COMBINING SIMULATED DISTILLATION (ASTM D7169) AND DETAILED HYDROCARBON ANALYSIS (ASTM D7900) FOR THE FULL BOILING POINT DISTRIBUTION OF CRUDE OILS

Introduction

Physical distillation is still considered the reference method for distillation. Simulated Distillation (SIMDIST) by gas chromatography offers significant advantages over the physical procedure, making this technique a quick, cheaper alternative to physical distillation. Analysis by Gas Chromatography (GC) typically has better precision, higher throughput, less hands-on time, and lower cost per sample. Also, SIMDIST requires considerably less sample to be run and can generally be considered the safer of the two techniques. SIMDIST is very suitable to characterise crude oils.

Knowledge of the boiling point distribution of stabilised crude oils is important for the marketing, scheduling, and processing of crude oil in the petroleum industry. ASTM methods D7900 and D7169 can be combined to determine the boiling point distribution of crude oils. For crudes with a significant light end this will be recommended.

SIMDIST method ASTM D7169 is widely used for determining the boiling point distribution of crude oils up to a final boiling point of 720°C. However, this method will give an incomplete result for the separation of C_4-C_9, due to the thin film column in the presence of large amounts of carbon disulfide. This problem can be solved by combining the results of ASTM D7169 with results from another GC, usually configured for ASTM D7900. This method will analyse the light end fraction of the crude oil, up to and including nonane. Results of both methods are merged into one boiling point distribution, which will give a more accurate data range of the crude oil.

Experimental

ASTM D7169 determines the boiling point distribution of crude oils and residual samples up to a final boiling point of 720°C. This corresponds to the elution of n-C100. The method determines the boiling point distribution of samples from n-C_9 up to n-C_{100}.

This method can also be used to obtain the boiling point distribution of samples that do not fully elute, such as atmospheric and vacuum residues. The amount of residue (or sample recovery) is determined using an external standard. This provides insight into composition and allows for the determination of intrinsic product value.

Table 1. Method Parameters of ASTM D7169 and ASTM D7900

	ASTM D7169	ASTM D7900
Injector	Cold on Column, Air Cooling, 0.5µL	Split/Splitless, Split 1:100, 0.2µL
Column	SCION-SIMDIST	Precolumn: SCION-1 Analytical Column: SCION-DHA
Oven	-20°C, 15°C/min to 430°C (10 mins)	35°C (30 mins), 2°C/min to 115°C,10°C/min to 200°C (5 mins)
Carrier Gas	Helium, 20mL/min	Helium
Detector	HT FID, 435°C	FID 300°C
Software	CompassCDS with SIMDIST	CompassCDS with DHA

A qualitative mixture of normal paraffins covering the range from C_5 up to C_{100} is used to determine the relationship of boiling point (BP) versus retention times (RT). Reference oil 5010, which fully elutes from the column, is used to determine the detector response factor. CS_2 blanks are run, and the resulting signal is subtracted from the response standard and the samples. Samples are injected and with the use of the response standard the recovery of the sample is calculated. A boiling point distribution can be calculated up to the recovered amount. Customised cut point reports can also be calculated.

ASTM D7169 yields an unreliable boiling point distribution for the front-end fraction of a crude, therefor ASTM D7900 is used. This method determines the boiling point distribution of hydrocarbons in crude oil up to n-C_9. Results of both methods are combined into one boiling point distribution.

An internal standard is quantitatively added to the crude oil. A small amount is injected onto a precolumn. When the front-end fraction ($<C_9$) has reached the analytical column, the precolumn is backflushed to vent the higher boiling components.

The components are identified by comparison of reference chromatograms and specialist DHA/SIMDIST software. The software can group individual components by hydrocarbon type. According to the composition of the front-end fraction the boiling point distribution will be calculated.

Samples included a D7169 Calibration standard, standard n-alkanes standard, Reference Oil 5010 and a Crude Oil.

Table 1 details the GC configuration and method parameters for the combined ASTM D7169 and D7900 analysis.

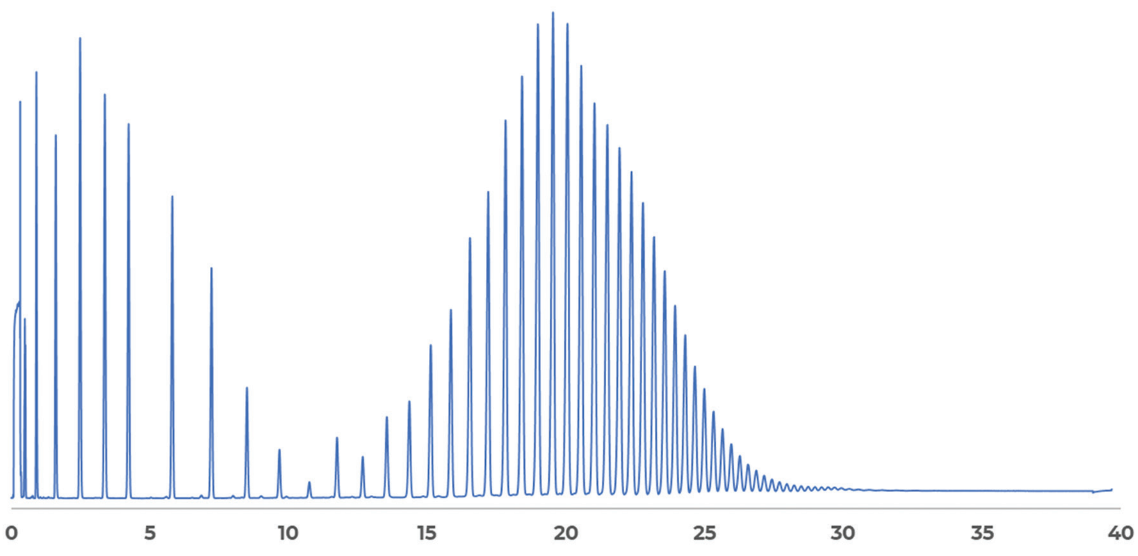

Figure 1. Chromatogram of D7169 calibration standard (C_5-C_{100})

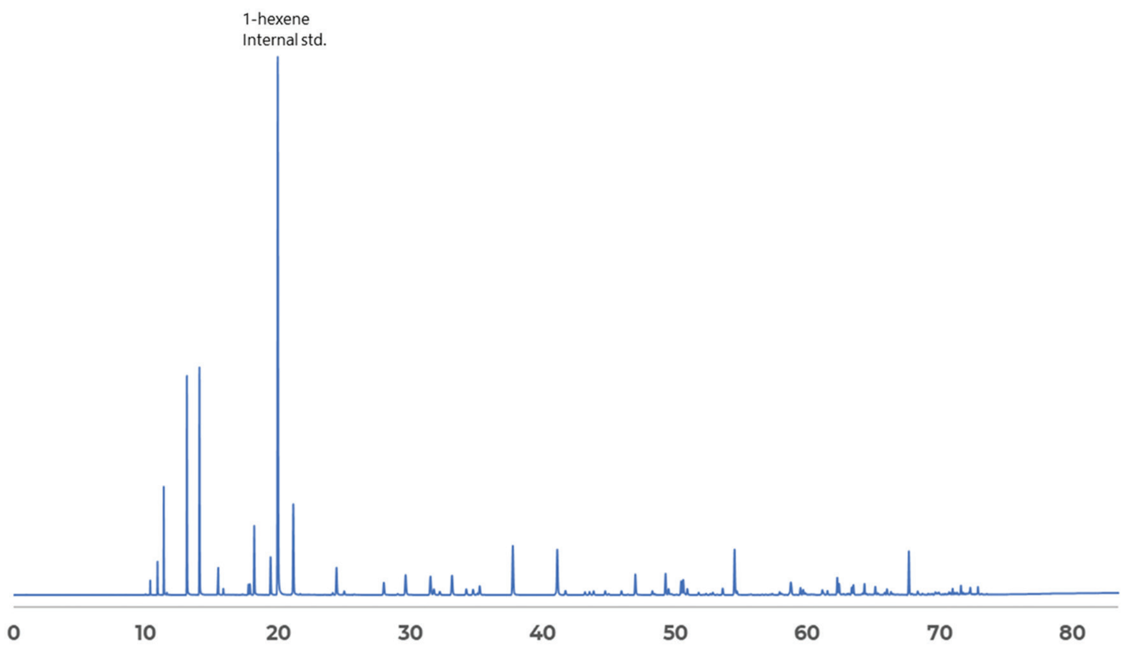

Figure 2. Front end analysis of crude oil sample to ASTM D7900 specifications

Table 2. Results of Reference Oil sample, reference values and allowable differences for ASTM D7169

% Off	CoA Result (°C)	Allowable Difference (°C) (ASTM Criteria ±)	Result (°C)	Actual Difference (°C)
IBP	427.4	9	431.5	4.1
10	493.3	3	492.5	0.8
20	510.5	3	509.5	1
30	524.5	4	523.5	1
40	537.1	4	535.5	1.6
50	548.7	4	547.0	1.7
60	560.4	4	558.5	1.9
70	572	4	570.0	2
80	585.1	4	583.0	2.1
90	602.1	4	599.5	2.6
FBP	656.3	18	644.0	12.3

Table 3. Merged Boiling Point Distribution Report of Crude oil (ASTM D7169 and ASTM D6900)

Recovery Mass (%)	TBP (°C)	Recovery Mass (%)	TBP (°C)
IBP	-10.9	55.0	368.2
5.0	31.3	60.0	402.3
10.0	67.6	65.0	436.4
15.0	98.8	70.0	475.0
20.0	136.1	75.0	520.9
25.0	165.6	80.0	577.6
30.0	202.1	85.0	639.8
35.0	238.4	90.0	710.5
40.0	271.4	95.0	NF
45.0	303.2	FBP	NF
50.0	333.8		

Results

Figure 1 shows a chromatogram of the ASTM D7169 Calibration standard, C_5-C_{100}.

A Reference Oil (5010) was analysed to verify that the requirements of ASTM D7169 were met with the above GC configuration. Table 2 details the requirements of ASTM D7169 and the results obtained from the analysis of the Reference Oil sample.

All obtained results successfully met the criteria of the ASTM D7169 method, highlighting that the above GC configuration can be used for the accurate qualification and quantification of boiling point distribution in crude oils.

Front end analysis was performed on a crude oil sample, as per ASTM D7900 specifications. Figure 2 shows the chromatogram of the front end analysis including 1-hexane as internal standard.

A group report of front end fraction (mass %) was merged with the data obtained during ASTM D7169 analysis to calculate a total boiling point distribution of the crude oil. Table 3 shows the merged boiling point distribution of the crude oil sample (using ASTM D7169 and ASTM D6900 data).

Conclusion

Simulated distillation can provide a very suitable alternative for conventional distillation methods. They typically provide a much more robust, economical, safe, automatable, and easy solution for obtaining accurate boiling point and cut point data for petroleum products, feedstocks and other petroleum fractions as specified in these different methods.

For crude oils with a significant light end it is advised to combine a High temp SIMDIST (ASTM D7169) with a front-end Detailed Hydrocarbon Analysis (ASTM D7900). Due to large amounts of CS_2 the SIMDIST method will give an incomplete result for the separation of C_4-C_9. Front-end DHA ASTM D7900 will cover this analysis. Merging data from both methods will give a more accurate data range of crude oil. A complete boiling point distribution can be calculated. Customised cut point reports can also be made.

SCION Instruments developed a solution for merged High Temp SIMDIST ASTM D7169 and Front-end DHA ASTM D7900 using specialist software, to produce the best results for analysing crude oils.

Author Contact Details

Esther Van Bloois,
Applications Specialist
– SCION Instruments,

- Amundsenweg 22-24, Goes, The Netherlands
- Tel: +31 (0) 113 287 600
- Email: estherv@scioninstruments.com
- **Web: www.scioninstruments.com**