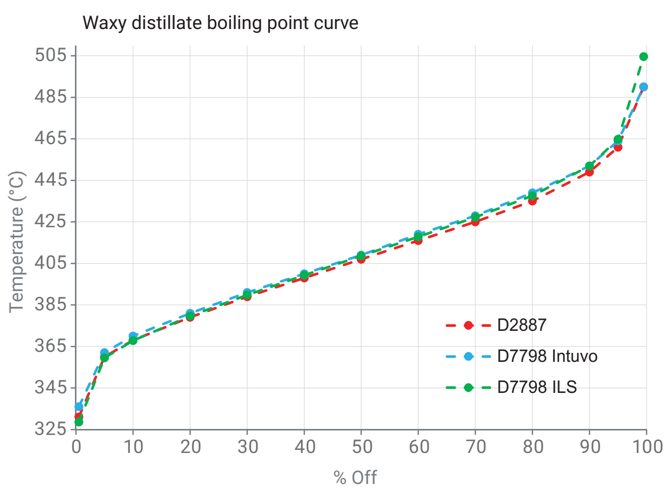
% Off	Temperature (°C) D2887	D7798 Intuvo	D7798 ILS
0.5	107	104	103
5	146	145	143
10	162	163	160
20	175	176	175
30	186	188	185
40	198	198	197
50	209	211	209
60	219	221	219
70	233	235	233
80	246	247	246
90	259	262	261
95	271	272	271
99.5	290	290	291

Figure 4. Comparison of the boiling point distribution of jet fuel obtained from an Agilent Intuvo 9000 GC running the D7798 (blue), D7798 ILS (green), and D2887 referee method (red).



% Off	Temperature (°C) D2887	D7798 Intuvo	D7798 ILS
0.5	246	247	246
5	268	269	267
10	275	276	274
20	288	288	287
30	294	295	293
40	302	303	301
50	307	307	306
60	313	314	313
70	320	320	319
80	327	329	327
90	335	338	336
95	344	346	345
99.5	363	365	364

Figure 5. Comparison of the boiling point distribution of diesel fuel obtained from an Agilent Intuvo 9000 GC running the D7798 (blue), D7798 ILS (green), and D2887 referee method (red).



% Off	Temperature (°C) D2887	D7798 Intuvo	D7798 ILS
0.5	331	336	329
5	360	362	360
10	368	370	368
20	379	381	380
30	389	391	390
40	398	400	399
50	407	409	409
60	416	419	418
70	425	428	427
80	435	439	438
90	449	452	452
95	461	464	465
99.5	490	490	505

Figure 6. Comparison of the boiling point distribution of waxy distillate obtained from an Agilent Intuvo 9000 GC running the D7798 (blue), D7798 ILS (green), and D2887 referee method (red).

References

1. ASTM D2887-16a, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM International, West Conshohocken, PA, **2016**, www.astm.org.
2. ASTM D7798-15, Standard Test Method for Boiling Range Distribution of Petroleum Distillates with Final Boiling Points up to 538 °C by Ultra Fast Gas Chromatography (UF GC), ASTM International, West Conshohocken, PA, **2015**, www.astm.org.
3. Research Report RR:D02-1806, Interlaboratory Study to Establish Precision Statements for ASTM D7798, Test Method for Boiling Range Distribution of Petroleum Distillates With Final Boiling Points up to 538°C by Ultra Fast Gas Chromatography (UF GC), ASTM International, West Conshohocken, PA, 2016, www.astm.org. October **2015**.

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