# Simulated Distillation System for ASTM D2887, Based on the Agilent 6890N GC

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

**An Agilent Simulated Distillation (SIMDIS) system is described for quality control and monitoring of refinery processes. The system uses an Agilent 6890N gas chromatograph (GC) equipped with a programmable temperature vaporizer (PTV) inlet designed specifically for high temperature analysis. A simulated distillation software program that couples with the Agilent GC ChemStation provides an easy-to-use solution for simulated distillation. The system allows analysts to quickly determine the boiling point distribution and cut points of petroleum products. This application note describes in detail the system needed to perform simulated distillation by ASTM method D2887. This method is applicable to petroleum products and fractions having an initial boiling point greater than 55 °C and a final boiling point less than 538 °C.**


## Introduction

The boiling range distribution of petroleum fractions provides insight into to the composition of feedstocks and products related to petroleum refining. Both physical distillation and simulated distillation methods can be used to determine boiling point (BP). However, physical distillation methods are time-consuming and require a high level of operator intervention compared to simulated distillation, resulting in wide specification ranges for reproducibility and repeatability. Simulated distillation, in contrast, allows accurate and fast determination of the BP distribution of petroleum fractions.

ASTM D2887 is widely used in the refinery industry [1]. It is designed to determine the boiling range distribution of petroleum products and fractions having a final boiling point of 538 °C or lower. The Agilent SIMDIS system offers a cost effective and easy-to-use package to practice ASTM method D2887.

## Experimental

The SIMDIS application uses an Agilent 6890N GC with electronic pneumatics control (EPC), configured with a flame ionization detector (FID) and a 10 m × 530 µm × 2.65 µm DB-1 capillary column. The Agilent 7683B automatic liquid injector, equipped with either an SGE 0.5 µL or Agilent 5-µL syringe was used for sample introduction into a JAS UNIS 3100 high temperature, air-cooled PTV inlet. A qualitative mixture of normal paraffins C5

to C44 (Supelco Part no. 500658) or C5 to C40 (Agilent part number 5080-8716) was used to determine the BP versus retention time (RT) relationship over the range required by method D2887.

### High Temperature PTV Inlet

This high temperature PTV inlet (HT PTV), 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 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 Agilent 7683B series injector operating in the fast injection mode is used with control and parameter setting 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 few minutes and then cooled back uncontrolled to the starting temperature, all during the first half of the GC run. High program rates of 400 °C or 500 °C/min can be used for thermally stable analytes as normally encountered in simulated distillation.

General instrumental conditions used for performing method D2887 are listed in Table 1.

The process of SIMDIS analysis includes blank analysis (for baseline subtraction), calibration (C5 to C40 or C5 to C44), validation (reference gas oil No.1 for ASTM D2887) and sample analysis. These analyses can be automated through the GC ChemStation coupled to the Agilent SIMDIS software.

### SIMDIS Software

The SIMDIS application software can operate standalone or be called to automatically execute as a post run event from ChemStation. The software is structured in functional modules including: Browse, Setup, SimDis, Report, and Automation. Each module provides specific functions to rapidly view data files, setup SIMDIS parameters, perform SIMDIS calculations, customize reporting, and track files used in automation.

The Agilent SIMDIS module provides a number of functions to correct artifacts such as solvent peaks and contributions from baseline, including a number of 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. The parameter selection and calculation functions are located at left of the menu for the SIMDIS module as shown in Figure 1. Also, icons for Start Elute, End Elute, initial-BP (IBP) display, and final-BP (FBP) display at the top left of the menu can be toggled to show the current selections graphically on the raw signal.

**Table 1. Gas Chromatographic Conditions**

| | |
|---|---|
| PTV inlet typical temperature program options | 1) 300 °C to 400 °C at 500 °C/min (4 min.), to 300 °C at 200 °C/min<br>2) 225 °C to 400 °C at 200 °C/min (4 min.), to 225 °C at 100 °C/min<br>3) 350 °C (no ramping) |
| Split ratio | 2:1 |
| Injection volume | 0.05 µL to 0.1 µL |
| Liner | HT PTV SimDis liner |
| Column | DB-1, 10 m × 530 µm × 2.65 µm (part number 125-10HB)<br>or DB-2887 (part number 125-2814) |
| Column flow (He) | 14 mL/min, constant flow mode |
| FID temperatures | 350 °C |
| $H_2$ flow | 40 mL/min |
| Air flow | 450 mL/min |
| Make up ($N_2$) | 45 mL/min |
| Oven program | 40 °C to 350 °C at 20 °C/min, hold 8 min |
| Data acquisition rate | 5 Hz typical |

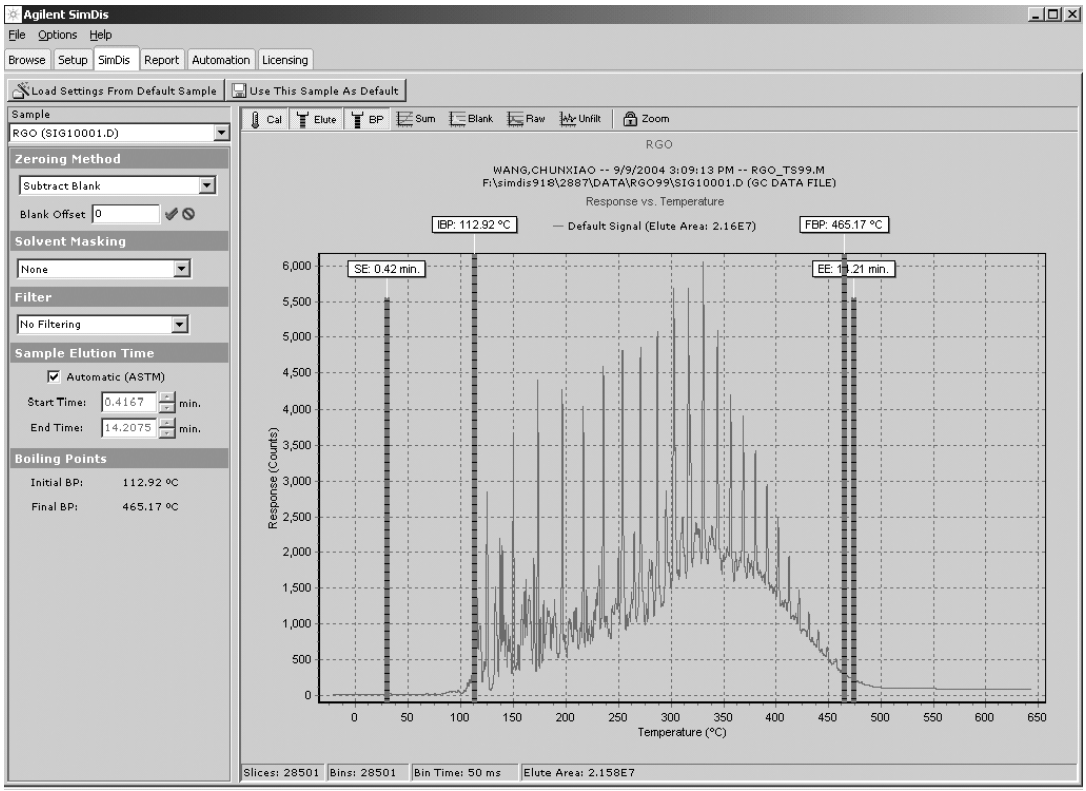


**Figure 1. SIMDIS analysis setup pane showing start (IBP) and end (FBP) values.**

The SIMDIS software Report tab offers several different report options for the results that can be displayed with a simple mouse click. The report list presents the available report formats and data treatment for output such as “calibration report”, “Engineering report”, “complete percentage yield”, “standard cut point”, “custom cut point”, and “D2887 to D86 correlation”. Figures 2a and 2b show examples of signature and custom cut point reports, respectively.

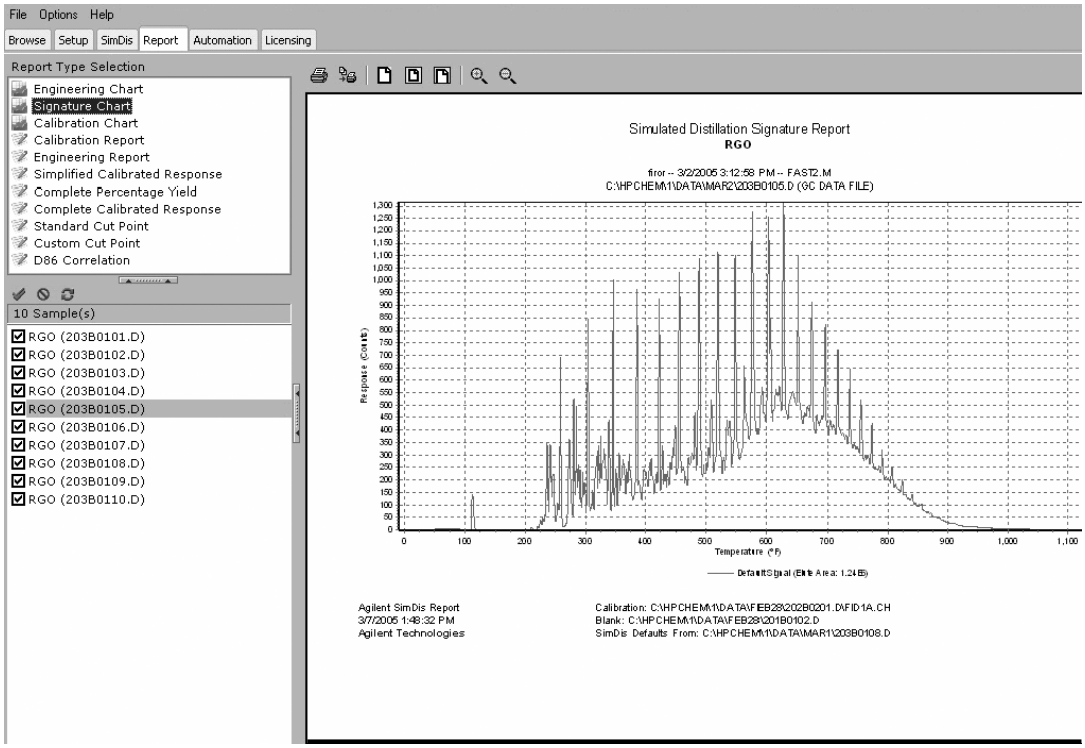


**Figure 2a. Signature report for reference gas oil (RGO).**

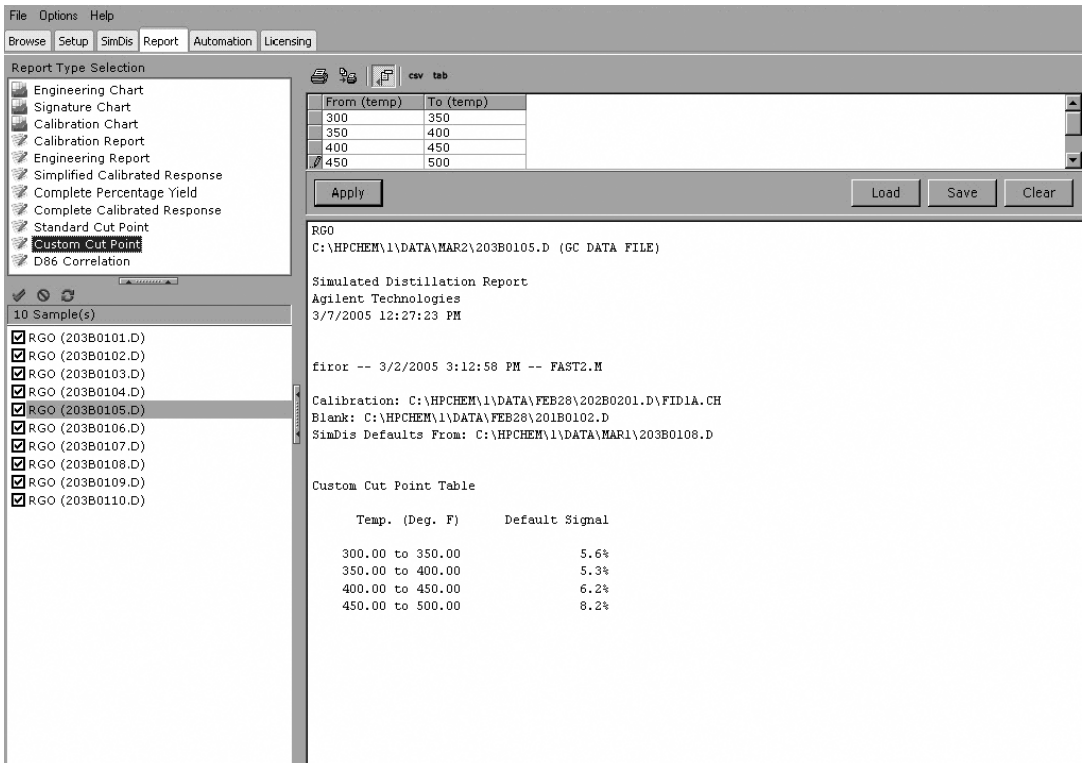


**Figure 2b. Report pane showing a custom cut point table.**

## Results and Discussion

### Blank Analysis

Two types of blank analyses are commonly performed; blank run without injection, and blank run with injection of solvent only. Blank analysis is performed with a method identical to the one used for sample and calibration runs. However, if the samples are too viscous, waxy, or require a reduction in concentration, dilution is required. The solvent often used is carbon disulfide ($CS_2$). It is injected neat as a blank run for subsequent subtraction from the sample runs. Thus, these blank analyses are used to correct for any baseline changes that may influence the baseline offset, such as column bleed. They are also useful to check for possible carryover from a previous overloaded injection. Also note in Figure 3, the overlay of two consecutive blank runs. It is always good practice to perform multiple blanks until a high degree of overlap is seen indicating a stable system ready to run test samples. An example of a valid calibration/$CS_2$ blank setup, as displayed by the software, is shown in Figure 4 (blank in bottom box).

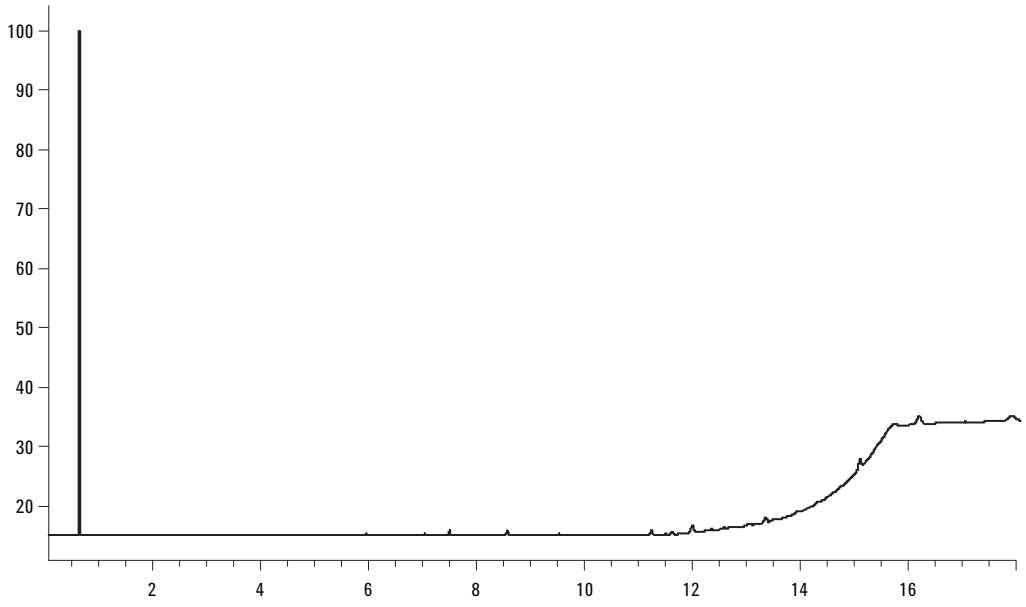


**Figure 3. Overlay of two consecutive blank runs showing stable baseline profile.**

## Calibration

Initially, the ChemStation calibration table functions are used to set up a calibration between BP and RT. Calibration mixtures containing a series of known n-alkanes from C5 to C40 or C5 to C44, are used to establish the BP-RT correlation. The SIMDIS software has the capability to edit the calibration file, adding peaks, deleting peaks, and assigning/changing carbon number, all accomplished easily using the mouse. An example of a complete BP calibration (C5 to C40) is shown in Figure 4 (top box). A second example (C5-C44) using the Sulpelco calibration mix (p/n 500658) is shown in Figure 5.

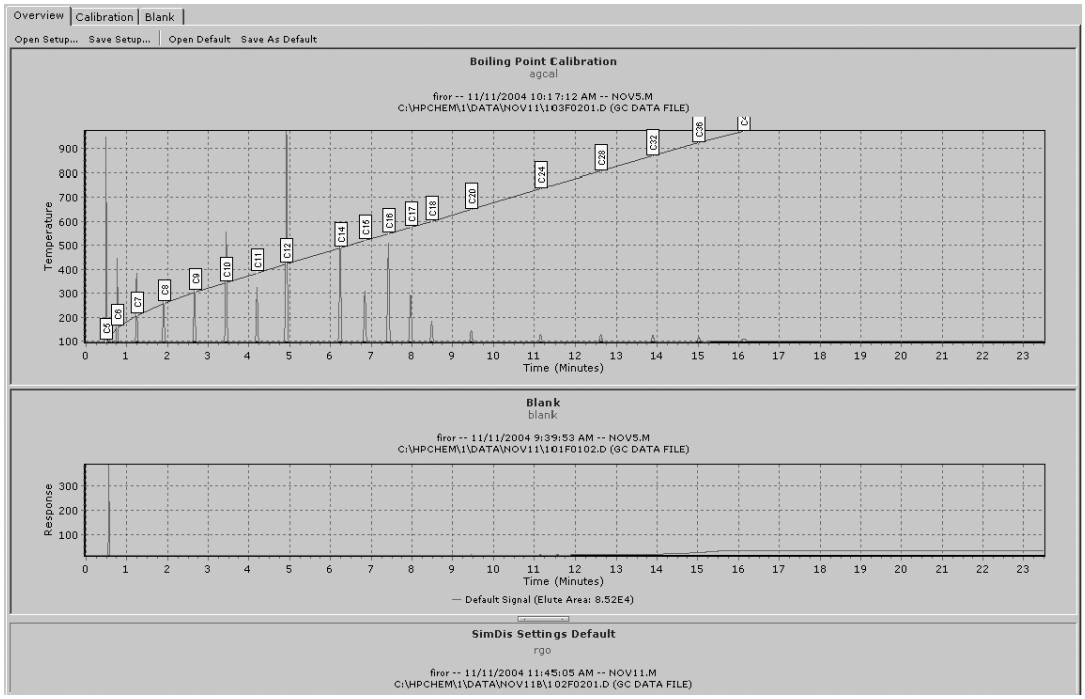


**Figure 4. Calibration overview pane showing calibration and blank runs selected for subsequent use in SIMDIS calculations.**

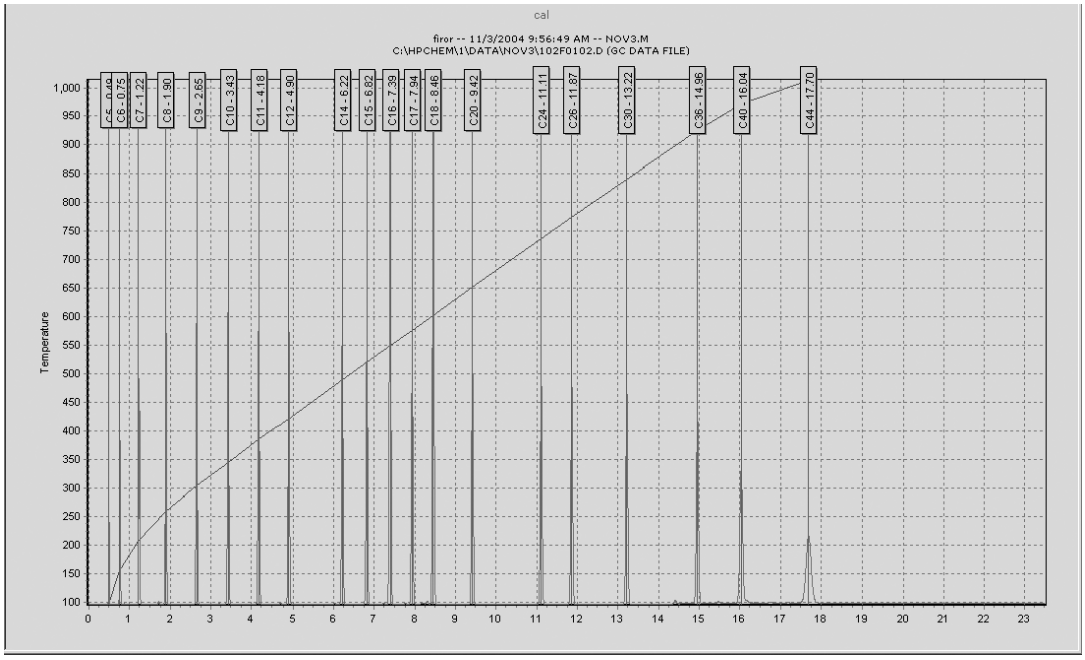


**Figure 5. Calibration pane showing C5 to C44 peak assignments.**

### RGO Analysis

To meet the requirements of ASTM D2887, the RGO sample analysis must be performed to verify both the chromatographic and calculation algorithms involved in this test method.

Figure 6 shows the chromatographic overlay of RGO and blank for a typical D2887 analysis. Table 2 shows the results for five runs of RGO analysis. The data demonstrates that the observed BP values agree with the ASTM D2887 consensus BP values within the allowable difference range.

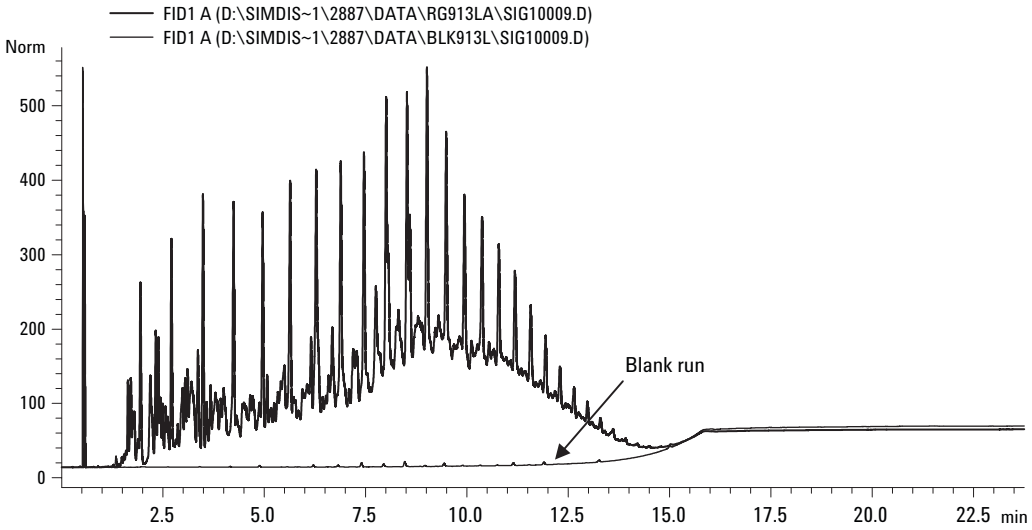


**Figure 6. Chromatographic overlay of RGO and $CS_2$ blank.**
Sample: ASTM RGO No. 1. Injection volume: 0.01 µL (no dilution). GC conditions are given in Table 1.

**Table 2. Typical Results for the RGO (°C)**

| ASTM D2887 Values | | | Observed values | |
|---|---|---|---|---|
| OFF% | BP | Allowable difference | BP | Difference |
| IBP | 115 | 7.6 | 113.3 | 1.7 |
| 10 | 176 | 4.1 | 177.8 | –1.8 |
| 20 | 224 | 4.9 | 227.2 | –3.2 |
| 30 | 259 | 4.7 | 262.8 | –3.8 |
| 40 | 289 | 4.3 | 292.2 | –3.2 |
| 50 | 312 | 4.3 | 314.4 | –2.4 |
| 60 | 332 | 4.3 | 332.8 | –0.8 |
| 70 | 354 | 4.3 | 355.6 | –1.6 |
| 80 | 378 | 4.3 | 379.4 | –1.4 |
| 90 | 407 | 4.3 | 409.4 | –2.4 |
| FBP | 475 | 11.8 | 466.7 | 8.3 |

In Figure 7, ten consecutive runs of the RGO are overlaid without normalization. Run to run deviations over the entire runtime are small, indicating good system performance (injector, syringe, inlet, column and detector).

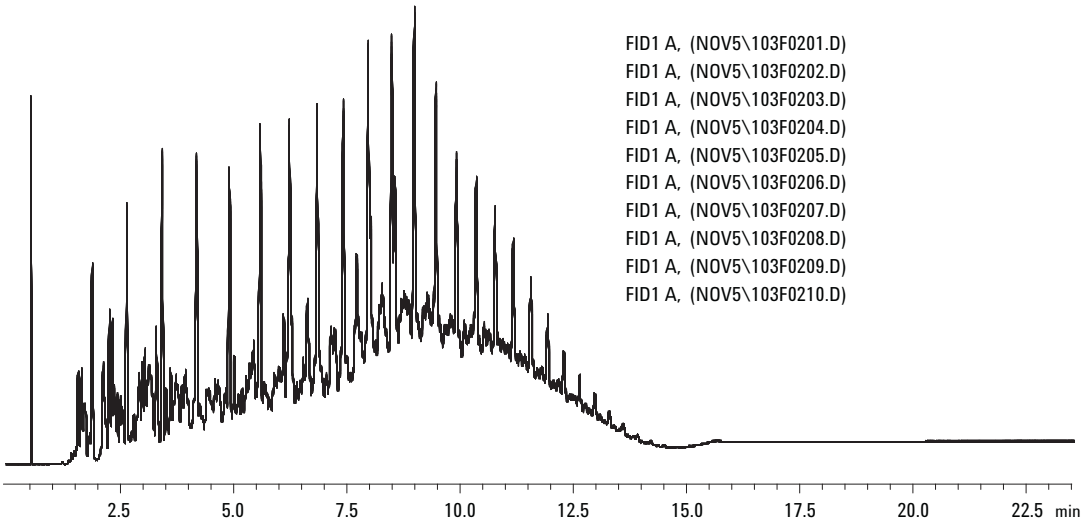


**Figure 7. Overlay of 10 consecutive runs of RGO. Less than 3% run to run variation in the area of any given slice across the entire chromatogram.**

An example of the engineering report format for analysis of the RGO is shown in Figure 8. The report indicates specific blank and calibration files used in calculating the results.

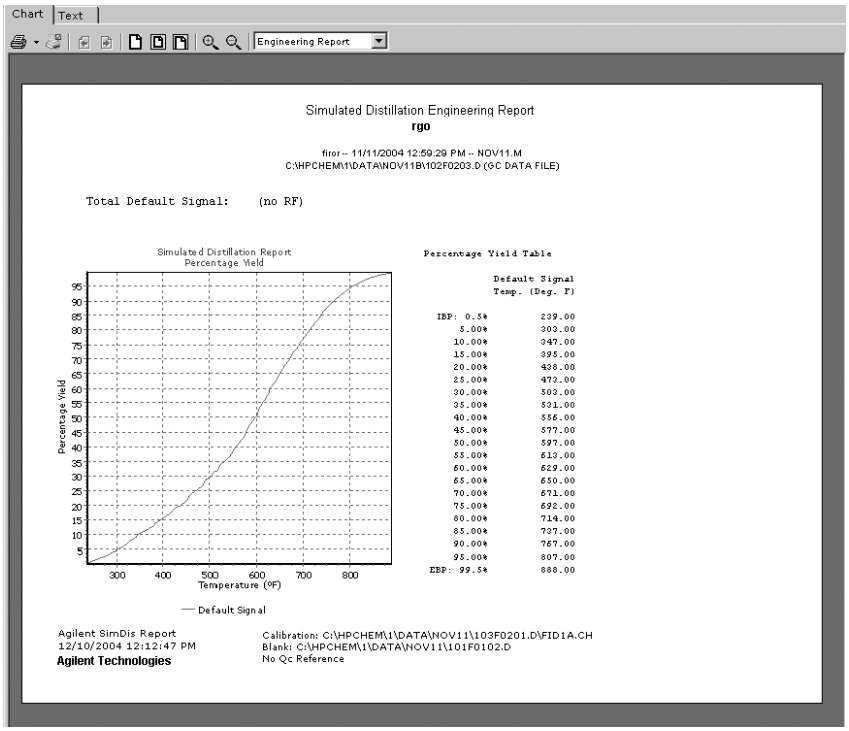


**Figure 8. Engineering report for a RGO sample.**

### Cracked Gas Oil

Figure 9 shows the chromatographic overlay of five runs of cracked gas oil for simulated distillation analysis. The overlays of the chromatograms guarantee reliable and repeatable results. Calculated results are shown in Table 3.

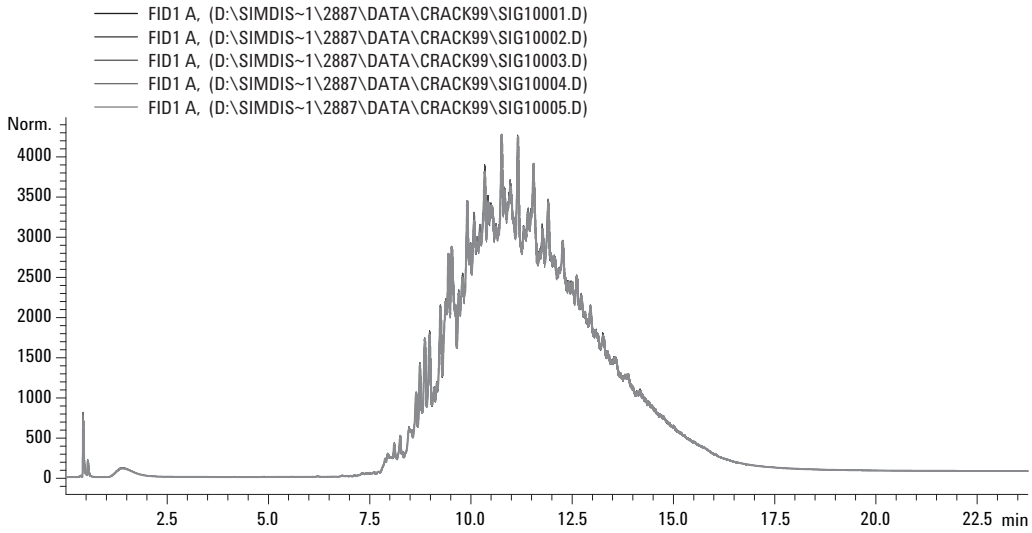


**Figure 9. Chromatographic overlay of five runs of a cracked gas oil analysis.**
Injection volume: 0.1 µL (4:1 approximate dilution in $CS_2$). GC conditions are given in Table 1.

**Table 3. Results for Cracked Gas Oil Samples in °C**

| Observed BP OFF% | BP °C | | | | | | | | | | | SD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Average | |
| IBP | 297 | 297 | 298 | 298 | 299 | 298 | 298 | 298 | 298 | 297 | 297 | 0.2 |
| 10 | 344 | 344 | 344 | 344 | 344 | 344 | 344 | 344 | 344 | 344 | 344 | 0 |
| 20 | 360 | 361 | 361 | 361 | 361 | 361 | 361 | 361 | 361 | 361 | 360 | 0.1 |
| 30 | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 0 |
| 40 | 384 | 385 | 385 | 385 | 385 | 385 | 385 | 385 | 386 | 386 | 385 | 0.1 |
| 50 | 397 | 397 | 397 | 397 | 397 | 397 | 397 | 397 | 398 | 398 | 397 | 0.1 |
| 60 | 410 | 411 | 411 | 411 | 411 | 411 | 411 | 411 | 411 | 411 | 411 | 0.1 |
| 65 | 417 | 417 | 417 | 417 | 417 | 417 | 417 | 417 | 418 | 417 | 417 | 0.1 |
| 70 | 424 | 424 | 424 | 424 | 424 | 424 | 424 | 424 | 425 | 425 | 424 | 0.1 |
| 80 | 442 | 442 | 442 | 442 | 442 | 442 | 442 | 442 | 443 | 442 | 442 | 0.1 |
| 90 | 467 | 468 | 468 | 468 | 468 | 468 | 468 | 468 | 469 | 468 | 468 | 0.1 |
| FBP | 516 | 516 | 517 | 516 | 516 | 517 | 515 | 516 | 517 | 519 | 517 | 0.2 |

## Conclusions

Knowledge of the BP distribution of petroleum fractions and feedstocks as input to catalytic crackers is essential to ensure a uniform quality of finished product and to optimize refinery processes. Simulated distillation provides a fast and reliable technique to determine the BP distributions with a high degree of confidence. The Agilent SIMDIS system consisting of a 6890N GC equipped with the HT PTV inlet, FID, ChemStation, and simulated distillation application software allows analysts to quickly and easily perform simulated distillation analysis according to ASTM D2887. The system and software can also perform the proposed D2887x (extended D2887), and D6352 (high temperature simulated distillation) methods. These latter two methods are described in a separate application note [2].

This simulated distillation system is available complete with hardware and software, including verification of performance using the RGO as option 651 to the 6890N.

## References

1. ASTM D2887-97a,"Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography", Annual Book of Standards, Volume 05.02, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428 USA.
2. C. Wang and R. Firor, "High-Temperature Simulated Distillation System Based on the 6890N GC", Agilent Technologies, publication 5989-2727EN www.agilent.com/chem

## For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.



Printed in the USA
May 9, 2005
5989-2726EN

Agilent Technologies