Application Note 10364

High Temperature Simulated Distillation According to ASTM D6352 using a Dedicated GC Analyzer

Vivek Dhole, Madhuli Narkesari
Thermo Fisher Scientific, Nasik, India

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Ioduction

The simulated distillation (SIMDIST) is a GC technique used to simulate the data of a laboratory distillation of medium and heavy petroleum distillate fractions. The boiling point determination of the petroleum compnents is an important component of the refinery processes. The GC SIMDIST analysis is a widely used method replacing the cumbersome and costly laboratory distillation methods.

A number of standard American Society for Testing and Materials (ASTM). ASTM methods need to be considered for GC-SIMDIST analysis. The important ones are:

(1) ASTM D2887 is used for the lower boiling point range from 55 ˚C to 538 ˚C
(2) ASTM D3710 is described for the gasoline fraction with a final boiling point up to 260 ˚C .
(3) ASTM D6352 is used for the analysis of the heavier petroleum fractions with an extended boiling range from the initial boiling point (IBP) of 174 ˚C to the FBP of up to 700 ˚C , representing a carbon chain number of approximately C10 to C90.

In this application the Thermo Scientific™ TRACE™ 1110 GC SIMDIST Analyzer is used for the characterization of various petroleum fractions for the quality control laboratories in petroleum refineries. This method is intended to describe and demonstrate the procedure of the SIMDIST Analyzer according to the ASTM D6352 standard method.

EXPERIMENTAL

GC Configuration

The Thermo Scientific SIMDIST Analyzer system comprises a Thermo Scientific TRACE 1110 GC equipped with flame ionisation detector (FID) and the dedicated MXT™-500 SIMDIST column, length 6 m, ID 0.53 mm, and a film thickness of 0.15 µm. This GC column is uniquely characterized by a special carborane dimethyl polysiloxane phase for high temperature applications up to 430 ˚C oven temperature. The column is a very solid unbreakable stainless steel tubing meeting the resolution criteria for high temperature simulated distillation.

A Polywax™ 655 standard is used as reference compound for determining the boiling points and calibration of the retention times for the carbon number and boiling ranges as required by the ASTM methods, especially by ASTM D6352 for the carbon number range of C10 to C90. The analytical GC conditions are summarized in Table 1.

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Table 1. TRACE 1110 GC SIMDIST Analyser analytical conditions.

Injector PTV temperature program	50 ℃ to 430 ℃ at 200 ℃ / min. hold 12 min.
Split ratio	4:1
Injection volume	2.0 µL
SIMDIST column, dimensions	MXT-500 metal column, length 6 m, ID 0.53 mm, 0.15 µm film thickness
Column flow	10 mL/min, Helium, constant flow mode
Oven program	35 ℃ , 6 min 5.5 ℃ /min to 90 ℃ 10 ℃ /min to 425 ℃ 425 ℃ , 10 min
FID temperature	430 °C
H_2 flow	45 mL/min
Air	255 mL/min
N_2 Make-up	20 mL/min

Calibration Mixture

Polywax calibration standard

A qualitative calibration mixture of C10 to C90 dissolved in CS_2 is required for the ASTM method D6352. This carbon range is obtained by mixing a CS_2 solution of Polywax-655 with the carbon range of C20 to C100 with a second mix standard of C6 to C18 range (Thermo calibration mixture).
The final concentrations of the n-paraffins are in the range of one in 50 parts of CS_2.
Carbon range: A mixture of even numbered n-paraffins from C20 to C100 was dissolved in 10 parts of CS_2.

SIMDIST Expert Software

A dedicated SIMDIST expert software is part of the Thermo Scientific TRACE 1110 GC SIMDIST Analyzer.

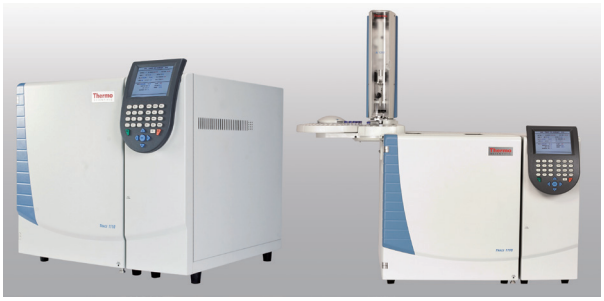

Figure 1. The Thermo Scientific TRACE 1100 GC SIMDIST Analyzer.

The Thermo Scientific™ Chrom-card software is used to acquire the chromatograms of the CS_2 solvent base line and those of the Polywax standards (Polywax-655 with the carbon range of C20 to C100 mixed with a second mix standard of C6 to C18 range) and the reference standard sample (Polywax-655 with the carbon range of C20 to C100 mixed with a second mix standard of C6 to C18 range and treated as a reference sample). Various SIMDIST reports are processed from the acquired chromatogram data to achieve the final results.

RESULTS AND DISCUSSION

Blank Analysis

For SIMDIST calculations a CS_2 solvent blank chromatogram is subtracted from the sample runs. This blank chromatogram is obtained by analysis of the pure solvent CS_2 which is also used for all sample dilutions. The baseline analysis is performed under the same analytical conditions used for the analysis of the standard and the samples. The acquired baseline profile is subsequently subtracted from the sample chromatograms for the SIMDIST calculations to compensate the effects of baseline drift or column bleed (see Figure 2).

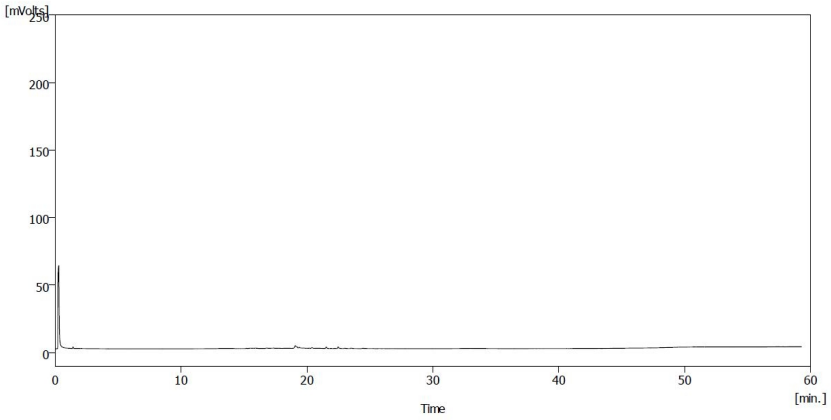

Figure 2. Chromatogram of a CS_2 solvent blank.

Calibration

The prepared Polywax calibration standard covering the required carbon range of C10 to C90 is used for the calibration of the boiling point to retention time (BP-RT) association. A representative chromatogram is shown in Figure 3.

Sample analysis and Repeatability

A reference sample typically comprising of n-paraffins as required in the ASTM method D6352 in the range of C10 to C90 is used for testing the performance of the gas chromatograph in the high temperature range and also to demonstrate the utility of SIMDIST calculation algorithms. The repeatability of retention times is critically important in SIMDIST system. The repeatability achieved with the TRACE 1110 SIMDIST Analyzer is shown with five overlaid chromatograms in Figure 4. The corresponding retention times for some selected carbon numbers are shown in Table 2 for six runs of the Polywax C10 to C90 reference sample.

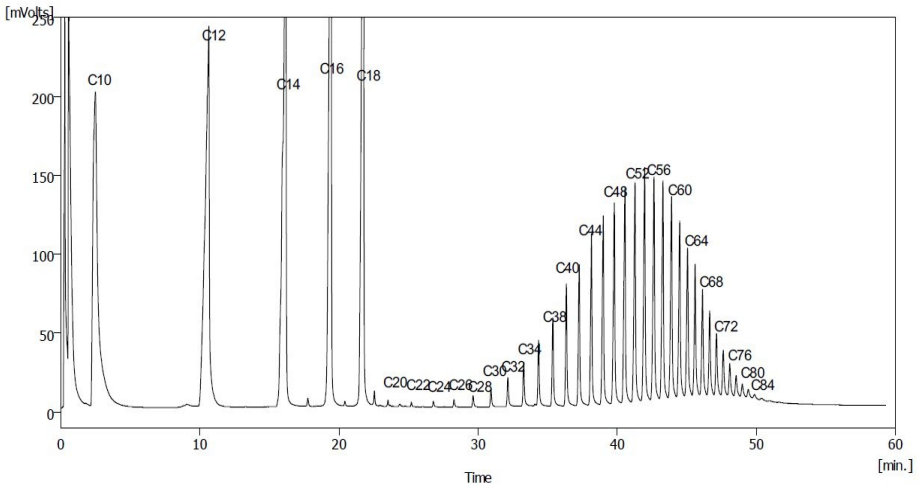

Figure 3. GC chromatogram of the prepared Polywax calibration standard.

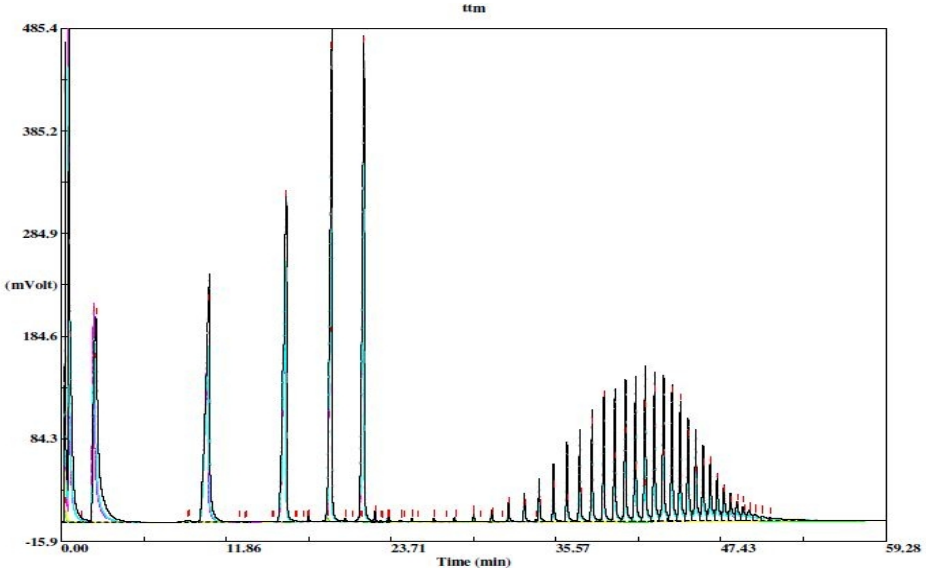

Figure 4. Repeatability of GC chromatograms for the reference sample C10 - C90 with the overlay from five injections as of Table 2.

Table 2. Repeatability of retention times for some selected carbon numbers taken from the GC chromatograms of the C10 to C90 reference sample.

Carbon No.	Run 1 [min]	Run 2 [min]	Run 3 [min]	Run 4 [min]	Run 5 [min]	% RSD n=5
C10	2.4171	2.5002	2.4172	2.4174	2.3338	2.4338
C20	23.5002	23.5001	23.5004	23.5001	23.5003	0.0006
C24	26.8332	26.8331	26.8334	26.8333	26.8332	0.0004
C26	28.3331	28.3335	28.3336	28.3333	28.3334	0.0007
C30	31.0004	31.0002	31.0005	31.0003	31.0002	0.0004
C32	32.1672	32.1678	32.1673	32.1674	32.1675	0.0007
C34	33.3332	33.3336	33.3331	33.3334	33.3335	0.0006
C36	34.4173	34.4171	34.4176	34.4172	34.4174	0.0006
C40	36.3337	36.4174	36.4173	36.3331	36.3335	0.1263
C44	38.1672	38.1676	38.1671	38.1674	38.1679	0.0008

Carbon No.	Run 1 [min]	Run 2 [min]	Run 3 [min]	Run 4 [min]	Run 5 [min]	% RSD n=5
C46	39.0003	39.0002	39.0008	39.0005	39.0004	0.0006
C50	40.5832	40.5838	40.5832	40.5837	40.5834	0.0007
C54	42.0001	42.0007	42.0003	42.0005	42.0004	0.0005
C56	42.6672	42.6675	42.6676	42.6674	42.6671	0.0005
C60	43.9177	43.9172	43.9173	43.9176	43.9175	0.0005
C64	45.0832	45.0836	45.0834	45.0837	45.0833	0.0005
C68	46.1674	46.1671	46.1672	46.1673	46.1675	0.0004
C70	46.6677	46.6674	46.6673	46.6675	46.6672	0.0004
C72	47.1673	47.1675	47.1671	47.1679	47.1674	0.0006
C74	47.6671	47.6675	47.6674	47.6678	47.6673	0.0005
C76	48.1675	48.1672	48.1671	48.1673	48.1679	0.0007
C78	48.5832	48.5837	48.5834	48.5833	48.5831	0.0005
C80	49.0835	49.0834	49.0833	49.0832	49.0837	0.0004
C82	49.5006	49.5003	49.5005	49.5001	49.5002	0.0004
C84	49.9173	49.9177	49.9179	49.9175	49.9176	0.0005

SIMDIS Profiles

For the reference sample comprising of C6 to C90 compounds the SIMDIS profiles using the SIMDIS Expert software have been calculated and shown in Table 3.

Table 3. Distillation ranges obtained by the expert SIMDIS software for different runs of the reference sample.

% Off	Run 1	Run 2	Run 3	Run 4	Run 5
	Temperature in °C				
IBP	56	50	51	54	52
5	111	106	114	115	117
10	135	130	130	124	125
15	174	173	173	174	170
20	183	177	177	180	175
25	215	215	216	216	216
30	251	253	253	251	252
35	253	255	254	253	254
40	284	286	286	284	285
45	287	287	287	287	287
50	313	308	305	313	315
55	315	316	315	315	317
60	464	460	461	461	463
65	541	533	532	535	544
70	566	565	556	566	565
75	584	584	582	584	584
80	603	600	599	600	600
85	621	620	615	616	615

% Off	Run 1	Run 2	Run 3	Run 4	Run 5
	Temperature in ℃				
90	640	640	635	635	635
95	665	666	660	659	658

Distillation Chart profile

This profile is acquired with the help of SIMDIST expert software using the reference RT values and sample chromatogram. A graphical representation gives information on the basic chromatographic profile, retention time and boiling point data either in ℃ or F units. A typical profile for reference standard mix is shown in Figure 5.

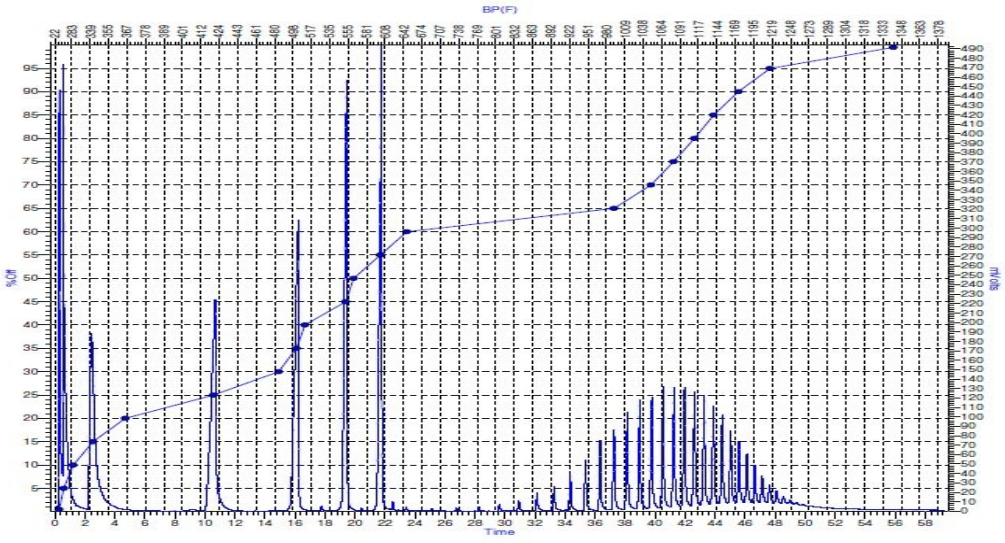

Figure 5. SIMDIST profile for distillation chart for the reference standard mix.

SIMDIST Profile Chromatogram

This profile is generated by the SIMDIST expert software and provides the information about the retention time data and separation of different components in the reference standard mix and samples. A typical chromatogram profile for the reference standard mix is shown in Figure 6.

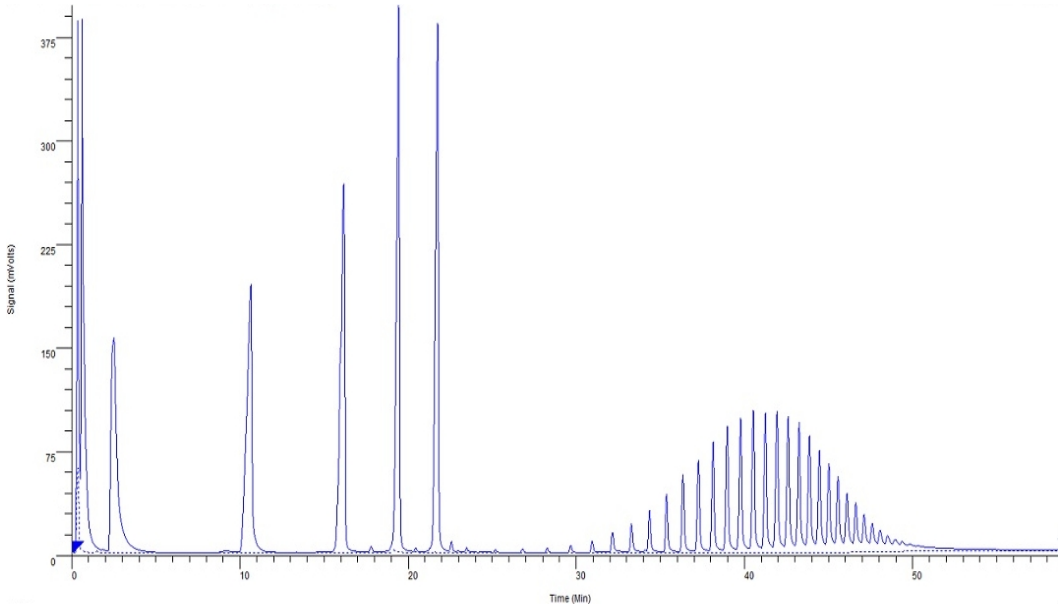

Figure 6. SIMDIST profile chromatogram

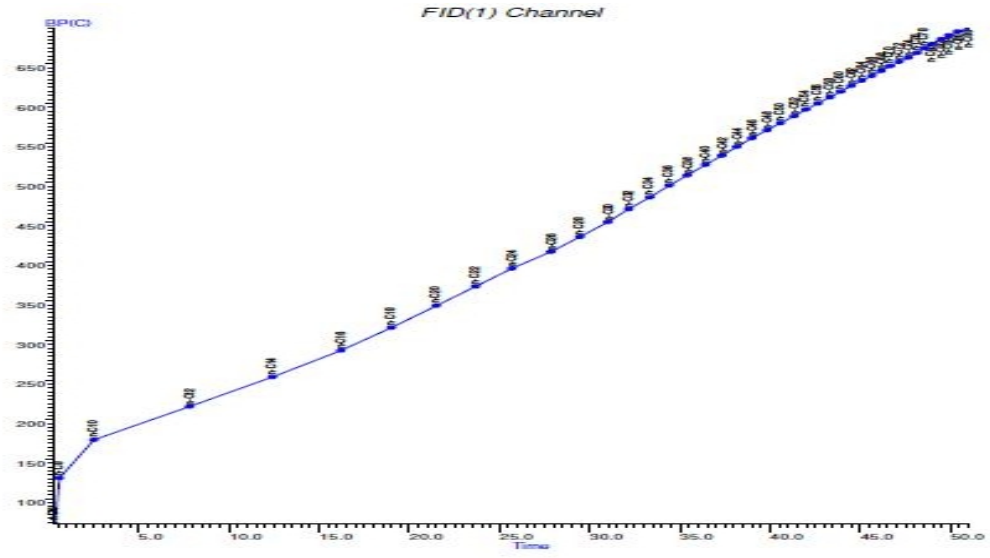

Figure 7. SIMDIS profile for RT calibration

RT Calibration profile

The calibration profile gives the data of SIMDIST retention time to boiling point correlation (RT-BP) calculated by the SIMDIST Expert software. It involves values for the reference standard mix and gives the profile for different samples. Figure 7 shows a typical profile generated for areference standard mix from the reference RT values for standard C-10 to C-90.

Conclusion

The Thermo Scientific SIMDIST Analyzer system is compliant with the performance required by the standard ASTM methods for the petroleum industry.
The repeatability of the retention times is of particular importance for SIMDIST analyses to provide reliable and repeatable RT-BP data for the petroleum fraction samples. The Thermo Scientific SIMDIST Analyzer system based on the TRACE 1110 GC offers excellent repeatability of the retention times and a good separation of the wide range of C10 to C90 petroleum hydrocarbons which are most important for SIMDIST analysis.
This application demonstrates that the SIMDIST Expert software can be successfully applied to perform the necessary SIMDIST calculations and documentations compliant with the ASTM specifications D2887, D3710 and D6352.

References:

1) ASTM D2887: Standard test Method for boiling range distribution of petroleum fractions by Gas Chromatography.
2) ASTM D3710: Standard test Method for boiling range distribution of gasoline and gasoline fractions by gas chromatography.
3) ASTM D6352: Standard test Method for boiling range distribution of petroleum distillates in boiling range from 174 to 700 ℃ by gas chromatography.

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