APPLICATION NOTE

Gas Chromatography

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Fast Simulated Distillation Analysis by Modified ASTM D2887, D7169, D6352, and D7500

Introduction

Simulated distillation (SimDis) 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 by the Wide Range Flame Ionization Detector (WR-FID). The Wide Range FID is designed with a larger dynamic range to be able to detect high and low concentrations of analytes within the same chromatographic run. Equipped with a smaller 0.011" ID jet, the wide range FID offers more sensitive detection of analytes. 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 SimDis applications have been widely used to obtain reliable and repeatable analysis given the specific parameters of each method. PerkinElmer has enhanced four popular ASTM® methods (D2887, D6352, D7169, and D7500) to allow quicker cycle times while still maintaining system-performance specifications. The expected boiling point range of the samples being tested will determine which method is best to use.

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See below the hydrocarbon ranges of six different methods.

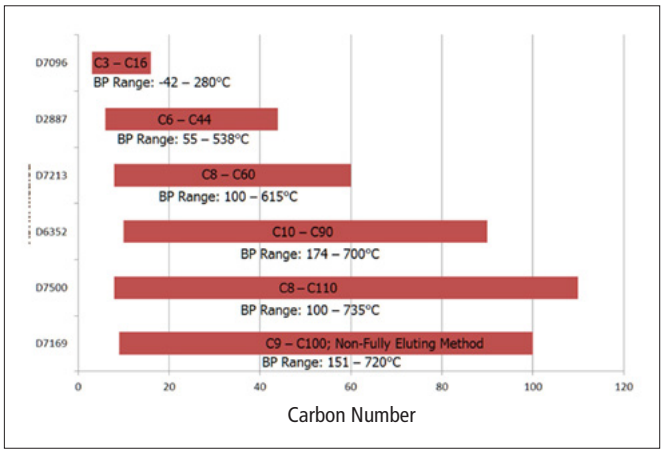

Figure 1. Hydrocarbon ranges of six different methods.

ASTM® Method D2887

ASTM® D2887 methodology is relatively simple due to its limited hydrocarbon range of C6 to C44. 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.

Table 1. ASTM® Method D2887 Gas Chromatograph Conditions.

Chromatograph	Clarus® 690 Gas Chromatograph
Column	10 m 0.53 mmID 2.65 um MXT-2887
Autosampler	0.5 µL syringe, injection volume 0.4 µL, normal injection speed
Oven	-20 °C, then 15 °C/min to 360 °C hold for 5.00 min
Injector	Programmable on column injector at 50 °C hold for 2.00 min, ramp 15 °C/min to 360 °C hold 7.66 min
Carrier	Helium, programmed flow, 21 mL/min
Detector	Wide Range Flame ionization (WFID) at 360 °C Air = 450 mL/min H2 = 30 mL/min Range x 1 Attenuation x 32
Data Handling	PerkinElmer TotalChrom® CDS and PKI Dragon® SimDis SW.

Figure 2 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 plottingthe 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 3).

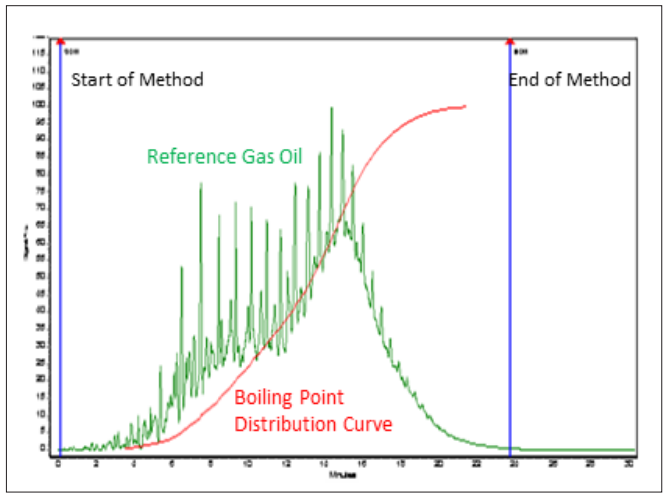

Figure 2. Reference gas oil and boiling-point distribution curve for an ASTM® D2887 analysis with Wide Range FID.

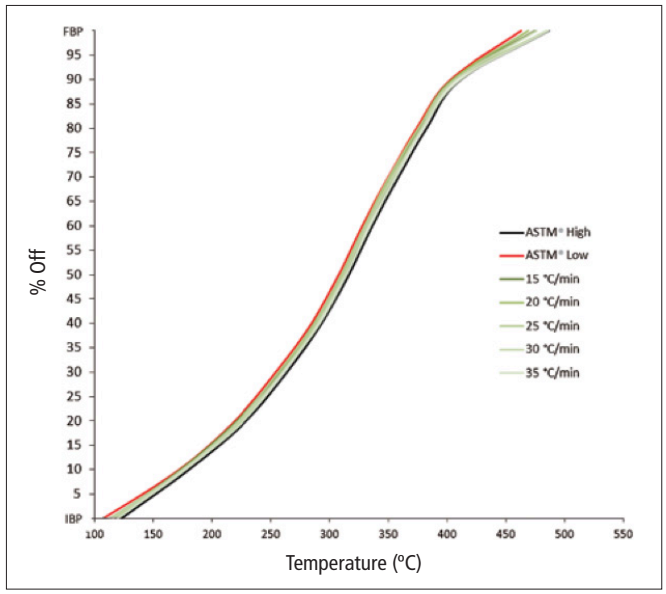

Figure 3. Boiling-point-range distribution vs. temperature for reference gas oil #1, lot 2 at different oven heating ramps

ASTM® Methods D6352, D7169 and 7500

ASTM® D6352 and D7169 methodologies are more challenging to optimize relative to D2887 due to its extended hydrocarbon range. D6352 focuses on the range of C10 to C90 and utilizes of a relatively short column and a linear heating ramp. All SimDis methods use 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; however, it really shows its value in the later methods, as this creates a refocusing effect which helps to limit peak broadening.

Table 2. ASTM® Method D6352 Gas Chromatograph Conditions.

Chromatograph	Clarus® 690 Gas Chromatograph
Column	Zebron ZB-1XT SimDis 5 m 0.53 mmID 0.09 um
Autosampler	0.5 µL syringe, injection volume 0.4 µL, normal injection speed
Oven	-20 °C, then 20 °C/min to 430 °C hold for 3.00 min
Injector	Programmable on column injector at 50 °C hold for 0.00 min, ramp 25 °C/min to 430 °C hold 999 min
Carrier	Helium, programmed flow, 14 mL/min
Detector	Wide Range Flame ionization (WFID) at 430 °C Air = 450 mL/min H2 = 30 mL/min Range x 1 Attenuation x 32
Data Handling	PerkinElmer TotalChrom® CDS and PKI Dragon® SimDis SW.

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.

Figure 4 shows a reference gas oil 5010 chromatogram produced using the ASTM® D6352 method described above, along with its associated boiling-point distribution curve.

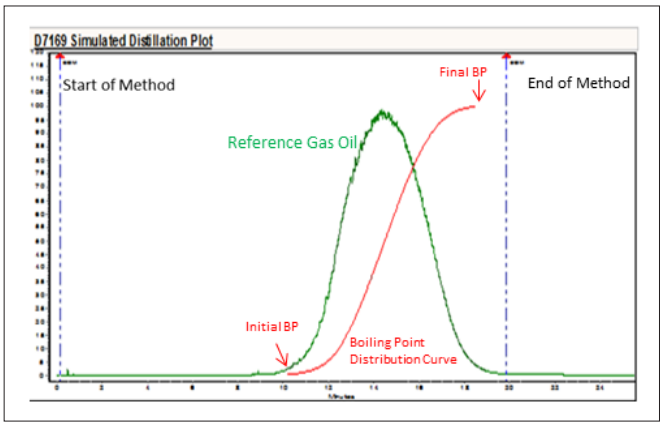

Figure 4. Reference gas oil and boiling-point distribution curve for an ASTM® D7169 analysis.

By analyzing a normal paraffin hydrocarbons calibration mix (Polywax® 655/1000), a sample blank and a reference-oil standard, we can observe the effect on the boiling-point distribution curve for this method. 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 5). 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.

ASTM® Method D7169 is an external standard method with % residue calculation which requires an addition step while setting up the SimDis procedure method in the PerkinElmer Dragon software. D7169 also covers an extended hydrocarbon range, C9-C100, and uses the same chromatographic method as D6352. The inclusion of the sample and solvent weights of the Reference Gas Oil used is vital in the calculations of this method. Figure 6 shows a screen shot of how to include the external standard file.

ASTM® Method D7500 has the broadest hydrocarbon range of C8 to C110. It is a standard test method developed by combining methods D6352 and IP 480. D7500 uses the same GC method parameters as D6352 and D7169 but with an option to increase hold times during the run to ensure that all hydrocarbons in the C8-C110 range elute prior to the oven reaching 430 °C.

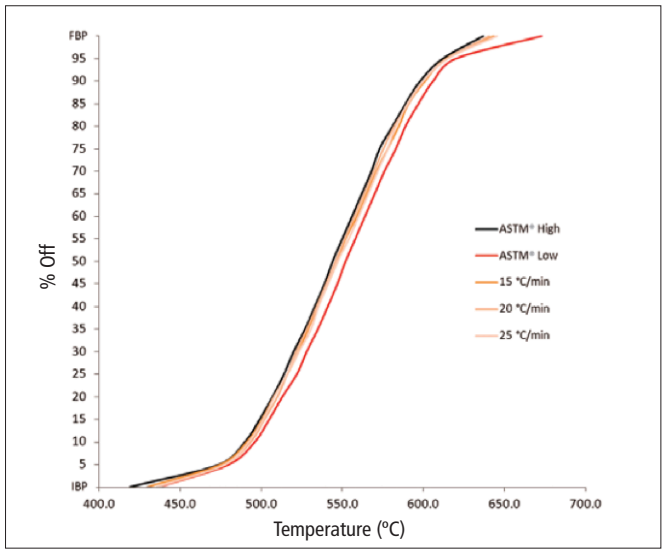

Figure 5. Boiling-point-range distribution vs. temperature for reference gas oil 5010 at different oven heating ramps.

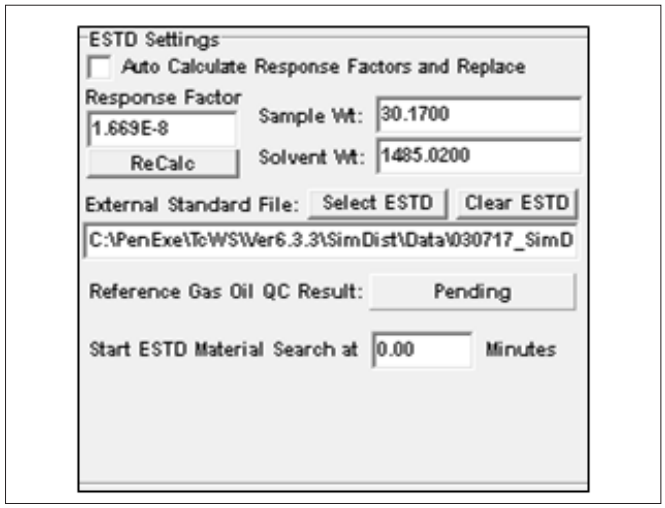

Figure 6. External Standards Settings tab in D7169 analysis method.

Complete Run Cycle Time

Figures 7 and 8 show a visual representation of advantages (as well as challenges) of increasing the temperature ramp to boost sample throughput.

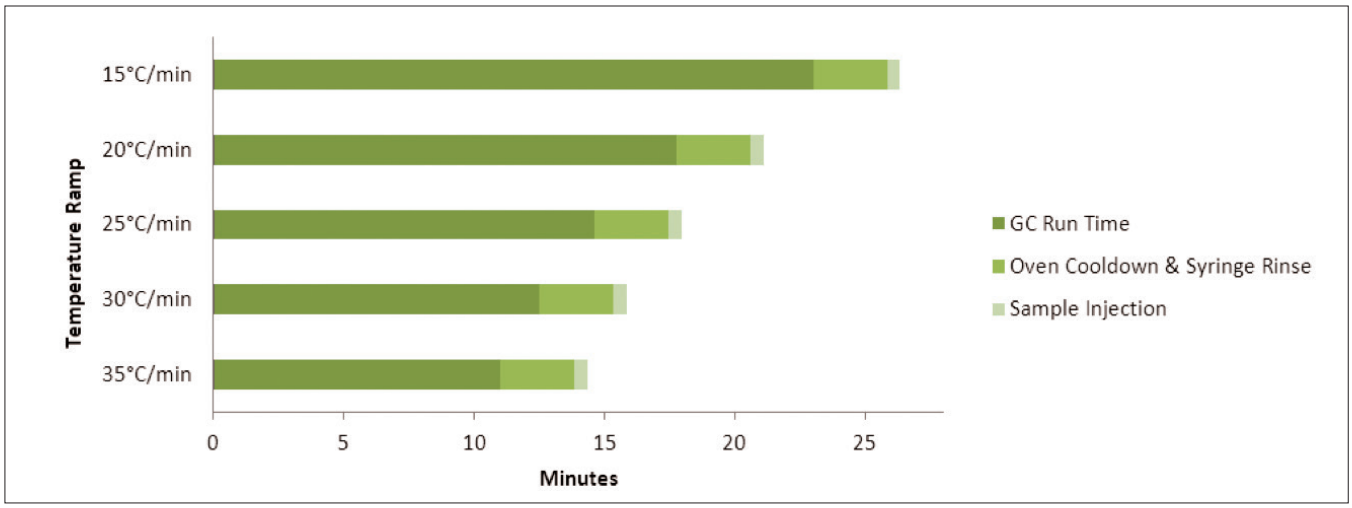

Figure 7. Effect of temperature ramp increasing on GC cycle time for ASTM® method D2887.

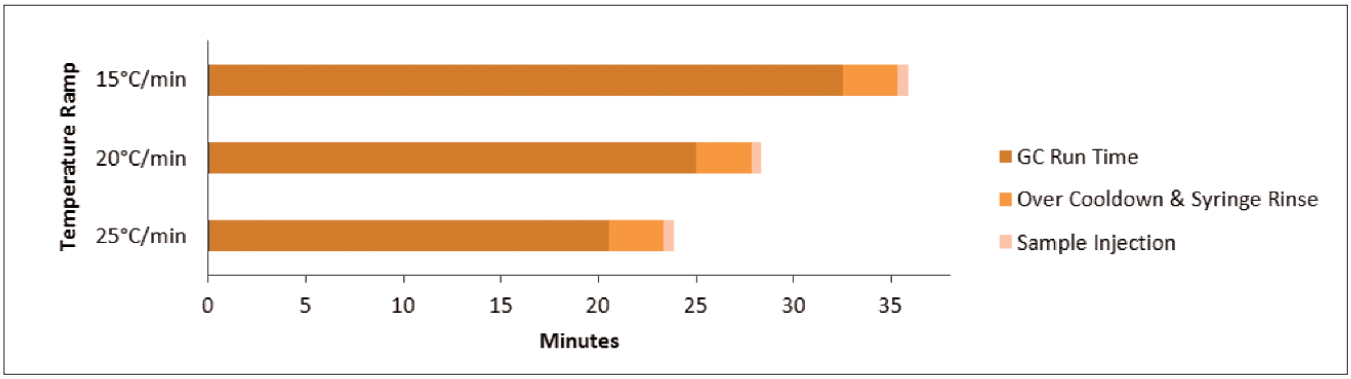

Figure 8. Effect of temperature ramp increasing on GC cycle time for ASTM® methods D6352 and D7169.

Wide Range Flame Ionization Detector

The Wide Range Flame Ionization detector has all of the same desirable attributes as the standard Flame Ionization detector (FID) that allows you to run successful SimDis methods. The Wide Range FID now allows a larger dynamic range that can detect low to high concentrations of analytes, all within the same chromatographic run. An additional benefit is ease of use due to no longer needing to change Range values in the method. Attenuation values can be used at one optimized setting to ensure all peaks are detectable and on-scale, from the lowest to highest concentrations. The new Wide Range FID and smaller ID jet now allow more sensitive detection of analytes as an added benefit.

Conclusion

While 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 690 GC allows the oven, as well as the programmable on-column injector, to cool down to ambient (430 °C to 30 °C) in less than three minutes. This allows the cryogen to further cool the system to sub ambient with minimal effort, which dramatically reduces the quantity used. The Clarus 690 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, injector pre-rinse, and Wide Range FID optimized detection technology leads to unsurpassed GC cycle times and analyte recognition compared to the original methods.

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