Agilent SimDis Applications

Houston June 27, 2013

Simulated Distillation Methods: Application to Petroleum Processes

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An Overview of Simulated Distillation Methods and Their Application to Petroleum Processes

There are a number of ASTM Simulated Distillation Methods that overlap in boiling range and scope.

In this presentation we discuss the ASTM methods and their merits and challenges for the analysis of petroleum streams and processes.

The critical differences of the methods and the appropriate method for the analysis of process distillates, transportation fuels and whole crudes will be covered.

Examples of analysis using the Agilent SimDis Package will be demonstrated.

Refinery Operational Controls

Temperature/Pressure/Flow Measurements

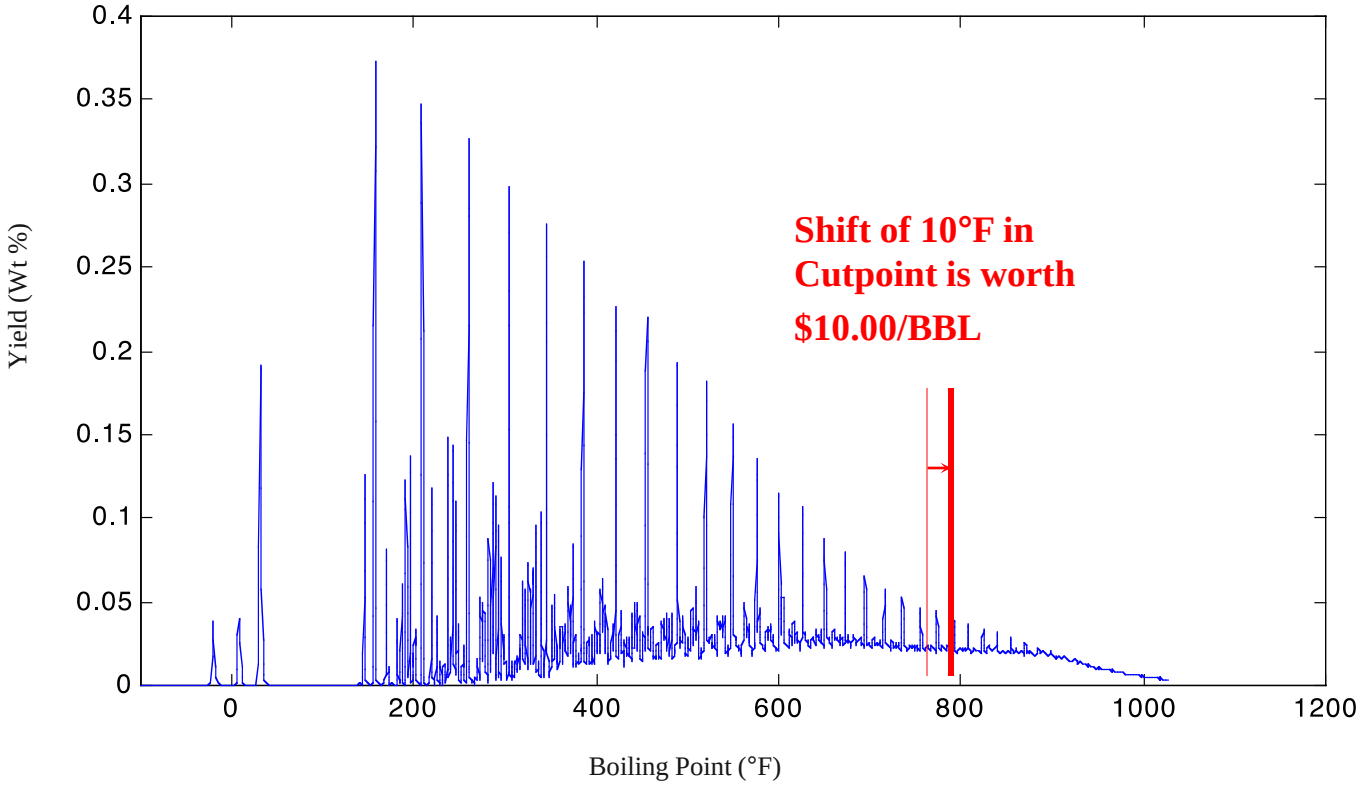
- Cut Point Temperature
- Cat. Avg. Bed Temp.
- Recycle Pressure
- Volumetric Product Yield

The Boiling Point is the single control variable consistently applied across all refinery process streams and operations.

The Value of Process Measurements

Applications	Realized Savings
Crude Unit Monitoring	$800K/Mo
LPG Stream Quality	$3MM Year
Effluent Monitoring	$200K/Day
FCC Operations	
Hydrocracking Operations	$5MM Year

The Value of Accurate Cut Points



What is True Boiling Point

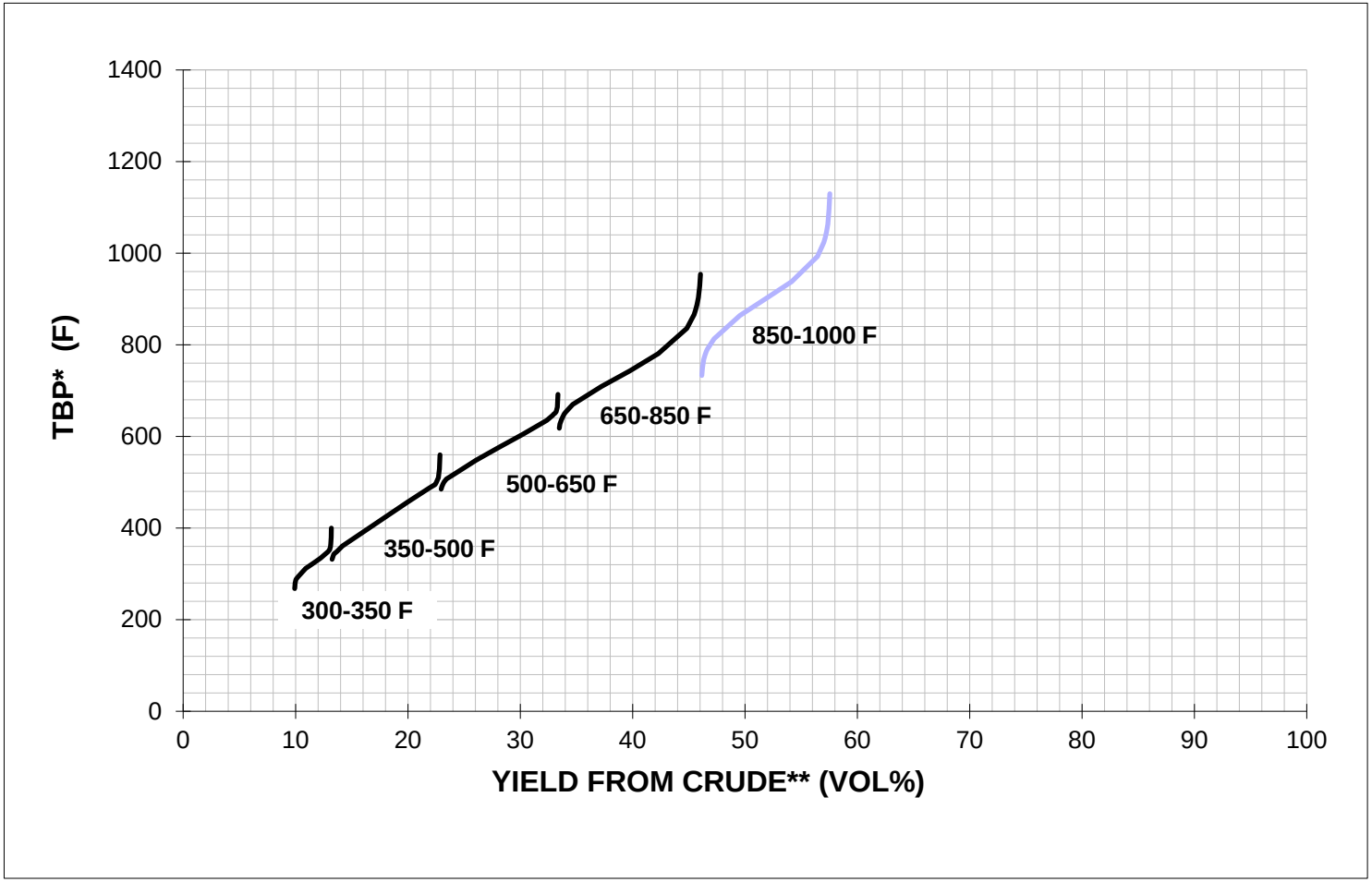
TBP is term describing the analytical results obtained from the distillation of stabilized crude petroleum to a final cut temperature of 400°C Atmospheric Equivalent Temperature (AET).

…

This test method details procedures for the production of a liquified gas, distillate fractions, and residuum of standardized quality on which analytical data can be obtained, and the determination of yields of the above fractions by both mass and volume. From the preceding information, a graph of temperature versus mass % distilled can be produced. This distillation curve corresponds to a laboratory technique, which is defined at 15/5 (15 theoretical plate column, 5:1 reflux ratio) or TBP (true boiling point).

True Boiling Point

TBP Curve for Distillation of a Whole Crude



True Boiling Point and SimDis of a Whole Crude

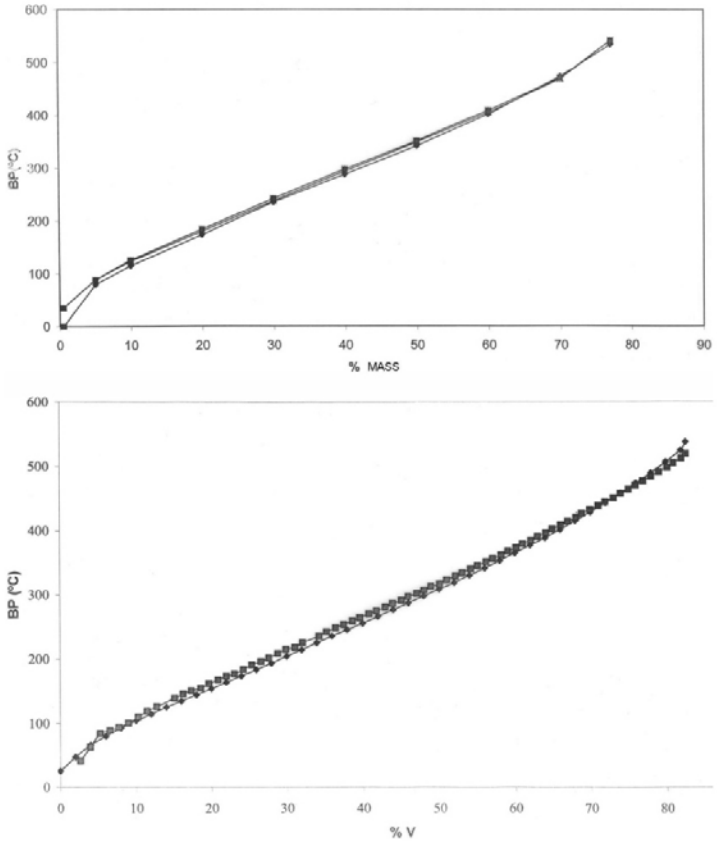


Figure 5. Comparison between physical distillation and SIMDIS mass curves (top) and volume curves (bottom) in Istmo crude. Legend for mass curve: (■) physical distillation, (*) SIMDIS 1, and (●) SIMDIS 2. Legend for volume curve: (◆) physical distillation and (■) SIMDIS.

Energy & Fuels **2004,** *18,* 1832−1840

Simulated Distillation Yield Curves in Heavy Crude Oils: A Comparison of Precision between ASTM D-5307 and ASTM D-2892 Physical Distillation

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SimDis

SimDis (short for Simulated Distillation) is a standardized chromatographic method which models the distillation curve of a hydrocarbon mixture and converts retention time to Boiling Point.

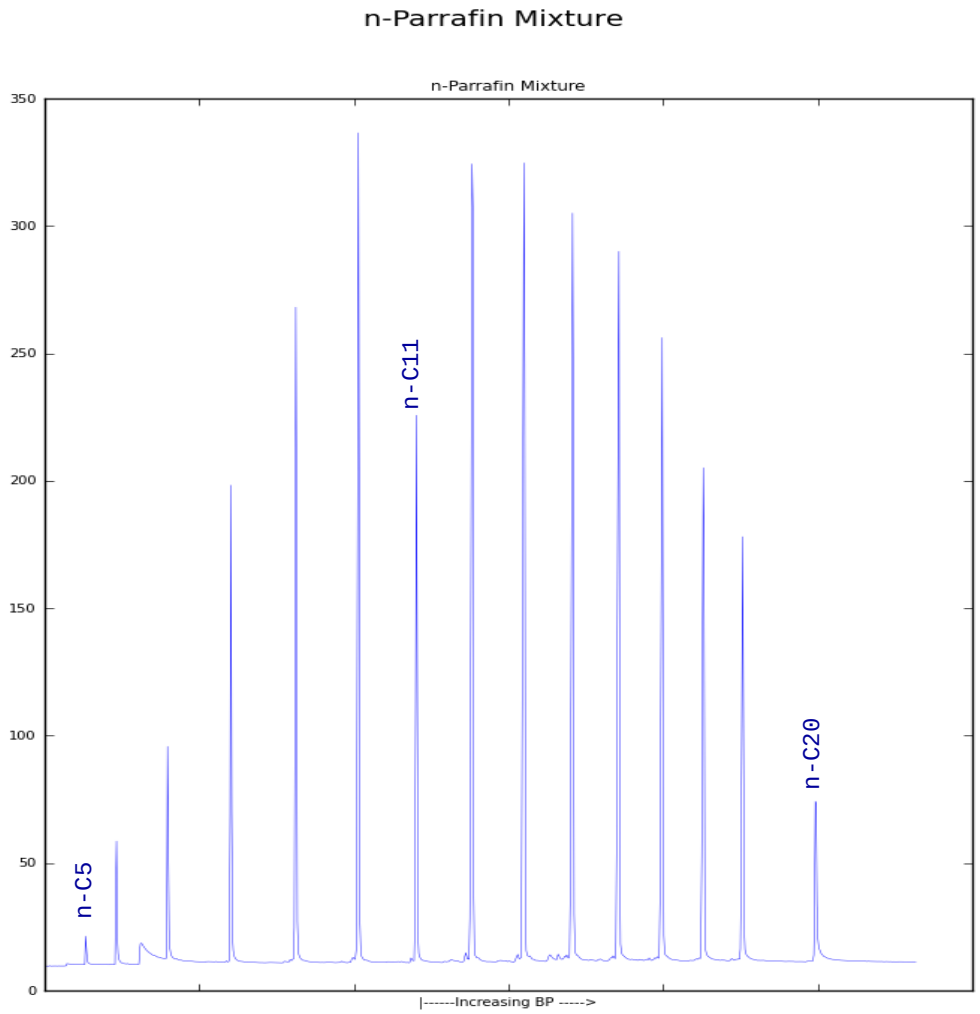
American Standards and Testing Methods (ASTM)currently uses 6 SimDis methods for a variety of sample types

SimDis is the only characterization method capable of analyzing the entire range of volatile hydrocarbons found in petroleum

(i.e from n-C3 through n-C120)

It is the methodology of choice for the self-consistent analysis of petroleum processes and products.

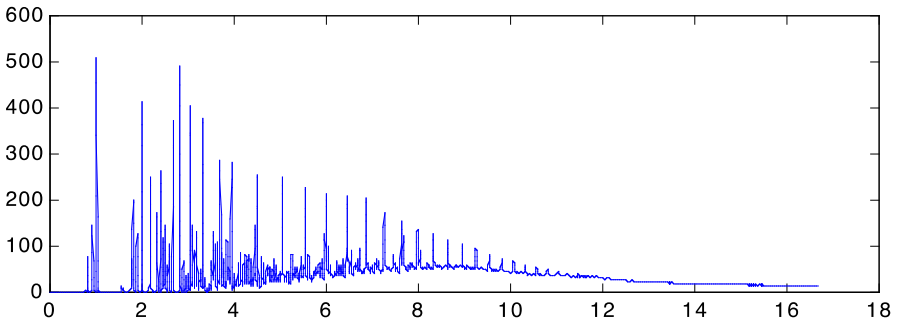
SimDis-GC

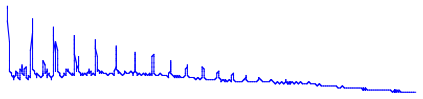


SimDis-Gas Chromatography partitions the sample based on the boiling points of the individual compounds contained in the sample.

Low boiling compounds (molecules) are eluted and characterized first followed by higher boiling compounds

Simulated Distillation

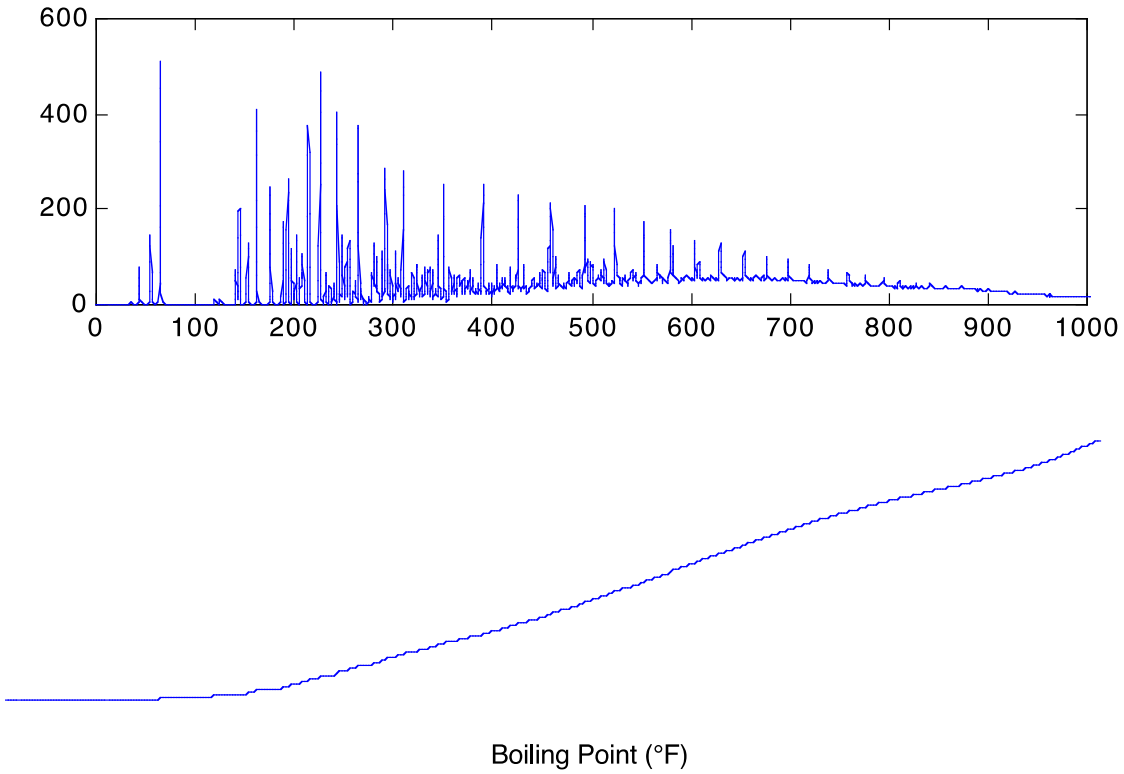




Boiling Point (°F)

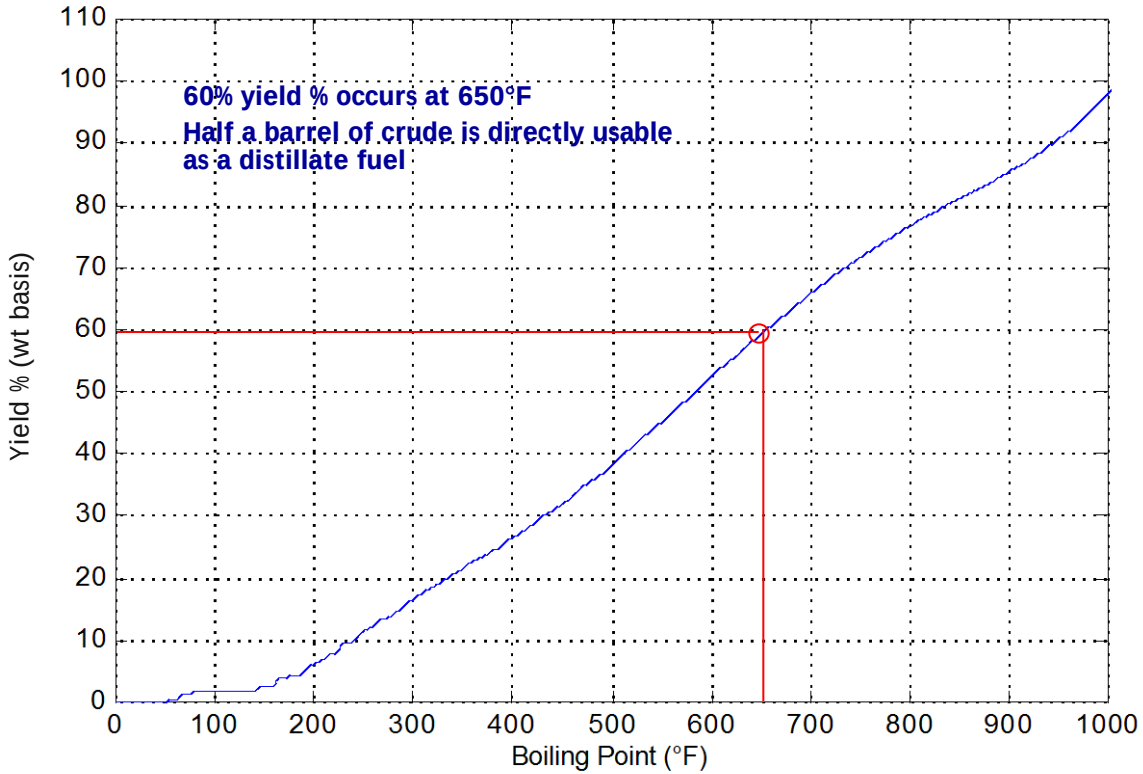
SIMDIS is a chromatographic procedure which translates retention time to boiling point….

D2887 SIMDIS



… and detector response to Yield Wt%

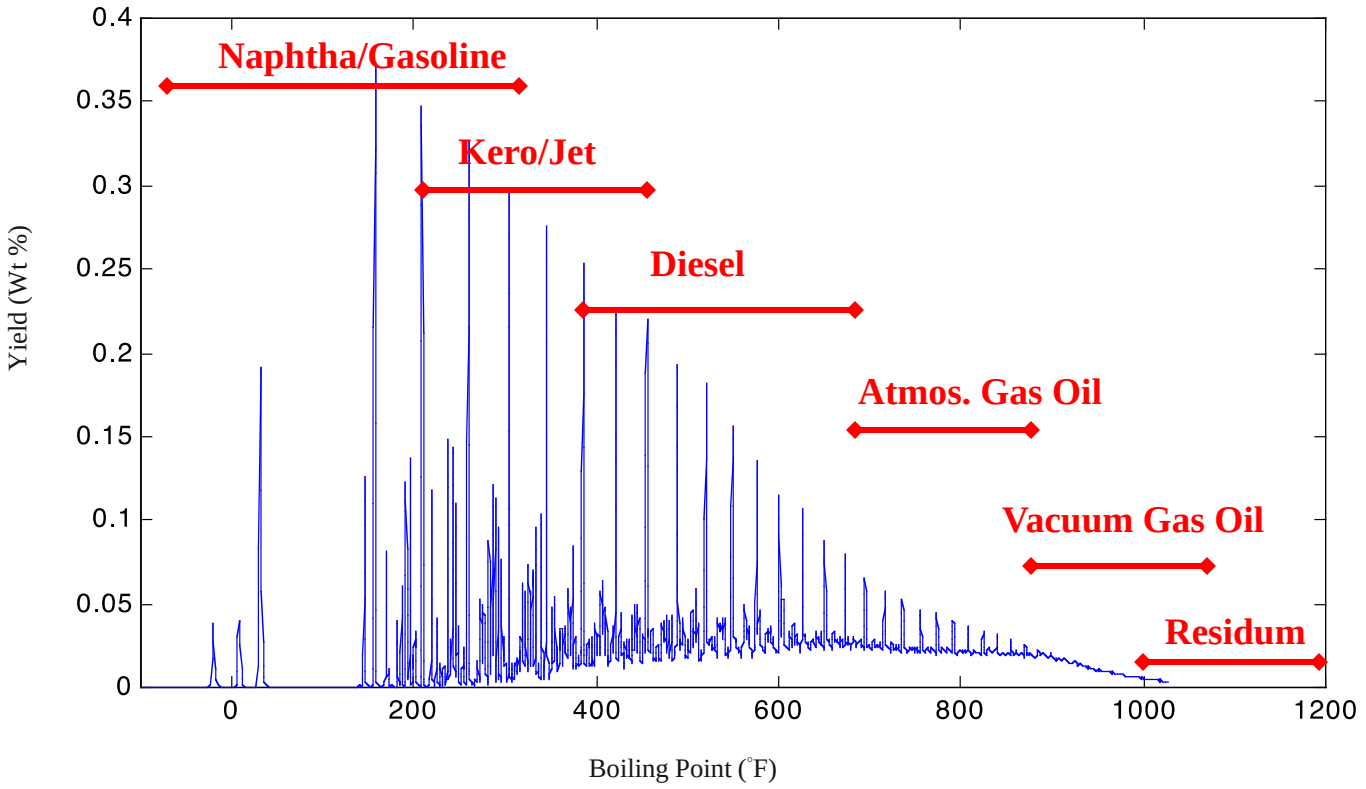
D2887 SIMDIS Yield % vs BP



Boiling point is the one common measurement applicable to all refining process streams

SIMDIS information is essential in assigning value to crude and develop refining operating plans

A Chromatographic View of Distillate Fractions



Current ASTM SimDis Methods

Active Standards:

D2887-13 Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

D3710-95(2009) Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography

D7096-10 Standard Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography

D7169-11 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

D7213-12e1 Standard Test Method for Boiling Range Distribution of Petroleum Distillates in the Boiling Range from 100 to 615°C by Gas Chromatography

D7500-12 Standard Test Method for Determination of Boiling Range Distribution of Distillates and Lubricating Base Oils—in Boiling Range from 100 to 735°C by Gas Chromatography

D7398-11 Standard Test Method for Boiling Range Distribution of Fatty Acid Methyl Esters (FAME) in the Boiling Range from 100 to 615°C by Gas Chromatography

D5399-09 Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography

Special (SimDis Like) Methods:

ASTM D6417 - 09 Standard Test Method for Estimation of Engine Oil Volatility by Capillary Gas Chromatography

ASTM D5442 - 93(2008) Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography

ASTM SimDis Methods

ASTM Method	BP Range (Carbon #)	Application
D3710	-162-260C (nC1-nC15)	Naphthas, Gasolines
D7096	-162-280C (nC1-nC16)	Naphthas, Gasolines (expands 3710)
D2887	-162-545C (nC1-nC44)	Naphthas thru VGO
D7213	100-615 C (nC7-nC60)	Hvy Naphtha, Kerosene, Jet, Diesel
D6352	174-715C (nC10-nC90)	Replaced by D7500
D7500	100-735 C (nC7-nC110)	VGO, HVGO, Lube Oils
D5307	162-545C (nC1-nC44)	Withdrawn Crude Oils
D7169	-162-720 C (nC1-nC100)	Crude Oil, Residua
D5399	37-285C (nC5-nC16)	Hydrocarbon Solvents
D7398	100-615 C(n C7-nC60)	Biodiesels

ASTM SimDis Methods

ASTM Method	BP Range (Carbon #)	Application
D3710	-259-500F (nC1-nC15)	Naphthas, Gasolines
D7096	-259-536F (nC1-nC16)	Naphthas, Gasolines (expands 3710)
D2887	-259-1000F (nC1-nC44)	Naphthas thru VGO
D7213	200-1100F (nC7-nC60)	Hvy Naphtha, Kerosene, Jet, Diesel
D6352	345-1292F (nC10-nC90)	Replaced by D7500
D7500	200-1430F (nC7-nC110)	VGO, HVGO, Lube Oils
D5307	-259-1000F (nC1-nC44)	Withdrawn Crude Oils
D7169	-259-1328F (nC1-nC100)	Crude Oil, Residua
D5399	100-550F (nC5-nC16)	Hydrocarbon Solvents
D7398	200-1100F (n C7-nC60)	Biodiesels

ASTM D2887

Analysis of Naphthas, Kerosene, Jet, Diesel, VGO's and HVGO's with FBP<1000F

Procedure:

For non-viscous samples: Inject neat

For viscous samples: Dilute sample with CS2

The sample must have a BP Range >100F

Run in order:

(Although Not a Requirement)

Blank

Calibration

QC Reference (2X)

ASTM D2887

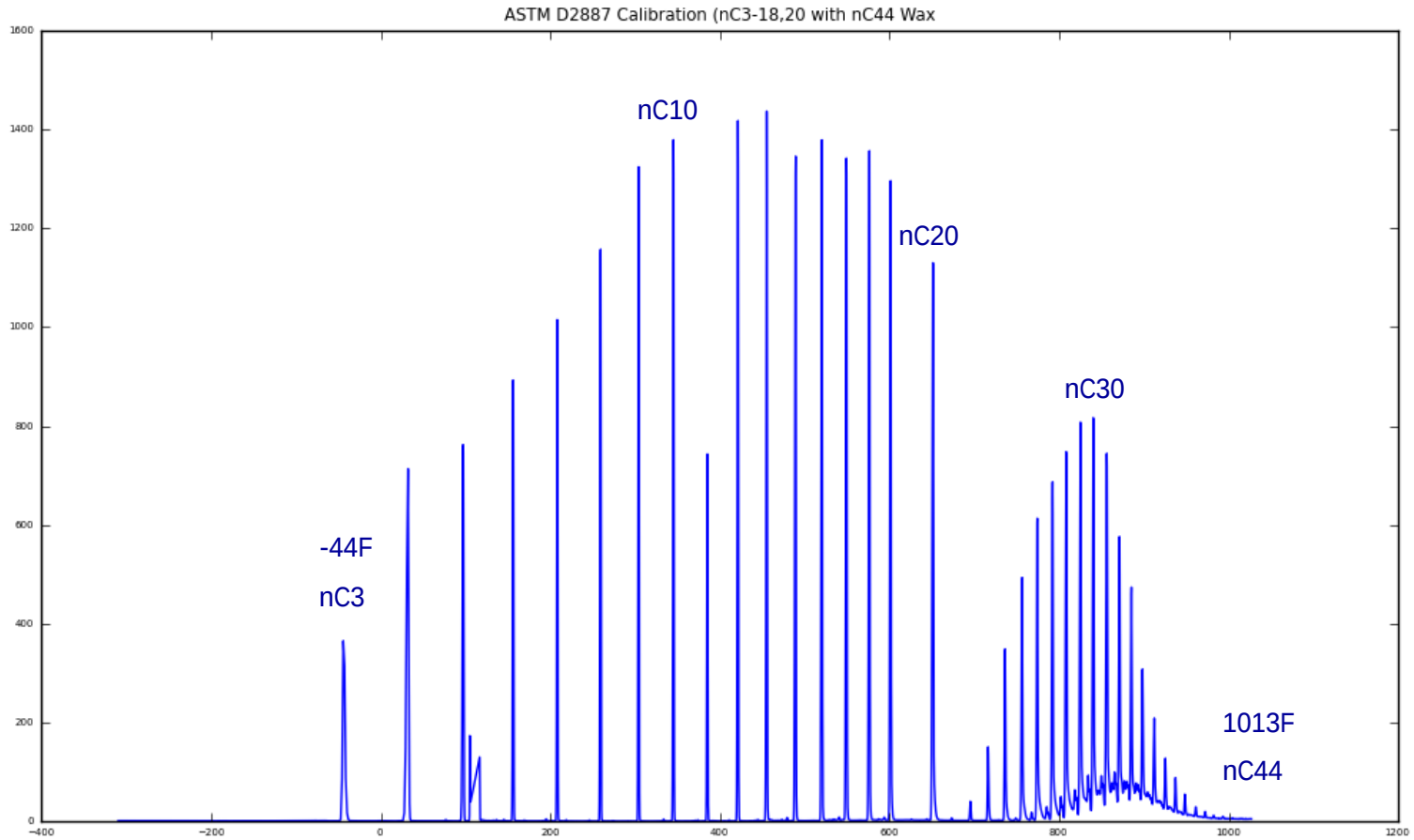
Hardware Requirements:

- Oven with Cryo Cooling to -20C
- Oven with 390C upper temperature
- PTV or Cool-On-Column Inlet with 390C Temp
- FID
- Column- 100% polydimethylsiloxane with upper Temp of 390C
- 99.999% N2,He, or H Carrier Gas

Method Requirements:

- Calibration Run (nC3-nC44)
  - (Maps Carbon Number Retention Time Axis to BP Axis)
- Blank Run
  - (determines EOR Baseline)
- Reference Oil #1 -QC Reference
  - (Establishes precision and repeatability to validate system performance)

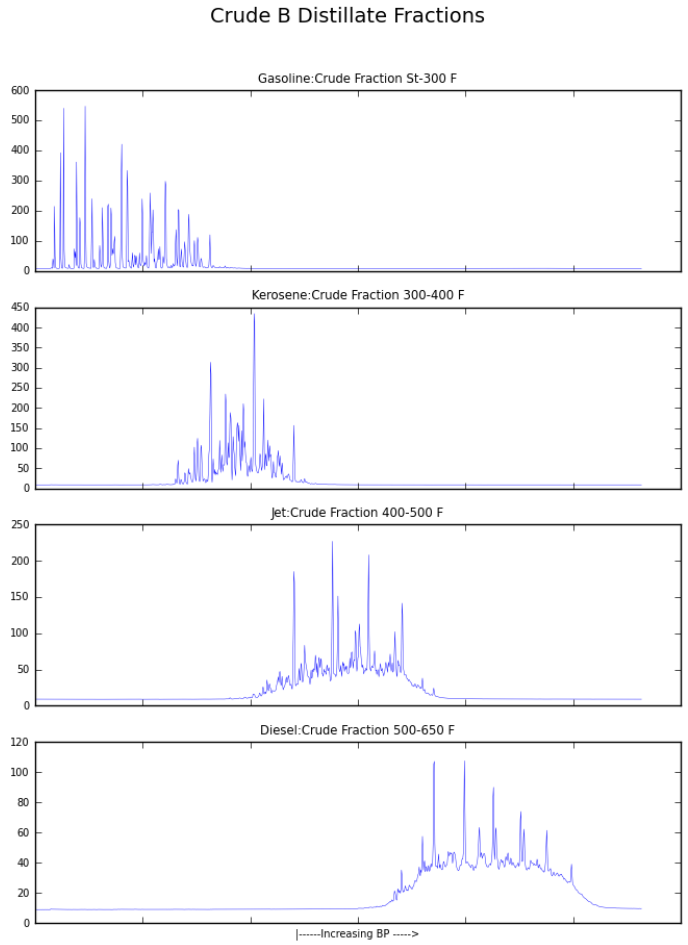
D2887 SimDis Calibration Mix



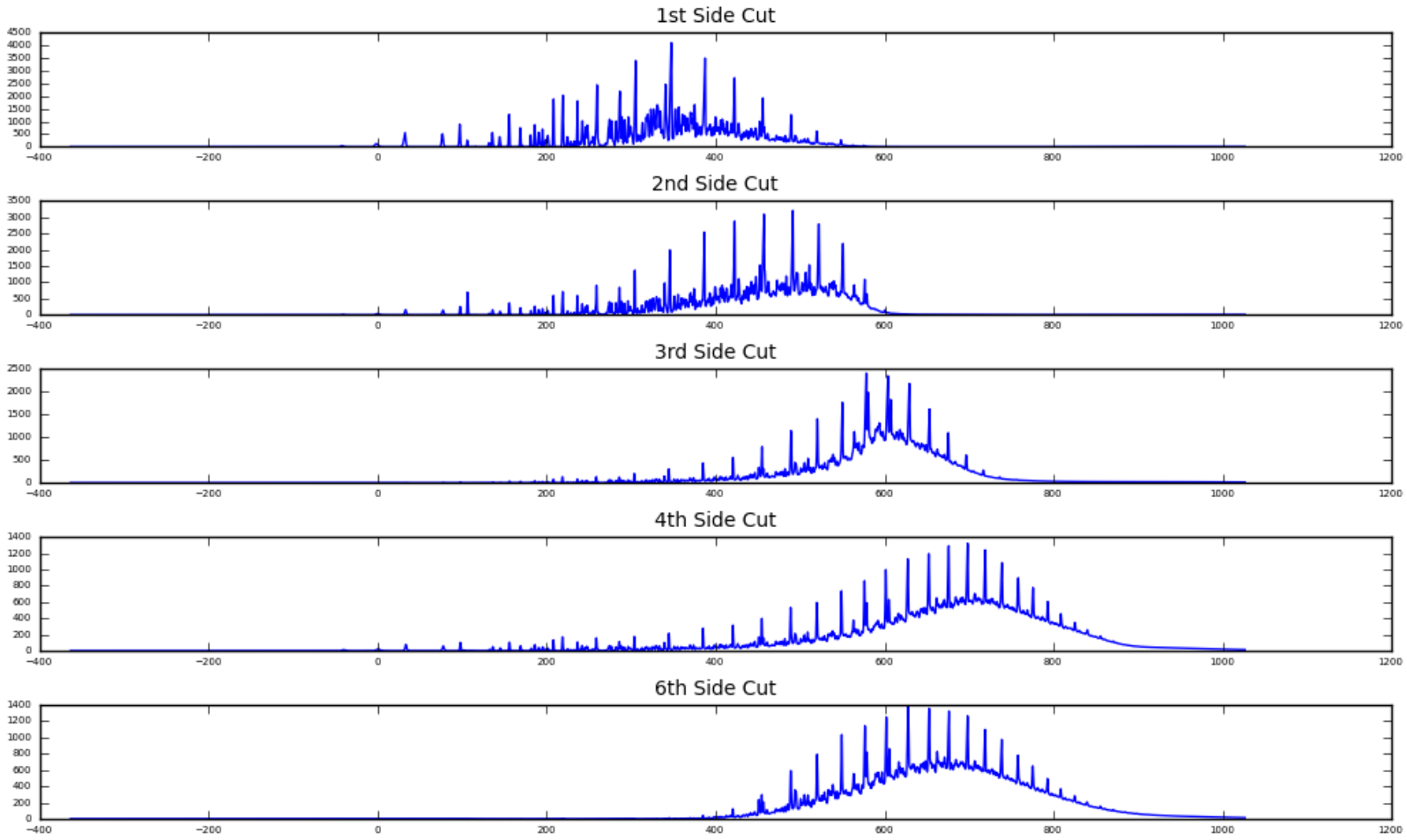
D2887 SimDis of Crude Fractions

SimDis Analysis of:

1. **Straight Run Gasoline**
2. **Kerosene**
3. **Jet**
4. **Diesel**



D2887 Analysis of Crude Unit Side Cuts

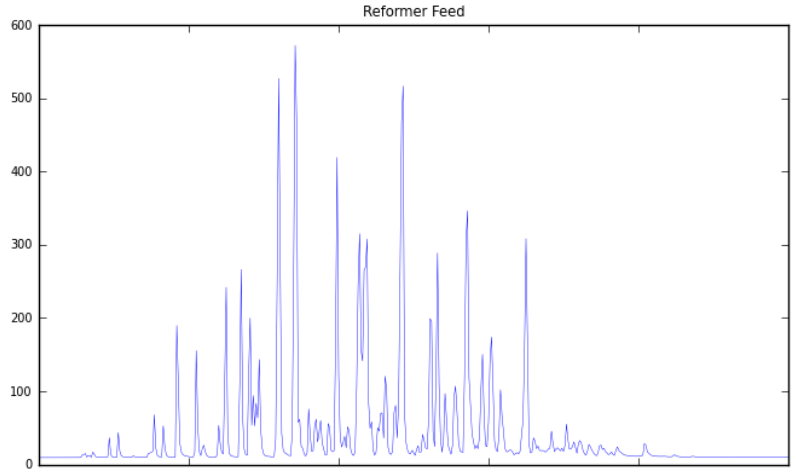


D2887 Analysis of a Reformer

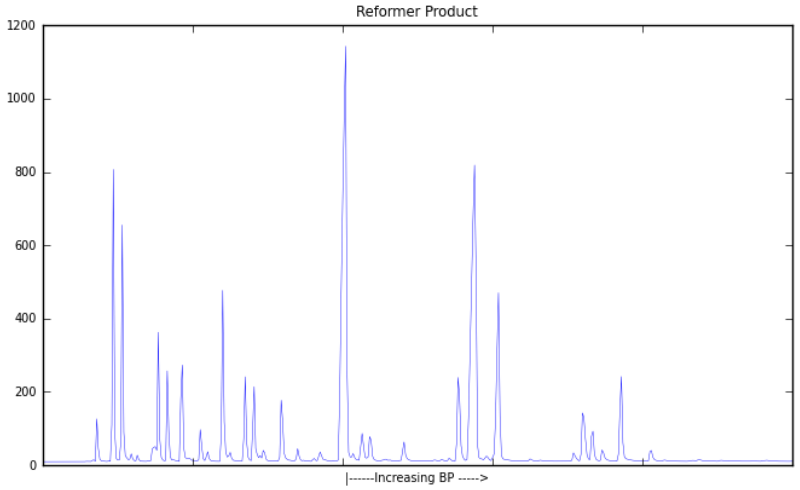
SimDis Analysis of:

Reforming Process which converts low octane components to high octane compounds

1. **Reformer Feed: Alkanes and Isoparaffins**



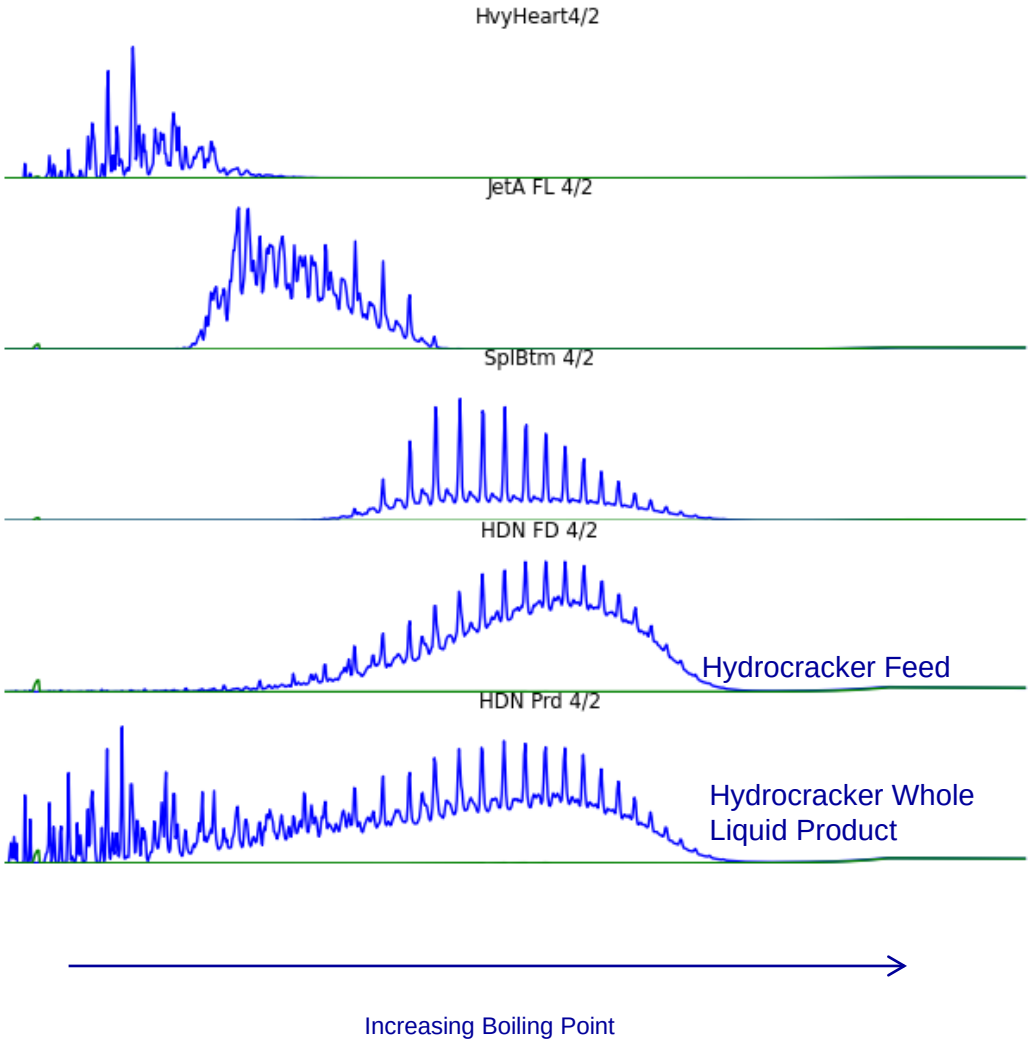
2. **Reformer Product: Aromatics**



D2887 Analysis of a Hydrocracker

SimDis Analysis of:

Hydrocracker Process which converts Gas Oils to Gasoline and Jet fuel Blending components



ASTM D7500

Analysis of Lube Oils, VGO's and HVGO's with FBP<1000F

Procedure:

Dilute the Sample to 1-3% solution with CS2

Run in order:

(Although Not a Requirement)

Blank

Calibration

QC Reference

ASTM 7500

Hardware Requirements:

Oven with 430C upper temperature

PTV or Cool-On-Column Inlet with 430Temp

FID

Column- 100% polydimethylsiloxane with upper Temp of 430C

99.999% N2,He, or H Carrier Gas

Method Requirements:

Calibration Run (nC3-nC110)

(Maps Carbon Number Retention Time Axis to BP Axis)

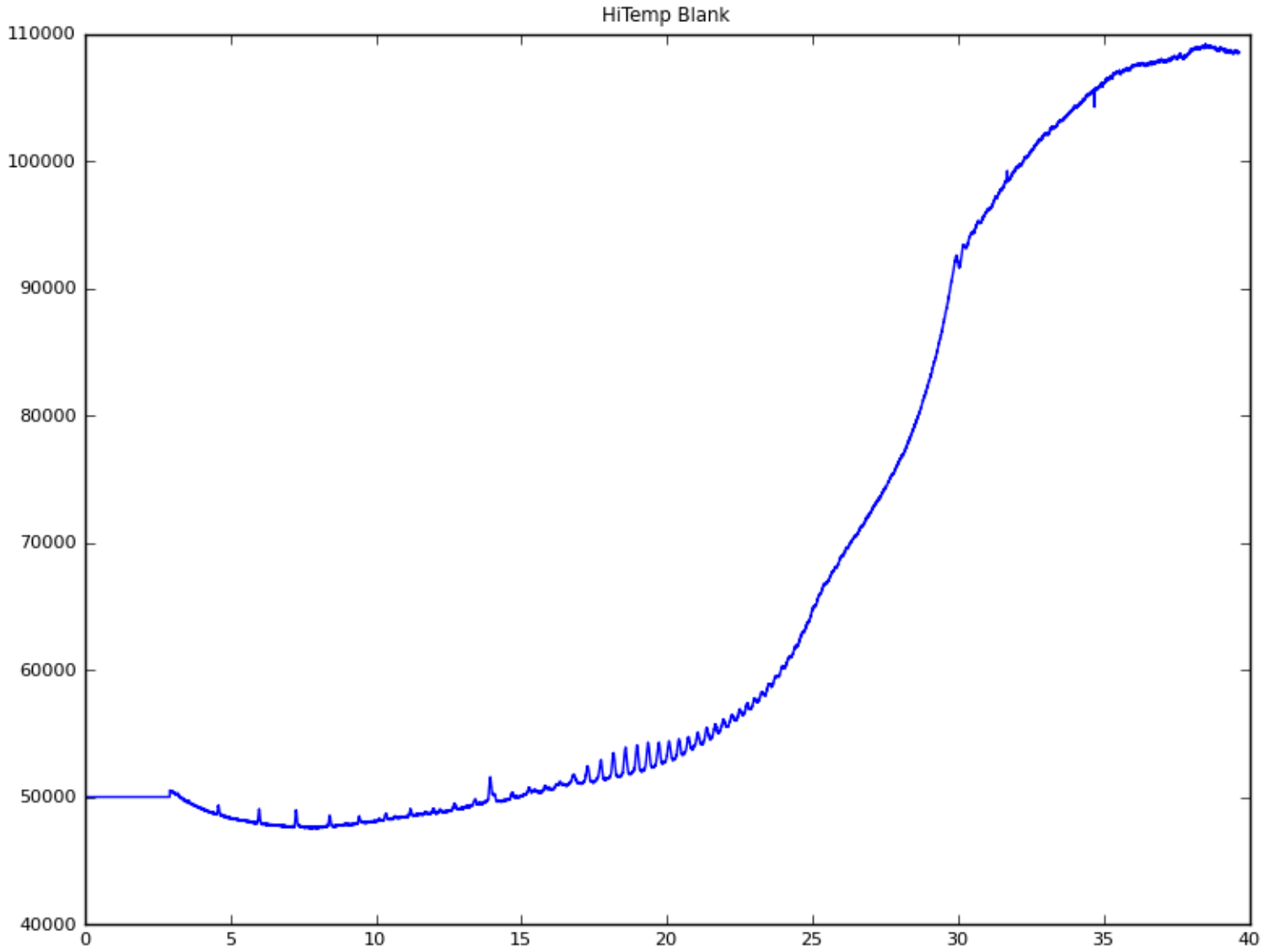
Blank Run (First run and after every 5 samples)

(determines EOR Baseline)

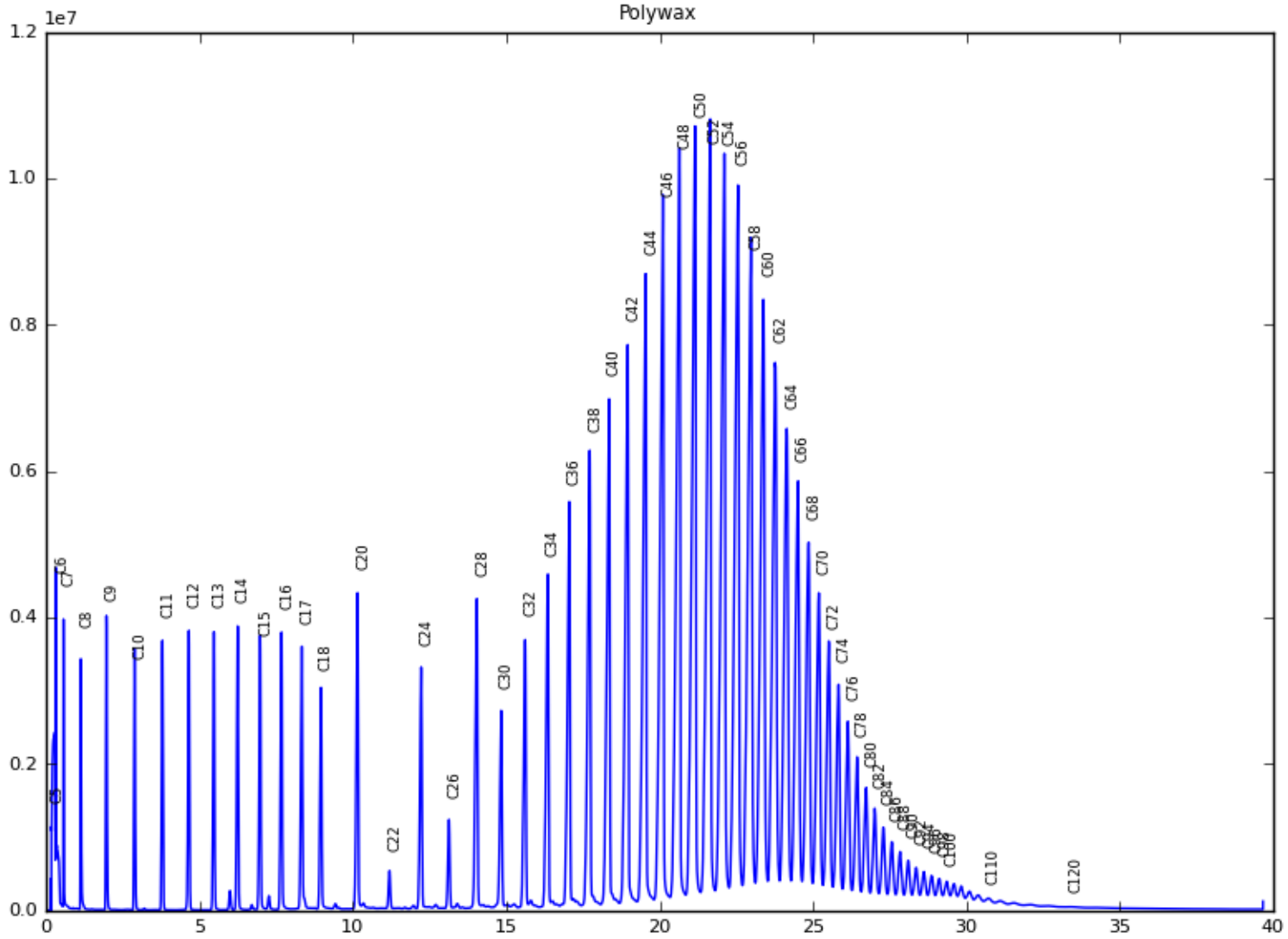
Reference Oil 5010 -QC Reference

(Establishes precision and repeatability to validate system performance)

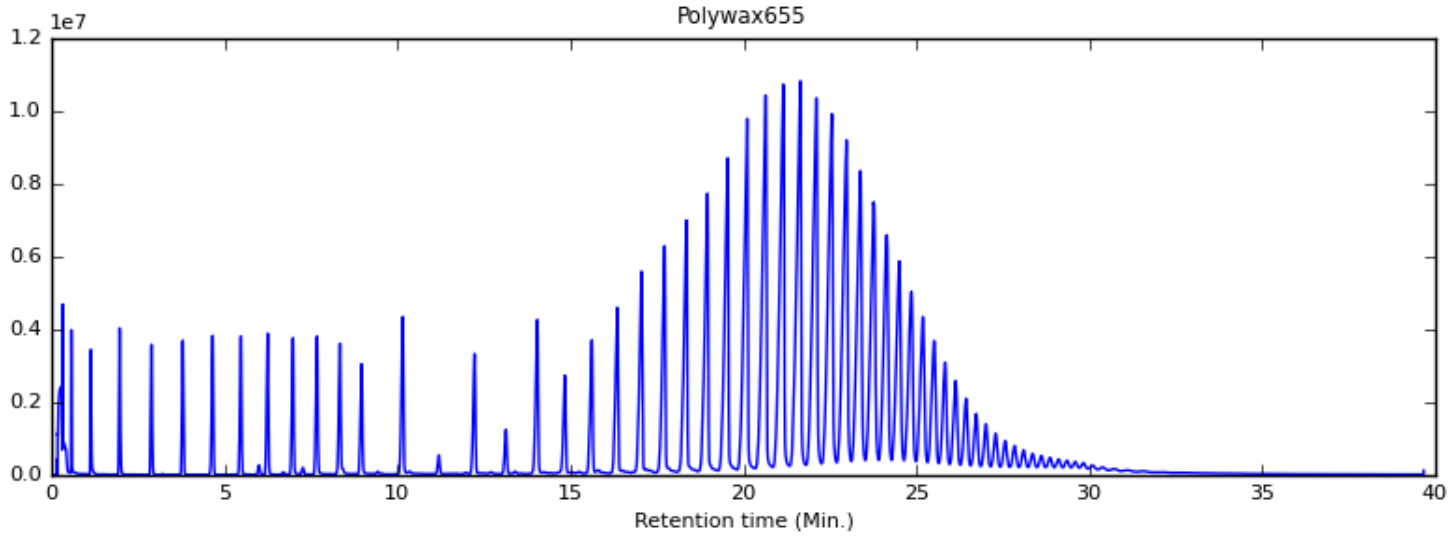
Hi-Temp Blank

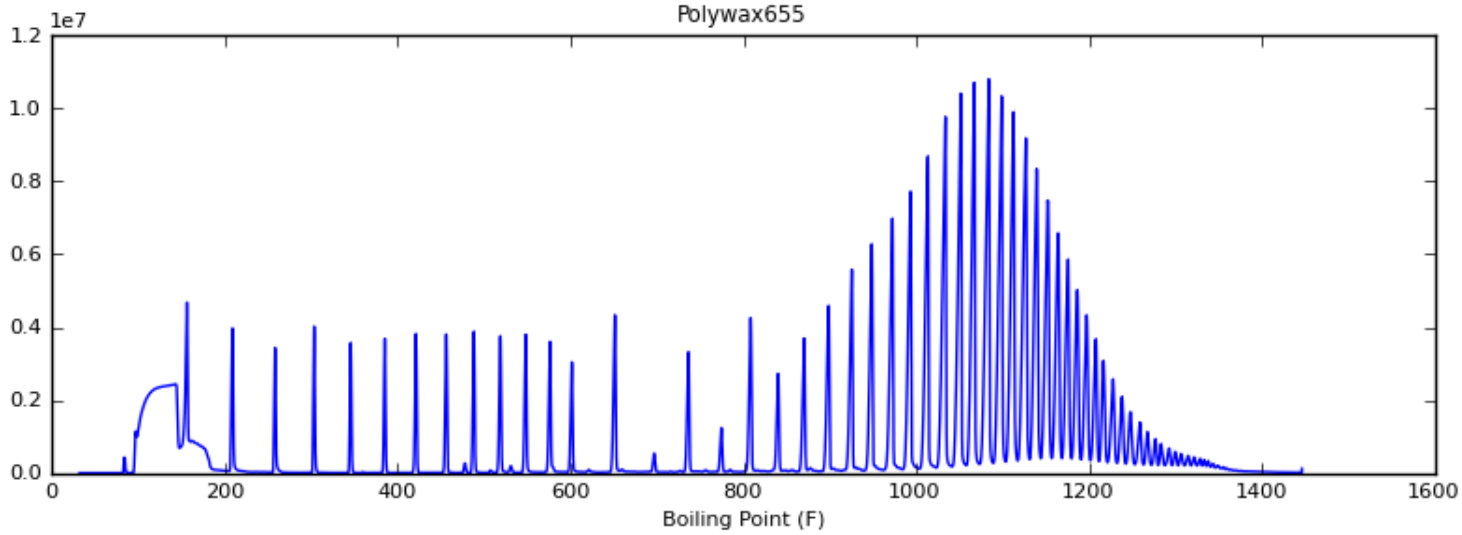


Hi-Temp SimDis Calibration



ASTM 7500: Time to Temp





ASTM D7169

Analysis of Whole Crudes, Residua and other partially eluted samples

Procedure:

Dilute 0.02 g sample with 10 ml CS2

Inject Diluted Sample

Run in order:

Blank (and blanks after every sample)

Calibration

QC Reference (2X)

ASTM D7169

Hardware Requirements:

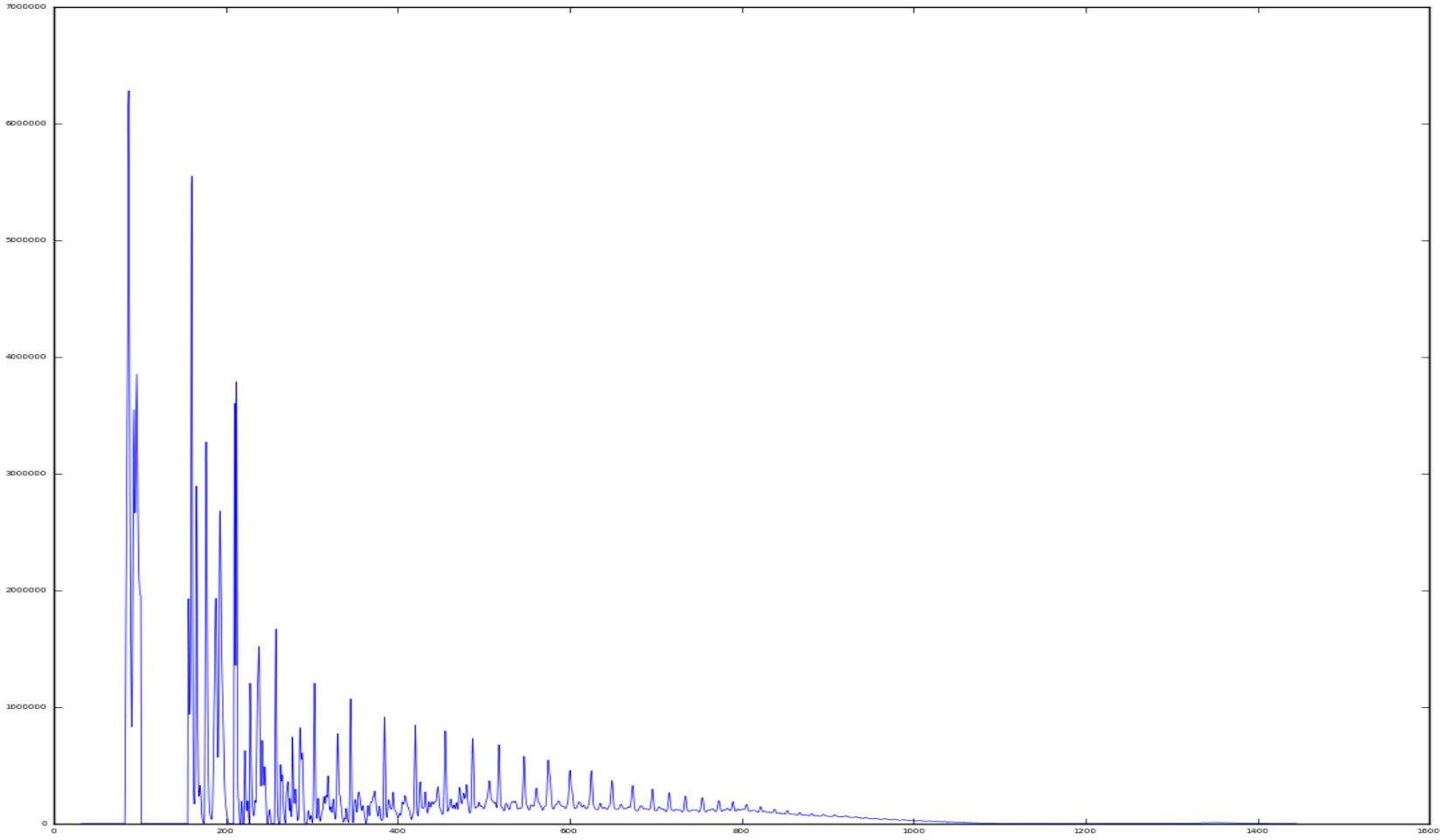
- Oven with Cryo Cooling to -20C
- Oven with 425C upper temperature
- PTV or Cool-On-Column Inlet with 425C Temp
- FID
- Column- 100% polydimethylsiloxane with upper Temp of 435C
- 99.999% N2,He, or H Carrier Gas

ASTM D7169

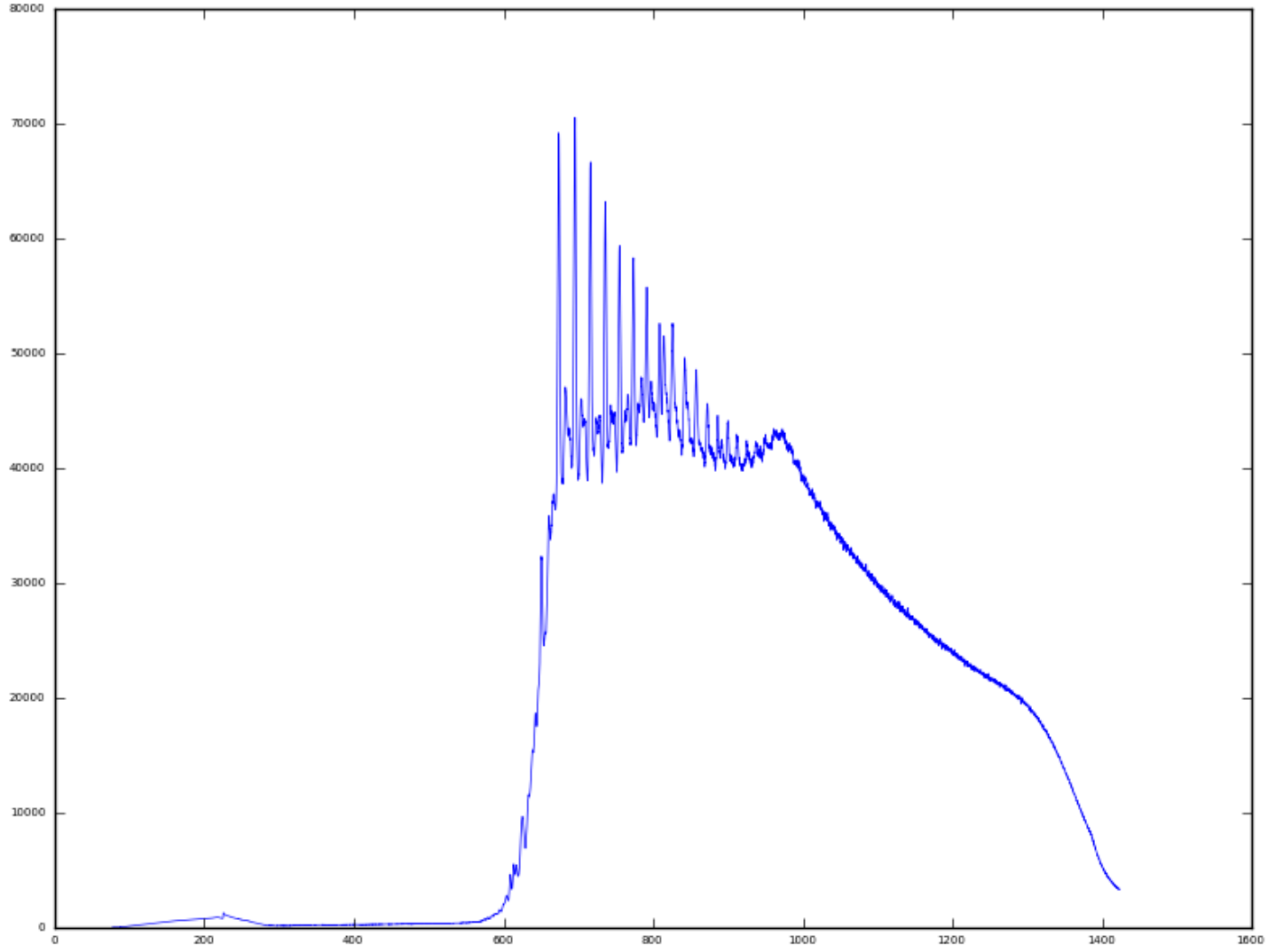
Method Requirements:

- Calibration Run (nC3-nC100)
  - (Maps Carbon Number Retention Time Axis to BP Axis)
- Blank Run
  - (determines EOR Baseline)
- Reference Oil 5010 -QC Reference
  - (sets the Carbon Response Factor for Yield Recovery Calculations)

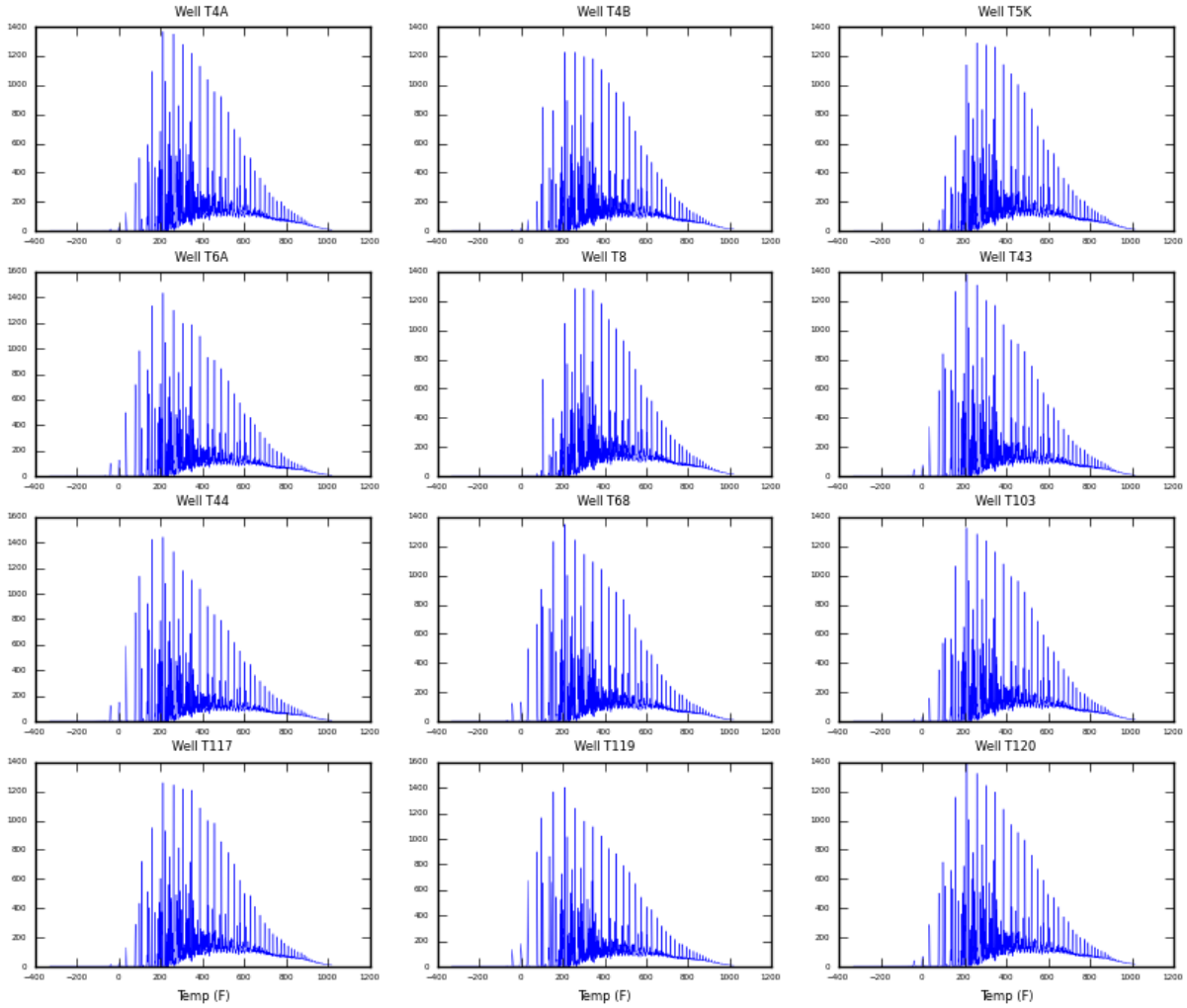
ASTM D7169: Crude Oil



ASTM D7169: Atmospheric Residua



D7169 of Whole Crude

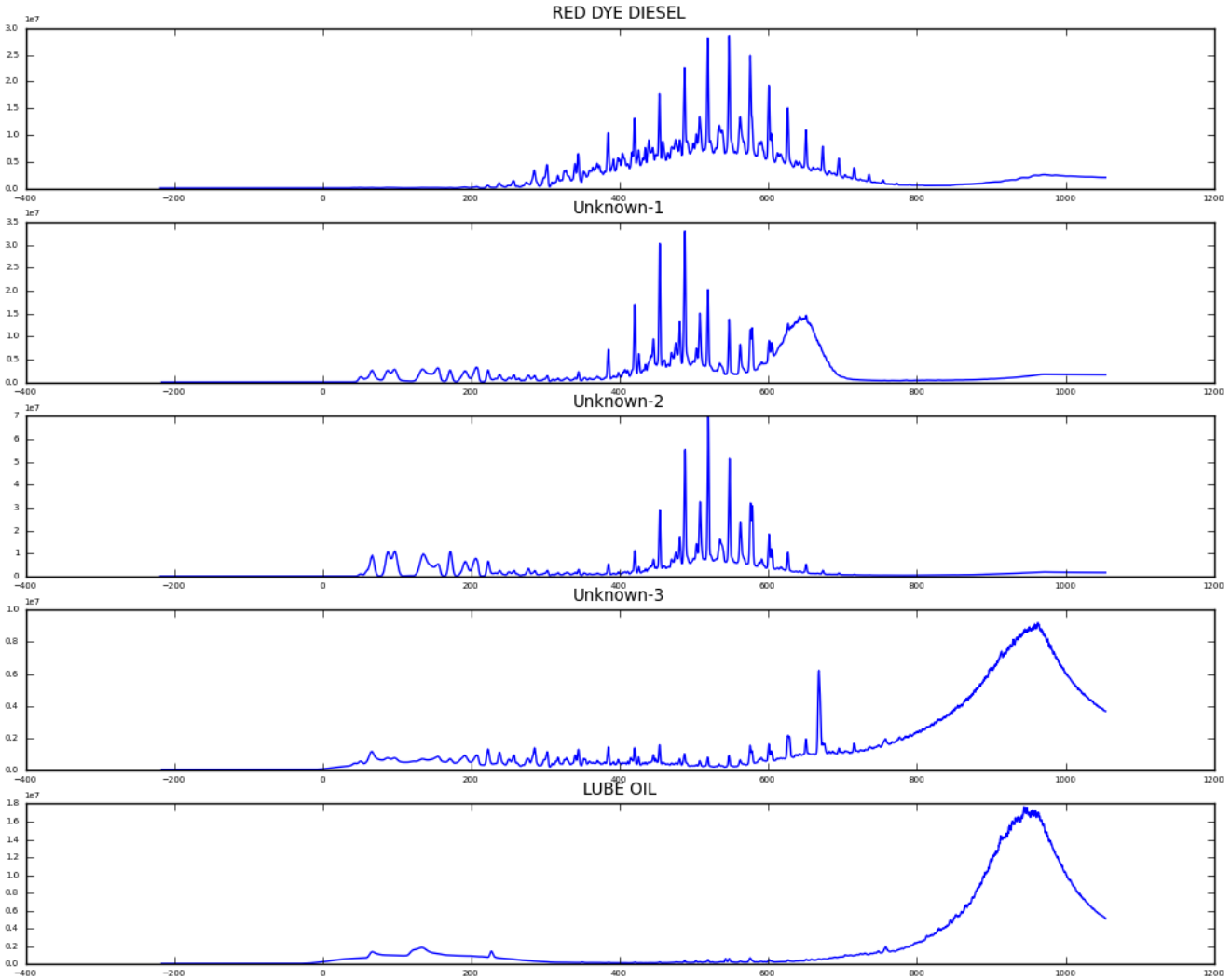


Fingerprinting Methods

Analytical Fingerprinting refers to the characterization of a sample by the use of techniques which use features obtained from the analysis to distinguish differences and similarities among samples and sample types.

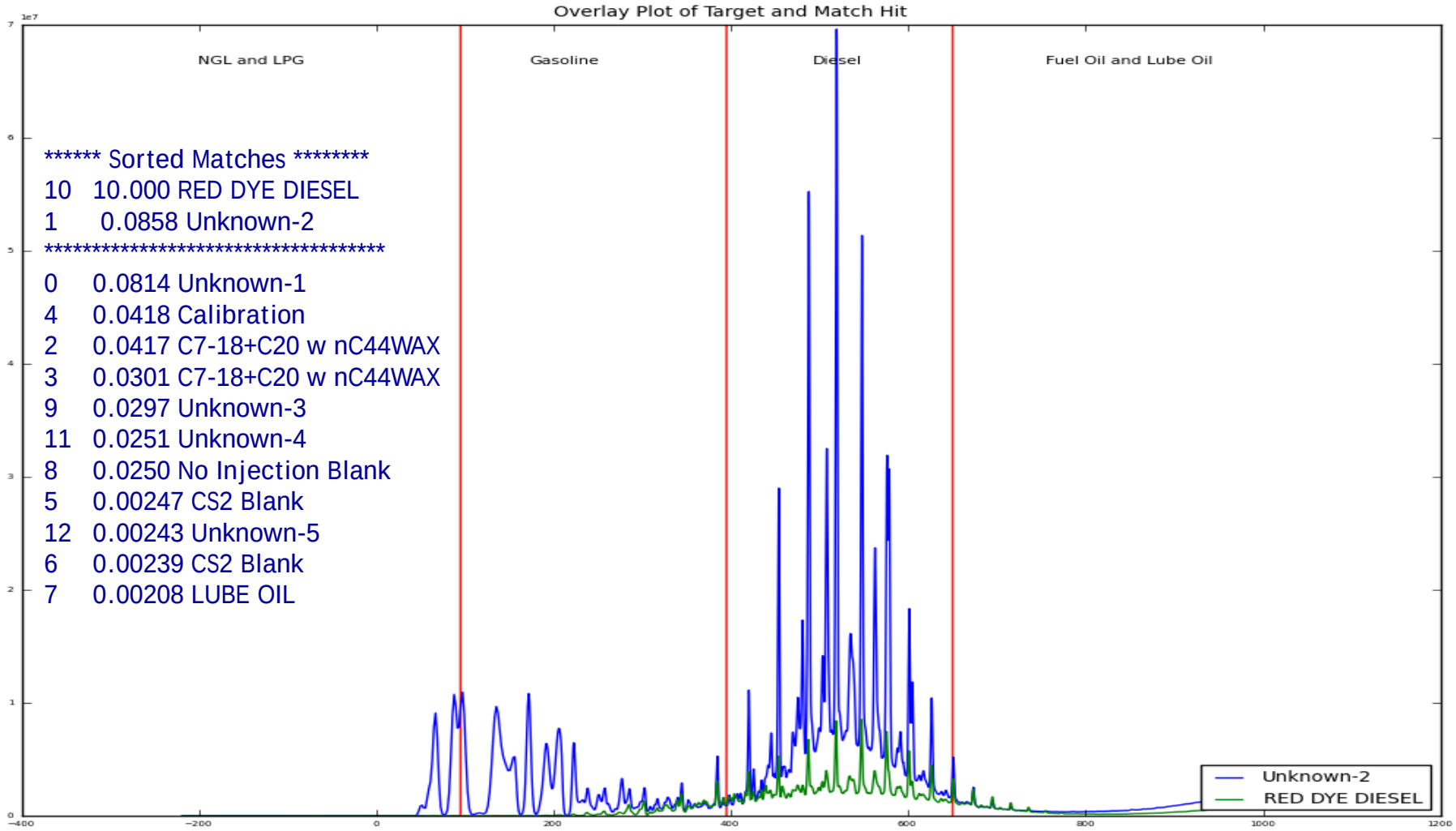
These methods are generally used to verify specification compliance for select product streams and often to identify the source of "fugitive" hydrocarbons

Fingerprint Example



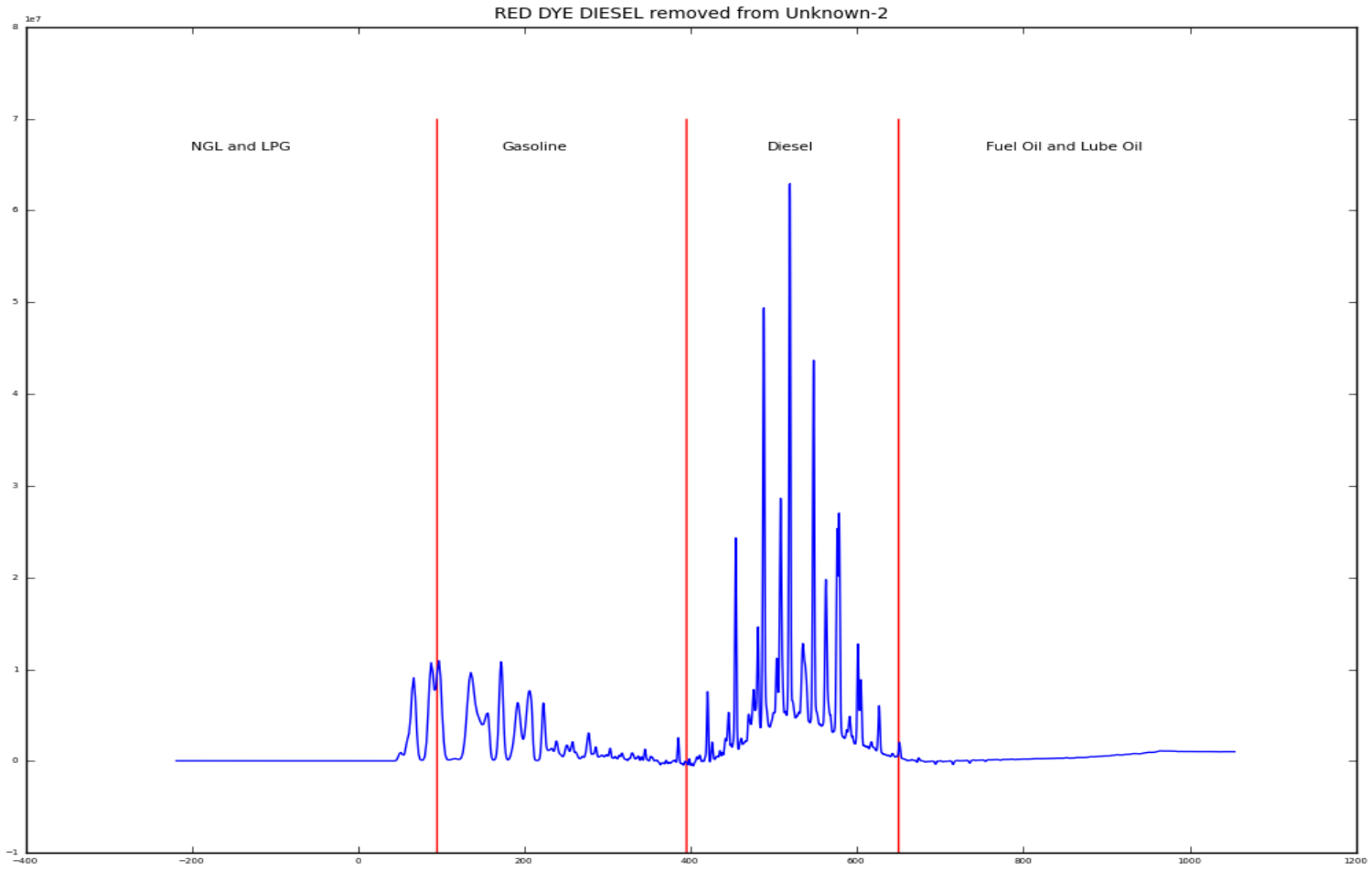
Hydrocarbons from a Pipeline Knockout Pots

Fingerprint Example



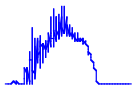
Overlay of best match to Red Dye Diesel

Fingerprint Example



Red Dye Diesel when removed from the Sample shows another diesel and a gasoline as contaminants

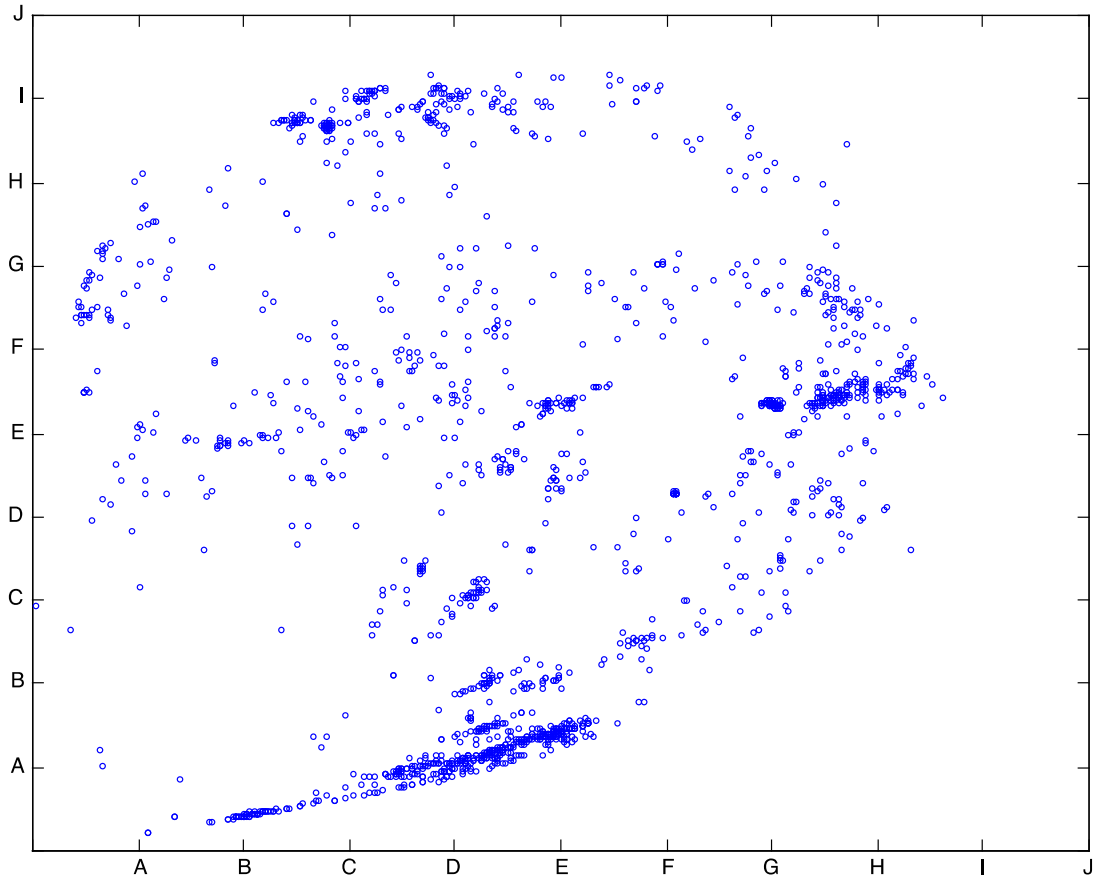
Crude Oil Signature Library



URALS EXPORT

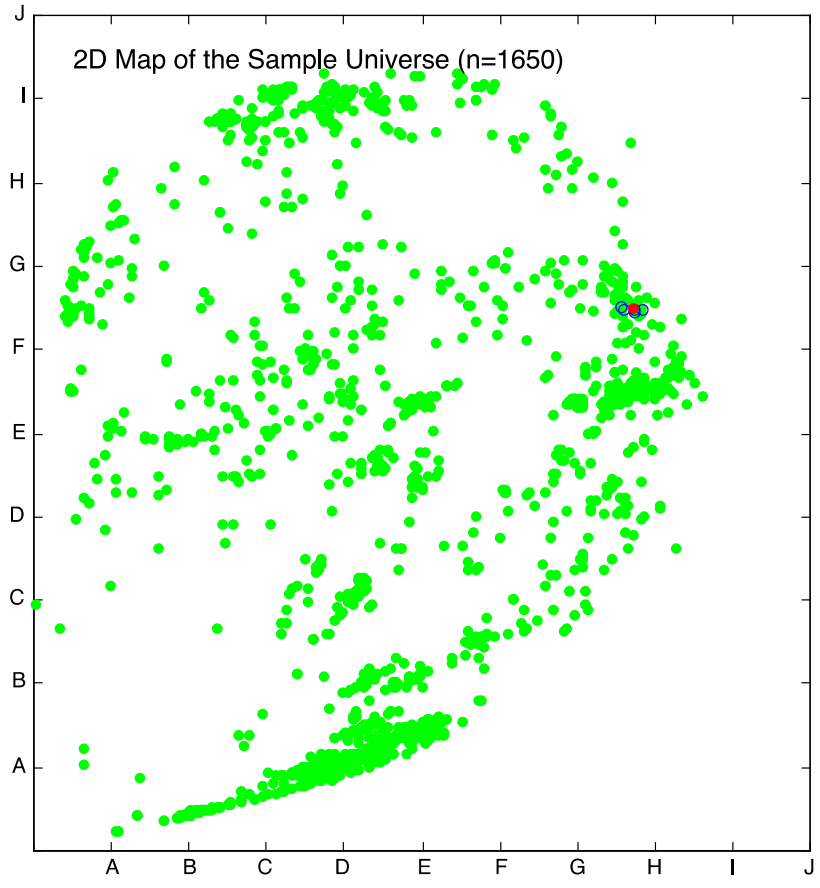
Reference Crude Oil Library

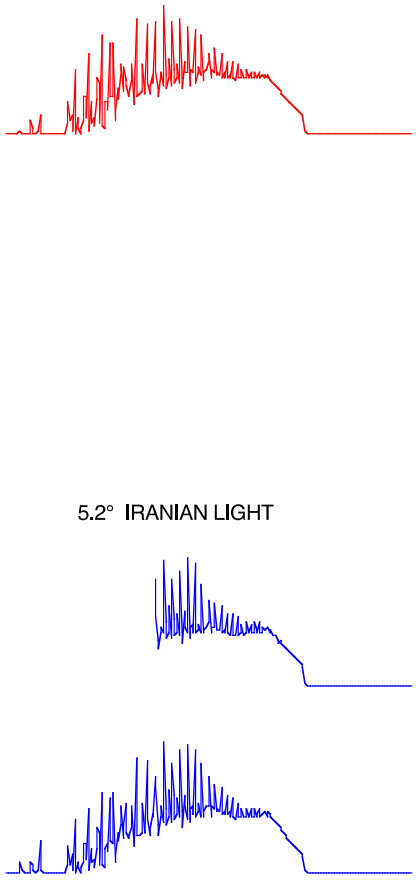
2D Map of the Sample Universe



This plot presents a visualization in a 2D mathematical space of the chromatographic profiles for 1650 samples including 200 crude oils

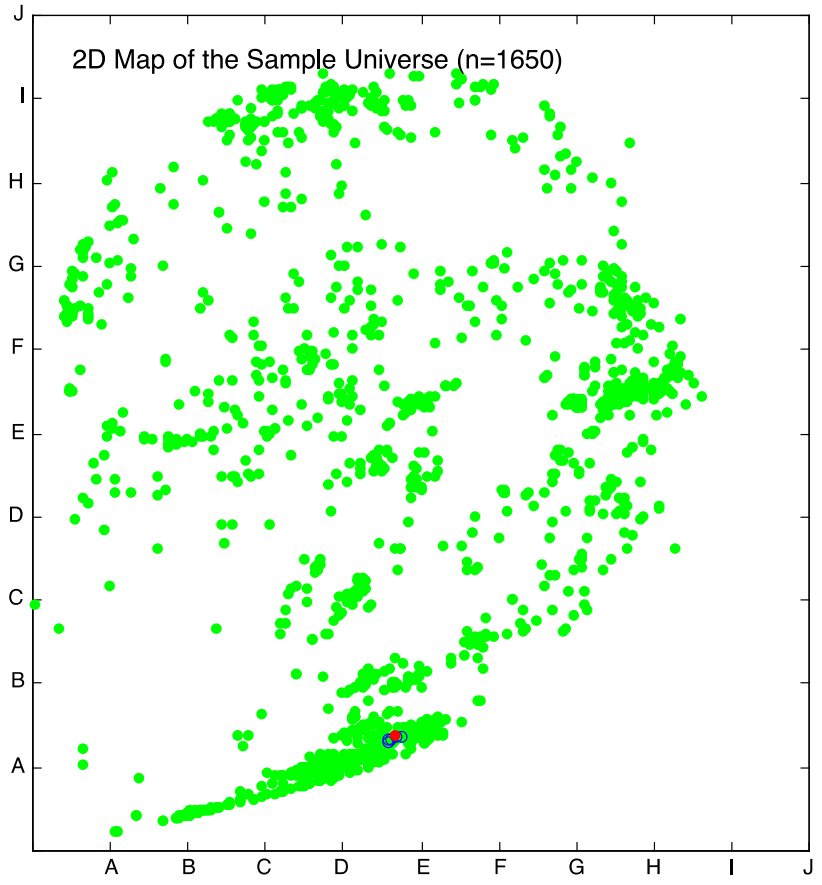
Identification and Extraction of Similar Samples-Crude Oils

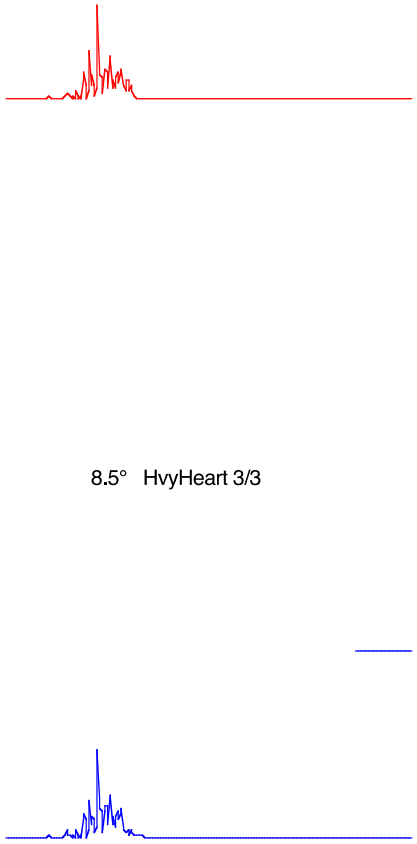




Here we show the utility of our approach to automatically extract the samples from the data base having the greatest similarity to the source sample

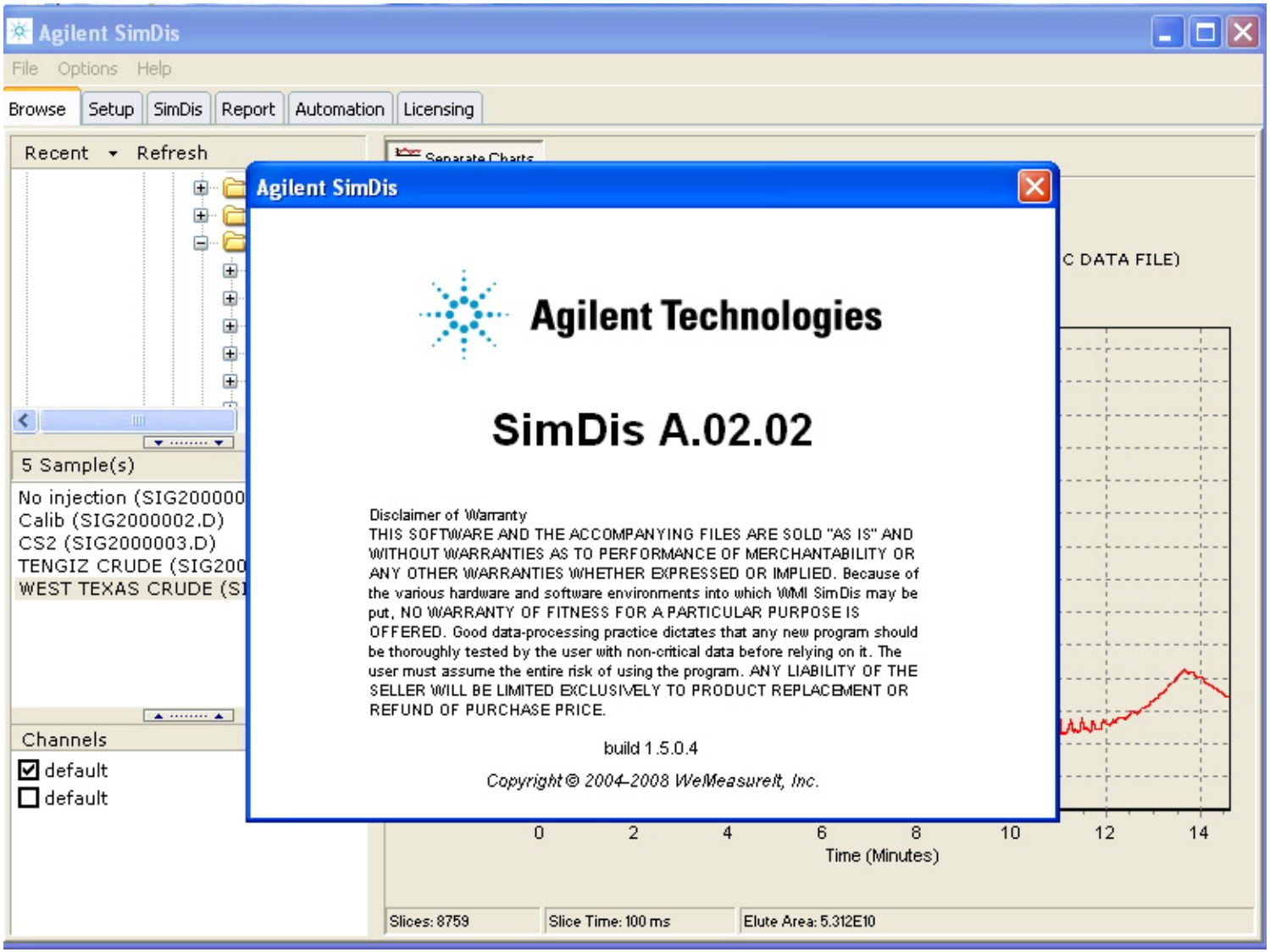
Identification and Extraction of Similar Samples-Naphthas



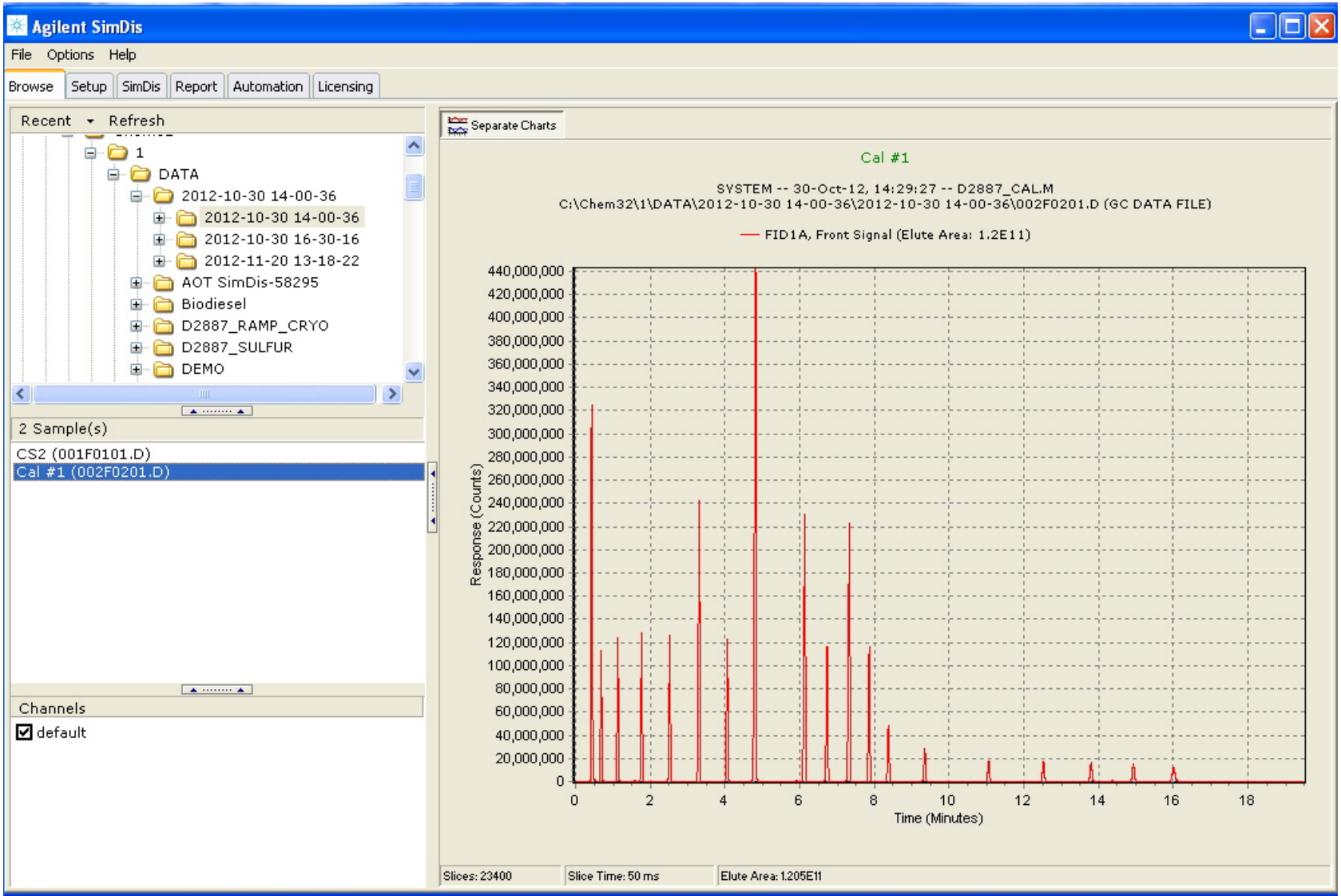


Here we show the utility of our approach to automatically extract the samples from the data base having the greatest similarity to the source sample

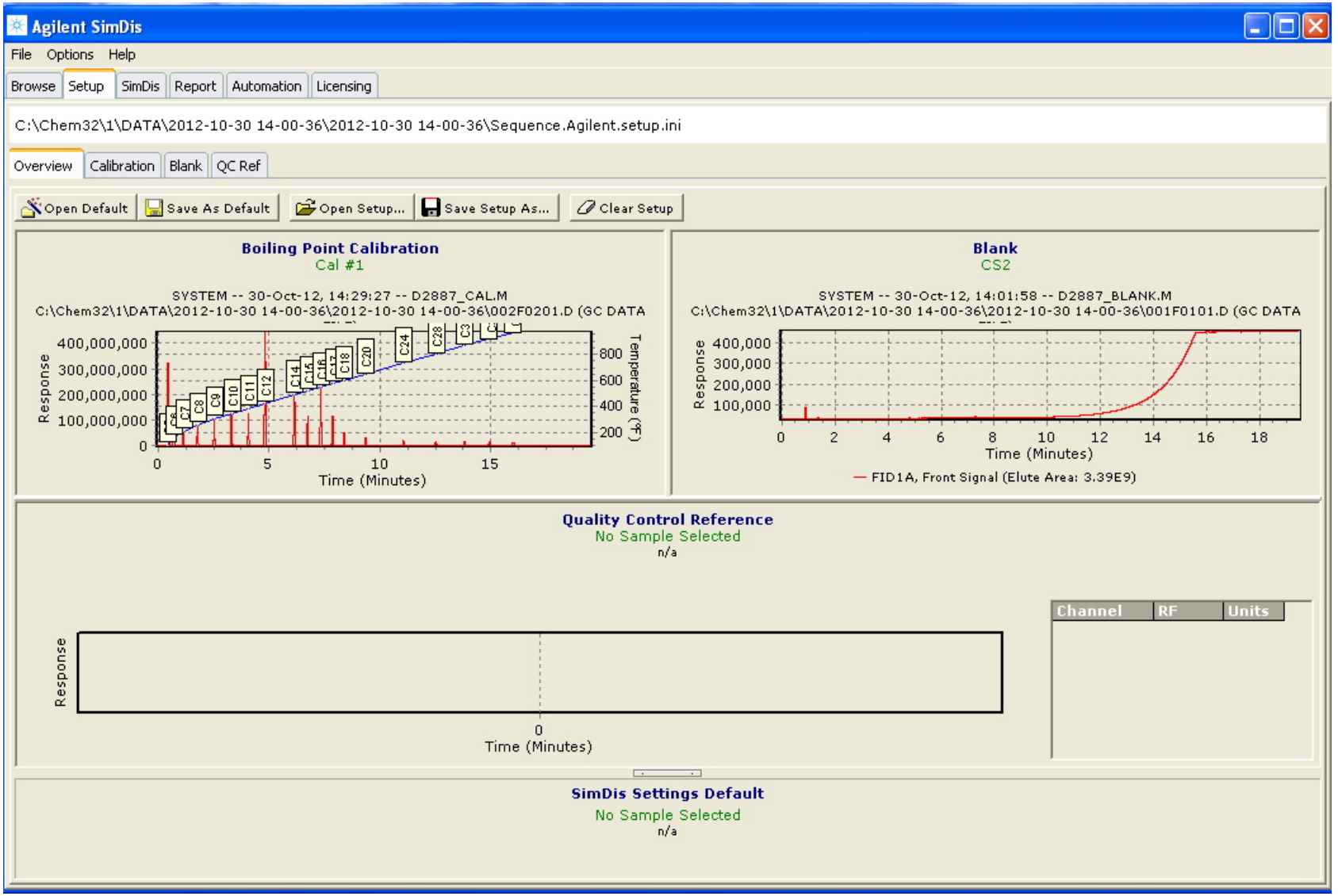
Agilent SimDis



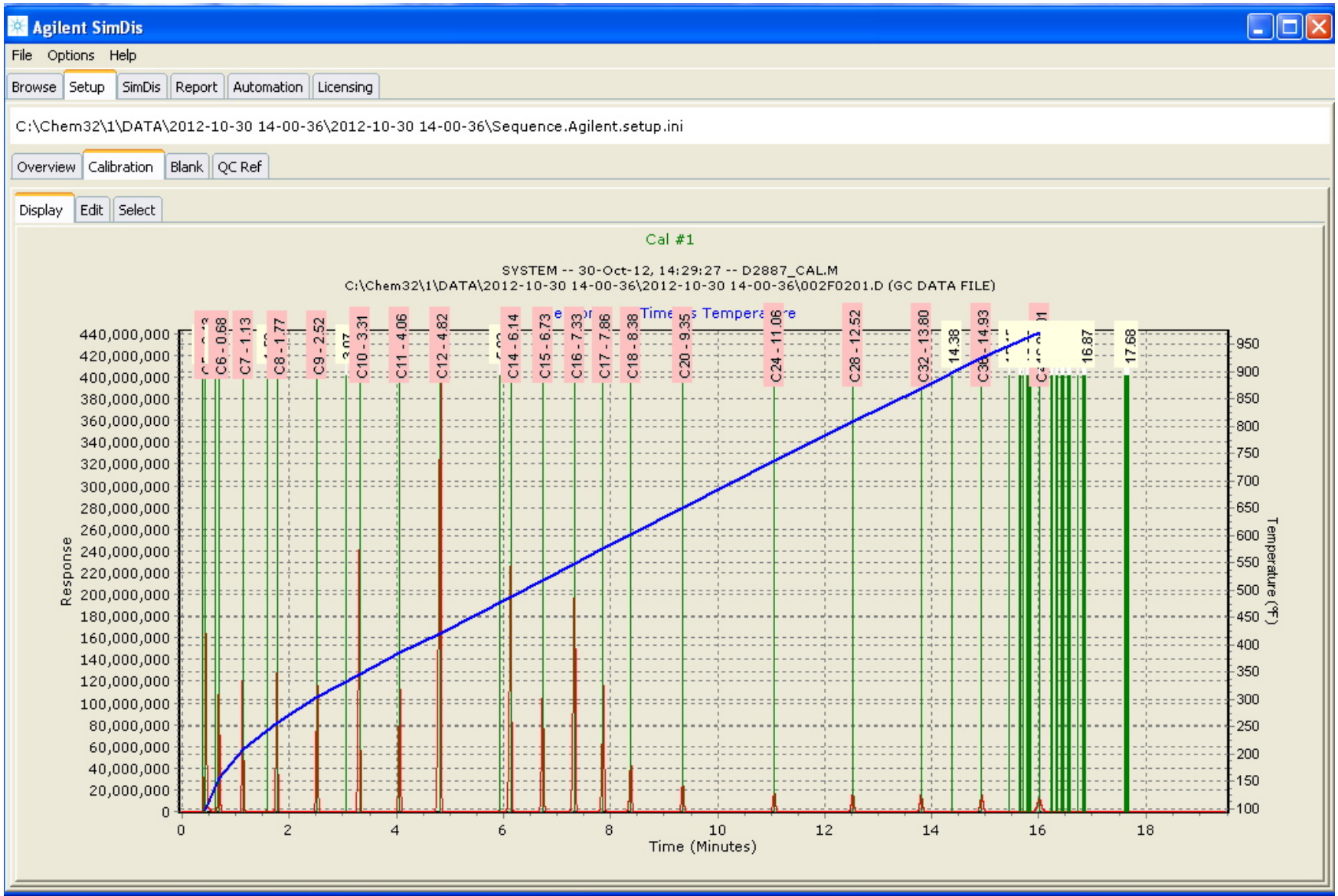
Agilent SimDis



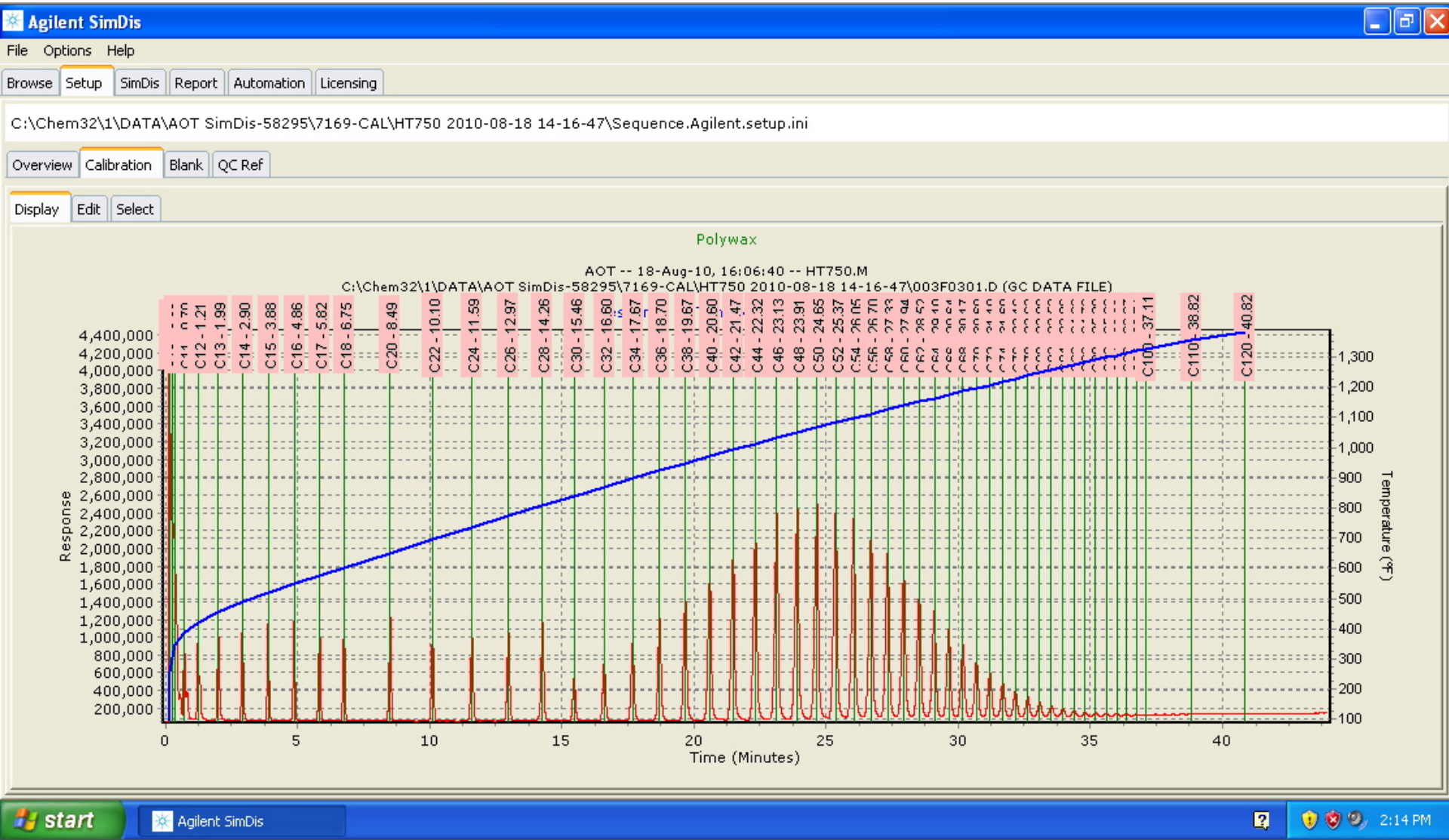
Agilent SimDis



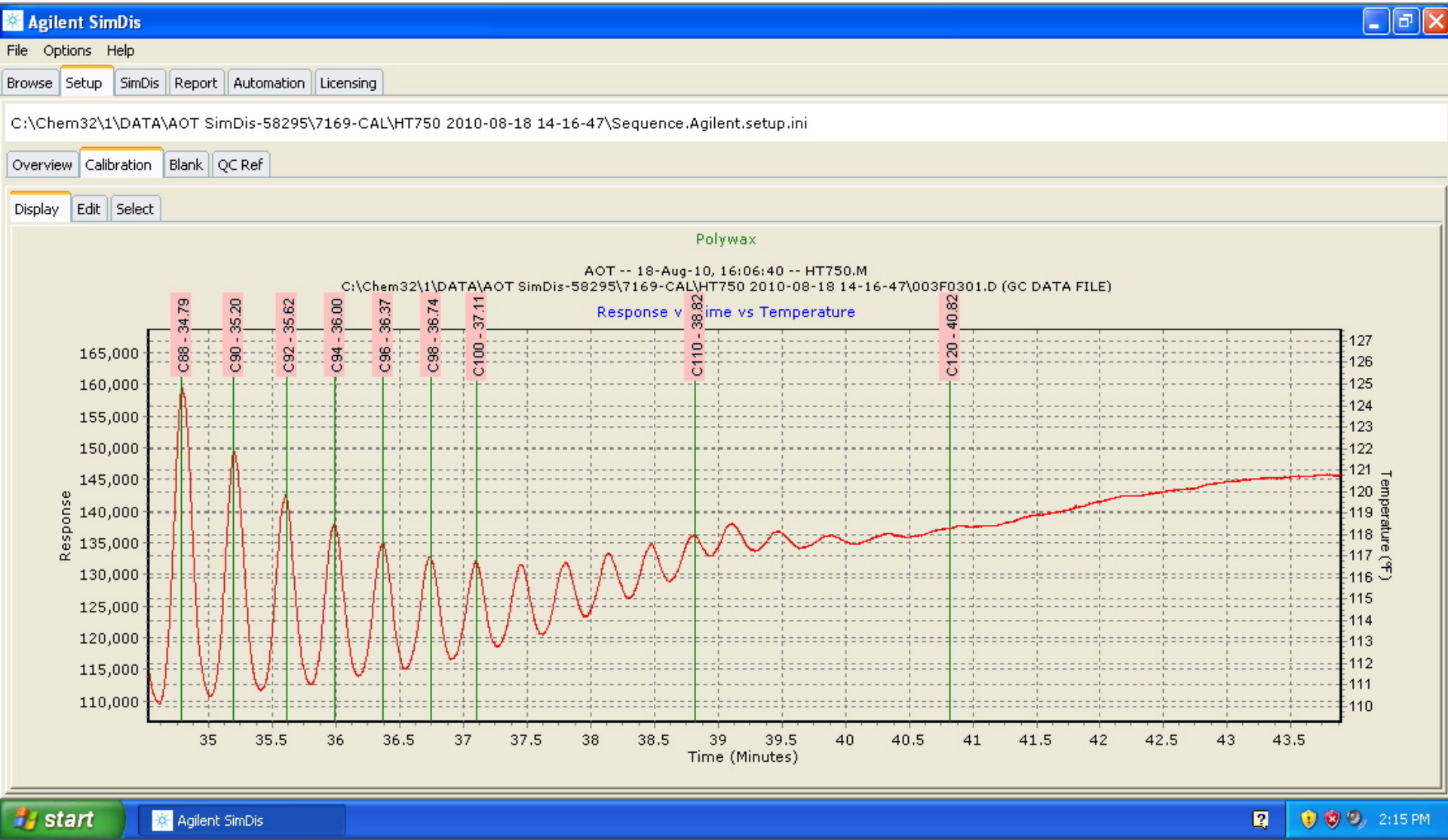
Agilent SimDis



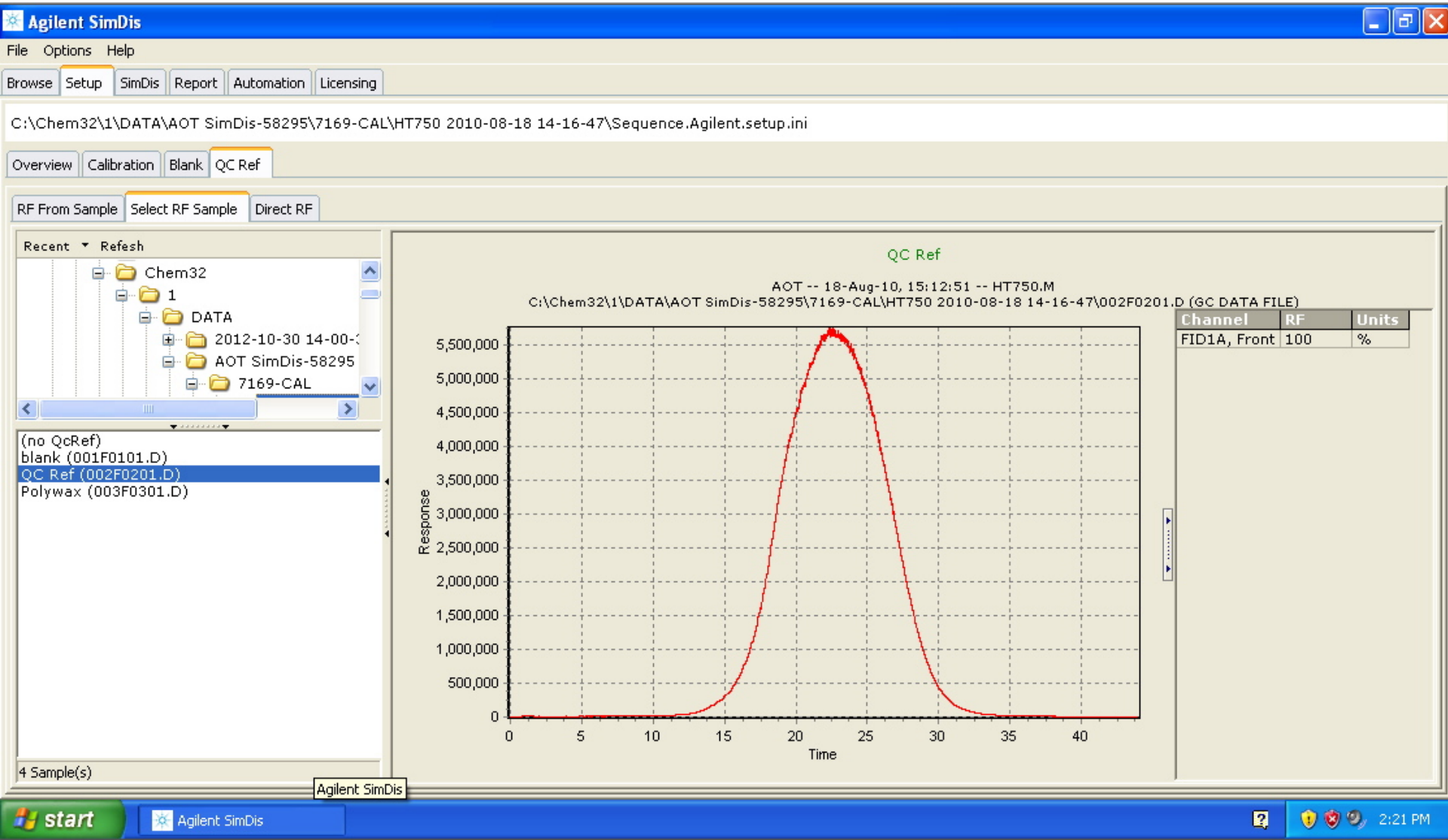
Agilent SimDis Calibration



Agilent SimDis Calibration



Agilent SimDis QC Reference



Agilent SimDis

File Options Help

Browse | Setup | SimDis | Report | Automation | Licensing

Load Settings From Default Sample | Use This Sample As Default

Sample
RGO (001F0101.D)
Channel
[0] default

Zeroing Method
Subtract Blank
Blank Offset 0

Dilution Factor
Original: 1.00000
Current: 1.00000

Solvent Masking
None

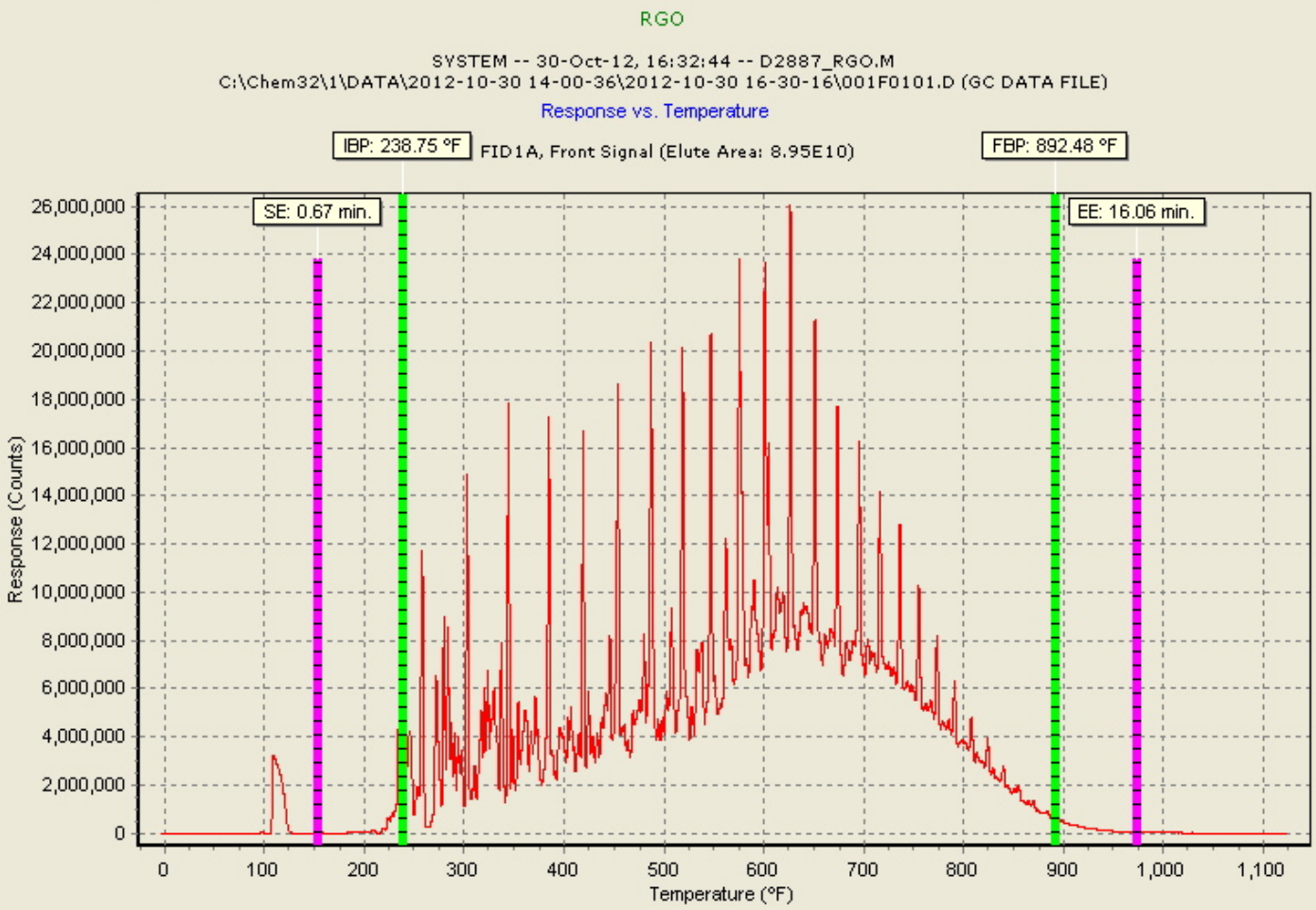
Filter
No Filtering

Elution Time
Automatic (ASTM)
Start Time: 0.6700 min.
End Time: 16.0617 min.

Boiling Points
Initial BP: 238.75 °F
Final BP: 892.48 °F

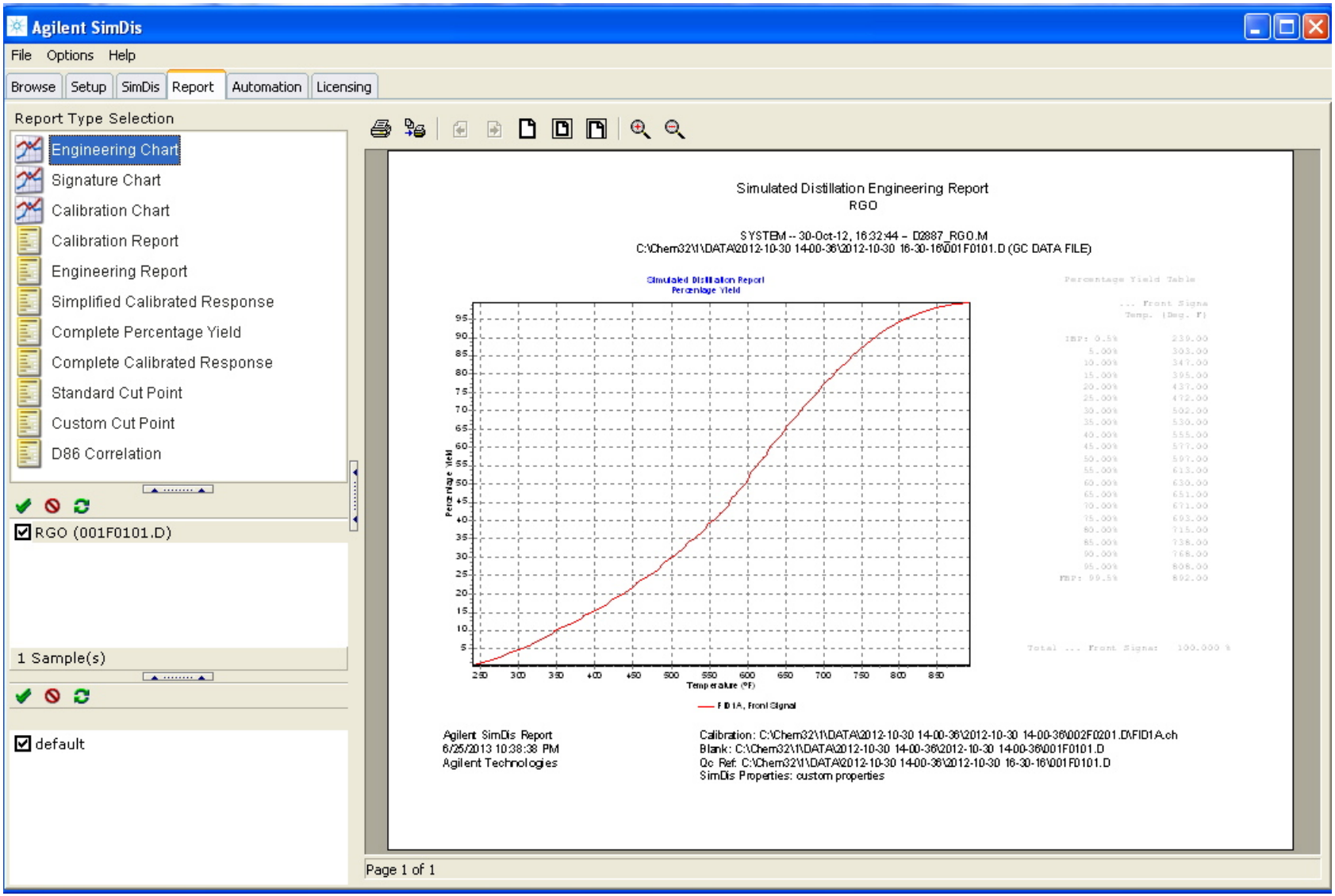
Percent Recovery
Recovery: 100.000 %
Normalize to 100%

Cal | Elute | BP | Sum | Blank | Raw | Unfilt | Lock Zoom

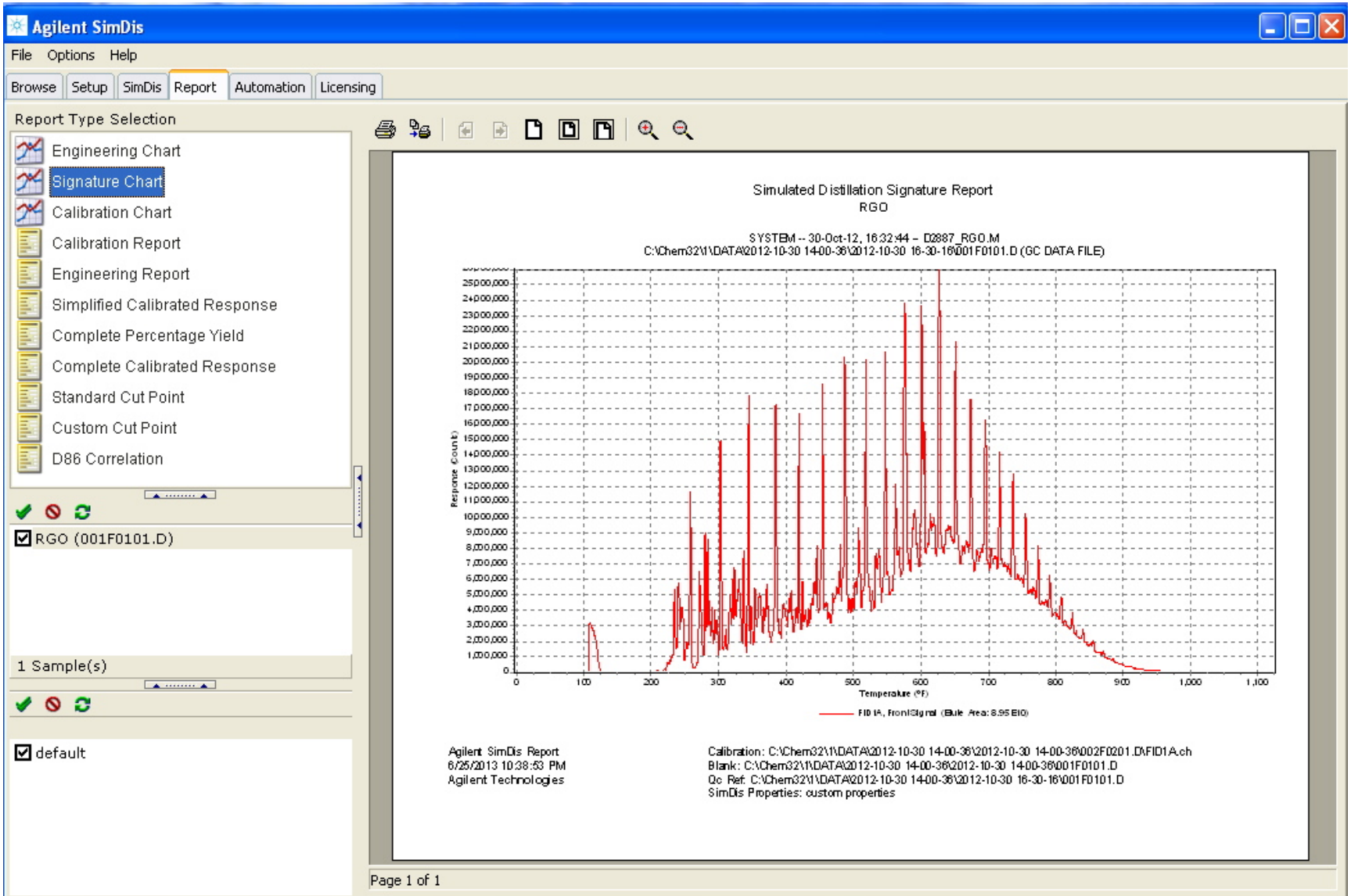


Slices: 23400 | Slice Time: 50 ms | Elute Area: 8.951E10

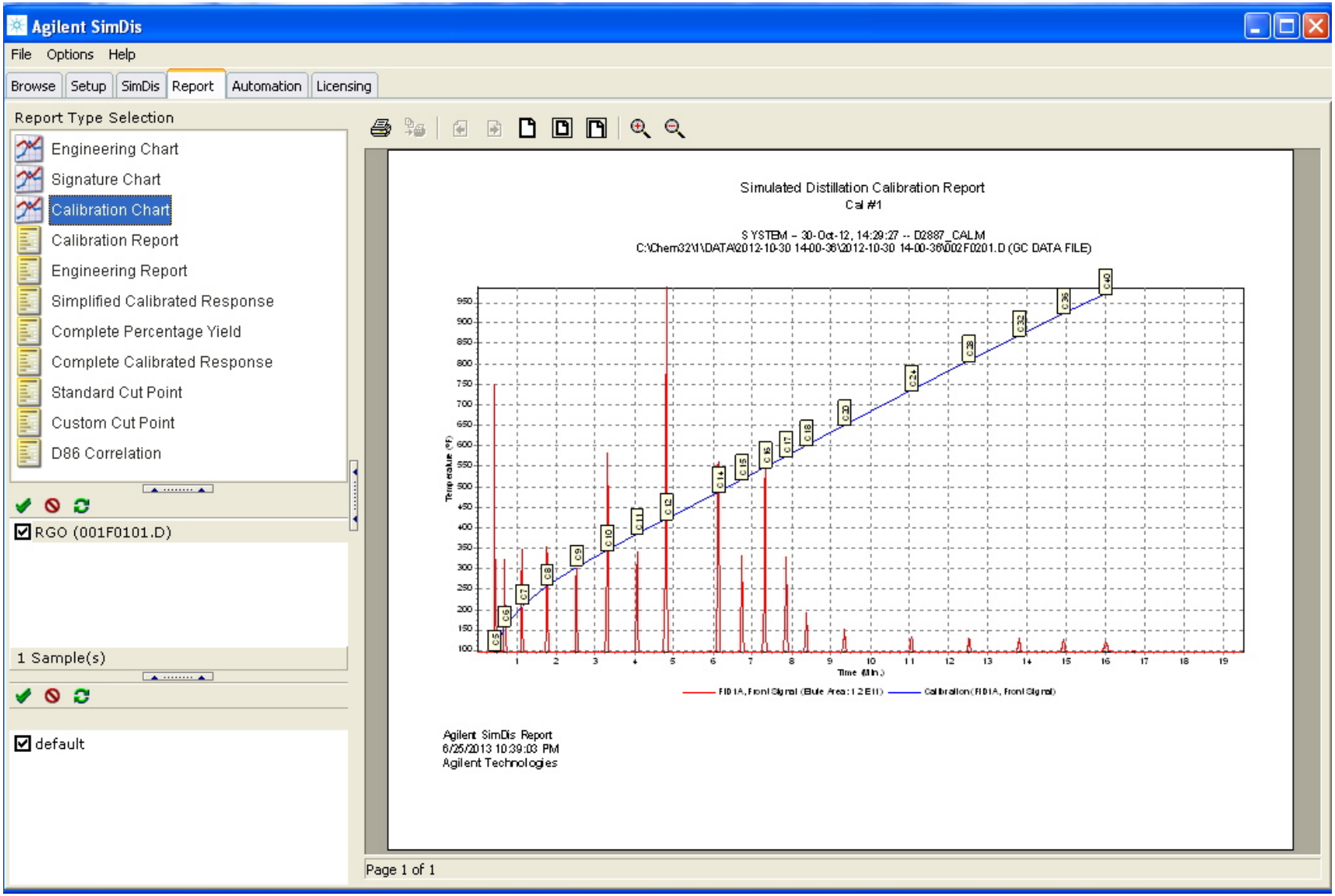
Agilent SimDis Engineering Report



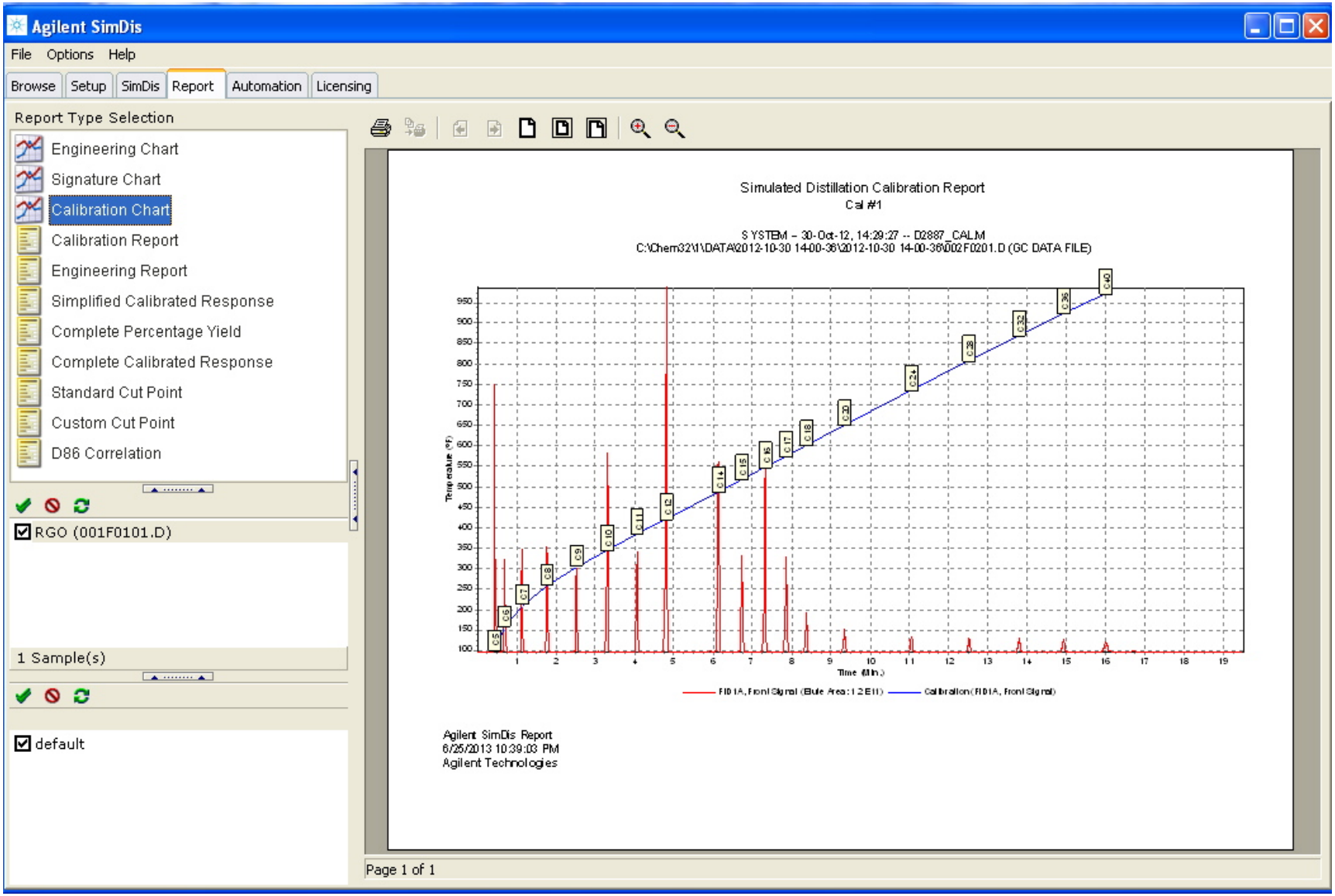
Agilent SimDis Signature Report



Agilent SimDis Calibration Report



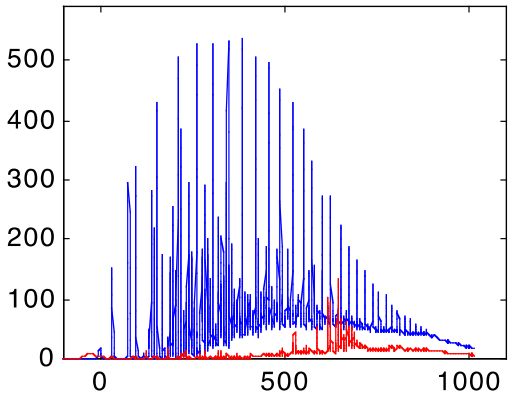
Agilent SimDis Calibration Report



Thank You

for your time and attention

Crude Oil Signature

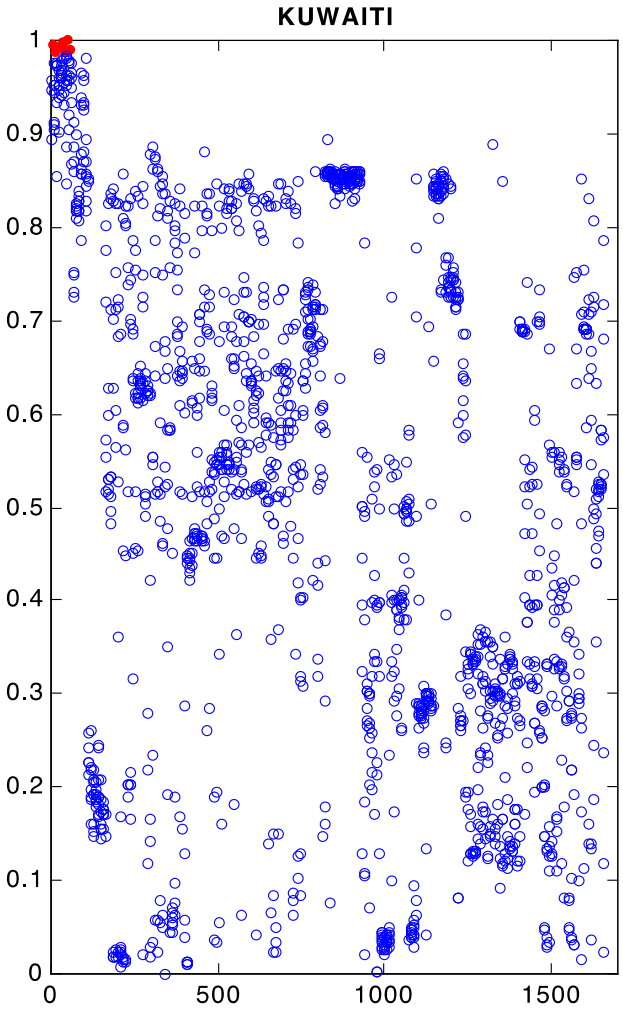


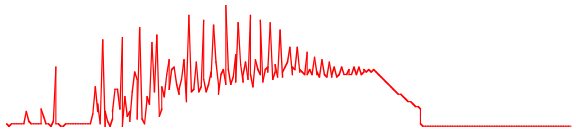
These Signatures (also often referred to as “Fingerprints”) map the crude composition to an invariant Boiling Point scale

W SIBERIAN CRUDE

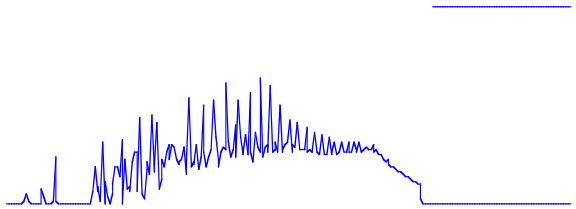
Boiling Point (°F)

Crude Oil Fingerprinting

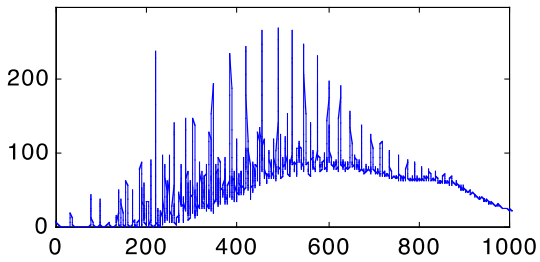




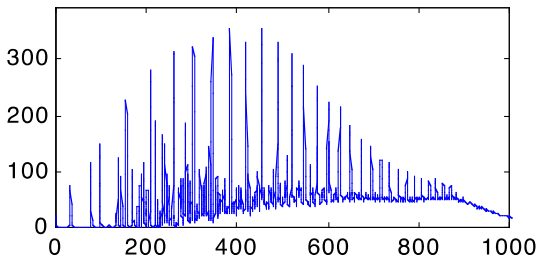
KUWAIT EXP Distance=5.1902°



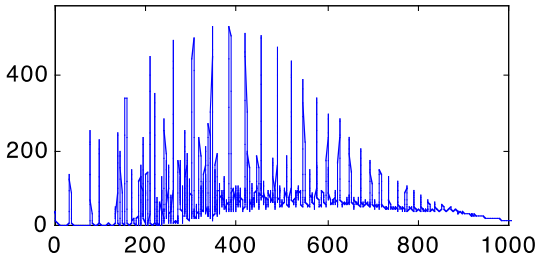
Crude Oil Characterization



Crude A (Asian)



Crude B (Mid-East)



Crude C (South American)

Carbon and Sulfur Distributions in Crude Oils

Hi-Temp Calibration