High-Temperature Simulated Distillation System Based on the 6890N GC

Application

Petroleum

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Abstract

An Agilent Simulated Distillation (SimDis) system is described for characterizing petroleum fractions for quality control and monitoring of refinery feedstocks and products. The system uses a 6890N gas chromatograph (GC) equipped with a high temperature programmable temperature vaporizer (HT PTV) inlet designed specifically for simulated distillation analysis. A SimDis software program that couples with the Agilent GC ChemStation provides an easy-to-use solution for simulated distillation analysis. The system allows for a quick determination of the boiling point distribution and cut points of higher boiling petroleum fractions. This application note describes in detail the system designed to perform simulated distillation by ASTM method D6352, and by the proposed ASTM method for petroleum fractions boiling between 100 °C and 615 °C, commonly referred to as D2887X.

Introduction

Determining the boiling point (BP) distribution of mid- and heavy petroleum distillate fractions is essential in monitoring and controlling petroleum refining processes, such as hydrocracking, hydrotreating, visbreaking, or deasphalting. The gas chromatographic simulation of this BP determination can be used to replace difficult and costly conventional distillation methods. Also, this method can be used for product specification testing.

The American Society for Testing and Materials (ASTM) has established several methods for simulated distillation specifying various BP ranges for petroleum fractions. Among them, ASTM D3710 is used to determine the BP distribution of gasoline and gasoline fractions with a final boiling point (FBP) up to 260 °C (500 °F), and ASTM D2887 for a BP distribution between 55 °C and 538 °C 1000 °F). See reference for details on the Agilent system for D2887 [1]. For the analysis of heavier fractions, ASTM D6352 [2] is applicable for distributions with an initial boiling point (IBP) greater than 174 °C (345 °F) and a FBP of less than 700 °C (1292 °F). Lastly, another procedure, commonly known as extended D2887 or D2887X, has been proposed by ASTM for determining the BP range of 100 °C to 615 °C (1114 °F) materials. The Agilent SimDis system is designed to perform any of the aforementioned methods: D2887, D2887X, and D6352.

This application note describes the setup and performance of the Agilent SimDis system for the ASTM D6352 and D2887X methods.

Experimental

The SimDis system uses the Agilent 6890N GC with electronic pneumatic control (EPC) configured with a flame ionization detector (FID) and a metal capillary column (DBHT-SIMD, 5 m × 530-µm id × 0.15-µm film of 100% dimethylpolysiloxane). The Agilent 7683B automatic liquid injector equipped with an SGE 0.5-µL micro-syringe was used for sample introduction into a JAS UNIS 3100 high temperature air-cooled PTV (HT PTV), with appropriate dilution levels, the Agilent 5-µL syringe can also be used. Polywaxes were used to determine the BP versus retention time (RT) relationship over the BP range required by the methods. To determine the BP versus RT relationships, a qualitative mixture of approximately C10–C62 was used for D2887X, while for D6352, a mixture of approximately C10–C90 was used. The Agilent SimDis software module performed the D6352 and D2887X method calculations.

The instrument conditions listed in Table 1 for both methods discussed above are the same except for the PTV inlet program, calibration standards and oven temperature profile.

HT PTV Inlet

This HT PTV inlet, developed by Joint Analytical Systems, GmbH, (Moers, Germany) provides efficient transfer of sample to the column without discrimination. It integrates a coiled wire cartridge for heating in a carefully constructed arrangement for an optimized thermal gradient. The low mass design allows for rapid heating/cool-down rates using only the GC inlet fan for cool down. For simulated distillation applications, the inlet is operated in a split/hot injection mode. The inlet has minimal seals providing a leak-tight system essential when operating the column at temperatures above 350 °C. The Agilent 7683B series injector operating in the fast injection mode is also used with control of the inlet integrated into the ChemStation. Typically, the inlet is ramped rapidly in temperature at the time of sample introduction, held at the maximum programmed temperature for a number of minutes and then cooled back (uncontrolled) to the starting temperature, all during the first half or two-thirds of the GC runs. Sufficient “hold time” at the highest programmed inlet temperature is critical for good peak shape of the higher carbon number peaks. High program rates of 400–500 °C/min can be used for thermally stable analytes such as the hydrocarbons normally encountered in simulated distillation.

The basic SimDis analysis includes column conditioning, blank analysis, calibration, system validation sample analysis, and percent off reporting.

Calibration Mixture

Method D6352 requires a qualitative calibration mixture of n-paraffins from approximately C10 to C90 dissolved in a suitable solvent. In this application note, the calibration is obtained through two steps: first, dissolution of polywax 655 in carbon disulfide (CS_2) followed by the addition of a suitable mixture of n-paraffins from C5 to C18 (Agilent SimDis calibration mix No.2). The final concentration should be approximately one part of n-paraffin to 50 (or 100) parts of CS_2.

Table 1. Gas Chromatographic Conditions for HT Simulated Distillation

HT PTV Temperature programs	40 °C to 440 °C at 200 °C/min, hold 11 min, cool to 40 °C at 100 °C/min (D6352) 50 °C to 420 °C at 200 °C/min, hold 10 min., cool to 50 °C at 100 °C/min (2887X)
Split ratio	2:1 typical
Injection volume for calibration	0.5 µL to 2.0 µL
Injection volume for sample	0.05 µL to 0.10 µL
Column	5 m × 530 µm × 0.15 µm, DBHT-SIMD, part no. 145-1001
Column flow (He)	16 mL/min, constant flow mode
FID temperatures	400 °C
H_2 flow	40 mL/min
Air flow	450 mL/min
Make up (N_2)	45 mL/min
Oven programs	40 °C to 435 °C at 20 °C/min, hold 3 min (ASTM D6352); 40 °C to 420 °C at 20 °C/min, hold 6 min (D2887x); 45 °C to 440 °C at 15 °C/min.
Data acquisition rate	5 Hz

Table 2. Calibration Standards

Standard	Carbon range *	Solvents	Part no.
Polywax 500	C20-C72	CS_2, Toluene, p-xylene	5188-5316
Polywax 655	C20-C100	CS_2, Toluene, p-xylene	5188-5317
Low Boiling Std	C5-C18	Added to PW 500 or 655	5080-8768

* Approximate ranges for Polywaxes

Method D2887X calibration uses Polywax 500. See Table 2 for more details on the BP-RT calibration standards.

Sample Size and Preparation

Careful consideration of the HT PTV inlet and column capacity is necessary for proper sample injection volume and concentration to avoid carry-over and column overload. In this application, the injected sample size ranges from 0.05 µL to 0.1 µL. One part of sample is diluted with about 10–50 parts of CS_2. Injected volumes of the Polywax standards are higher due to the very low solubilities encountered. In this work, CS_2 was used exclusively as the solvent, however; reasonably good solubilities of the Polywaxes in toluene and p-xylene were found, making these an acceptable less toxic alternative to CS_2.

SimDis Software

The SimDis application software can operate standalone or be called to automatically execute as a post-run event from the ChemStation. The software includes the functional modules: Browse, Setup, SimDis, Report, and Automation. Each module provides specific functions to rapidly view data files, set up SimDis parameters, perform SimDis calculations, customize reporting, and track automation.

The Agilent SimDis module provides a number of functions to correct artifacts such as solvent peaks and contributions from baseline, including options for baseline treatment that optimize the SimDis analysis. Once optimized, this collection of parameters can be saved and applied to all future sample analyses.

As an example, the Setup module used for configuring the BP calibration selection (Polywax 655) and Blank (CS_2) selection files is shown in Figure 1. Each chromatogram can be moved about the window and zoomed in or out using simple (left - right button) mouse functions.

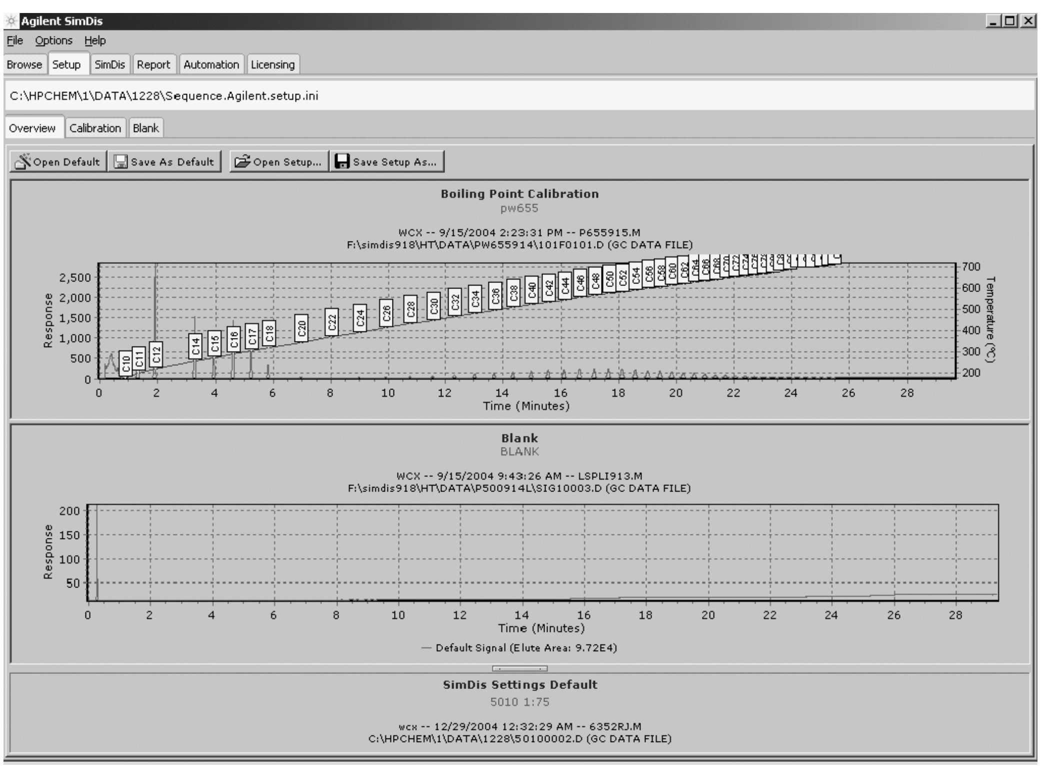

Figure 1. Examples of calibration and blank software panels after editing and selection.

The SimDis module is the core of the software where parameters dealing with the actual simulated distillation calculation are defined and set. For example, this module can set the calculation parameters used for setting the baseline, determining the start-elute (SE) and end-elute (EE) for calculations, eliminating solvent effects, and removing extraneous peaks. Typically, a reference or QA sample is run first to establish appropriate parameters. This setup is then saved (use this sample as default). Now all sequences run from the ChemStation will automatically use these parameters. Figure 2 shows an example software panel where selected parameters are displayed graphically, overlaid on the sample chromatogram. In this screen, the presence of a solvent or extraneous peak that may interfere with the accuracy of SimDis calculations can be factored out. The Sample Elution time function can correct inaccurate calculations by setting the SE time after the extraneous peak (see the marked regions). Also, icons of Elute, EE, the IBP and the FBP at the top left of the menu can be toggled to show the current calculations on the raw signal.

The Report module offers a number of ways to customize reporting of the SimDis analytical results. The dropdown report list presents available report formats and data treatment options for output such as “Calibration Report”, “Engineering Report”, “Complete Percentage Yield”, “Standard Cut Point”, and “Custom Cut Point.”

Result and Discussion

Blank Analysis

Blank analysis is performed to establish and record a baseline profile for subsequent subtraction during simulated distillation calculations. It is done using an identical method as used for sample analysis, usually with the pure solvent that is being used for sample dilution. In this application, an injection of carbon disulfide was used. The CS_2 injection volume was 0.1 µL. Blanks are typically performed prior to sample analysis, and subtracted from the sample signal to remove effects of column bleed that influence baseline offset. It can also be used to check for possible carryover resulting from previous too large injections. See Figure 6.

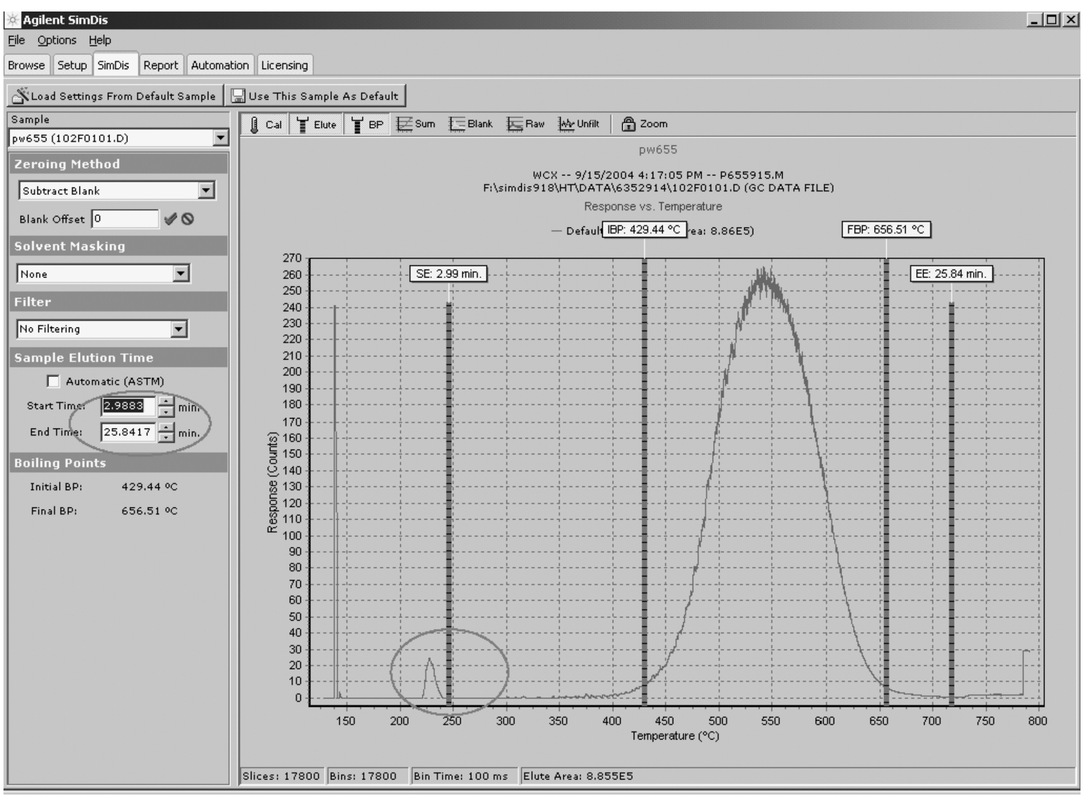

Figure 2. Parameter setup screen example from the SimDis module graphically showing SE, EE, IBP, and FBP.

Calibration

A calibration mixture containing a series of known n-alkanes was used to establish the BP-RT correlation. Polywax 655 plus C5–C18 is used for method D6352. A representative chromatogram is shown in Figure 3.

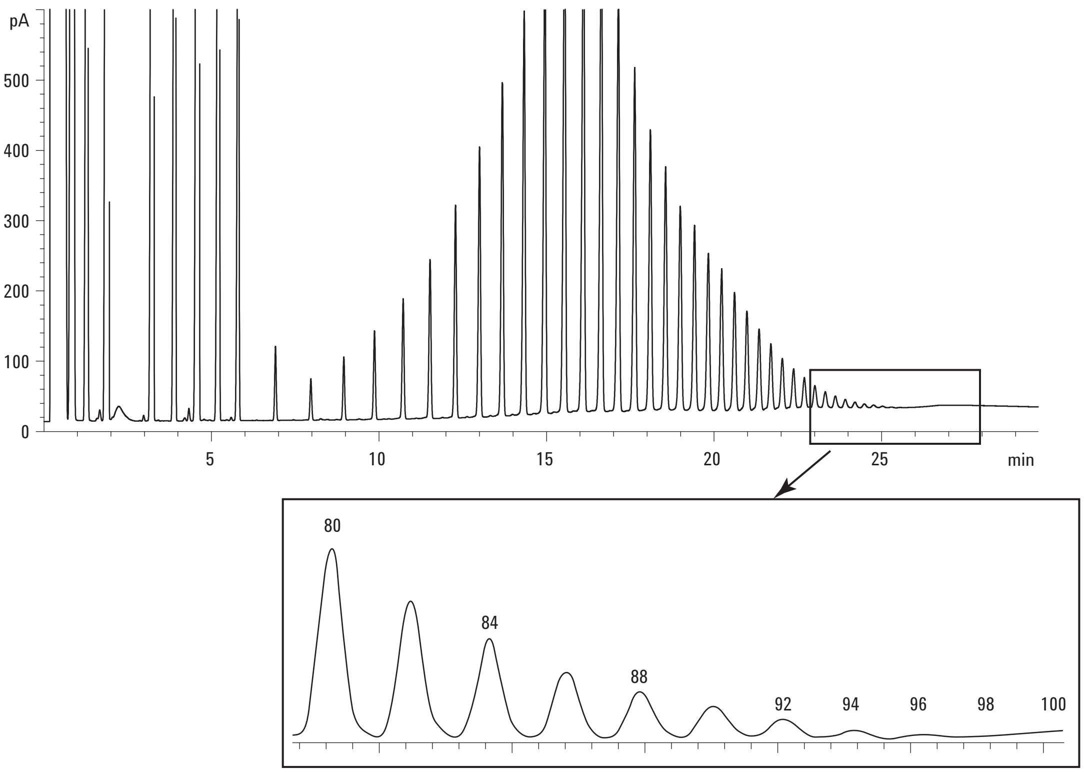

Figure 3. Chromatogram of Polywax 655 + C5–C18. Injected 0.1 µL. GC conditions given in Table 1.

Figure 4 shows the corresponding BP-RT plot. Polywax 500 plus C5–C18 was used for the calibration of method D2887X.

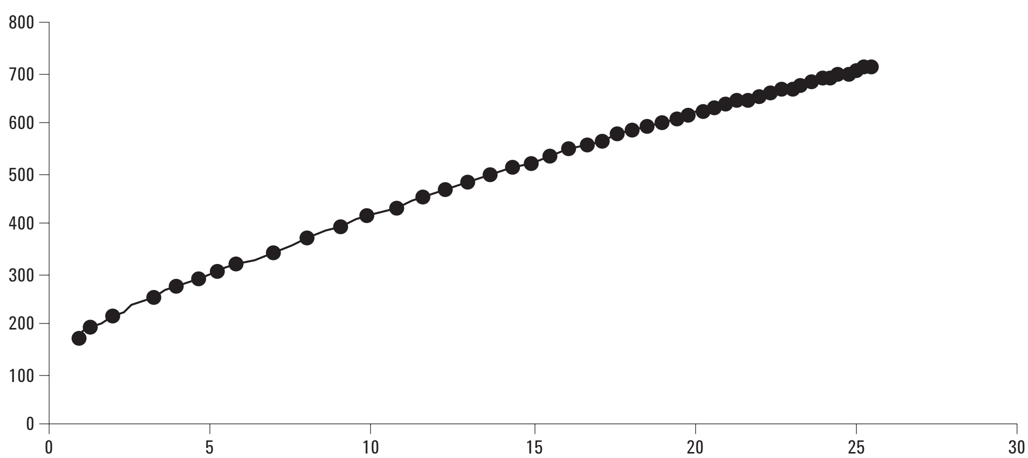

Figure 4. Plot of BP versus RT (min).

The chromatogram of PW500 shown in Figure 5 demonstrates excellent peak shape, a result of the focusing characteristics of the HT PTV inlet equipped with a specialized multirestricted liner.

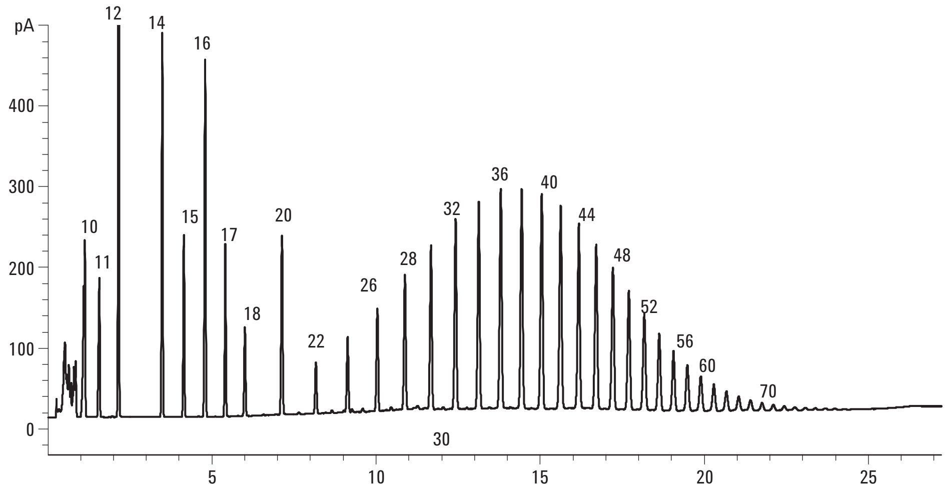

Figure 5. Chromatogram of Polywax 500 plus C5-C18 added. Injected volume 0.1 µL. GC conditions are given in Table 1.

Reference Sample Analysis

Reference sample 5010, as published in method D6352, can be analyzed to verify both chromatographic system performance and the calculation algorithms used. A chromatogram of standard 5010 is shown in Figure 6A. The chromatogram shows a return to baseline by the end of the temperature program, indicating that the sample has completely eluted from the column as required by the method. An engineering report and results are shown in Figure 6B and Table 3, respectively. The data demonstrate that the observed BP values agree with the D6352 consensus values within the allowable difference range published in the method.

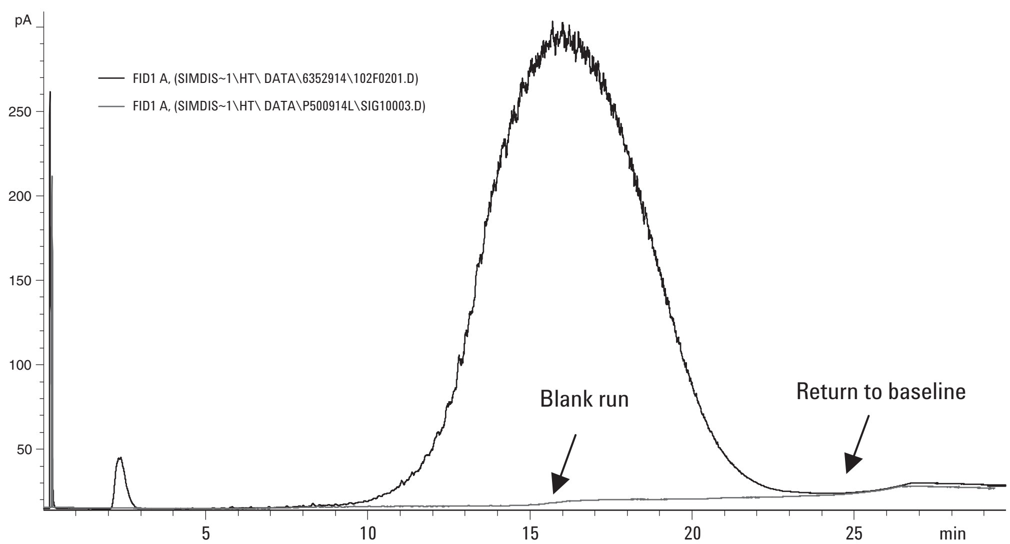

Figure 6A. Chromatographic overlay of reference sample 5010 and blank. Injected volume 0.1 µL (50:1 approximate dilution in CS_2). GC conditions given in Table 1. Polywax 655 was used for calibration.

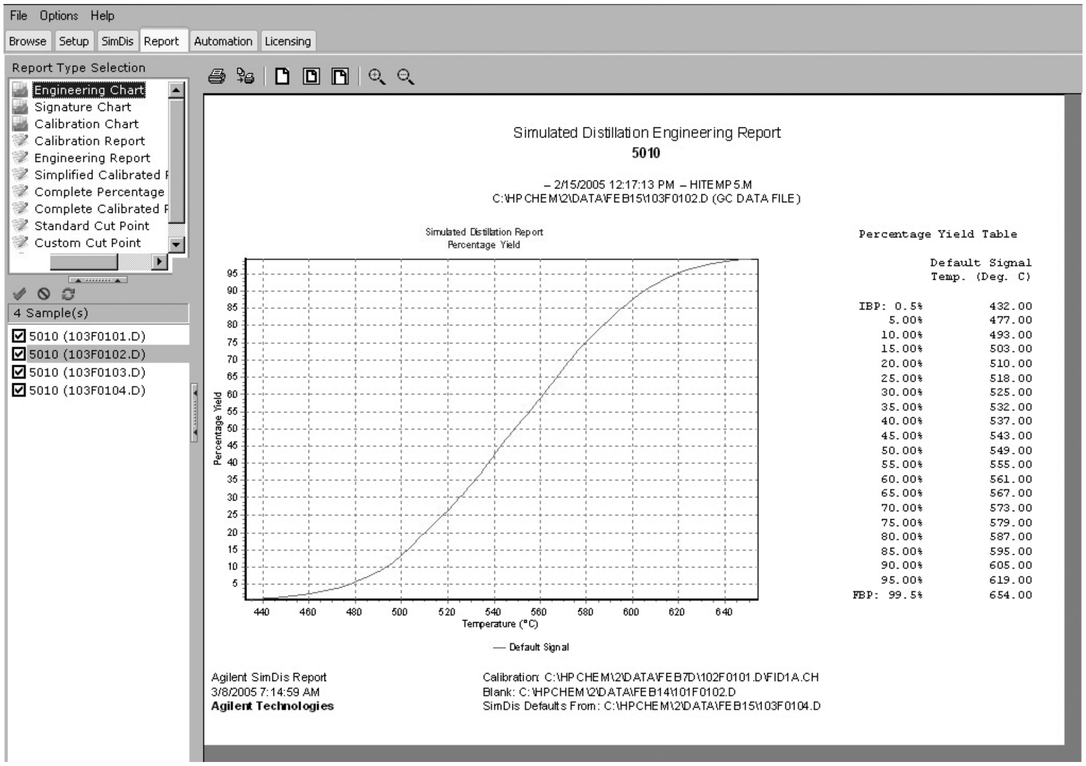

Figure 6B. Engineering report for reference sample 5010.

Table 3. Reference Sample 5010. Results in °C.

ASTM D6352 Values			**Typical observed values**	
OFF%	**IBP**	**Allowable difference**	**FBP**	**Difference**
IBP	428	9	429.4	–1.4
5.0	477	3	479.4	–2.4
10.0	493	3	493.3	–0.3
15.0	502	3	502.8	–0.8
20.0	510	3	510.6	–0.6
25.0	518	4	517.8	0.2
30.0	524	4	524.4	–0.4
35.0	531	4	530.6	0.4
40.0	537	4	536.1	0.9
45.0	543	4	542.2	0.8
50.0	548	5	547.8	0.2
55.0	554	4	553.9	0.1
60.0	560	4	560.0	0
65.0	566	4	566.1	–0.1
70.0	572	4	572.2	–0.2
75.0	578	5	578.3	–0.3
80.0	585	4	585.6	–0.6
85.0	593	4	593.9	–0.9
90.0	602	4	603.9	–1.9
95.0	616	4	620.0	–4.0
FBP	655	18	657.2	–2.2

Repeatability of Reference Sample 5010

Although injected volumes are very small (typically 0.05 µL to 0.1 µL), performance of the 7683B injector and HT PTV are exceptional. An overlay of eight sample runs of standard 5010 and two blanks are shown in Figure 7. Results as calculated from the SimDis module are given in Table 4.

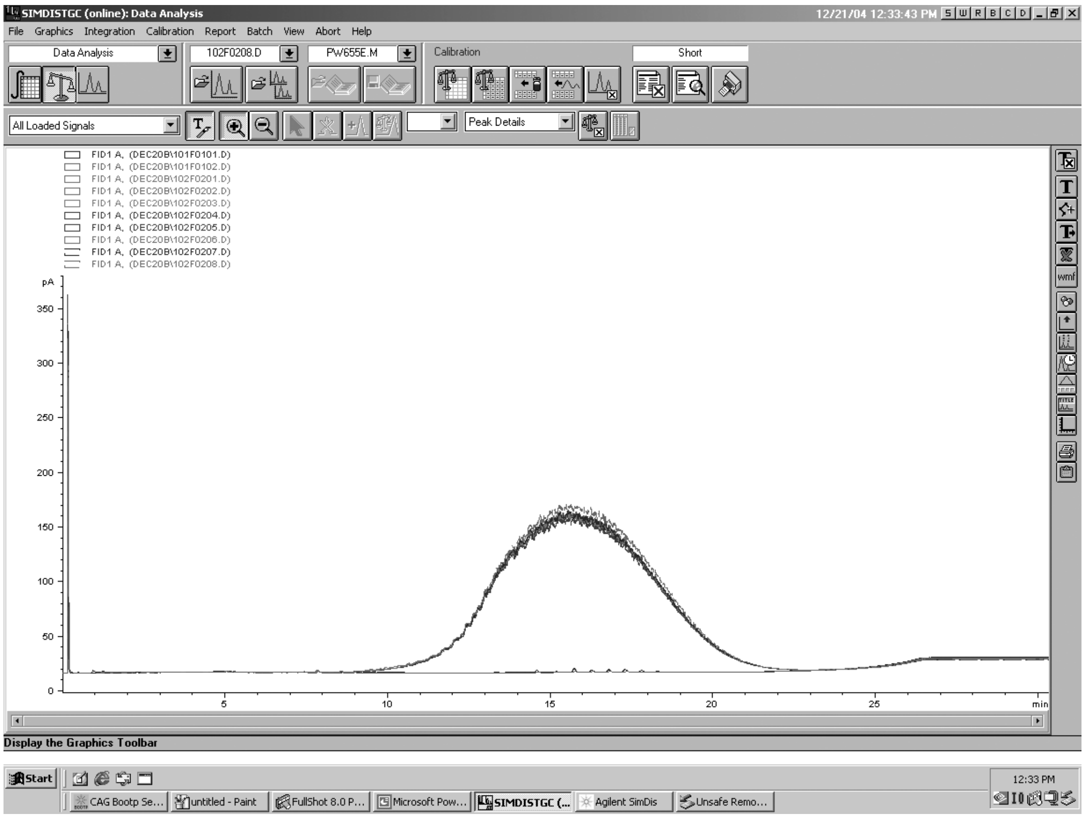

Figure 7. Eight runs of sample 5010 and two blanks are overlaid. Oven program: 45 °C (0 min) to 440 °C (4 min) at 15 °C/min.

Table 4. Values for Eight Sample Runs of D6352 Reference Material 5010 (% Off Numbers Listed)

Run	IPB	20%	40%	50%	60%	80%	FPB
1	428	508	535	546	558	583	648
2	427	508	535	546	558	584	649
3	426	509	535	547	559	584	645
4	427	508	535	546	558	584	649
5	426	508	535	546	558	584	649
6	423	507	534	546	558	584	650
7	430	509	535	546	558	583	646
8	428	508	535	546	558	583	648

Heavy Vacuum Gas Oil Analysis

Figure 8 shows the chromatographic overlay of five runs of heavy vacuum gas oil (HVGO) simulated distillation analysis. This sample falls within the requirements of the proposed method D2887X. The overlays of five chromatographic runs demonstrate that repeatable results are obtained. Table 5 lists numeric results for this HVGO sample.

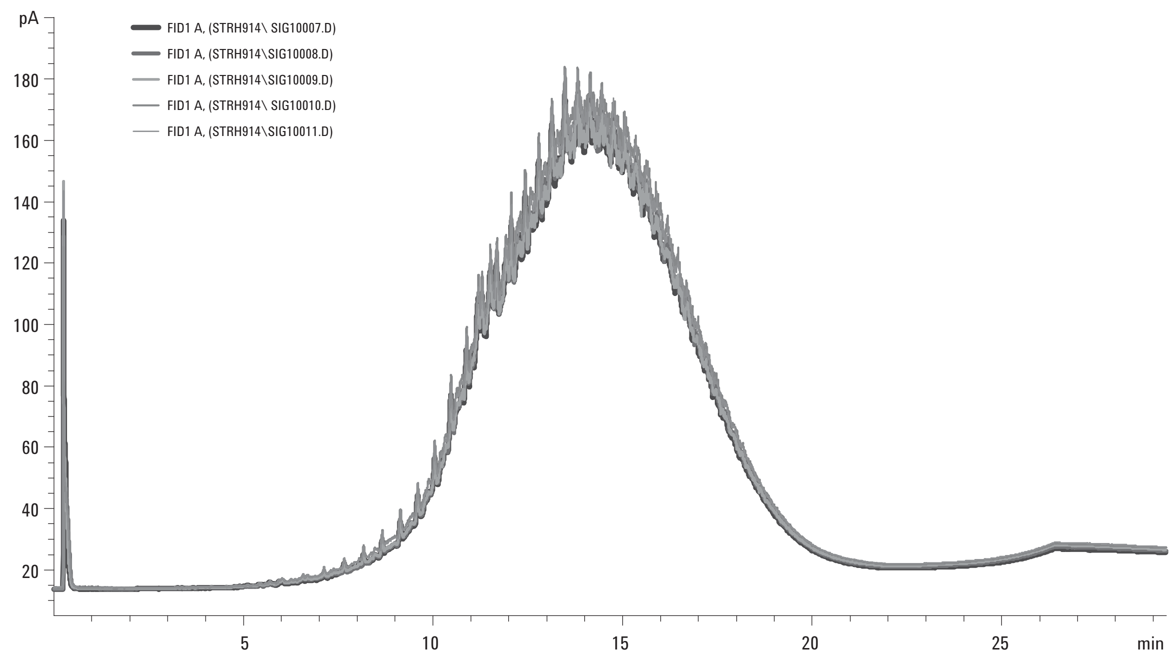

Figure 8. Chromatographic overlay of five runs of HVGO. Injected 0.1 µL (55:1 approximate dilution in CS_2). GC conditions given in Table 1.

Table 5. HVGO Results

OFF%			Observed BP °C			Repeatability
	1	2	3	4	5	
IBP	140	141	141	141	141	1.1
5.0	282	282	282	286	284	3.9
10.0	369	369	368	371	369	3.3
20.0	433	433	432	433	432	1.1
30.0	458	459	458	458	458	0.6
40.0	478	479	478	478	478	1.1
50.0	496	496	496	495	496	1.1
60.0	511	511	511	510	511	1.1
70.0	527	528	527	527	527	1.1
80.0	546	546	545	544	545	1.7
90.0	569	571	569	568	569	2.2
95.0	587	588	586	584	586	3.9
FBP	606	607	604	601	604	6.1

Conclusions

Accurate determination of the cut point distribution of heavy petroleum fractions is essential in optimizing the efficiency of refining operations as the use of heavier feedstocks become more prevalent. The Agilent SimDis System provides an easy-to-use and efficient means to automate simulated distillation through the GC ChemStation. Analysts can quickly set up and perform simulated distillation analysis using the Agilent SimDis software module. The system supports ASTM D6352, D2887 and the proposed extended D2887 methods. The HT PTV inlet provides efficient and reproducible transfer of the high boiling calibration samples and petroleum fractions to the column without discrimination. Agilent's 5-meter metal thin-film column offers a stable HT stationary phase with long life even when programmed to 440 °C.

References

1. C. Wang and R. Firor, "Simulated Distillation System for ASTM D2887" Agilent Technologies, publication 5989-2726EN, www.agilent.com/chem.

2. ASTM D6352-02, "Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700 °C by Gas Chromatography" Fractions by Gas Chromatography", Annual Book of Standards, Volume 05.02, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.

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Printed in the USA
April 27, 2005
5989-2727EN

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