Advances in Gas Chromatography for **Sulfur Analysis** in Petroleum Upstream, Refining, and Petrochemical Applications

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FALCON
Analytical Systems & Technology

Talk Outline

Background

The System

Performance

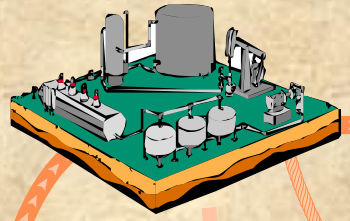
Comparisons

Conclusion

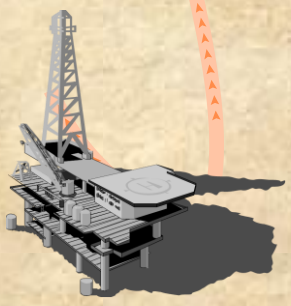
Integrated Oil Company Business Areas

Exploration

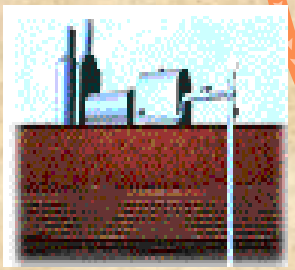
Shipment & Storage



Refining



Production



Production

Marketing

Background

- Routine analysis of hydrocarbons is well known, since the elements Carbon and Hydrogen combined comprise > 90% by weight of a barrel of oil.

- Sulfur is the next most prominent element in crude oil ranging from about 0.1 to 4 wt%.

- Further, sulfur content is important information for optimizing the performance refinery processes and is limited in light transportation fuels by regulations.
  - For example, gasoline is currently limited to 30 ppm by wt, with new proposals to reduce this limit. Diesel fuel is limited to less than 15 ppm by wt sulfur.

- Sulfur types include Mercaptans, Disulfides, Thiols, "Thiophenics", Sulfones and Sulfoxides

Molecular Composition of Petroleum

Each crude oil component can be described by the general formula:

$$C_nH_{2n+Z}X$$

where:

C - Carbon
n - Number of carbon atoms in a molecule
H – Hydrogen

X - Heteroatoms (S, N, O, V, Ni)

Z - Hydrogen deficiency value

defined as:

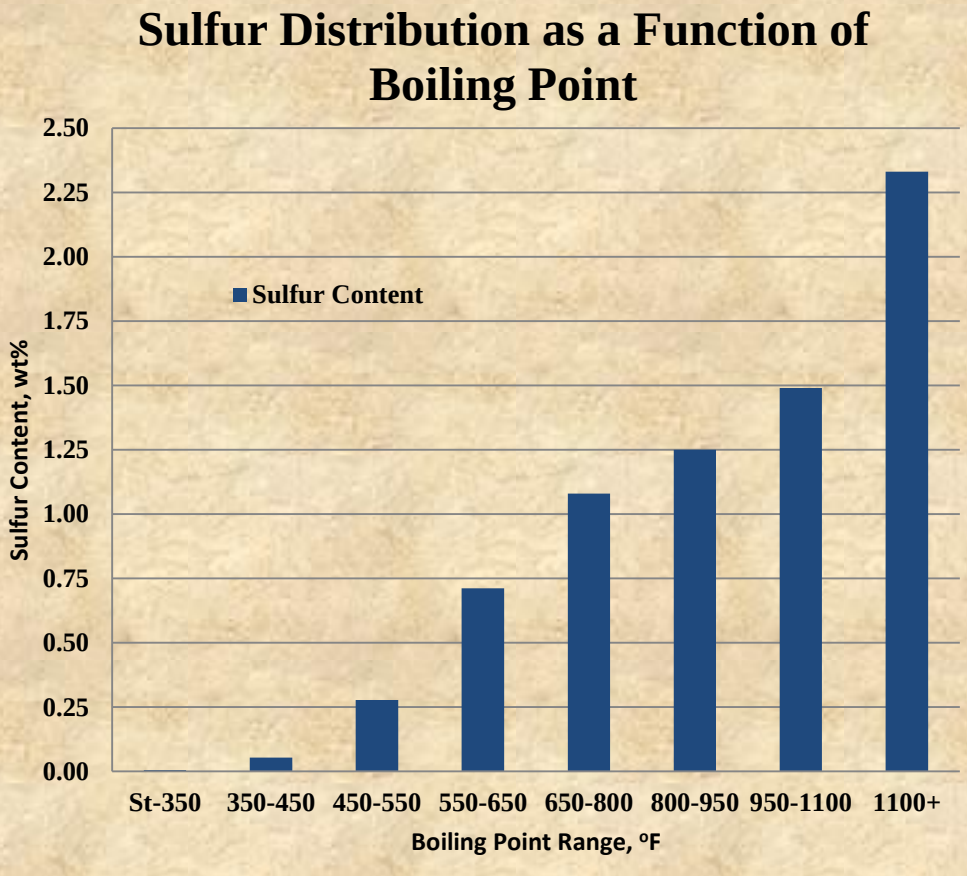
$$Z = 2 - 2*(R + DB)$$

R - a number of rings
DB - a number of double bonds

Representative Sulfur Distribution

BP Range °F	Sulfur[1] wt%	Crude Yield wt%
St-350	0.005	23.02
350-450	0.054	7.88
450-550	0.278	9.26
550-650	0.711	10.56
650-800	1.08	14.01
800-950	1.25	11.79
950-1100	1.49	5.56
1100F+	2.33	17.92

31°API Crude

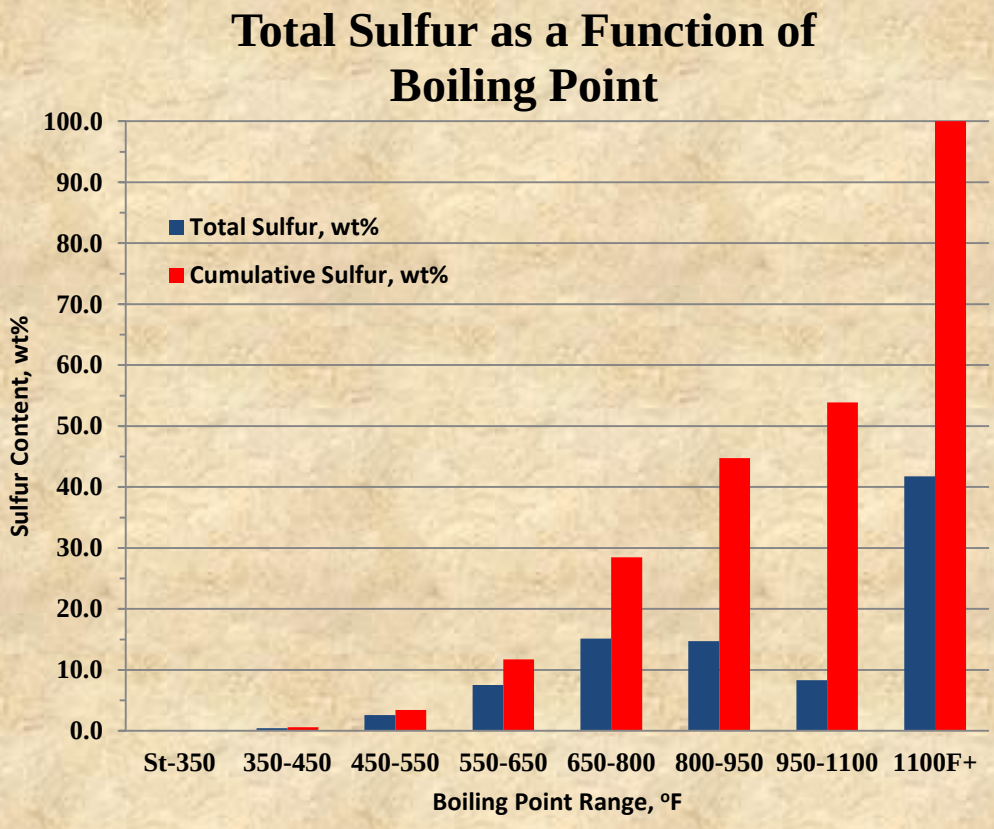


[1] content in fraction

Sulfur Distribution - 2

BP Range °F	Sulfur[1] wt%	Cum. Sulfur wt%
St-350	0.13	0.13
350-450	0.47	0.60
450-550	2.84	3.44
550-650	8.29	11.73
650-800	16.71	28.45
800-950	16.28	44.73
950-1100	9.15	53.88
1100F+	46.12	100.00

31°API Crude



[1] content on crude basis

The Compact, Fast System

A modular design is essential for the system to be usable and serviceable in the variety of potential applications area from lab, to process line, to field.

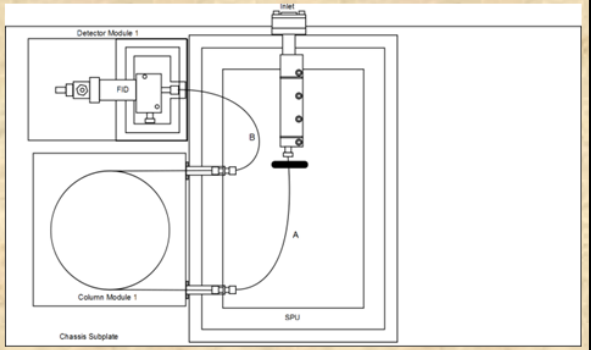
The system used in this work consists of:

Falcon Analytical, Inc.'s	Calidus GC
Justice Laboratory Software's	Chromperfect 7 software
Infometrix Inc.'s	LineUp software

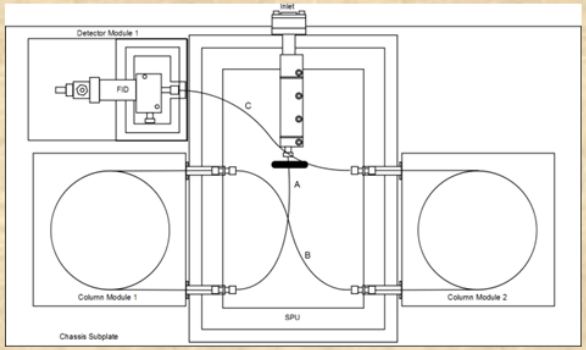
Modular Calidus GC

Single injector Configurations

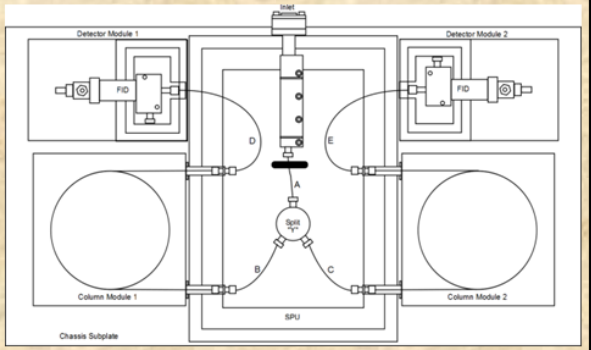
Single Injection in All Examples



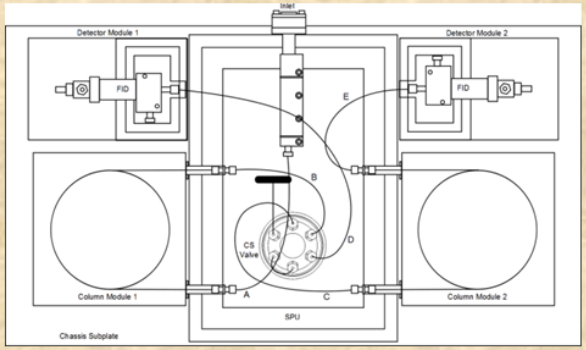
One Column, One Detector



Two Columns, One Detector in Series Operation



Two Columns, Two Detectors in Parallel Operation



Two Columns, Two Detectors with Column Switching

TCD, FID, FPD and DBD* Detectors Available

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* Dielectric Barrier Discharge Detector

Calidus 101 for Simulated Distillation GC

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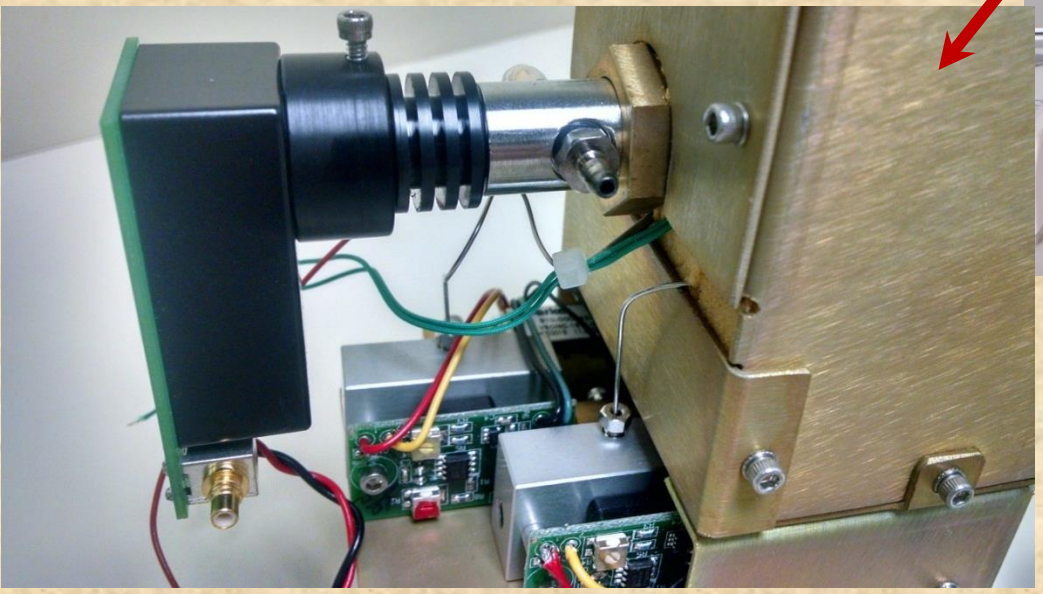
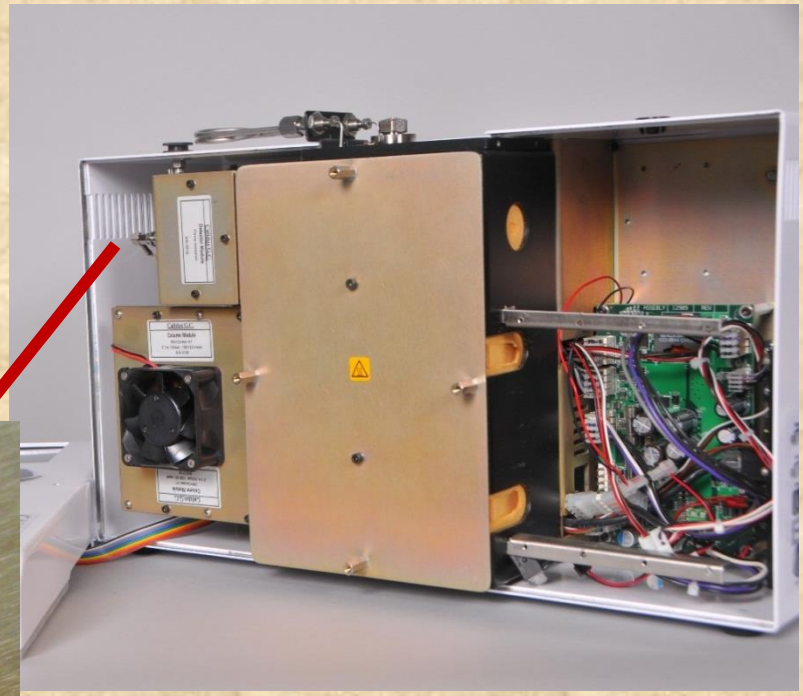
Calidus 101 with FPD Detector

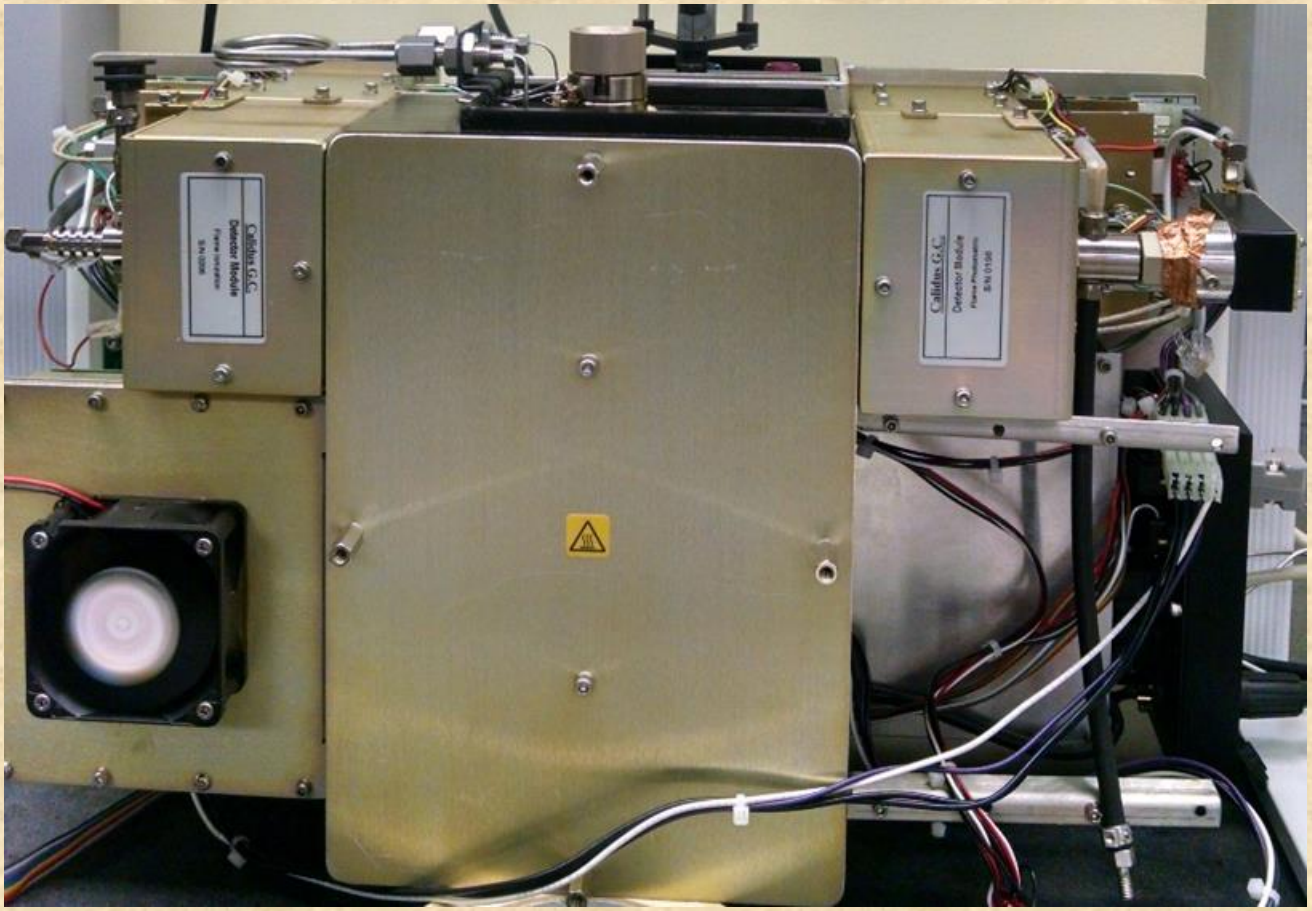




Calidus 101 Configured with Dual Detectors
(used in this work)

FID

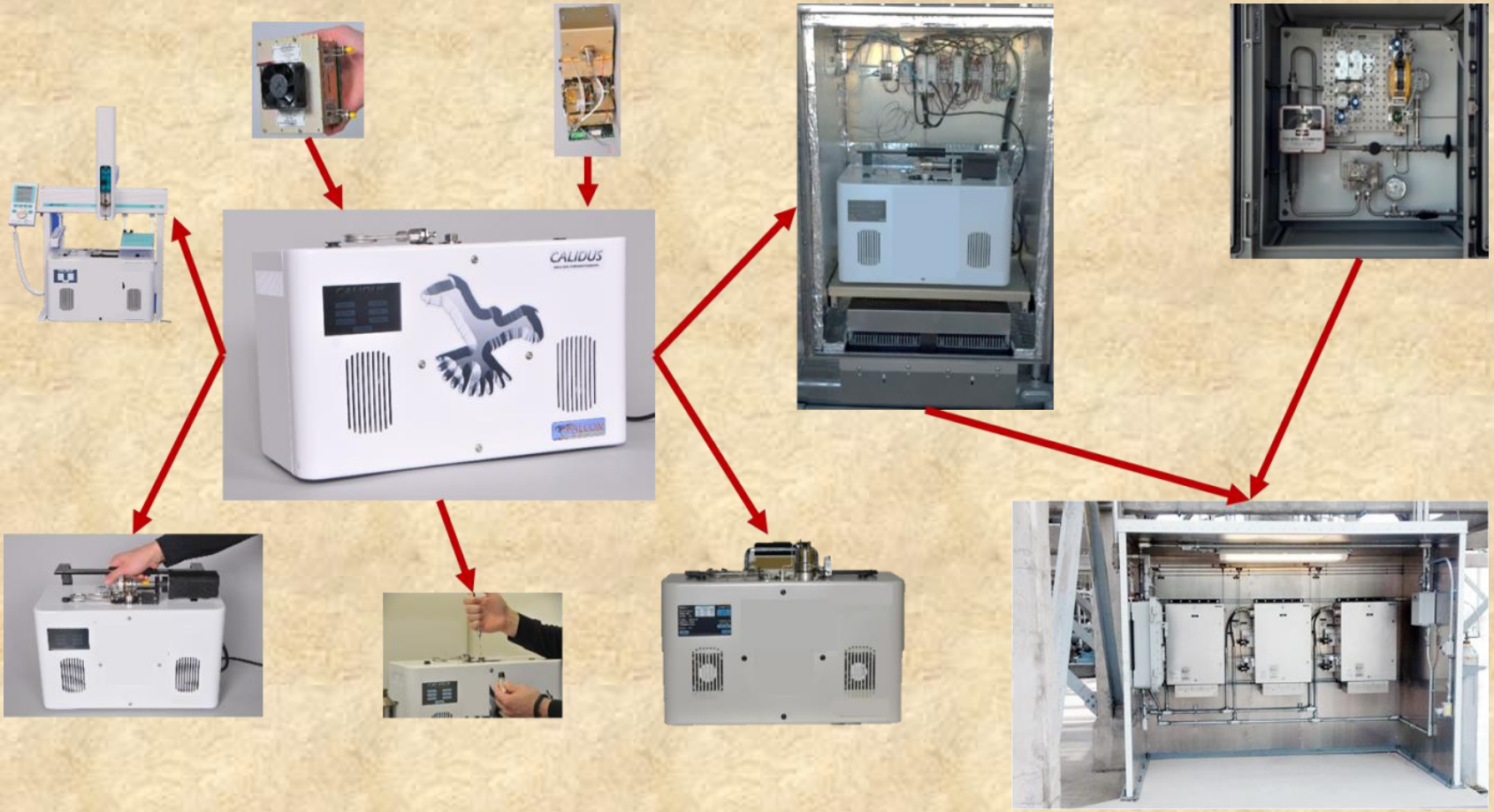
FPD



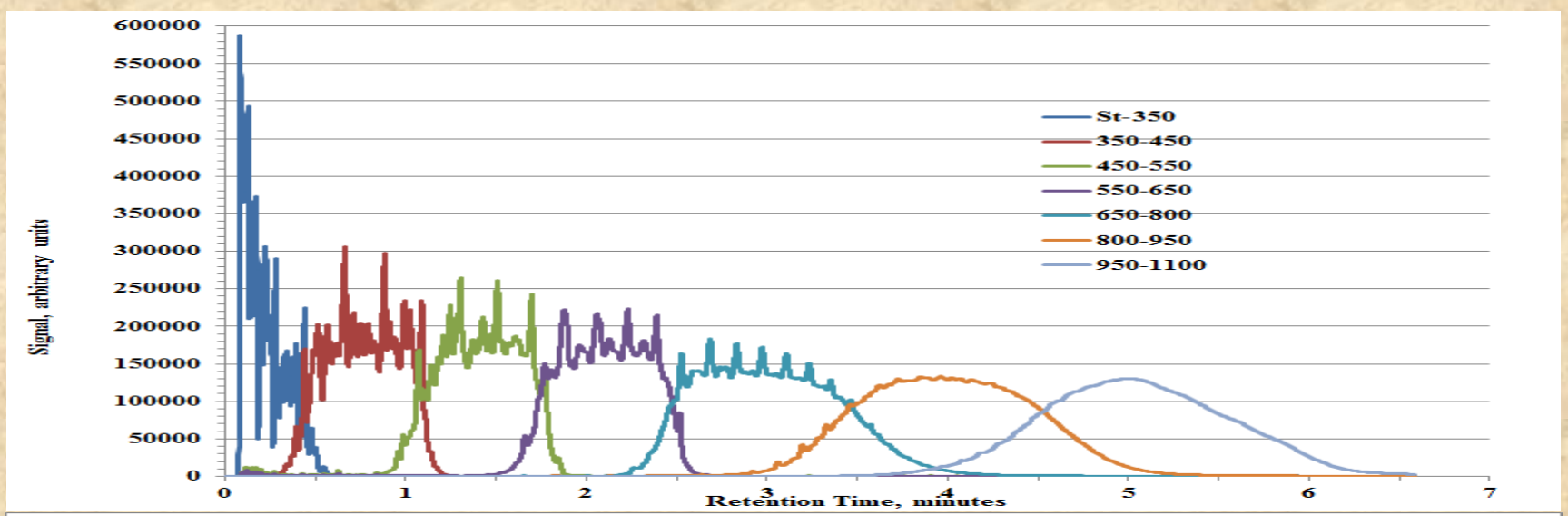
Column

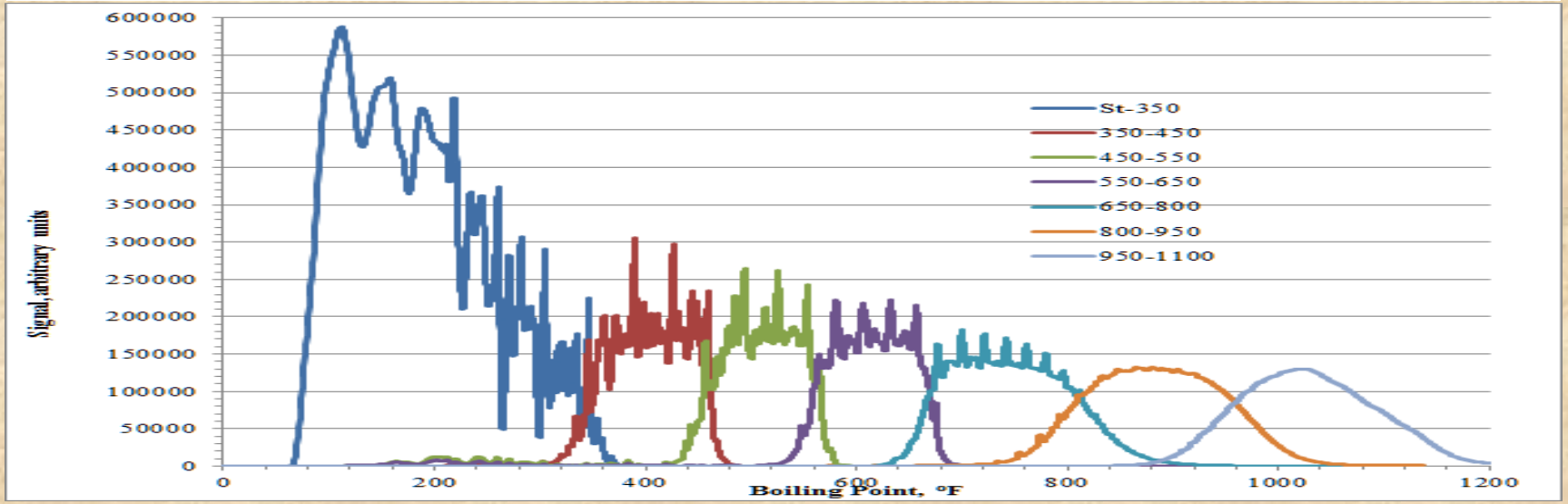
Injector and column effluent splitter

Modular Design Allows Flexible Usage



Chromatographic Traces (FID)





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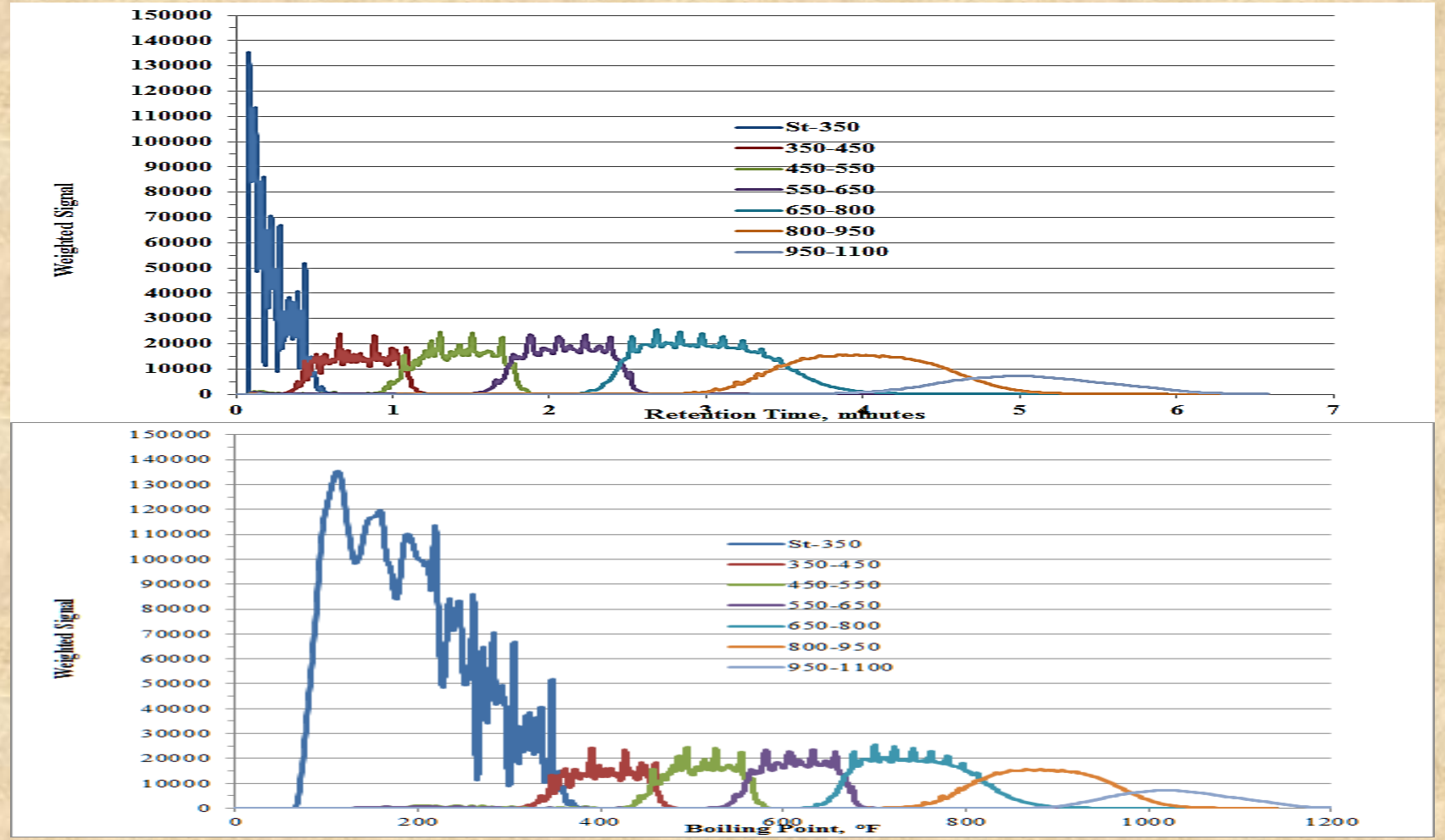
Chromatographic Traces Weighted by Fraction Yield



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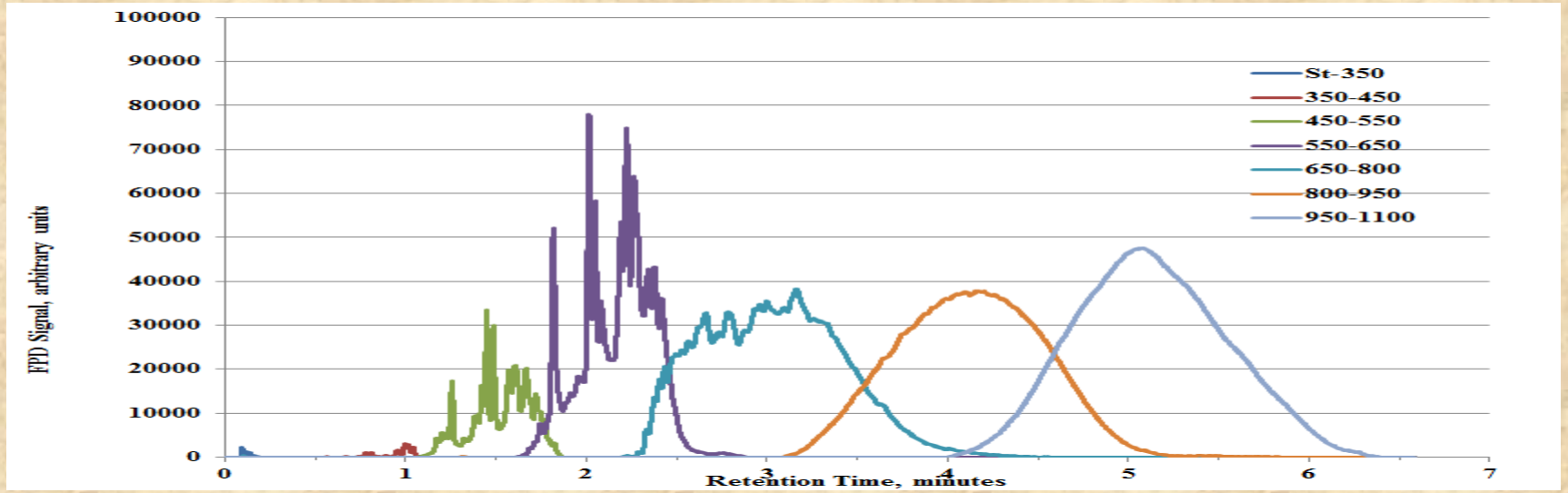
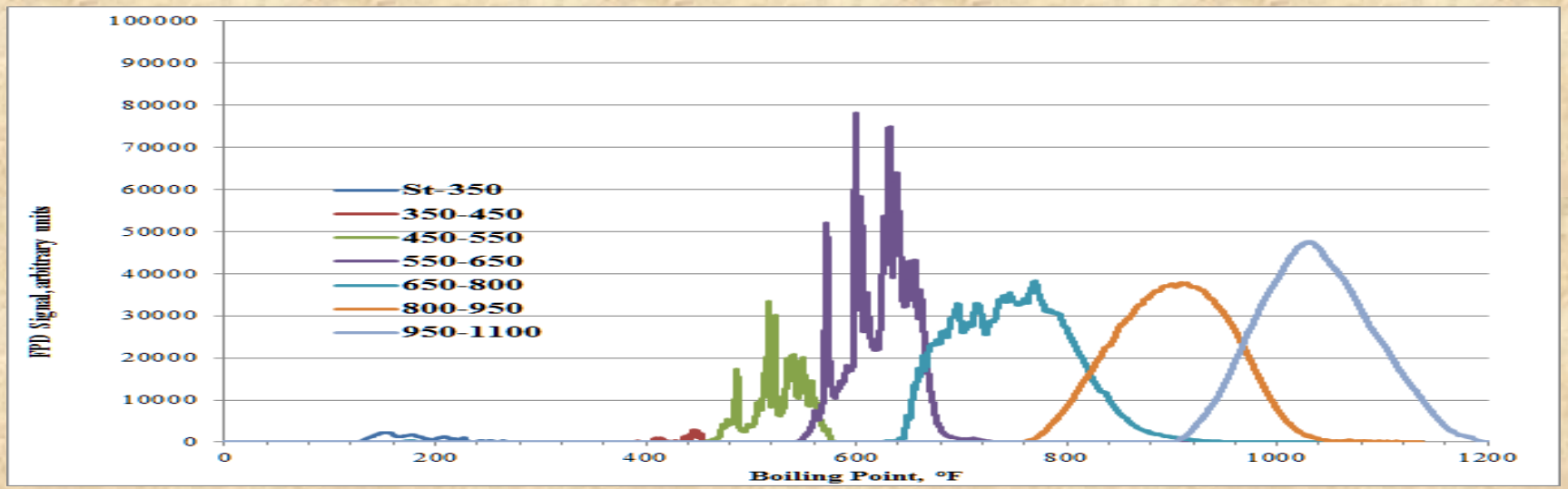
Sulfur Traces (FPD)





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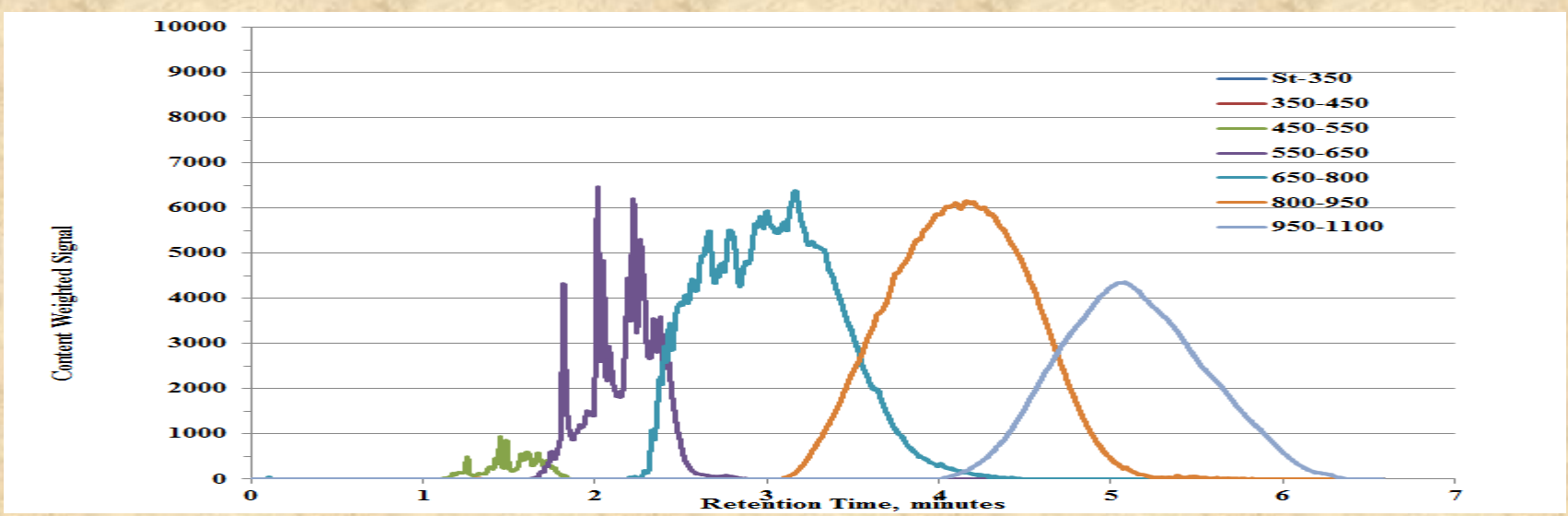
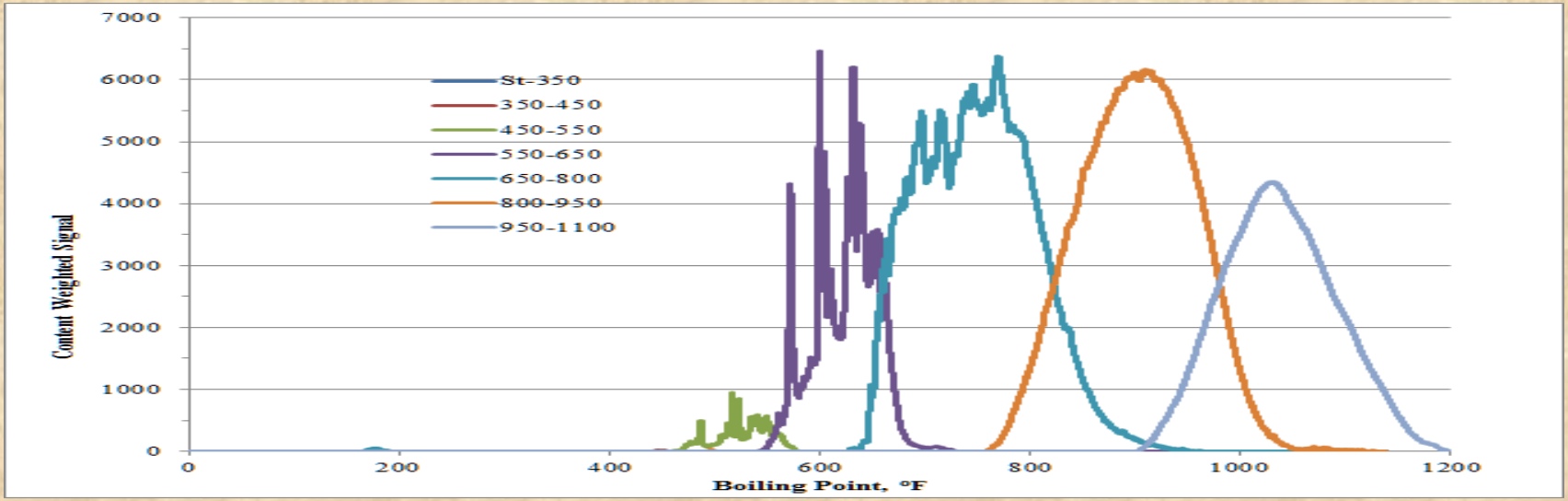
Sulfur Traces (FPD) Weighted by Content





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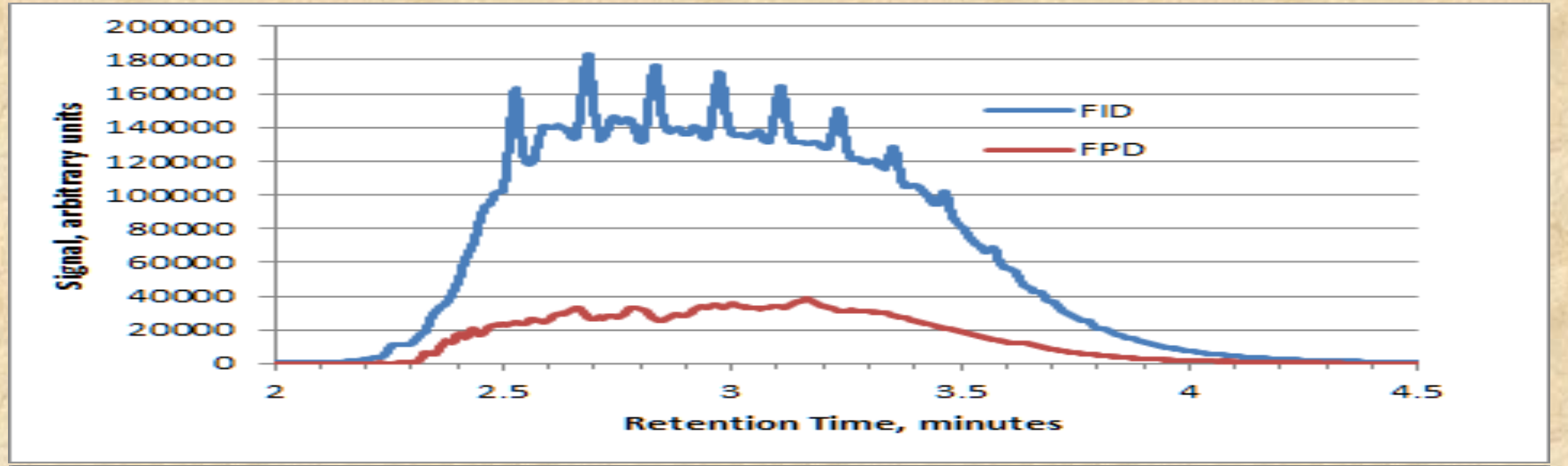
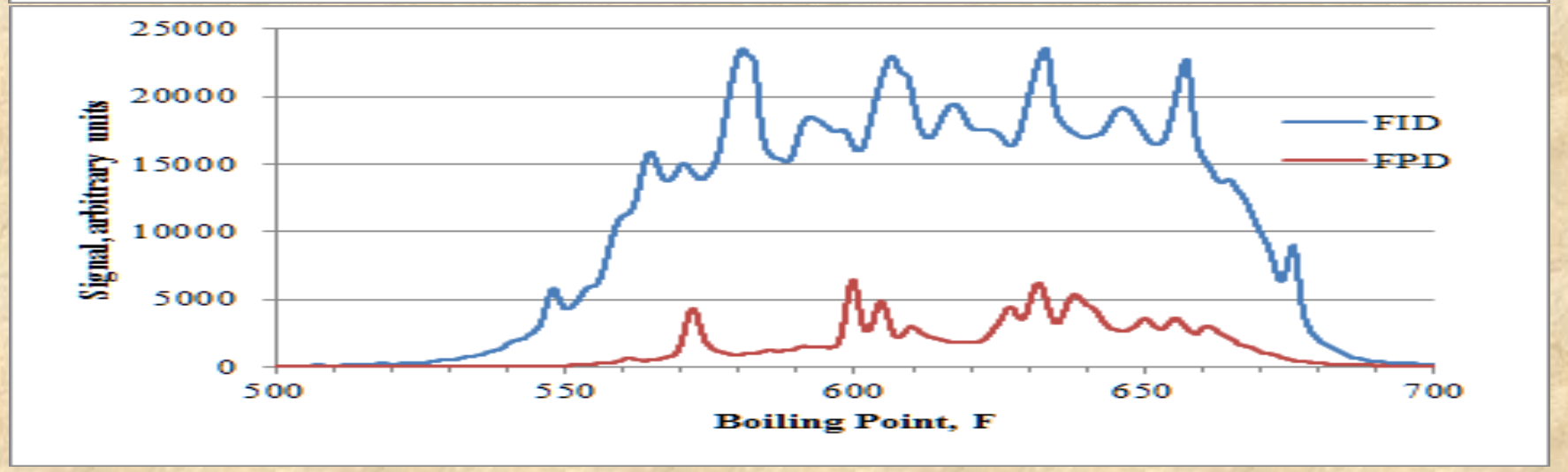
Comparison of FID and FPD Signals

(550-650 °F)





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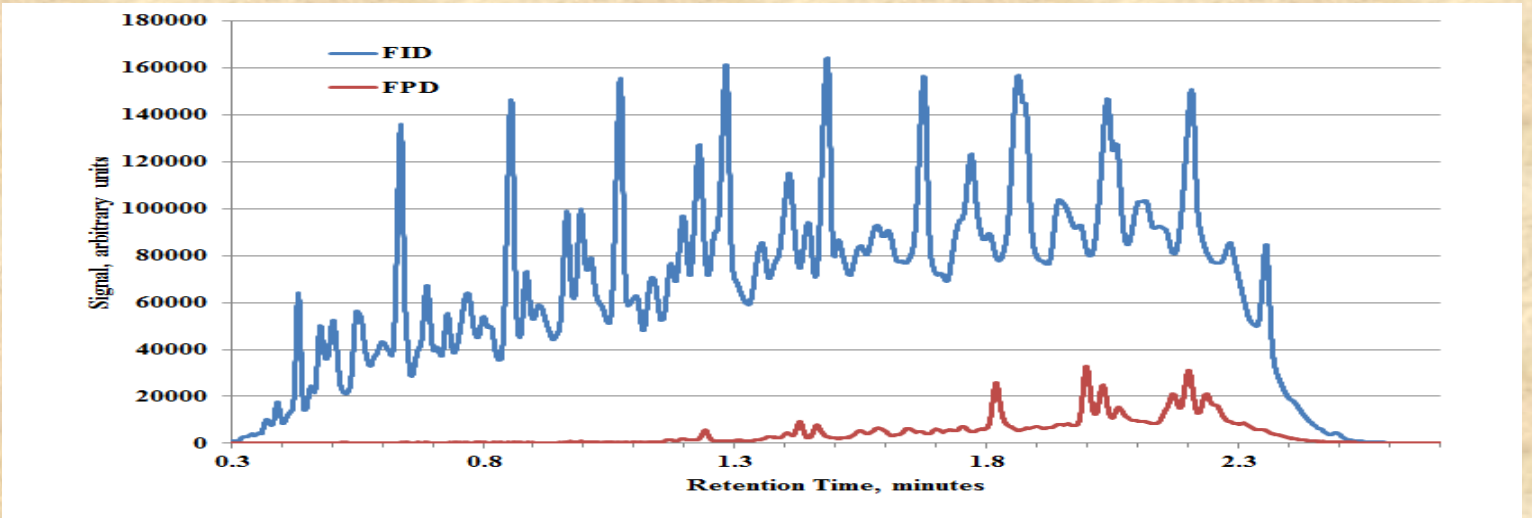
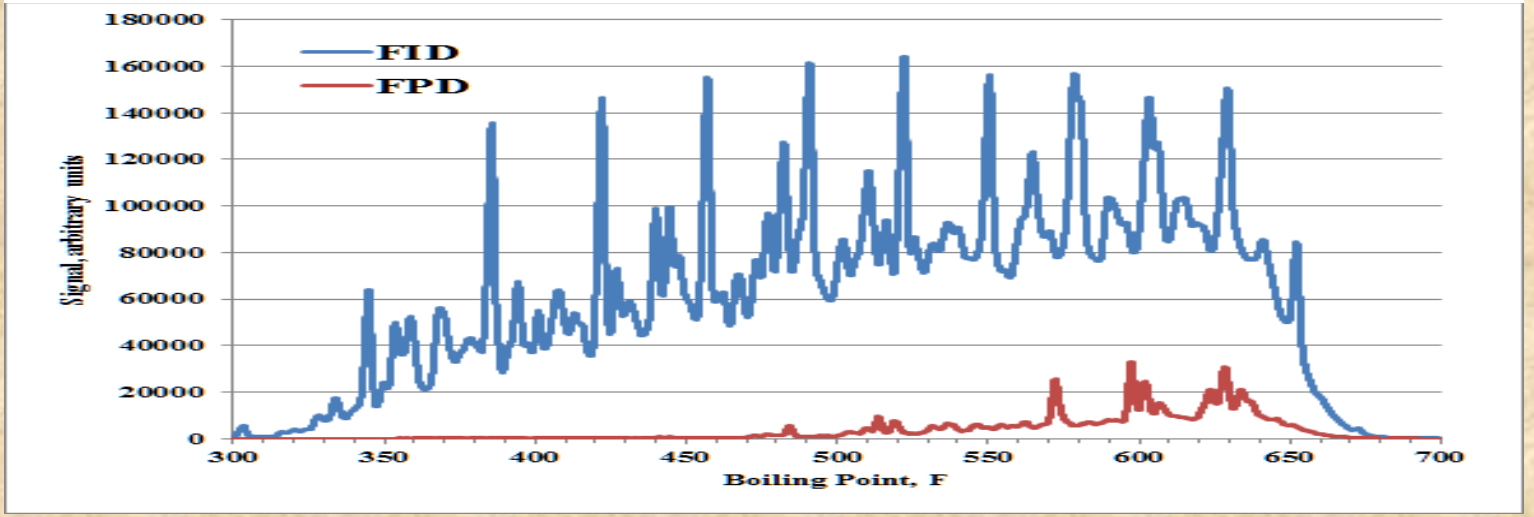
Comparison of FID and FPD Signals

(350-650 °F - weighted to crude basis)

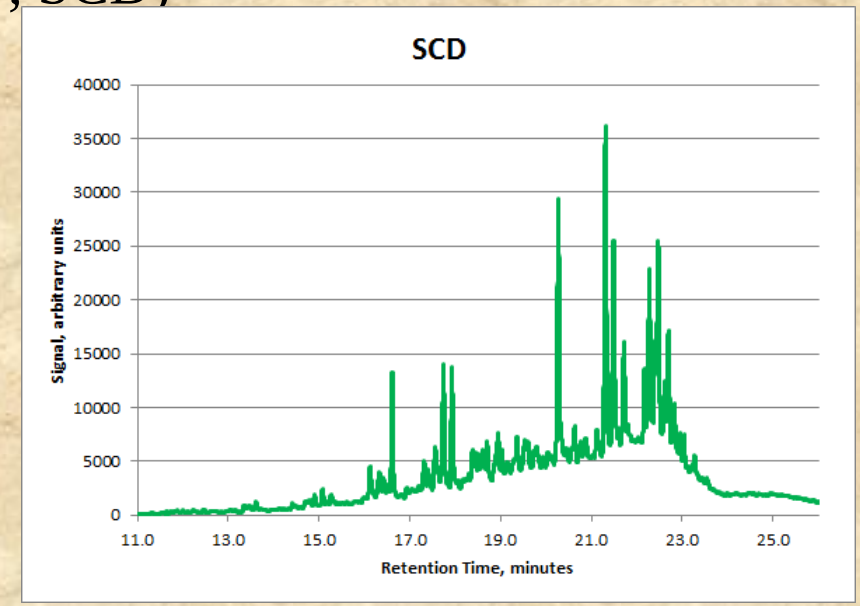


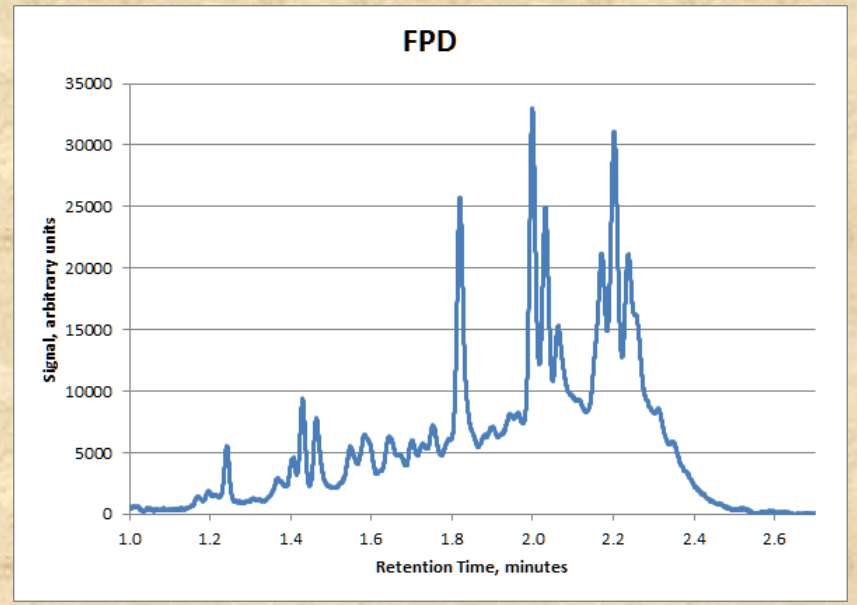


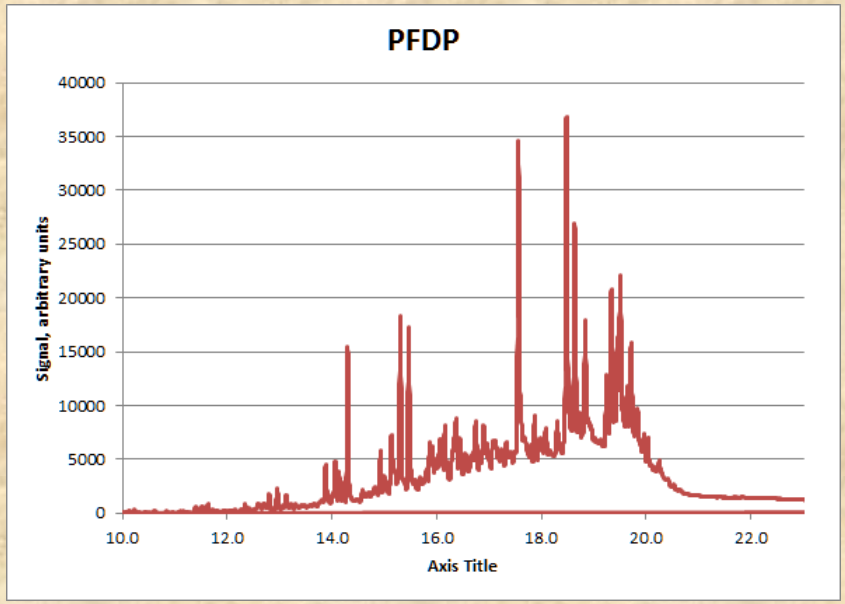
Comparison of Sulfur Signals

(FPD, PFPD, SCD)

- 350-650F crude fraction
- Different chromatography conditions
- FPD conditions compatible with ASTM D-7798







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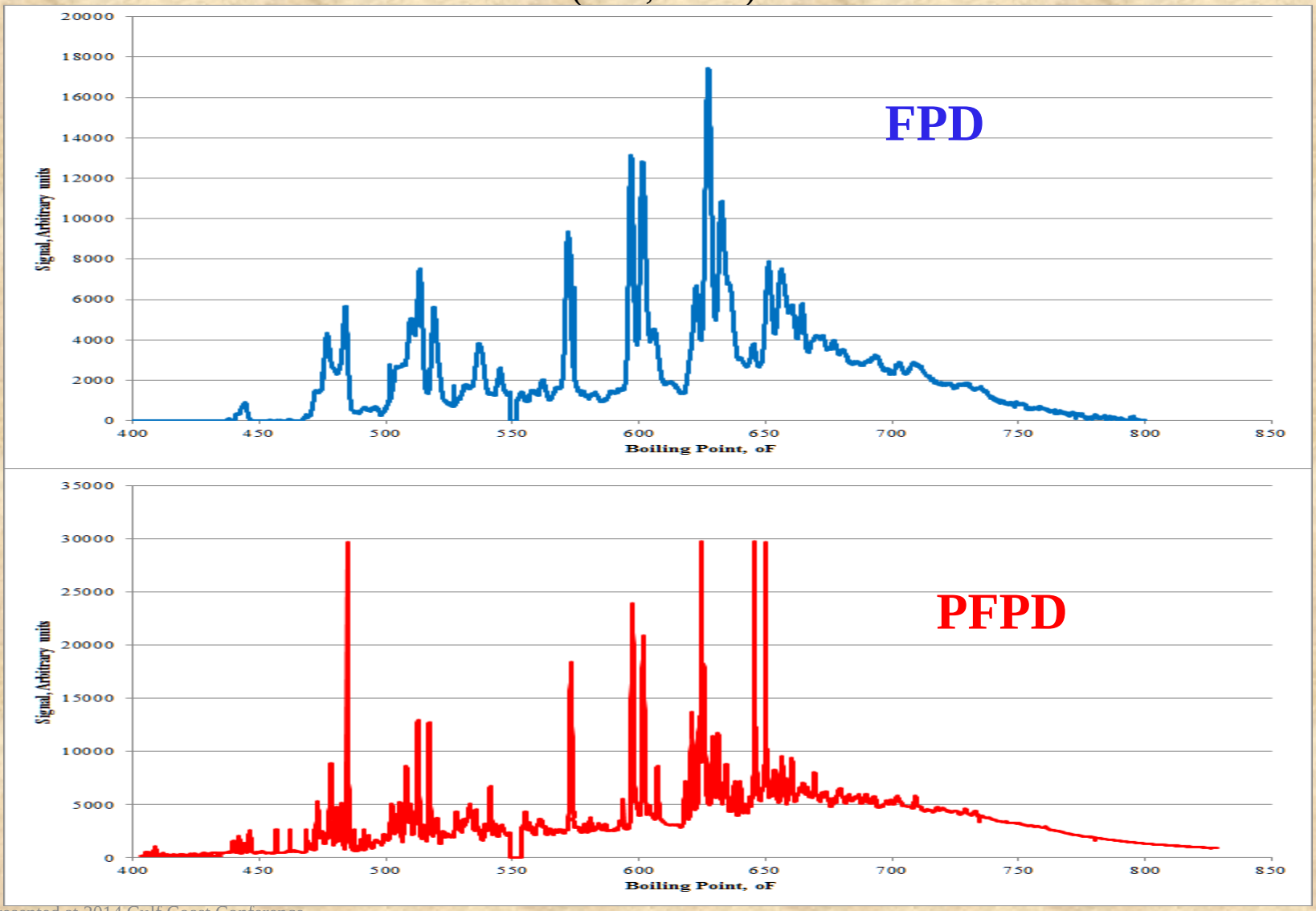
Diesel Hydrotreater Feed

(FPD, PFPD)



Comparison of GC-based Sulfur Detection Systems[1]

Characteristic	FPD	PFPD	SCD
Selectivity	10^5	10^6	10^6
Dynamic Range	10^3	10^3	10^5
Quenching	Yes	Yes	No
Robustness	Good	OK	Fragile
Approximate Detector Cost	$	$$	$$$
Total System Cost (per sample basis)	$	$$+	$$$+

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[1] partially from Agilent Technologies Application Note, "A Comparison of Sulfur Selective Detectors for Low Level Analysis in Gaseous Streams", August 16, 2001, Roger Frior

Summary

This presentation demonstrated the capabilities of a novel FPD design for the measurement of sulfur distribution in petroleum streams and fractions. The system simultaneously measures both the bulk carbon and signal and the sulfur specific signals needed to characterize such streams.

The speed of this system, nominally 10 times faster than conventional, research grade GCs, can be exploited to move from after the fact measurements to on-line control applications.

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The authors would like to thank Chevron Energy Technology Company for allowing previously presented information to be presented again.

The authors would also like to thank Rob Lorenz and Brian Morlan of Chevron Energy Technology Company for PFPD and SCD data for comparison.