ASTM Method D-2887 – Fast Simulated Distillation – with the Clarus 600 Gas Chromatograph

Author
Clarence Wentzel
Robert Cardillo
Arnel Inc.
3145 Bordentown Ave.
Parlin, NJ 08859

Andrew Tipler
PerkinElmer, Inc.
710 Bridgeport Ave.
Shelton, CT 06484

Introduction

Crude Assay Distillation (ASTM D-2892) is a commonly accepted and sanctioned method for providing an estimate of the yields of the fractions of various boiling ranges for crude oil. The results of this method, when properly conducted, are extremely important in the characterization and commercial trading of crude oil and heavy fuels. This method, however, suffers from several shortcomings. "Fast Simulated Distillation" using new GC technology and based upon ASTM method D-2887 provides a powerful and rapid analytical tool to overcoming the many limitations found in crude assay distillations.

Discussion

While crude assay distillation provides vital information and is essential in modeling actual physical distillations, it is very manpower intensive, fundamentally slow, provides only limited data, offers only attended automation and finally, is user subjective. Modern gas chromatographic instruments and, in particular, those that incorporate column ovens with rapid heat-up and cool-down facilities, can quickly and easily provide throughput and productivity gains in a Simulated Distillation analysis. The PerkinElmer®-Arnel Model 3023 Simulated Distillation Analyzer is a turnkey solution that includes a Clarus® 600 GC and reporting software for a fully-automated and unattended solution for ASTM method D-2887.

The analysis time for method D-2887 has typically been performed in the range of 30-35 minutes and, when added to the oven cool-down time of approximately 10 minutes, the total analysis time is now lengthened to 40-45 minutes (Figure 1). Decreasing the analysis time to improve sample throughput may, however, have an adverse affect on retention-time repeatability; a critical and important measure in performing Simulated Distillation. The Model 3023 Simulated Distillation Analyzer makes use of the novel oven design of the Clarus 600 GC to provide a marked improvement in not only total run time but improved retention-time precision without the use of cryogenic cooling fluids.

Experimental

A Clarus 600 GC was utilized with a programmable on-column (POC) injector, flame ionization detector (FID) and a liquid autosampler. A 100% dimethyl polysiloxane fused-silica capillary column (5 m x 0.05 mm ID x 0.2 micron film thickness) was used. Method conditions are shown in Table 1.

A boiling-point calibration blend (C_6-C_{44}) was run (Figure 2). Of particular interest is the run time: approximately 7 minutes. This is a dramatic improvement versus the conventional run time of approximately 30-35 minutes. With the rapid and efficient oven cool-down of the Clarus 600 GC and an equilibration time of 0.5 minutes, the total GC cycle time (time to next injection) has been reduced to approximately 6.83 minutes. This represents more than a 35-minute reduction in cycle time per sample or a gain of 700% in productivity.

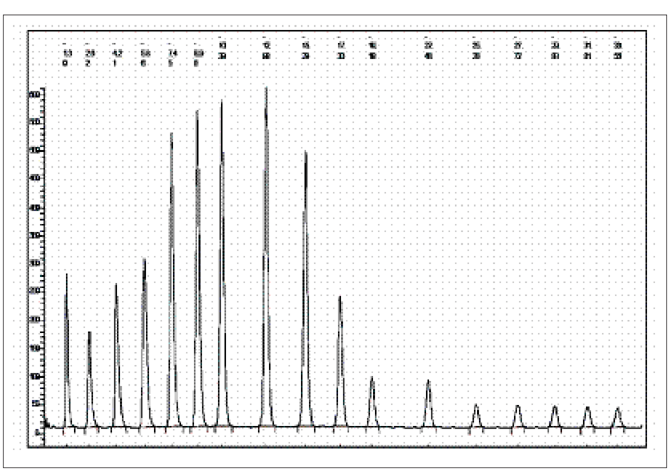


Figure 1. ASTM method D-2887 cryogenic start with an analysis time of almost 34 minutes.

Equally as important in the reduction in cycle time is the ability to maintain or improve the retention-time precision. Retention-time measurement requires precise carrier-gas control (programmable pneumatic control – PPC) and temperature programming, plus accurate control of the injection pulse and start synchronization. The Clarus 600 GC fulfills all of these requirements as illustrated in the retention-time precision shown in Table 2 (Page 3).

Table 1. GC Method.

Injector Temperature:	350 °C
Detector Temperature:	350 °C
Carrier Gas:	Hydrogen @ 40 psi
Split Ratio:	4000:1
Injector Mode:	Fast
Sample Volume:	0.3 µL
Oven Program:	
Initial Temperature:	40 °C
Ramp 1:	60 °C to 300 °C
Rate:	60 °C/min
Equilibration Time:	0.5 min

Reference Gas Oil (RGO) is a highly-characterized ASTM-sponsored standard for D-2887 and is a good system-performance indicator. Using a Reference Gas Oil (Figure 3, Page 3) the total analysis time is approximately 6 minutes. As with the boiling-point calibration blend, excellent retention-time precision can be observed with the RGO (Table 3, Page 3).

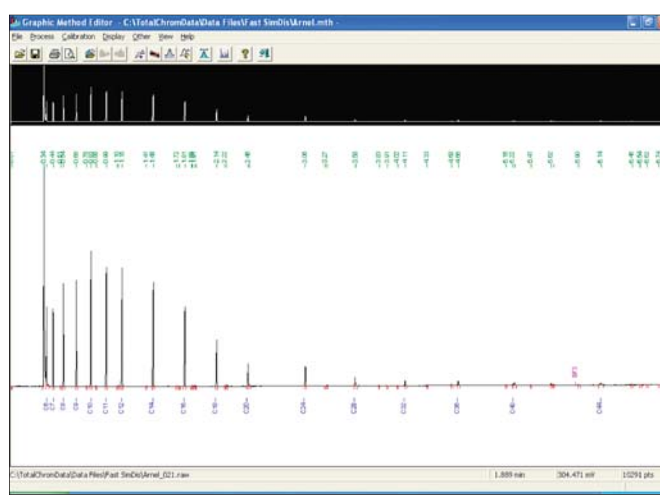


Figure 2. Boiling-point calibration blend.

The Model 3022 Simulated Distillation Software is a fully 32-bit enabled calculation and reporting package that is included in the Model 3023 Simulated Distillation Analyzer. It boasts a number of features and includes a unique data template that can be used to create custom correlations. %-off, cut-points and QC-reporting functions extend the capability of the software into a powerful post-run tool. An example of the %-off RGO report can be seen in Figure 4.

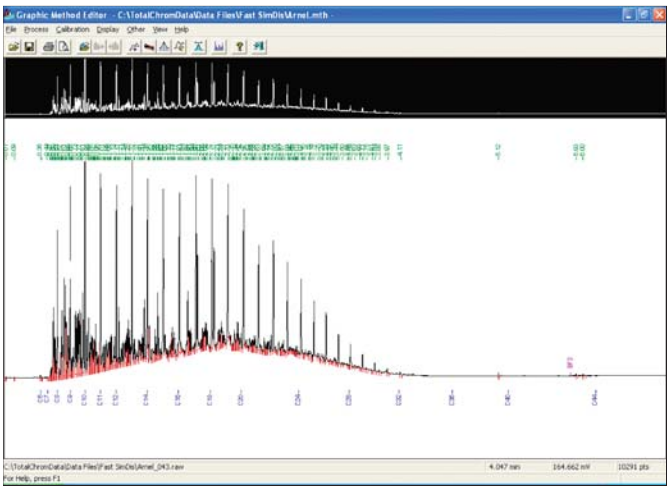
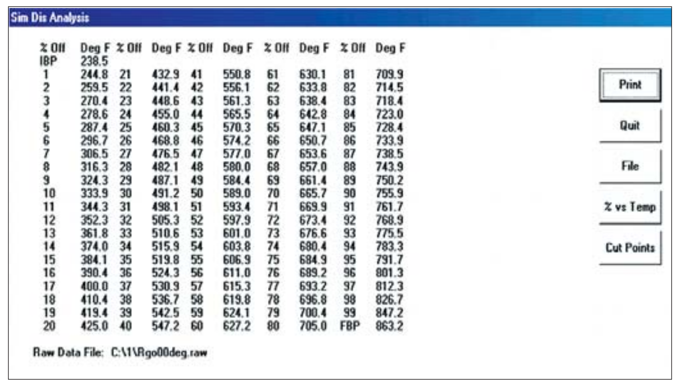


Figure 3. Reference Gas Oil.

The Clarus 600 GC oven design offers enhanced stability and the ability to cool and control near-ambient temperature. This feature permits samples with moderate volatility to be run without the use of cryogenic start temperatures.

Table 4 shows retention-time precision of the Reference Gas Oil run at a start temperature of 30 ˚C. The ambient room temperature during the experimental work was approximately 78 ˚F. Again, excellent precision was obtained without increasing equilibration time before injection.



Sim Dis Analysis

% Off	Deg F	% Off	Deg F	% Off	Deg F	% Off	Deg F	% Off	Deg F
IBP	238.5								
1	244.8	21	432.9	41	550.8	61	630.1	81	709.9
2	259.5	22	441.4	42	556.1	62	633.8	82	714.5
3	270.4	23	448.6	43	561.3	63	638.4	83	718.4
4	278.6	24	455.0	44	565.5	64	642.8	84	723.0
5	287.4	25	460.3	45	570.3	65	647.1	85	728.4
6	296.7	26	468.8	46	574.2	66	650.7	86	733.9
7	306.5	27	476.5	47	577.0	67	653.6	87	738.5
8	316.3	28	482.1	48	580.0	68	657.0	88	743.9
9	324.3	29	487.1	49	584.4	69	661.4	89	750.2
10	333.9	30	491.2	50	589.0	70	665.7	90	755.9
11	344.3	31	498.1	51	593.4	71	669.9	91	761.7
12	352.3	32	505.3	52	597.9	72	673.4	92	768.9
13	361.8	33	510.6	53	601.0	73	676.6	93	775.5
14	374.0	34	515.9	54	603.8	74	680.4	94	783.3
15	384.1	35	519.8	55	606.9	75	684.9	95	791.7
16	390.4	36	524.3	56	611.0	76	689.2	96	801.3
17	400.0	37	530.9	57	615.3	77	693.2	97	812.3
18	410.4	38	536.7	58	619.8	78	696.8	98	826.7
19	419.4	39	542.5	59	624.1	79	700.4	99	847.2
20	425.0	40	547.2	60	627.2	80	705.0	FBP	863.2

Raw Data File: C:\1\Rgo00deg.raw

Print

Quit

File

% vs Temp

Cut Points

Figure 4. Reference Gas Oil %-off report.

Table 2. Retention-Time Precision for C_6-C_{44} Boiling-Point Calibration Blend.

	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{24}	C_{28}	C_{32}	C_{38}	C_{40}	C_{44}
RT Ave.	0.37	0.44	0.54	0.68	0.83	0.99	1.15	1.47	1.8	2.13	2.46	3.05	3.58	4.1	4.65	5.23	6.13
St. Dev.	.005	.004	.003	.004	.003	.003	.000	.004	.003	.004	.005	.004	.005	.005	.005	.007	.007
%RSD	0.33	0.39	0.42	0.41	0.33	0.27	0.22	0.18	0.18	0.16	0.15	0.13	0.12	0.11	0.09	0.1	0.1

Table 3. Reference Gas Oil Retention-Time Precision at 40 ˚C.

	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{24}	C_{28}	C_{32}
RT Ave.	0.43	0.54	0.67	0.83	0.99	1.15	1.47	1.80	2.13	2.45	3.04	3.57	4.10
St. Dev.	.005	.003	.003	.004	.004	.000	.005	.006	.015	.005	.006	.012	.004
%RSD	1.152	0.613	0.613	0.452	0.379	0.000	0.339	0.325	0.684	0.187	0.197	0.348	0.100

Table 4. Reference Gas Oil Retention Time Precision at 30 ˚C.

	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{24}	C_{28}	C_{32}
RT Ave.	0.74	1.32	2.05	2.82	3.57	4.30	5.63	6.83	7.98	8.89	10.57	11.96	12.80
St. Dev.	.011	.015	.024	.026	.028	.032	.034	.034	.038	.038	.040	.040	.076
%RSD	1.49	1.18	0.99	0.89	0.79	0.69	0.60	0.52	0.48	0.45	0.39	0.36	0.59

Summary

Simulated Distillation will remain a valuable tool in the daily operation of a modern refinery. The need to improve throughput and efficiency, while maintaining accuracy and precision, continue to push the envelope of chromatographic-instrumentation design. The Clarus 600 GC, with its rapid oven heat-up/cool-down time and stability, provides the analyst with state-of-the-art performance without sacrificing accuracy and precision. The results presented in this document show that the PerkinElmer Clarus 600 GC, combined with PerkinElmer-Arnel Model 3022 Simulated Distillation Software, can achieve 7-minute analysis times with excellent precision. The powerful features of the reporting software further enhance the effectiveness of this high-throughput integrated system.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
Phone: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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