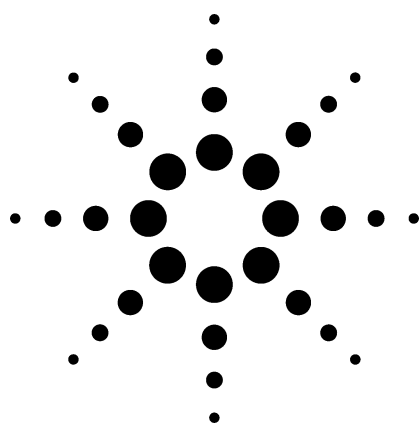


Fast Simulated Distillation Based on Agilent 6890N Gas Chromatograph

Application



Petroleum

Authors

ChunXiao Wang
Agilent Technologies (Shanghai) Co.,Ltd.
412 YingLun Road
Waigaoqiao Free Trade Zone
Shanghai 200131 P.R. China

Roger Firor
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

A rapid simulated distillation method is described for analysis of petroleum fractions boiling within the range of ASTM D2887 [1]. The method employs an Agilent 6890N gas chromatograph (GC) equipped with a split/splitless inlet, flame ionization detector (FID), oven insert, and 3-meter 180- μ m id capillary column. A SIMDIS software package is partially integrated into the GC ChemStation for data analysis and SimDis calculations. Compared to conventional ASTM D2887, the accelerated method yields run times at least two times faster. It yields results comparable to traditional D2887, and agrees with the guidelines of ASTM method D2887 based on published results for the reference gas oil (RGO).

Introduction

ASTM D2887 is widely used in the refining industry. The method is designed to determine the boiling range distribution of petroleum products and

fractions having a final boiling point of 538 °C or lower. Agilent has developed a SimDis system including an easy-to-use software package. For details see reference [2]. High-throughput labs can benefit from the faster cycle times possible when short, narrow-bore capillary columns are used. This application employs 180- μ m id columns as a good compromise between speed and ease of use. Faster D2887 runs (greater than 2X speed gain) are certainly possible, however, high oven ramp rates, available only with a 220 V GC and/or 100- μ m id columns, are needed. For example, using the 220 V GC with oven insert will allow oven ramps of up to 65 °C/min when programmed from 30 °C to 450 °C. This configuration is recommended if faster analyses are required. Use the Agilent method translation software available as a download from www.chem.agilent.com to investigate other column/oven ramp rate scenarios.

Experimental

Experiments were performed on an Agilent 6890N GC (120 V version) with electronic pneumatics control configured with a split/splitless inlet, 7683 automatic liquid injector, FID, and a 3 m \times 180 μ m \times 0.4 μ m DB-1 capillary column. An oven insert (Agilent part/number G2646-60500) was used for fast chromatography in order to reduce the oven volume so that the column and sample are heated more quickly and yield faster separation and chromatography. Furthermore, the smaller volume oven cools faster than a full-sized one, thus reducing the overall analytical cycle time. A qualitative mixture of normal paraffins, C5 to C40, is used to



determine the boiling point (BP) versus retention time (RT) relationship over the range required by method D2887. In this application it is critical to choose the appropriate liner for the split/splitless inlet. A single taper liner (Agilent part/number 5183-4647) with glass wool positioned to “wipe” the syringe needle is required. The column is prepared by measuring and cutting a 3-meter piece of a 10-meter column (Agilent part/number 121-1013).

General instrument conditions used for this method are listed in Table 1.

Table 1. Gas Chromatographic Conditions

Inlet temperature	325 °C
Split ratio	50:1
Injection volume	0.1 µL
Column	DB-1, 3 m × 180 µm × 0.4 µm
Column flow program (He)	1.5 mL/min, hold 0.5 min, 80 °C /min, 5 mL/min, hold 8 min
FID temperature	350 °C
H ₂ flow	40 mL/min
Air flow	450 mL/min
Make up (N ₂)	45 mL/min
Oven program	35 °C to 350 °C at 30 °C/min, hold 0.5 min
Data acquisition rate	5 Hz

The process of SimDis analysis includes blank analysis, calibration (C5–C40), validation (reference gas oil No.1 for ASTM D2887) and sample analysis. The analysis process can be automated through the GC ChemStation coupled to Agilent SIMDIS software (G2887-90020).

SIMDIS Software

The SIMDIS application software can be operated in a stand-alone mode for post-run processing or called automatically to execute as a post-run event from on-line ChemStation. Its function is described in greater detail in other application notes. For details see references [2] and [3].

Result and Discussion

Calibration

Calibration mixtures containing a series of known n-alkanes from C5 to C40 are used to establish the BP-RT correlation. The 3-meter column provides a fast separation of hydrocarbons while maintaining

good separation between C5 and C6 alkanes. The Agilent 6890 GC (120 V) configured with oven insert for fast temperature programming allows an oven ramp rate of 30 °C/min over the temperature range 35 °C to 350 °C, resulting in a twofold speed gain over a conventional D2887 analysis. An oven ramp rate of 30 °C/min is approximately the maximum possible using a 120 V 6890 with oven insert over the temperature range required for D2887.

Figures 1 and 2 compare the calibration standard analyzed using the fast SIMDIS method and the conventional D2887 method respectively. Conventional D2887 is performed on the 6890 GC configured with a 10 m × 530 µm × 2.65 µm DB-1 column [2].

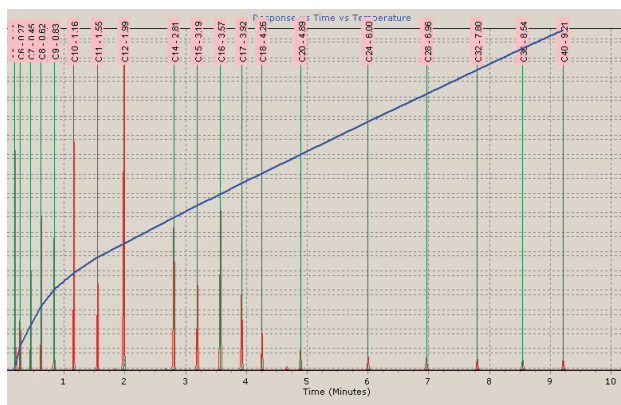


Figure 1. Calibration standard analysis using the fast SimDis method, showing C5–C40 peak assignments. Column: DB-1, 3 m × 180 µm × 0.4 µm. Oven program: 35 °C to 350 °C at 30 °C/min, and hold 0.5 min.

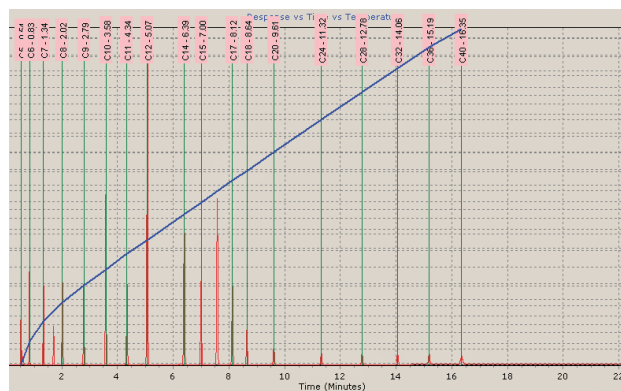


Figure 2. Calibration standard analysis using conventional D2887 method, showing C5–C40 peak assignments. Column: DB-1, 10 m × 530 µm × 2.65 µm. Oven program: 40 °C to 350 °C at 20 °C/min, and hold 8 min.

RG0 Analysis

Figure 3 shows a chromatographic overlay of 20 consecutive injections of RG0. Run-to-run deviations over the entire chromatographic time range are small, indicating good system performance. Statistics for these runs are shown in Table 2.

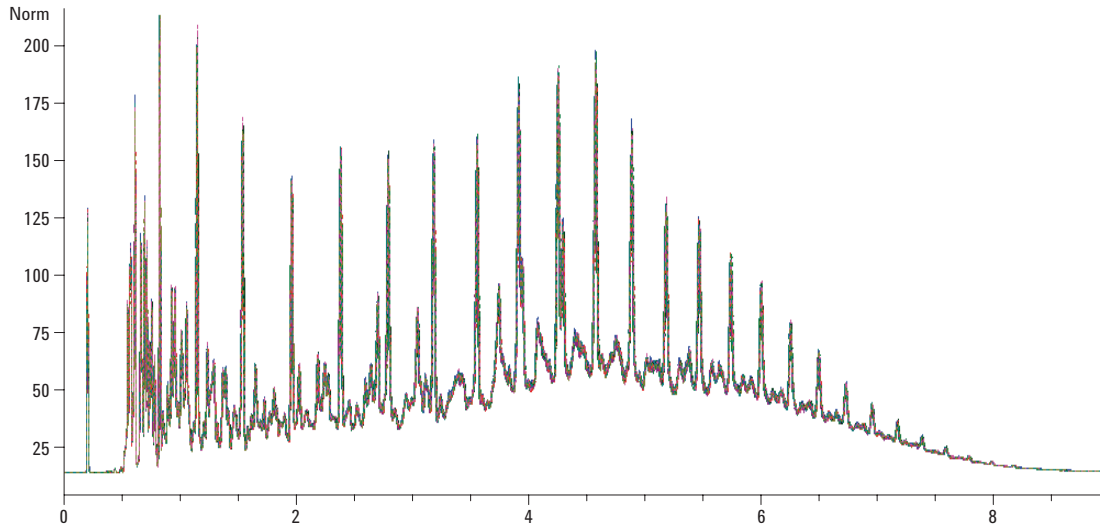


Figure 3. Chromatographic overlay of 20-run RG0 fast analysis. Column: DB-1, 3 m × 180 μm × 0.4 μm
Oven program: 35 °C to 350 °C at 30 °C/min, hold 0.5 min.

Table 2. Statistics for 20 Consecutive Runs of RG0

% OFF	Average	STDEV	% RSD
IPB: 0.5	118.0	0.00	0.00
5	150.0	0.00	0.00
10	174.0	0.00	0.00
15	200.8	0.37	0.18
20	224.3	0.57	0.25
25	243.0	0.51	0.21
30	258.6	0.50	0.19
35	272.6	0.50	0.18
40	287.4	0.50	0.17
45	301.6	0.49	0.16
50	310.1	0.31	0.10
55	318.0	0.00	0.00
60	329.1	0.37	0.11
65	339.5	0.51	0.15
70	350.6	0.49	0.14
75	362.6	0.50	0.14
80	374.9	0.31	0.08
85	388.3	0.49	0.13
90	403.0	0.39	0.10
95	424.0	0.60	0.14
FBP: 99.5	466.1	1.02	0.22

Table 3 shows results for the 20 RG0 analyses. The data demonstrate that observed BP values agree with the ASTM consensus BP values within the allowable difference range.

Table 3. Results for RG0 Fast SimDis. Results in °C

ASTM D2887 values		Observed values		
OFF%	BP	Allowable difference	BP (Average n = 20)	Difference
IBP	115	7.6	118.0	-3
10%	176	4.1	174.0	+2
20%	224	4.9	224.3	-0.3
30%	259	4.7	258.6	+0.4
40%	289	4.3	287.4	+1.6
50%	312	4.3	310.1	+1.9
60%	332	4.3	329.2	+2.8
70%	354	4.3	350.7	+3.3
80%	378	4.3	374.9	+3.1
90%	407	4.3	403.1	+3.9
FBP	475	11.8	466.1	+8.9

Table 4 shows a comparison of RGO fast analysis to conventional D2887 analysis. The results indicate good consistency between the two methods.

Table 4. Comparison of RGO Fast SimDis to Conventional D2887. Results in °C

OFF%	ASTM D2887 values		Fast (Ave BP, n=10)	D2887 (Ave BP, n=10)
		BP		
IBP		115	118.0	113.3
10		176	174.0	177.8
20		224	224.0	227.2
30		259	258.3	262.8
40		289	287.2	292.2
50		312	310.0	314.4
60		332	329.1	332.8
70		354	350.5	355.6
80		378	374.9	379.4
90		407	403.2	409.4
FBP		475	466.5	466.7

Cat Cracker Feed Analysis

Table 5 lists the results for 10 consecutive runs of cat cracker feed. The results show excellent repeatability.

Table 5. Repeatability of Cat Cracker Feed Analysis. Results in °C

OFF%	1	2	3	4	5	6	7	8	9	10	Average	RSD%
IBP	196	196	196	196	196	197	197	197	197	200	196.8	0.27
10	299	299	299	299	300	300	300	300	300	301	299.7	0.18
20	333	333	334	333	334	334	334	334	334	335	333.8	0.15
30	358	358	359	358	359	359	359	359	359	360	358.8	0.14
40	379	380	380	379	379	380	380	380	380	380	379.7	0.13
50	399	399	399	399	399	399	399	399	399	400	399.1	0
60	417	418	418	417	418	418	418	418	418	418	417.8	0.11
70	437	437	437	437	437	437	437	437	437	437	437.0	0
80	459	460	460	460	460	460	460	460	460	460	459.9	0.07
90	493	493	494	493	493	494	494	493	494	494	493.5	0.11
FBP	566	568	568	569	568	568	569	568	568	568	568.0	0.15

Conclusions

A 10-min simulated distillation method was demonstrated on the Agilent SimDis system. The fast method is suitable for petroleum fractions in the range covered by ASTM D2887. The procedure using a short, small-diameter capillary column, 3 m × 180 μm × 0.4 μm, achieves a two-fold speed gain over a conventional D2887 analysis while maintaining the same ease-of-use associated with 530-μm id columns. The results obtained from the fast SimDis method are comparable to that from D2887, and agree with the ASTM D2887 consensus BP values within the allowable percent off windows. The method can easily be deployed in routine labs where high throughput is required. Additional time savings can be achieved using the 220 V 6890 GC with oven insert. This configuration allows oven ramp rates up to 65 °C/min (35°C to 450°C).

References

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