🕀 SHIMADZU

Application News

Gas Chromatography

SSI-GC-001

High Temperature Simulated Distillation using Shimadzu GC-2010

Introduction

ASTM D 7169, a simulated distillation GC (DGC) method that extends the boiling point profile up to 720°C (corresponding to the elution of n-C100), is used in the petro-refinery industry to monitor the refining process of a feedstock by profiling the boiling point distribution characteristics.

Differing from existing ASTM DGC methods such as D2887, 3710, 5307, 6352, etc, D7169 is for crude oil applications, primarily targets at high boilers that do not easily elute out of a GC column. In this study, a Shimadzu GC-2010 based DGC system was employed to determine boiling point distribution of crude oil samples.

Principle

To improve productivity, DGC methods have been widely practiced to replace old distillation methods such as D86 and D1160, which are time and labor consuming, and also require complicated operating procedures. In DGC methods, retention times are directly correlated to boiling points and detector responses are correlated to the hydrocarbon concentrations.

A calibration curve can be generated by plotting boiling points of n-alkanes as a function of retention times, and sliced peak intensities represent the sample amount distilled. To do so, reproducible retention times and automated software are highly desirable. The GC-2010, equipped with an advanced flow controller, meets the hardware requirements, and Shimadzu distillation GC software for GCsolution is able to achieve automation by integrating calibration, integration, calculation, and report functions.





Experimental

GC system:	Shimadzu GC-2010, OCI/PTV injector, FID detector, AOC-20i/20s autosampler.
Software:	Shimadzu GCsolution 2.31 and Distillation GC software 2.00
Column:	Restek MXT-1HT, 5m X 0.53mm X 0.2µm
Inj. Liner:	Stainless steel OCI liner
Inj.:	0.2 µL Direct, He carrier, Column Flow: 18.00mL/min; Purge Flow: 0.5mL/min.
Inj. Temp:	40°C to 430°C @ 10°C/min, hold 5 min
Oven Temp:	35.0°C to 430°C @ 10°C/min, hold 10 min
DET Temp:	430°C, He Makeup, Makeup 12.0mL/min, H ₂ 40.0mL/min, Air 400.0mL/min.

Sample Preparation

Standard samples: Prepared 0.5% Polywax 655 CS_2 solution, then mixed with equal volume of D2887 SimDist standard. Both Polywax 655 and D2887 standards are from AccuStandard. **Sample Pretreatment**: 0.2g sample were measured and dissolved in 20 mL CS_2 . Three replicate runs were conducted from different 1.5mL vials. A solvent blank run was performed between each sample as a negative control. The solvent blank was also subtracted from sample chromatograms when processing the data.

Chromatograms



Figure 1: Chromatogram of ASTM D2887 Standard



Figure 2: Chromatogram of Polywax 655 Standard



Figure 3: Chromatogram of ASTM D2887 Standard plus Polywax655



Figure 4: Solvent blank



Figure 5: Reproducibility Study: RSD% < 0.05% for most of the peaks



Figure 6: Chromatogram of Sample I



Figure 7: Chromatogram of Sample II



Figure 8: Chromatogram of Sample III

Calculations and Report



Figure 9: Calibration curve: Boiling point *vs.* retention time, calibration curve is calculated by the software, based on n-paraffin chromatography

📲 Distilla	ation GC In	itial Setti	ng(GC 1)-	[C:\GC	solution \	dgc1\par.	×		
<u>F</u> ile <u>E</u> dit	<u>H</u> elp			C	istillation GC Ini	tial Setting(GC 1	.)-[C:\		
	6 🖻 💼								
Entry	Parameter File Setting								
	FILE : 7169.PAR								
Calibration Initial	Method :	Total Area		-					
Setting	ASTM Correction Terminus Automatic								
	O D-86	30 EFV	/TBP Correcti	on	Variety Proportion(%):	0.010			
Parameter File Setting	Internal Star	ndard Range (C):						
The Setting	IBP	FBP	Upper Limit Temperature	e					
	240.	0 310.	0 720.	0					
Report File	Number of	Specified Te	mperature Ra	ange :	1	(C)			
Setting	Range	IBP	FBP	Range	IBP	FBP			
	1	0.0	720.0	6					
	2			7					
	3			8					
	4			9					
	5			10					

Figure 10: Parameter settings







Figure 12: Simulated distillation curve

**** BOILING RANGE DISTRIBUTION ****

SAMPLE NAME	VTB
SAMPLE ID	10-027
SAMPLE TYPE	UNKNOWN
ANALYSIS TIME	0201/03/24_0_8:40:22 PM
TOTAL AREA	TOTAL AREA
OUTPUT FILE	C:\GCsolution\dgc1\data\VTB1.DAT
CALIBRATION FILE	C:\GCsolution\dgc1\Calib\SIM_High_Temp.CLB
PARAMETER DATA FILE	C:\GCsolution\dgc1\PARM\7169.PAR
REPORT DATA FILE	C:\GCsolution\dgc1\PARM\7169.REP
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GC DATA

%OFF	BP	BP	Rt (min)	
	(0)	())	1207	
	374.0	700.2	15.07	
	400.5	702.0	17.24	
2	433.5	8295	18.21	
 	440.0	8597	18.99	
5	468.9	876.0	19.62	
10	498.0	9285	21 71	
15	5161	9610	23.05	
20	530.6	9871	24 12	
25	542.4	1008.3	25.02	
30	55.3.2	10278	25.83	
35	563.3	1046.0	26.61	
40	572.6	1062.7	27.36	
45	582.1	1079.7	28.12	
50	591.2	1096.2	28.88	
55	600.7	1113.3	29.67	
60	610.6	1131.1	30.48	
65	620.4	1 1 48.8	31.33	
70	631.1	1168.0	32.22	
75	641.7	1187.0	33.18	
80	653.8	1208.8	34.22	
85	667.0	1232.5	35.33	
90	682.4	1260.3	36.57	
95	698.7	1289.7	38.02	
96	703.0	1297.4	38.34	
97	707.6	1305.6	38.67	
98	712.3	1314.2	39.03	
99	717.5	1323.6	39.41	
L FBP	720.3	1328.6	39.61	
VABP	591.194	(C)	1096.149 ((F)

Figure 13: Simulated distillation data

Discussions

Robust hardware and automated software are critical to ASTM D7169. The GC-2010, with an advanced flow controller running at 'Linear velocity' mode, has proved to be effective. The reproducibility study has shown retention time RSD% are less than 0.05% for most of the peaks, except for low and high boilers, as shown in Figure 5. The adoption of a CO₂ cryo-cooling unit could potentially lower the initial boiling point to 0°C (corresponding to n-C4). However, this configuration has not been investigated in this study. With improved GC column technology, seeing n-C100 is no longer a problem. It is worth to note though, heterogeneous sampling may affect final results. One abnormal result observed during the study is that it disagreed with the other two parallel runs. In this case, the results from the other two runs can be considered to be accurate results. Additional runs can be performed to further confirm the results.

DGC software has achieved fully automated data analysis. Two data processing methods were adopted. First, a calibration method was used to generate a calibration curve, establishing correlations between retention times and alkane boiling points, as illustrated in Figure 9. Second, an integration method was created to define an integration retention window and make slice cuts. Then the results can be automatically calculated and reported, depicted in Figures 10 to 13.

Furthermore, solvent blank runs are important not only to verify the system cleanness but also to compensate for baseline drifts by being subtracted from sample chromatograms to obtain undistorted DGC results.

Conclusions

The robust GC-2010 hardware, integrated with Distillation GC software, has achieved fully automated DGC boiling points determination, in compliance with method ASTM D 7169. The reproducibility study has shown retention time RSD% are less than 0.05% for most of the peaks, except for low and high boilers.

References

- (1) Shimadzu Application Note "Simulated Distillation Analysis of Heavy Canadian Crude Oil by ASTM D 5307", 2009.
- (2) ASTM D7169-05 "Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography", September 2005.

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