

Abstract

Fast Multi-element SimDis for Petroleum Analyses using an Atomic Emission Detector

The advent of element specific detectors in the 1990's introduced new capabilities for the analysis and monitoring of petroleum processes. A Gas Chromatograph with an Atomic Emission Detector (GC-AED) is capable of directly measuring more than twenty elements and can simultaneously monitor Carbon, Sulfur, and Nitrogen at ppm levels.

New designs in GC inlet and chromatograph - detector interface have expanded the scope of the multi-element capabilities. A low-mass split/splitless temperature programmable inlet and a temperature programmable GC-AED interface permit high temperature analysis up to 450°C in less than twenty minutes.

The Simulated Distillation analysis (SimDis) of petroleum streams is the singular most important method in the analysis of refinery processes. SimDis provides information for cut point control, stream processability and ultimately process mass balance. This information allows refiners to optimize product yields and their operating margins.

Multi-element SimDis can now be performed on the entire distillable range of petroleum feedstocks (from naphthas to residua) with the new GC-AED configuration. Multi-element SimDis analysis requires new considerations in signal processing and data treatment. The direct measurement of elemental yield must be equivalent to other total element analyses and also accurately represent the elemental distribution in the sample.

A discussion of the Multi-Element SimDis in D2887, D2887-EX and D6253 analogues with example applications for gasolines, diesels, vacuum gas oils, residua and whole crudes are presented.



Fast Multi-element SimDis for Petroleum Analyses using an Atomic Emission Detector

joint analytical systems USA

Pittsburg Conference 2005
February 28, 2004

SIMPLY SMART SOLUTIONS



The jas Atomic Emission Detector



Detects more than 20 elements:
C,S,N,H,O,Ni,V,Fe,Cl,Pb,Mn,P...

High Temperature Operation:
Split/Splitless Programmable Inlet
Temp. Programmable Transfer Line
(Both to 500°C)

Large Linear Dynamic Range
Low Level Sulfur Detection

PPM and PPB Detection Limits for
many elements



jas UNIS Injector

A Low Mass Programmable Split/Splitless Injector

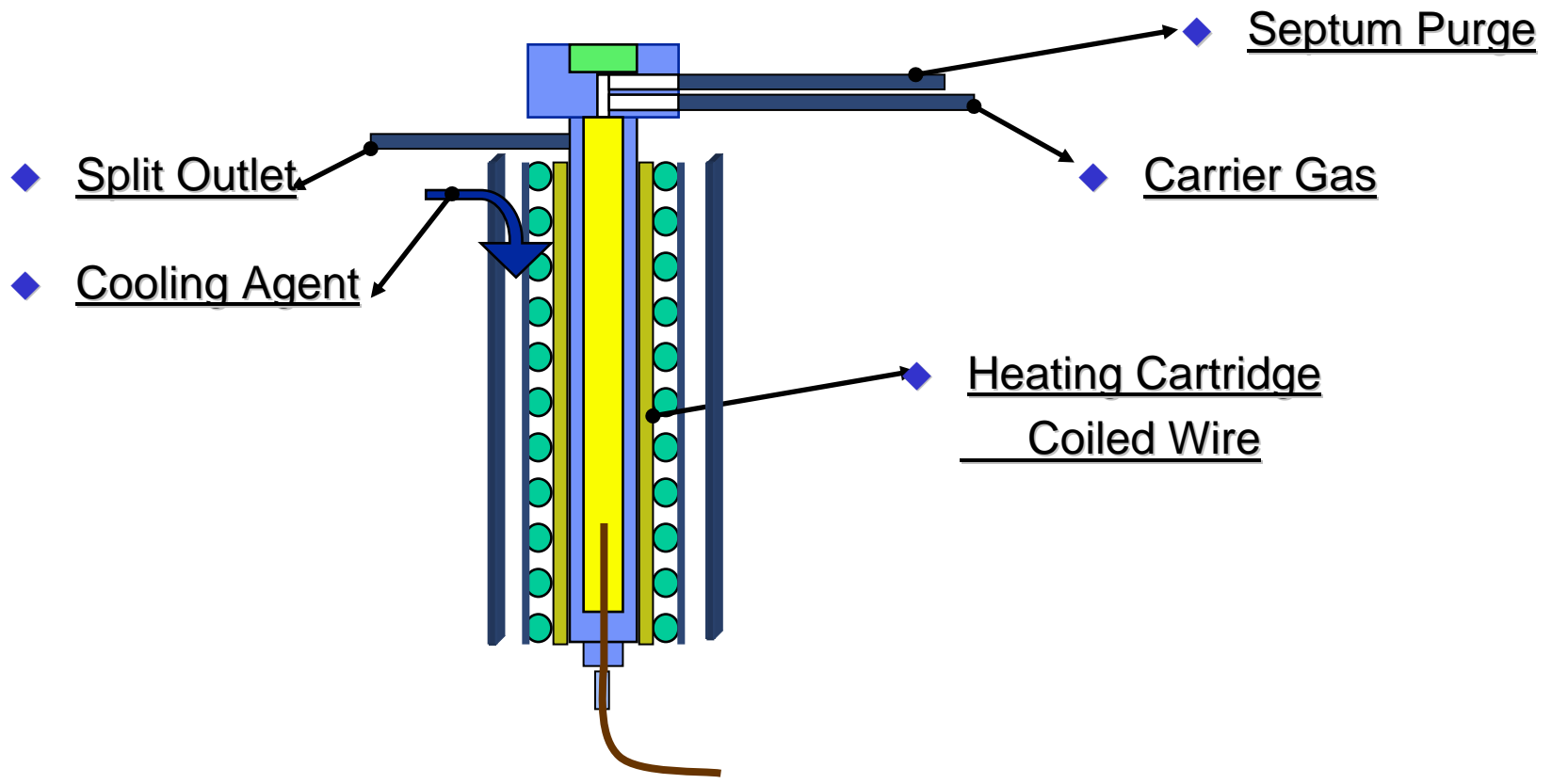
Reproducible injections with fast cycle time
Unique jas inlet liner design

Specifications

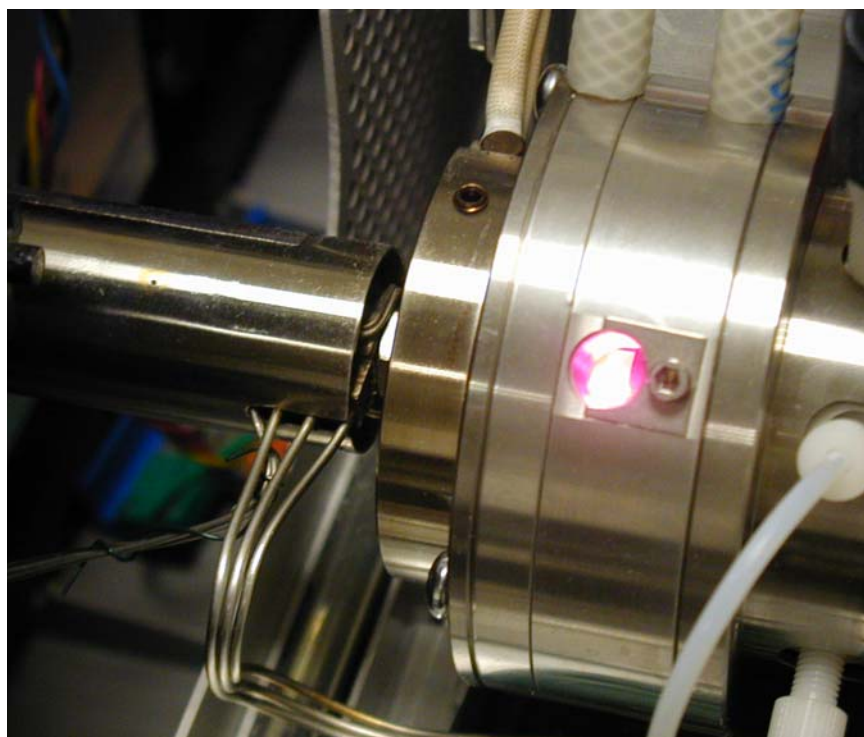
- Max Temperature 500°C
- Max Ramp Rate for PTV Mode 720°C/min
- Min Temp -160°C (Liquid Nitrogen)



jas UNIS Injector Design



New AED Transfer Line Design



Temperature Programmable
Transfer Line

Thermally Isolated (No Cold Spots!)

Improved integration of GC column and
AED gas flows

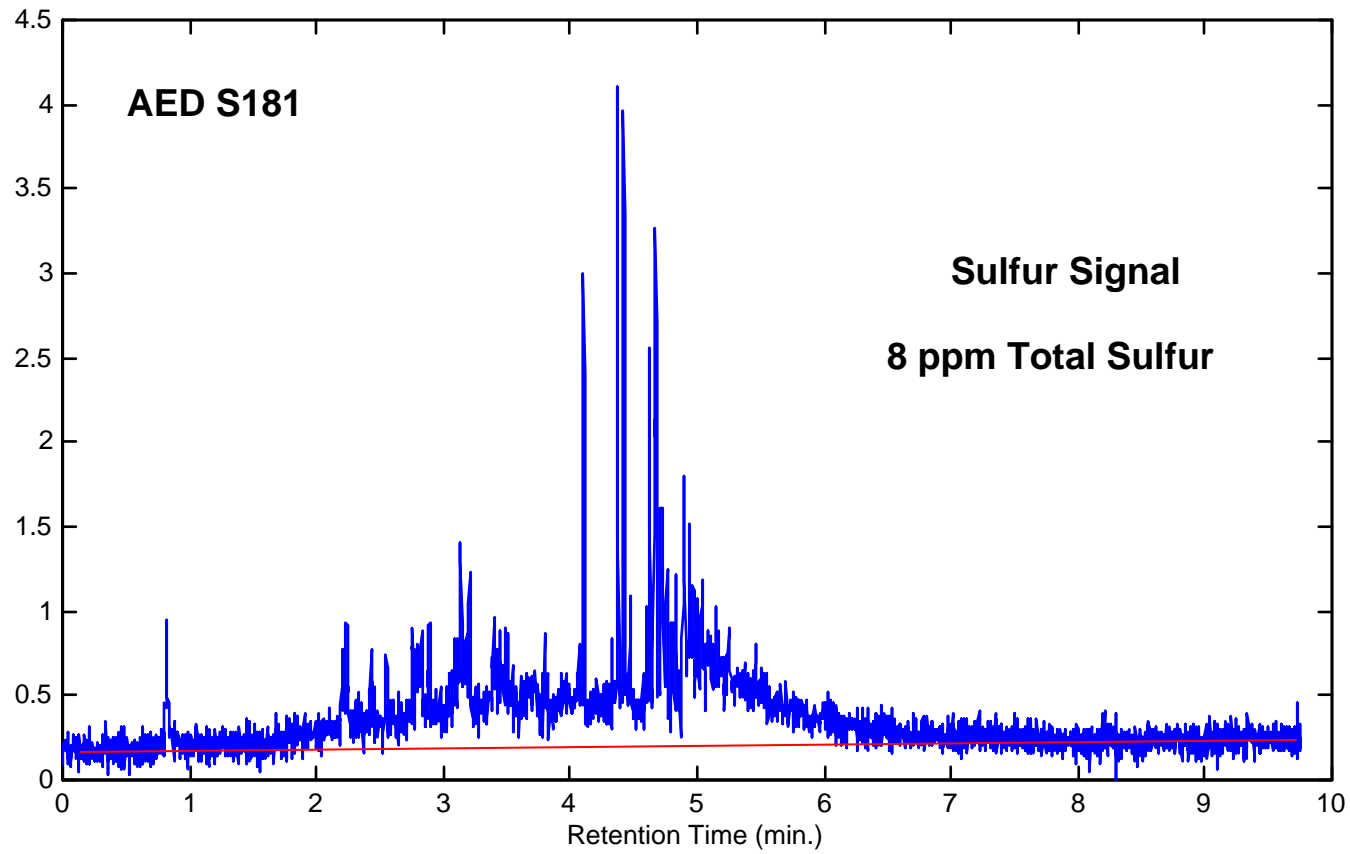


Technologies for Multi-Element SimDis Analysis

	Sulfur MDL(ppm)	Elements	Linear Range	Advantages Limitations
AED	Low ppm/ppb	8 ppm	10^5	Dynamic Range Cost
SCD	Low ppm/ppb	15 ppm	10^4	Sulfur Specific Response Factor Drift
FPD	200 ppb	20 ppm	10^3	Low cost non-linear response
PFPD	20 ppb	10 ppm	10^3	High sensitivity MDL is Matrix Dependent
XRF	10-50 ppm	10-50 ppm	10^4	Measures Total Sulfur Measure Total Sulfur

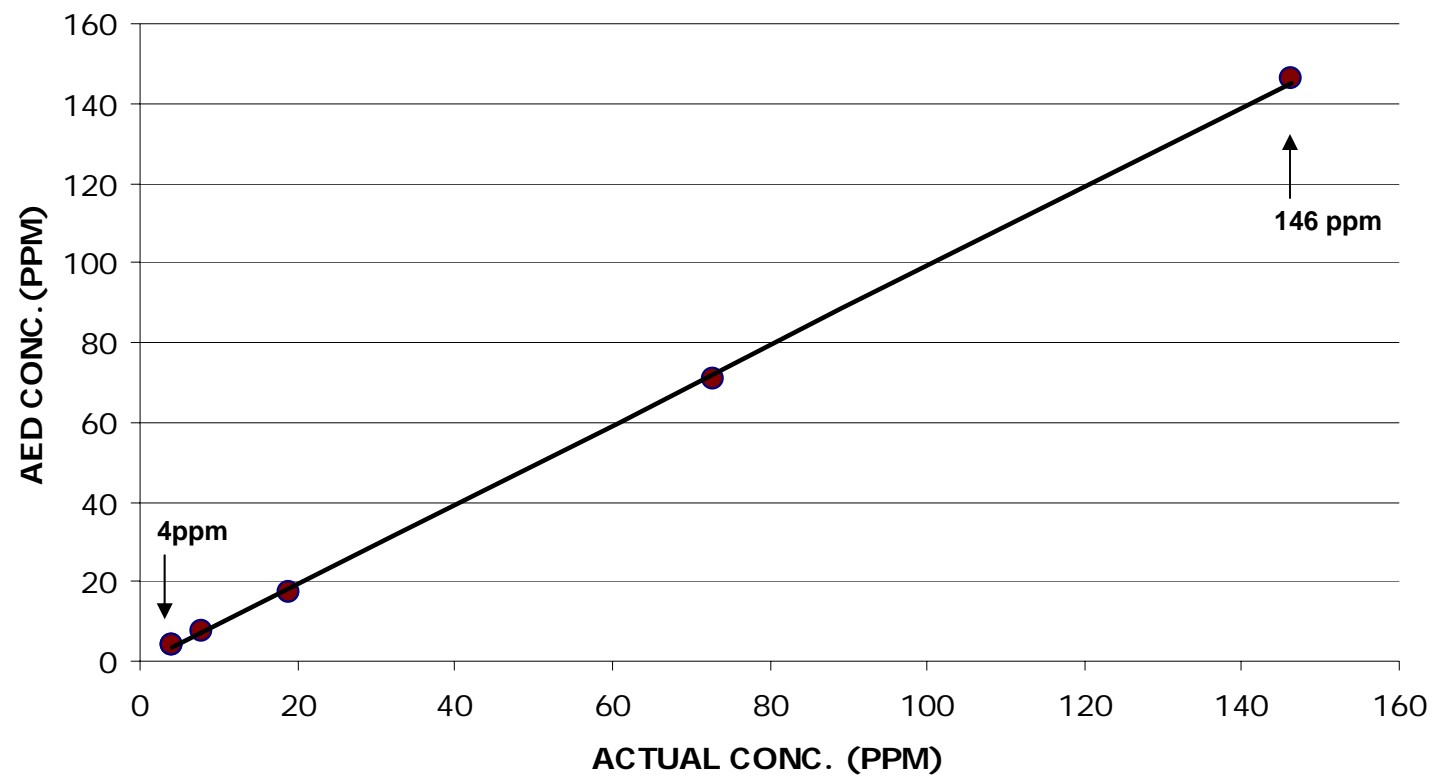


Optimized-Low Sulfur Mode



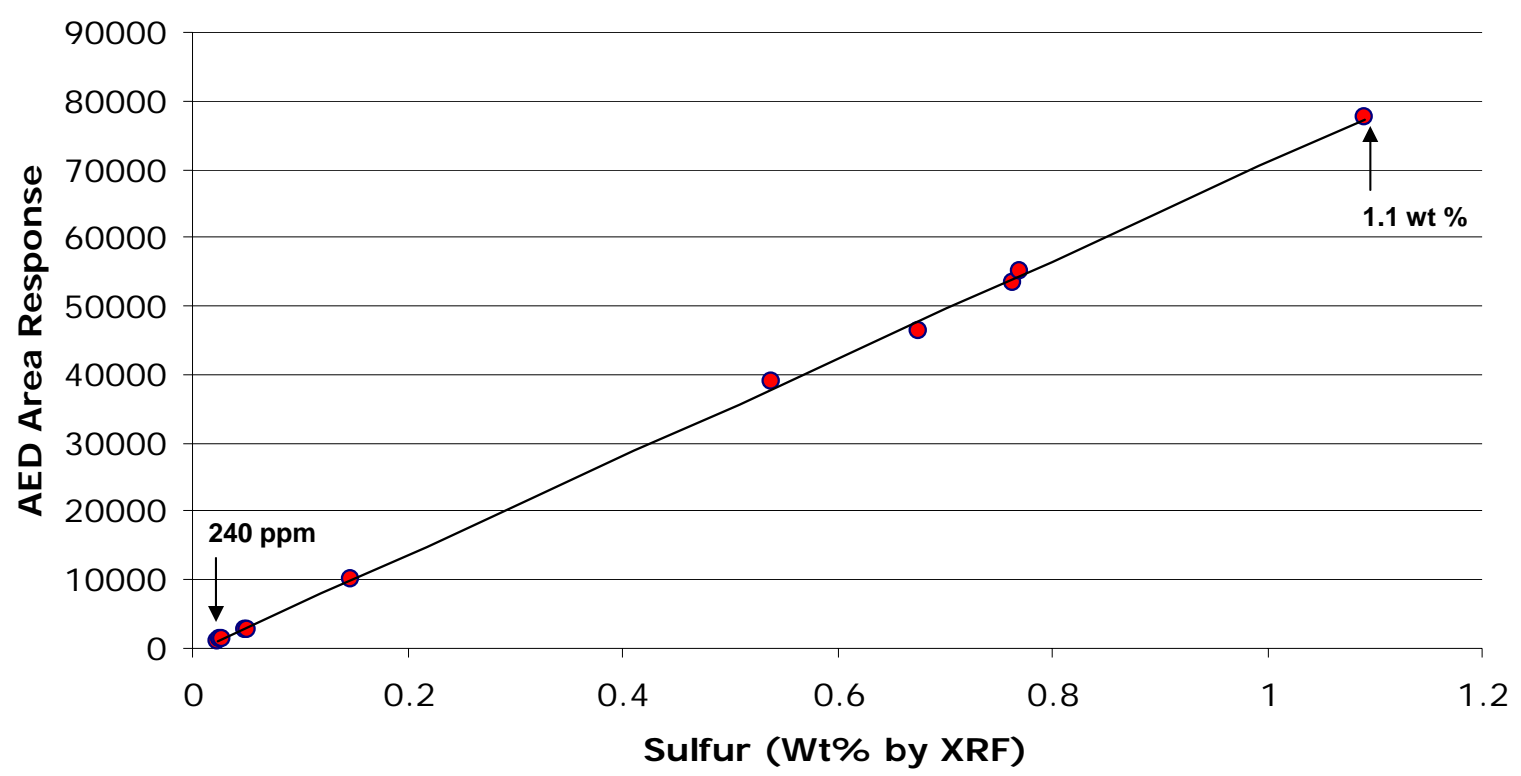
Sulfur Linearity

NIST BLENDS

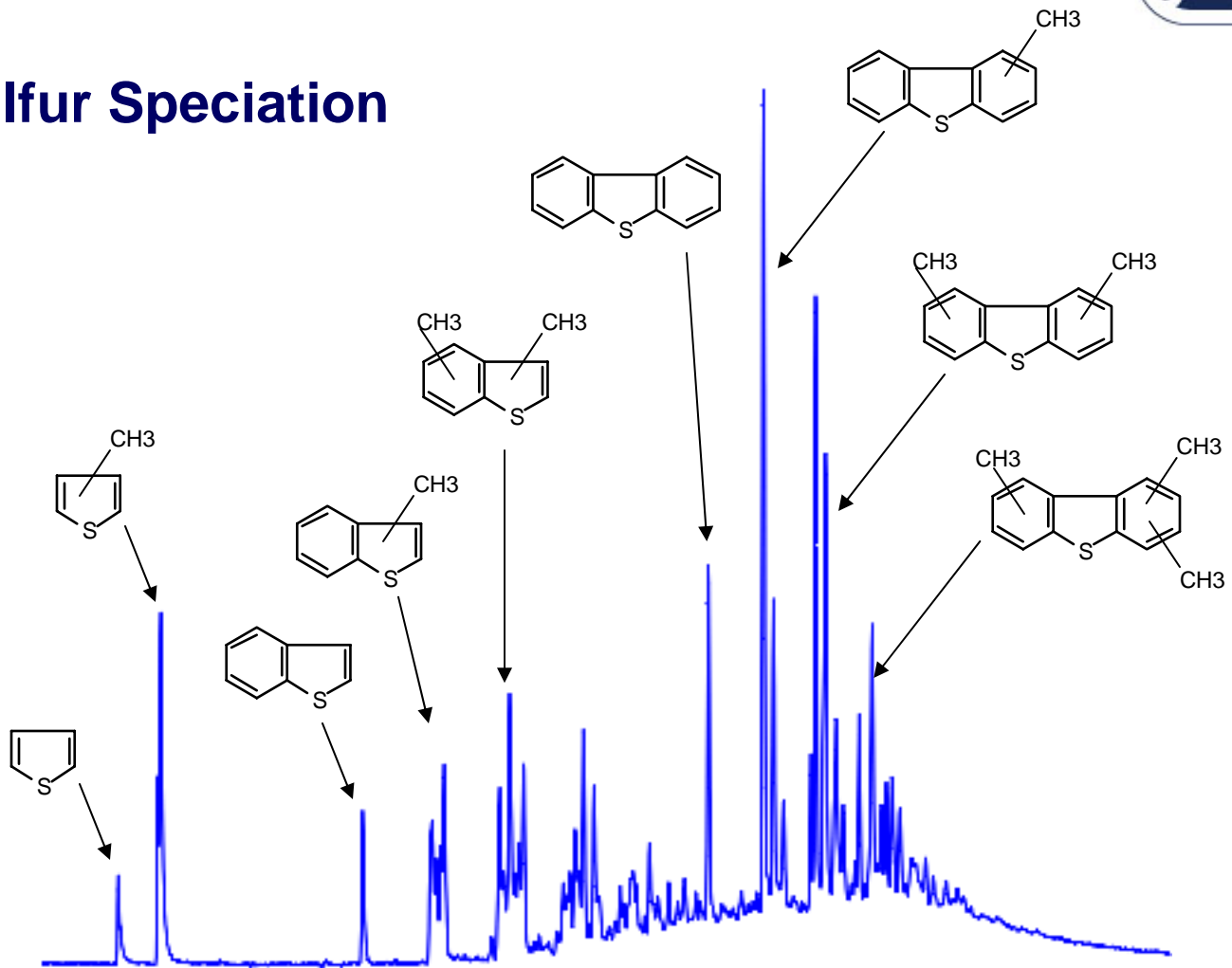


Linearity of Total Sulfur in Diesel Samples

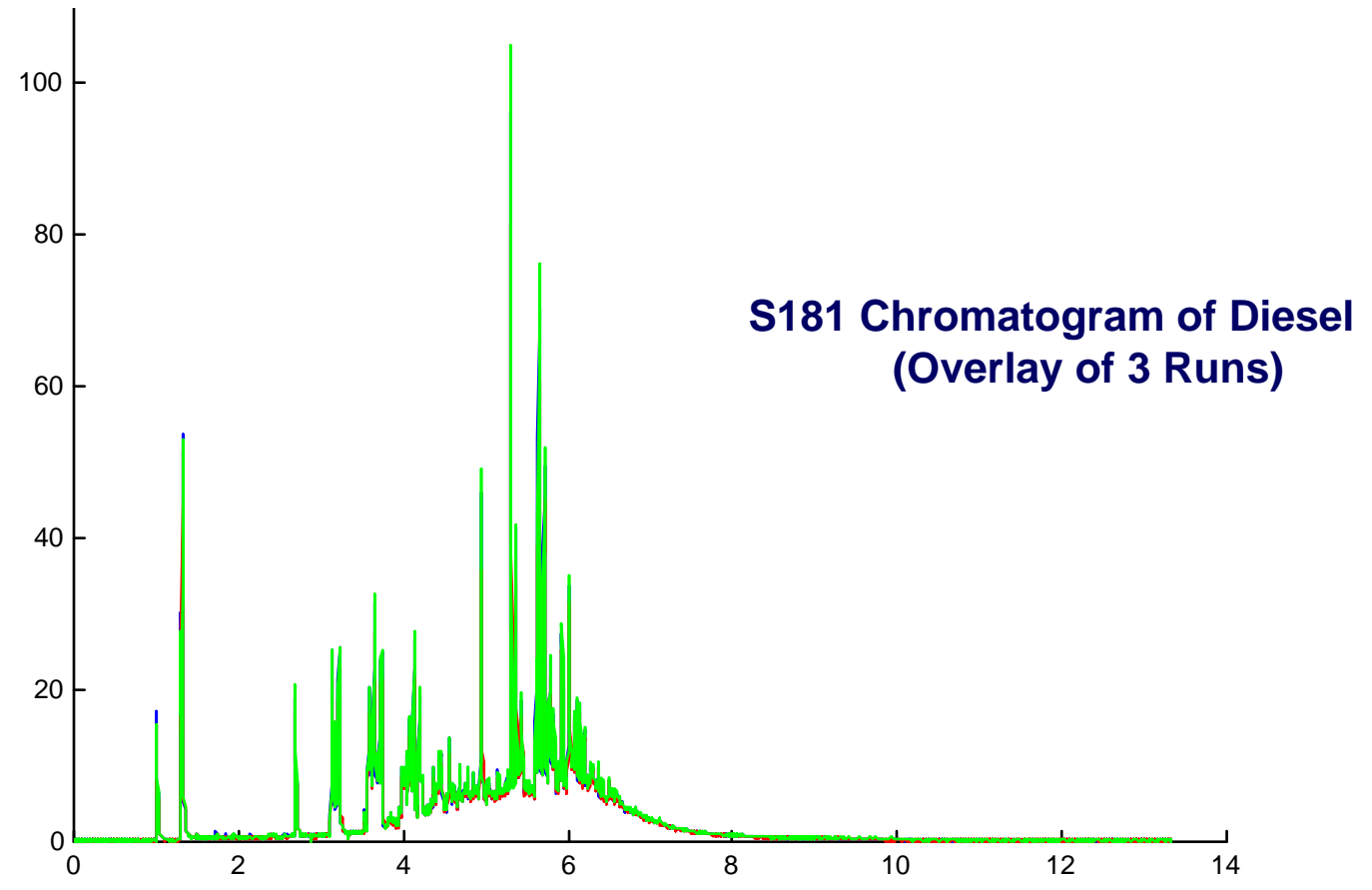
AED Sulfur Response (Diesel samples)

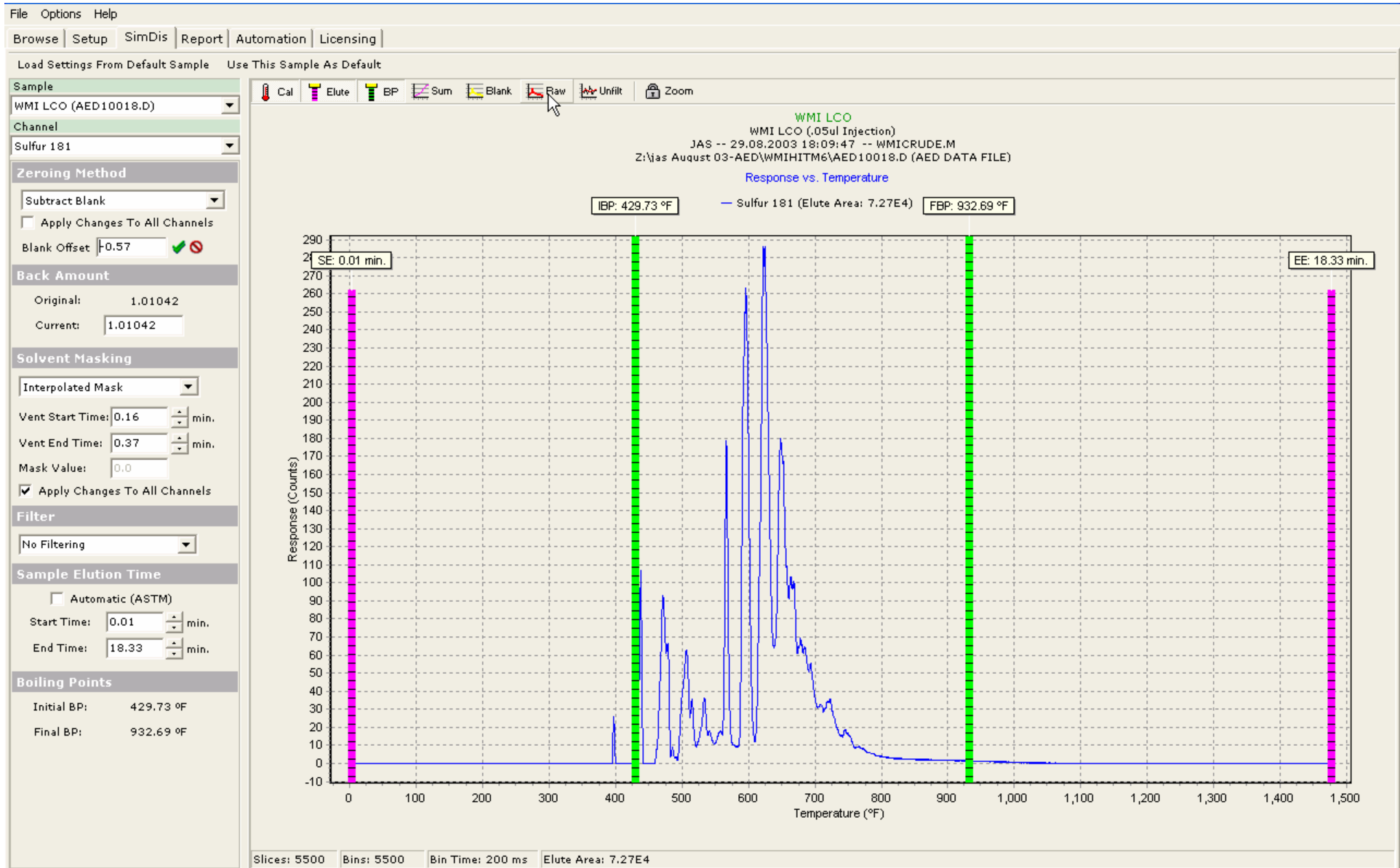


Sulfur Speciation

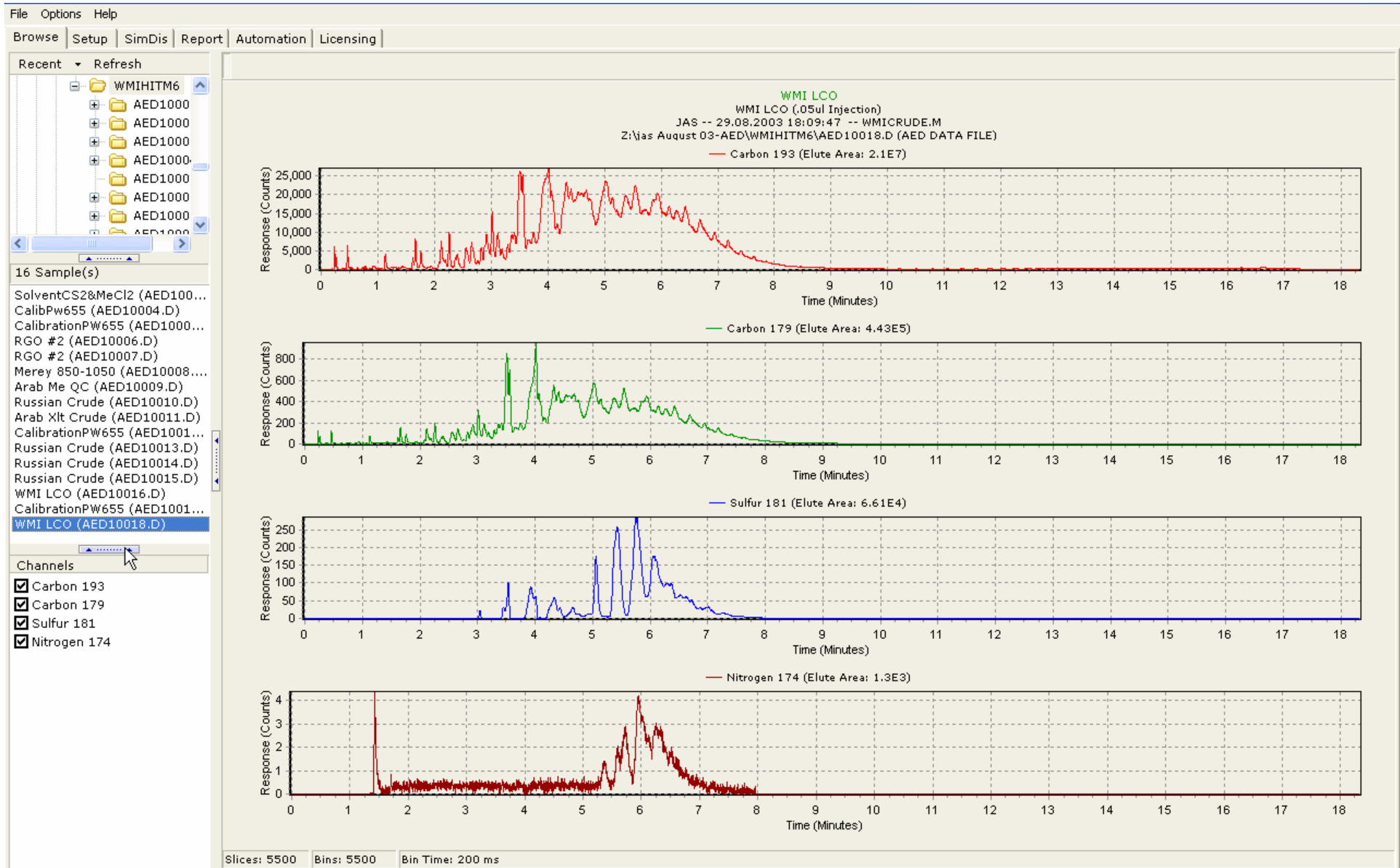


Sulfur Repeatability

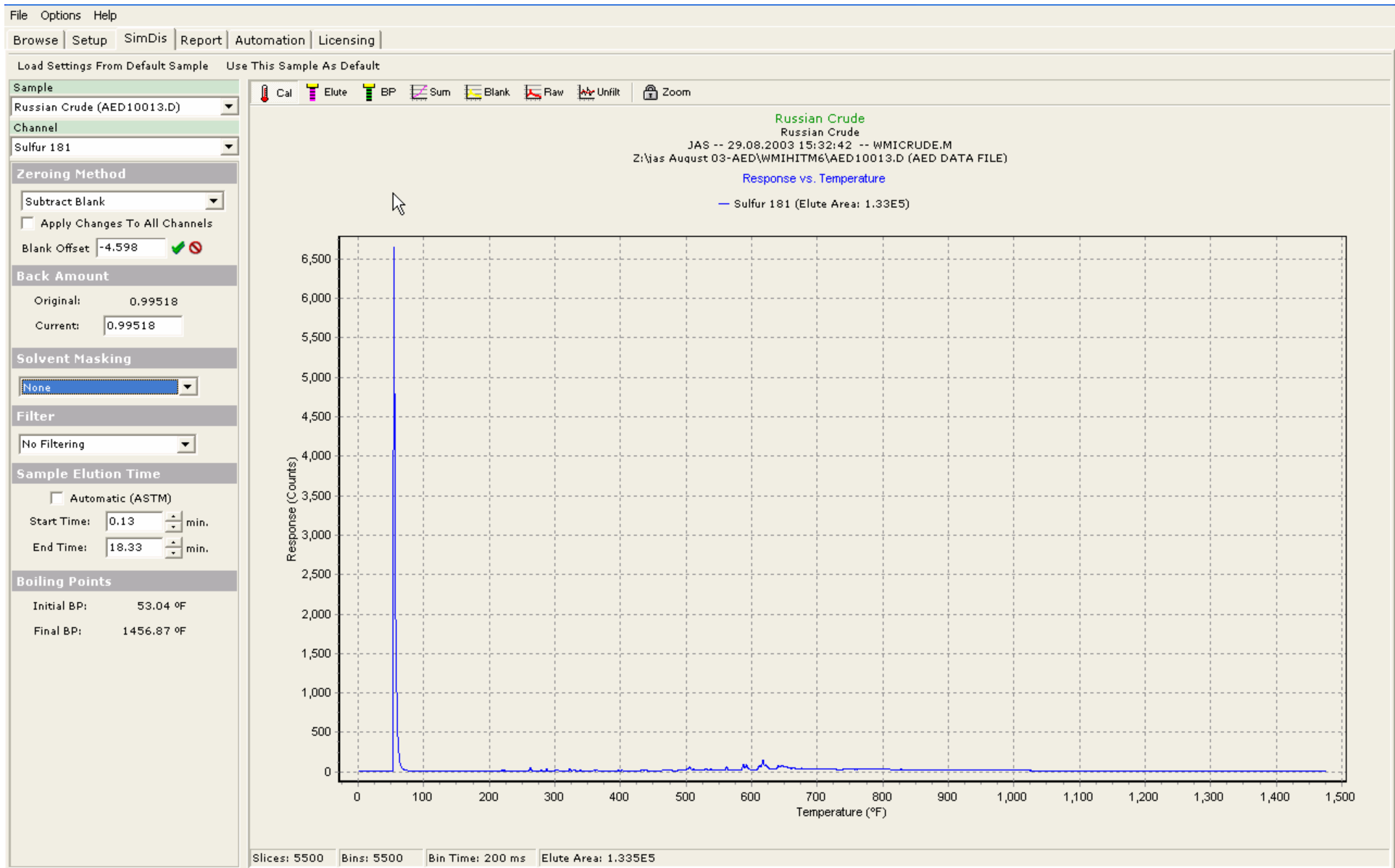




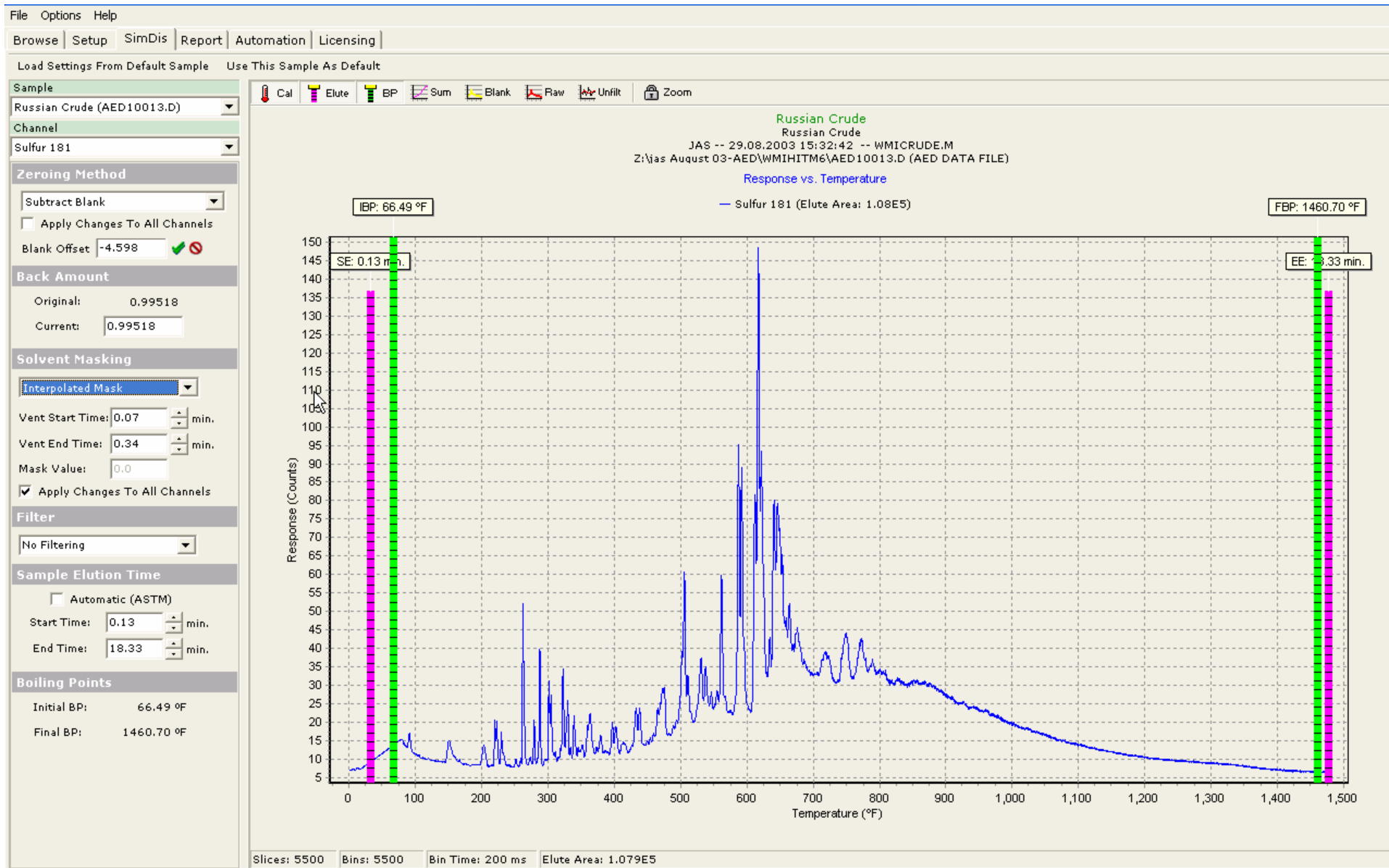
BP Distribution Measurements



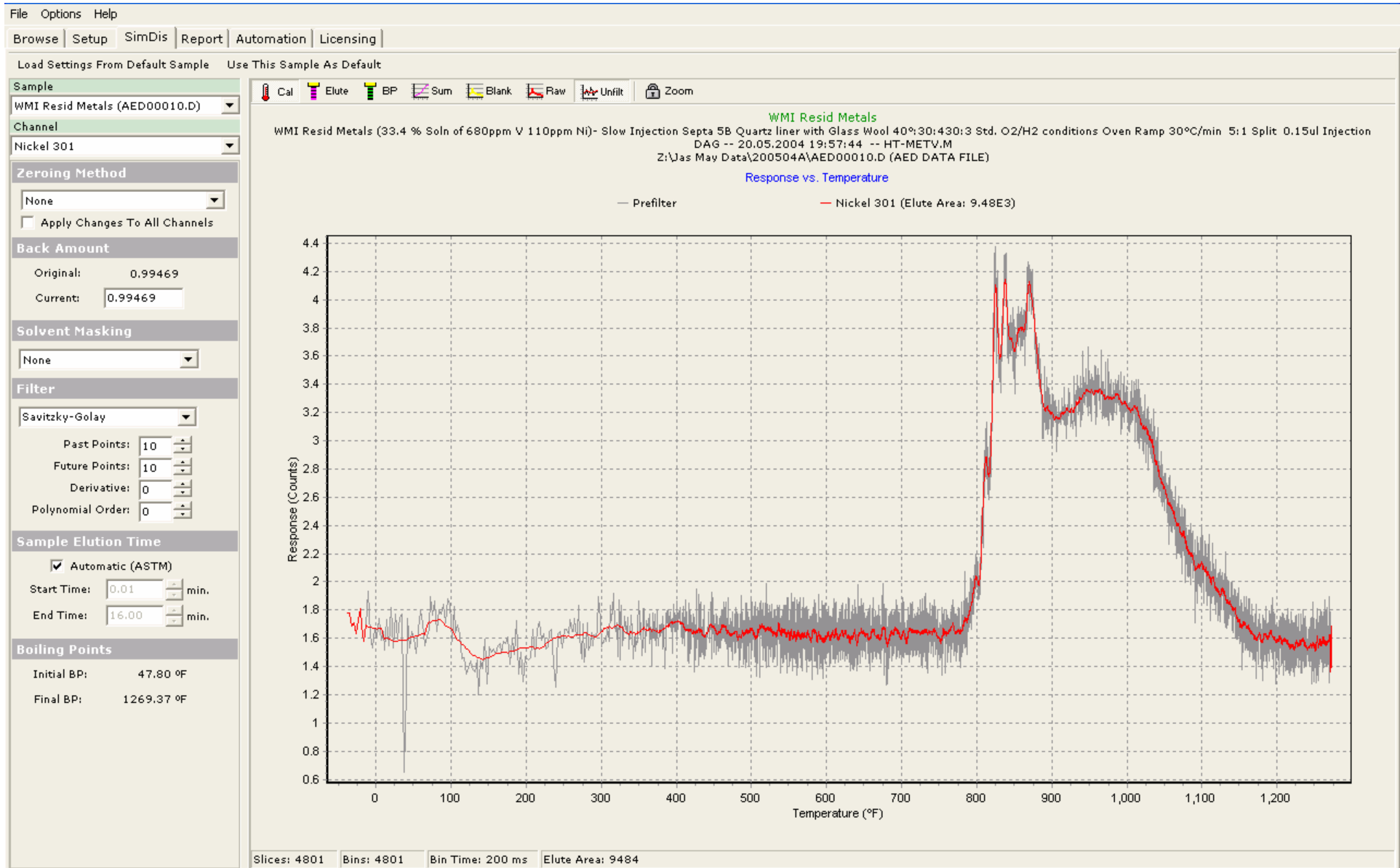
SimDis Browse Pane



SimDis Parameters-Blank Subtraction



SimDis Parameters-Solvent Masking

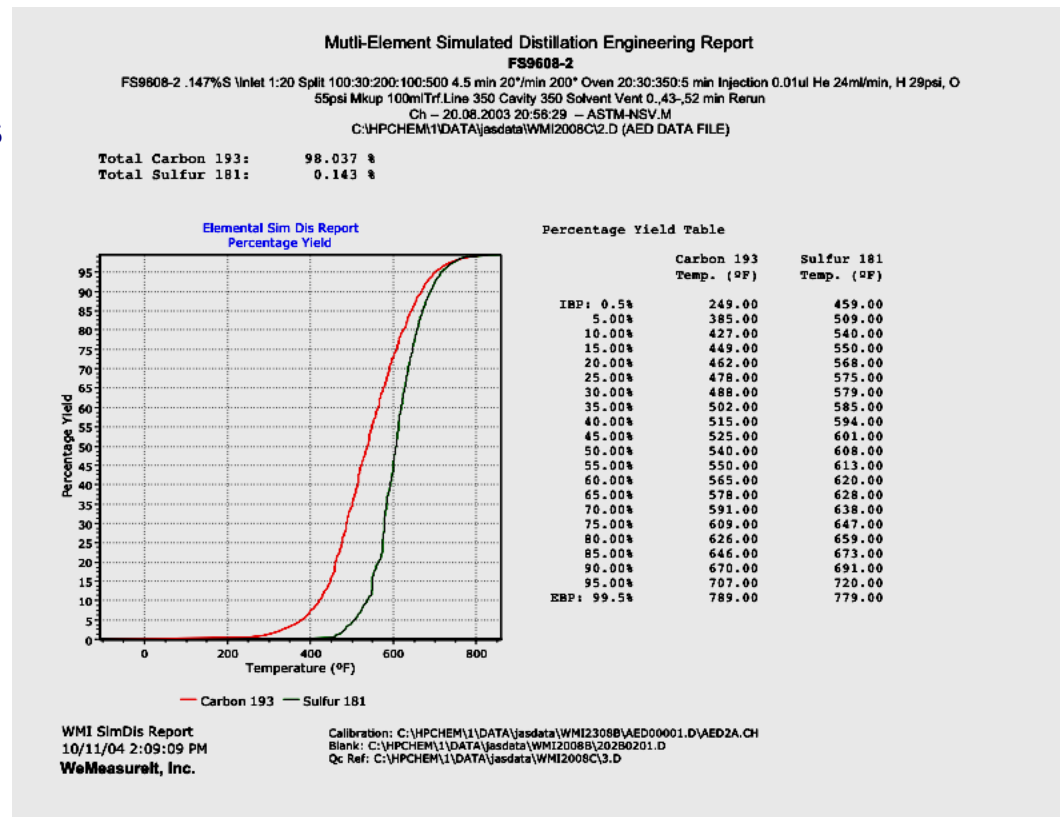


SimDis Parameters-Filter

SimDis Engineering Report

The Engineering Report presents the temperature at which a given yield% off occurs.

This is used by Engineers and Planners to optimize plant performance and assure product liftings

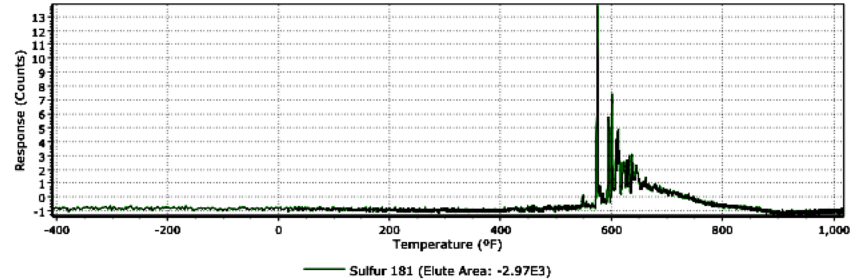
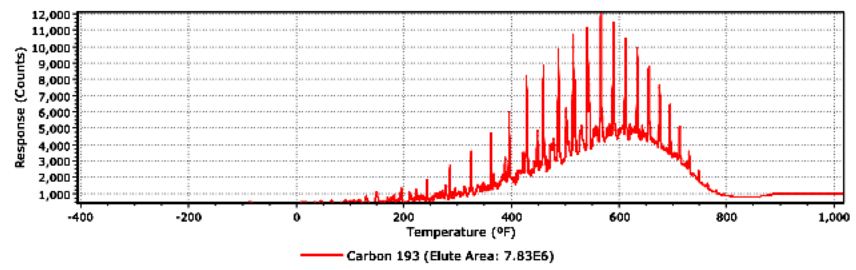


SimDis Signature Report

The Signature Report presents the chromatographic trace versus a boiling point (temperature) axis providing a compositional view of the sample

Multi-Element Simulated Distillation Signature Report FS9594-1

FS9594-1 .052% Inlet 1:20 Split 100:30:200:100:500 20*/min 200* Oven 20:30:350:5 min Injection 0.05ul He 12ml/min, H 29psi, O 55psi Mkup
100mTf.L. Line 350 Cavity 350 NO Solvent Vent 0.43-.52 min Rerun
Ch - 20.08.2003 20:32:21 -- ASTM-NSV.M
C:\HPCHEM\1\DATA\jasdata\WMI2008C\1.D (AED DATA FILE)



WMI SimDis Report
10/11/04 2:10:06 PM
WeMeasureIt, Inc.

Calibration: C:\HPCHEM\1\DATA\jasdata\WMI2308B\AED00001.D\VAED2A.CH
Blank: C:\HPCHEM\1\DATA\jasdata\WMI2008B\20280201.D
Qc Ref: C:\HPCHEM\1\DATA\jasdata\WMI2008C\3.D



File Options Help

Browse Setup SimDis Report Automation Licensing

11 Sample(s)

- Blank (AED00001.D)
- 1157B Diesel (AED00002.D)
- 1157B Diesel (AED00003.D)
- 1157B Diesel (AED00004.D)
- Blank (AED00005.D)
- Calibration (AED00006.D)
- Paraffins w S (AED00007.D)

Channels

- Carbon 179
- Sulfur 181
- Nitrogen 174

Chart Text

csv tab Custom Cut Point

From (temp)	To (temp)
110	580
580	680
680	800
800	

Apply Load Save Clear

Diesel
Z:\WMI0225D\AED00001.D (AED DATA FILE)

Simulated Distillation Report

Diesel :
JAS -- 25.02.2004 15:02:44 -- 0221.M

Calibration: Z:\WMI0224\AED00006.D\AED2A.CH
Blank: Z:\WMI0225D\AED00005.D
No Qc Reference

Total Carbon 179: (no RF)
Total Sulfur 181: (no RF)
Total Nitrogen 174: (no RF)

Custom Cut Point Table

Temp. (Deg. F)	Carbon 179	Sulfur 181	Nitrogen 174
70.00 to 110.00	0.1%	5.8%	0.0%
110.00 to 580.00	68.9%	12.0%	100.0%
580.00 to 680.00	23.3%	52.8%	0.0%
680.00 to 800.00	7.9%	28.6%	0.0%
800.00 to +	0.0%	0.9%	0.0%

SimDis Report- Custom Cutpoint

AED SimDis Cut Point Report

The Cut Point Report presents the yield off for selected Boiling Ranges

For example: for a hydrotreated diesel the elemental yield % of the distribution for selected Boiling Ranges can be found

Hydrotreated Diesel 36 ppm

Total Carbon 179: 100.000 %
Total Sulfur 181: 36.000 ppm

Custom Cut Point Table

Temp. (°F)	Carbon 179	Sulfur 181
180.00 to 600.00	75.5%	17.7%
600.00 to 800.00	24.5%	82.3%



AED SimDis Cut Point Report

Cut Point Report

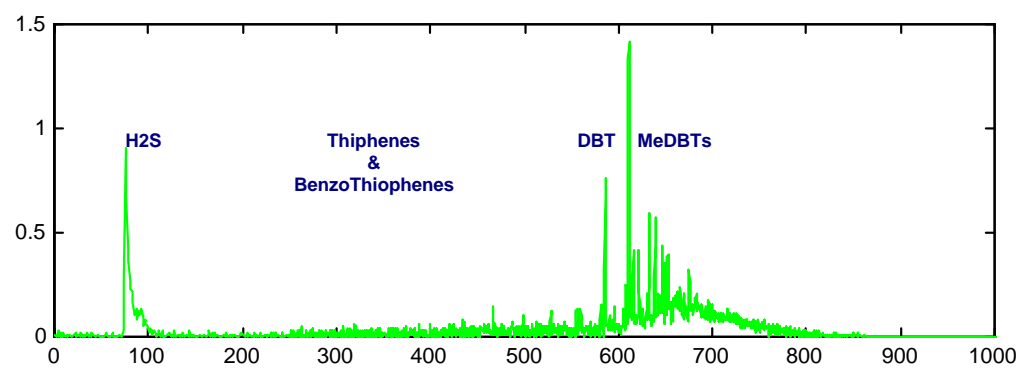
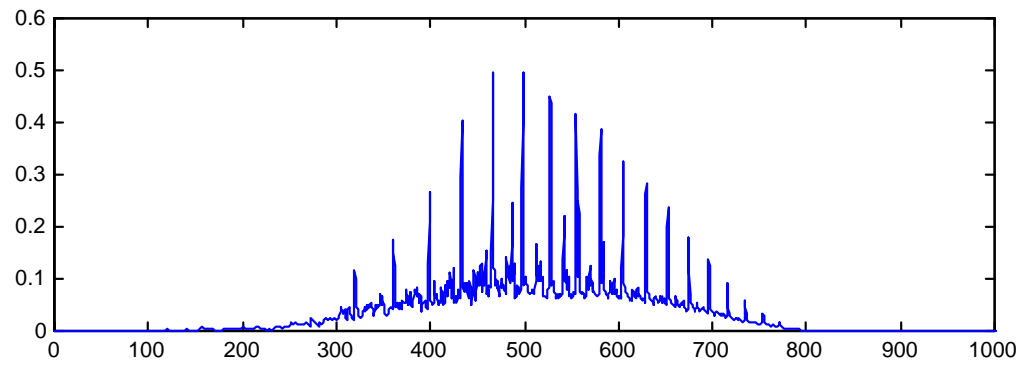
Hydrotreated Diesel
 C:\HPCHEM\1\DATA\WMI0225D\AED00001.D (AED DATA FILE)

Multi-Element Simulated Distillation Report
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Total Carbon 179: 100.00 %
 Total Sulfur 181: 36.00 ppm

Custom Cut Point Table

Temp. (°F)	Carbon 179	Sulfur 181
70.00 to 110.00	0.0%	5.0%
110.00 to 580.00	68.9%	23.2%
580.00 to 600.00	6.4%	6.1%
600.00 to 680.00	17.0%	40.3%
680.00 to 800.00	8.0%	24.5%
800.00 to +	0.0%	0.7%



Jas Multi-Element AED SimDis

3x Higher Analysis Throughput (C100 in less than 18 min)
jas Hi-Temp analysis is 3 times faster than other commercial systems

High Analytical Precision

No Inlet carry over or memory effects

UNIS Inlet upper temperature limit of 500°C is essentially self-cleaning
(reduces number of bake-out runs to restore baseline)

Detect more than 20 elements with one detector

C,S,N,O,H,V,Ni,Fe,
Br,Cl,F,I,
B,Ge,P,Si
As,Sn,Pb,Mn,As,Hg,Se,
C13,N15,H3
etc.



Thank You for Your Attention

SIMPLY SMART SOLUTIONS

