

## Gas Chromatography

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## Fast Simulated Distillation Analysis by Modified ASTM® D2887, D6352 and D7169

### Introduction

Simulated distillation (SimDist) is a gas chromatographic technique used to simulate the results of a distillation tower, separating crudes or other multicomponent blends into component fractions by boiling points.

As the oven temperature is raised at a reproducible rate, analytes are eluted and the areas under the chromatogram are recorded. Boiling points are assigned to the time axis from a calibration curve, known as the boiling-point distribution curve, based on a known mixture of normal paraffin hydrocarbons over a fixed range. These paraffin hydrocarbons serve as markers, which identify the time that specific paraffins of known boiling points elute. From these data, we can plot the area between these markers against the boiling-point ranges to create boiling-point distributions for specific crudes or other multicomponent blends.

ASTM® methods used for SimDist applications have been widely used to obtain reliable and repeatable analysis given the specific parameters of each method. PerkinElmer has enhanced three popular ASTM® methods (D2887, D6352, and D7169) to allow quicker cycle times while still maintaining system-performance specifications.

## ASTM Method D2887

ASTM® D2887 methodology is relatively simple due to its limited hydrocarbon range. The method utilizes a relatively short column length, a thicker film to improve resolution of early-eluting compounds, and a linear heating ramp to emulate a true distillation process as closely as possible. Since higher-molecular-weight hydrocarbons are excluded from this method, limitations to column resolution are less of an issue, and the boiling-point distribution markers vary little with the increased oven temperatures.

By increasing the column-temperature ramp, we trade resolution for speed and deliver a reduced analysis runtime. With this reduced runtime, it is important to maintain a boiling-point distribution curve which will meet the method reference standard (Figure 2 – shown in red).

**Table 1. ASTM® Method D2887 Gas Chromatograph Conditions.**

Chromatograph	PerkinElmer® Model Arnel 3023 SimDist Analyzer, with Clarus® 680 Gas Chromatograph
Column	10 m x 0.53 mm x 2.65 µm MXT-2887
Autosampler	0.5 µL syringe, injection volume 0.2 µL, slow injection speed
Oven	35 °C, then 15 °C/min to 350 °C, hold for 2.00 min
Injector	Packed injector, 350 °C
Carrier	Helium, programmed flow, 12 mL/min
Detector	Flame ionization (FID) at 370 °C Air = 450 mL/min H <sub>2</sub> = 45 mL/min Range x1 Attenuation x32
Data Handling System	PerkinElmer TotalChrom® CDS

Figure 1 shows a reference gas oil #1, lot 2 chromatogram with its associated boiling-point-distribution curve. By running this sample, a subtracted blank baseline, and a normal paraffin hydrocarbons calibration mix for each of the different oven ramps in increments of 5 °C/min, we can observe the effect the oven ramps have on the boiling-point distribution curves.

By plotting the boiling-point-range distribution from initial boiling point (IBP - 0.5%) to final boiling point (FBP - 99.5%) versus temperature, we can see that even at a maximum temperature ramp of 35 °C/min we are still within the ASTM® method limits (Figure 2).

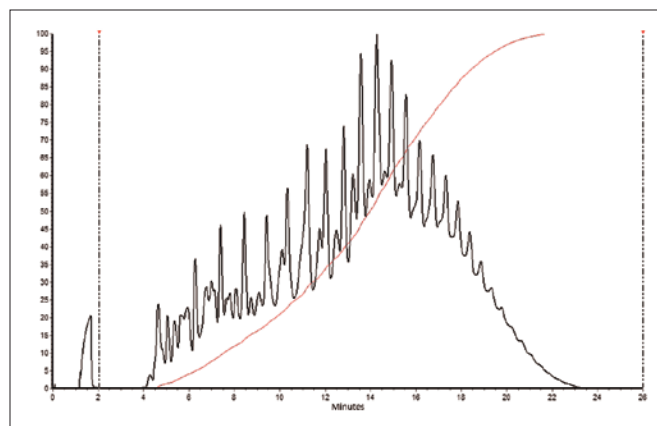


Figure 1. Reference gas oil and boiling-point distribution curve for an ASTM® D2887 analysis.

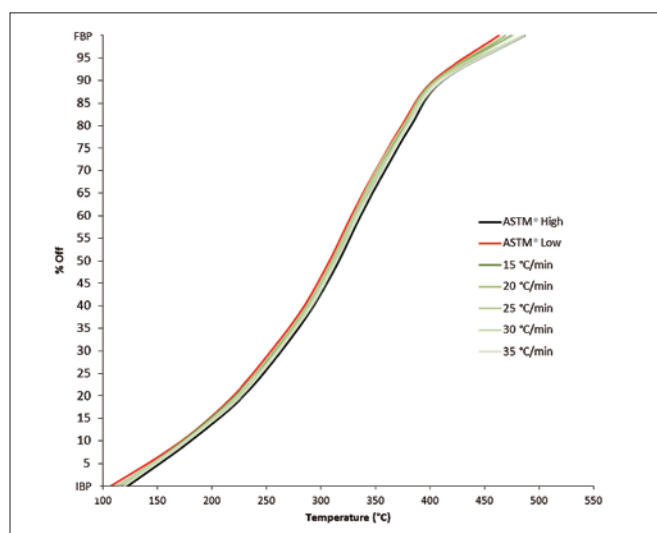


Figure 2. Boiling-point-range distribution vs. temperature for reference gas oil #1, lot 2 at different oven heating ramps.

## ASTM® Methods D6352 and D7169

ASTM® D6352 and D7169 methodologies are more challenging to optimize relative to D2887 due to their extended hydrocarbon range. These two methods are very closely related, but we will focus on the ASTM® D7169 method for the following example. Both of these methods utilize a relatively short column and a linear heating ramp, but differ from the D2887 method in that they utilize a programmable on-column injector which heats at a constant rate equal to the oven temperature ramp, with an offset to keep the injector at a higher temperature than the oven. This creates a refocusing effect which helps to limit peak broadening.

Because of the extended hydrocarbon range, correctly resolving accurate boiling-point distribution markers presents a challenge. As the oven temperature increases, peaks generally broaden until they become undistinguishable. This results in uncertainty in the higher boiling regions of the boiling-point distribution curve.

**Table 2. ASTM® Method D7169 Gas Chromatograph Conditions.**

Chromatograph	PerkinElmer Model Arnel 3023 SimDist Analyzer, with Clarus 680 Gas Chromatograph
Column	5 m x 0.53 mm x 0.10 µm MXT-1 HT SimDist
Autosampler	0.5 µL syringe, Injection volume 0.2 µL, slow injection speed
Oven	-20 °C to 425 °C at 15 °C/min, hold for 2.50 min
Injector	Programmable on-column injector 50 °C to 450 °C at 15 °C/min, hold for 5.00 min
Carrier	Hydrogen, programmed flow, 20 mL/min
Detector	Flame ionization (FID) at 430 °C Air = 450 mL/min H <sub>2</sub> = 45 mL/min Range x1 Attenuation x32
Data Handling System	PerkinElmer TotalChrom CDS

Figure 3 shows a reference gas oil 5010 chromatogram produced using the ASTM® D7169 method described above, along with its associated boiling-point distribution curve. By analyzing a normal paraffin hydrocarbons calibration mix (Polywax® 655/1000), a sample blank and a reference-oil standard at various oven heating ramps, we can observe the effect on the boiling-point distribution curve for this method.

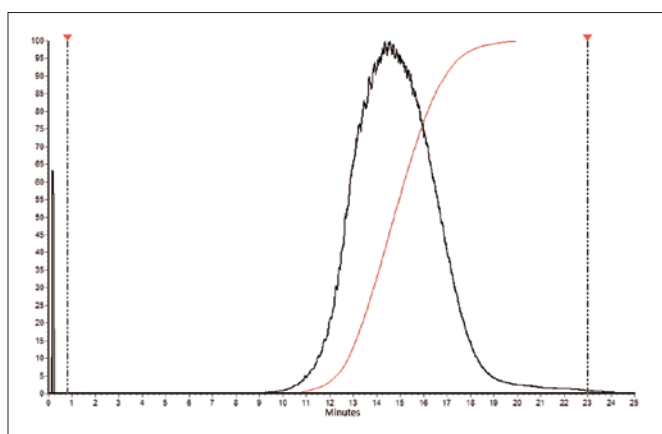


Figure 3. Reference gas oil and boiling-point distribution curve for an ASTM® D7169 analysis.

By plotting the boiling-point-range distribution versus temperature, we can see that temperature ramps in the 15 °C/min to 25 °C/min were well within the ASTM® method limits (Figure 4). If the GC oven ramp exceeds 25 °C/min, the curve will fall outside of the ASTM® limits and fail the required quality control (QC) reference.

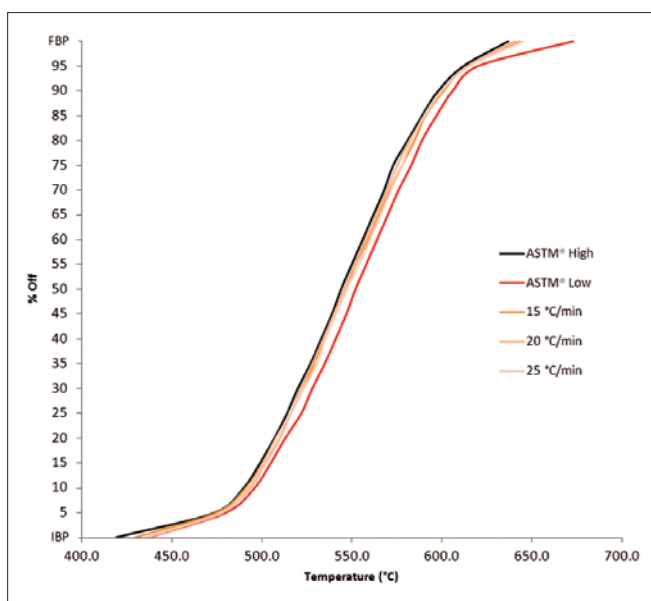


Figure 4. Boiling-point-range distribution vs. temperature for reference gas oil 5010 at different oven heating ramps.

### Complete Run Cycle Time

Figures 5 and 6 show a visual representation of advantages (as well as challenges) of increasing the temperature ramp to boost sample throughput.

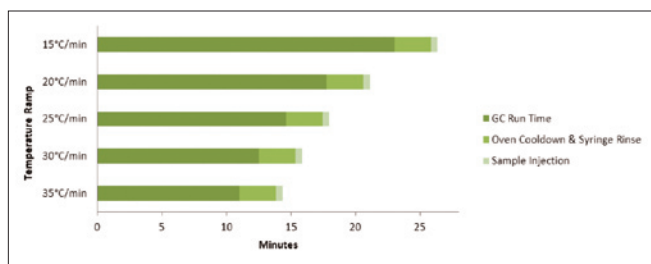


Figure 5. Effect of temperature ramp increasing on GC cycle time for ASTM® method D2887.

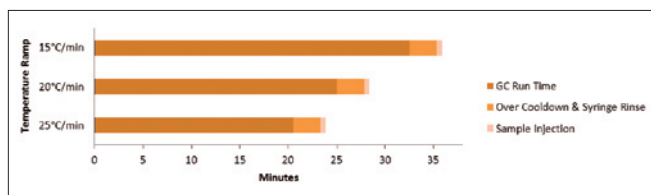


Figure 6. Effect of temperature ramp increasing on GC cycle time for ASTM® methods D6352 and D7169.

## Conclusion

While increasing the linear temperature ramp has an impact on analysis time, it is the total cycle time (analysis time + cool down + sample injection) that determines the overall GC injection-to-injection time. The unique construction of the Clarus 680 GC allows the oven, as well as the programmable on-column injector, to cool down to ambient (400 °C to 30 °C) in less than 3 minutes. This allows the cryogen to further cool the system to subambient with minimal effort, which dramatically reduces the quantity used. The Clarus 680 GC also pre-rinses the syringe before the end of the previous analysis, saving additional time. This combination of optimized oven heating, advanced cool down and injector pre-rinse leads to unsurpassed GC cycle times, increasing throughput compared to the original methods.

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