Determination of Total and Speciated Sulfur in Petrochemical Matrices Using a Pulsed Flame Photometric Detector (PFPD)

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Introduction to the PFPD

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Introduction

- The Pulsed Flame Photometric Detector (PFPD) is a new generation of Flame Photometric Detectors (FPD).
- The PFPD has several distinct advantages over the static FPD, for example:
  - Increased sensitivity (10–100x, depending on FPD)
  - Increased selectivity (10x or more, depending on FPD)
  - Linear, equimolar response for sulfur and phosphorus, and easier calibrations
  - Decreased gas requirements
  - Self cleaning
  - Requires only minimal maintenance

Introduction (cont.)

- The Pulsed FPD can be used for any application or method that calls for a static FPD with improved results.
- It can also be easily configured for a wide variety of additional applications that are not easily done with a traditional, static FPD.
- The PFPD has the unique ability produce simultaneous, mutually selective chromatograms for sulfur and hydrocarbons using one detector with a small footprint and single PMT.
- And, the PFPD can detect up to 28 different elements for unique applications.

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Introduction (cont.)

- Some of the distinctive applications of the PFPD include:
  - Low-level sulfur speciation in gasoline and diesel
  - Sulfur speciation in other petrochemical matrices
  - Simultaneous sulfur and carbon chromatograms
  - Simultaneous organophosphorus and organosulfur pesticides
  - Parallel configuration with MS for complex matrices
  - Sulfur speciation in flavor and fragrance matrices
  - Sulfur quantitation in food and beverage samples
  - Organotin analysis in environmental samples
  - Arsenic, selenium, and silicone detection
  - Chemical warfare agent monitoring

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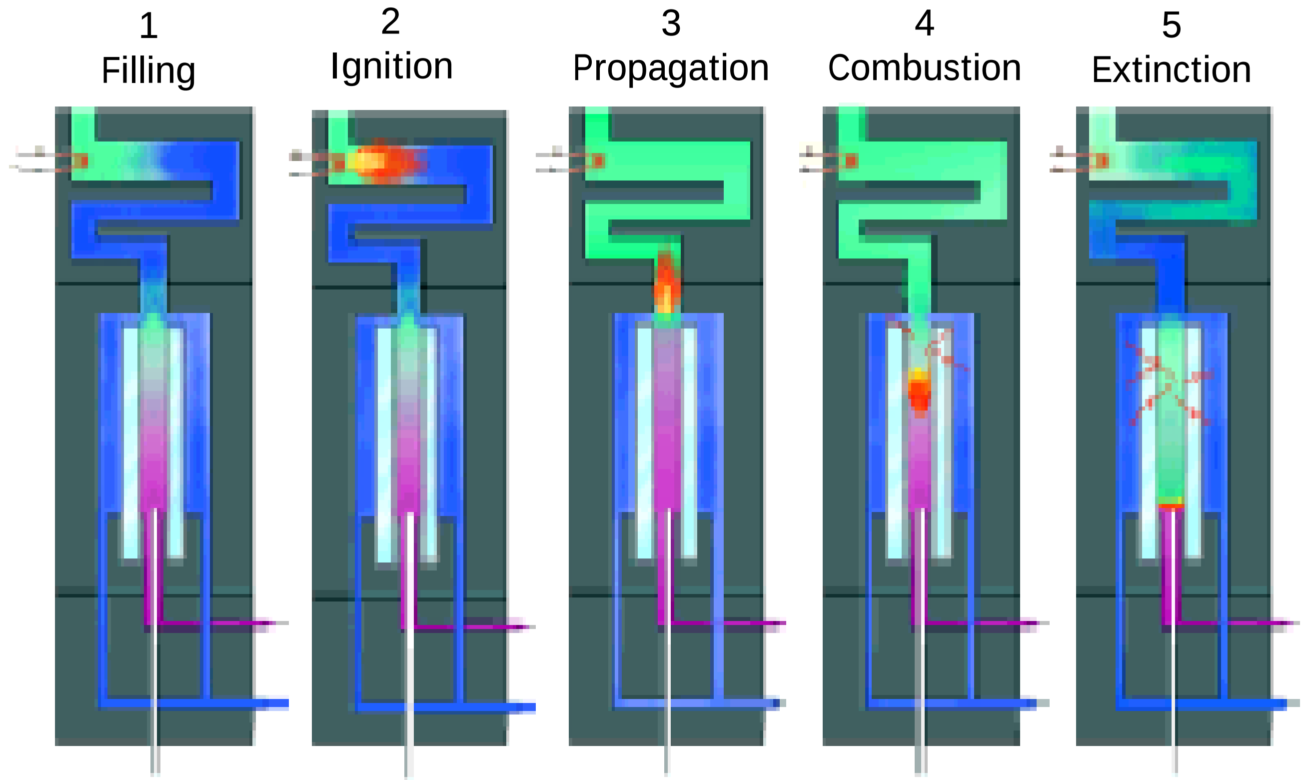
Self-Cleaning Detector



- 2200 °C flame
- Pulsing at 3–4 times per second
- “Self-cleaning” detector

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PFPD Advantages Over FPD

- The principle advantages of the Pulsed FPD over the traditional, static FPDs include:
  - Dual-element capability for the cost of a single detector
  - Better sensitivity and selectivity
  - Simultaneous, mutually selective S/C and S/P chromatograms
  - Linear, equimolar response
  - Wider range of applications and methods
  - Long-term stability
  - Lower cost of ownership and less gas usage
- A detailed comparison in shown in the tables in the following slides.

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Comparison of FPDs: Sulfur Mode

	FPD	Enhanced FPD	Pulsed FPD
Sulfur sensitivity	20 pg S/second	3.6 pg S/second	<1 pg S/second
S/C selectivity	10^5	10^6	>10^6 Adjustable to ∞
Linear?	No	No	Yes
Equimolar?	No	No	Yes
Linear range	~3 orders	~3 orders	~3 orders
Quenching	Yes	Yes	Minimal
Gas usage	230–240 mL/minute	230–240 mL/minute	30–40 mL/minute
Temperature	Maximum 250 °C	Maximum 250 °C	200–400 °C
Comments	• Poorest sensitivity and selectivity. • Subject to quenching. • High cost of operation.	• If broadband filter used to improve sensitivity, it may reduce selectivity. • S/C selectivity may be concentration dependent, with reduced selectivity near the detection limit.	• Stabilizes quickly & remains stable. • Infinite S/C selectivity. • Simultaneous, mutually selective S and C chromatograms from a single detector.

Comparison of FPDs: Phosphorus Mode

	FPD	Enhanced FPD	Pulsed FPD
Phosphorus sensitivity	900 fg P/second	60 fg P/second	<100 fg P/second
P/C selectivity	10^5	10^5	$>10^5$
P/S selectivity	Poor	Poor	Excellent with Dual Gate Subtraction
Equimolar?	Unknown	Unknown	Yes
Linear range	~3 orders	~3 orders	~3 orders
Temperature	Maximum 250 °C	Maximum 250 °C	200–400 °C
Comments	• Poorest sensitivity and selectivity. • High cost of operation.	• The low maximum temperature restricts FPD use for OP pesticides and can lead to tailing, reduced response, and poor reproducibility for late eluting compounds.	• Best sensitivity for all OP pesticides, with excellent peak shape. • Analyze for P and S simultaneously with mutually selective chromatograms.

Comparison of FPDs: General

	FPD	Enhanced FPD	Pulsed FPD
Simultaneous S/C and S/P detection?	Yes, but at double the cost.	Yes, but at double the cost.	Yes, using a single detector.
Simultaneous S and C detection?	May be possible, but will double the cost.	May be possible, but will double the cost.	Simultaneous, mutually selective chromatograms for petrochemical matrices with a single detector.
Other elements?	Not easily	Not easily	As, Se, Si 28 total elements
Cost of operation	High (gas usage and frequent cleanups)	High (gas usage and frequent cleanups)	Low gas usage Low maintenance

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PFPD Advantages Over SCD

- The principle advantages of the PFPD over the SCD include:
  - ½ the initial capital expense
  - Lower cost of ownership and less gas usage
  - Ease of use with minimal maintenance
  - Long-term stability
    - Months rather than days!
  - Dual-element capability for the cost of a single detector
  - Simultaneous, mutually selective S/C chromatograms
  - Wide range of applications and methods
- A detailed comparison is shown in the tables in the following slides.

PFPD Compared to SCD

	SCD	PFPD
Detectivity	<1 pg sulfur per second	<1 pg sulfur per second
Selectivity	>10^6	>10^6 Adjustable to ∞
Linear range	>3 orders linear range	~2.5 orders linear range Up to 3 orders with Dual Gate techniques
Long-term stability	Inherently more complex and less stable. Ozone generator, vacuum system, ceramic tubes.	Simple, self-cleaning design. Stable for months with little or no maintenance.
Calibration frequency	Daily or weekly	Calibrations can last many months or longer.
Gas and gas consumption	10x higher gas consumption Requires O_2 tank	Total combined gas flows of about 25–30 mL/min (He and air)
Equimolar response	Yes	Yes (FPD is NOT equimolar)

PFPD Compared to SCD (cont.)

	SCD	PFPD
Quenching	Low due to high gas flows	Yes, but can be minimized with proper conditions
Chromatography	Broad peaks with some tailing, up to 2 sec wide	Narrow, symmetric sulfur peaks
Simultaneous hydrocarbon chromatogram?	No	Yes
Multiple element detection?	No	Yes, 28 elements including S, P, N, C, As, Si, Sn
Size and weight	Takes up extra bench space and requires under-bench rotary pump	Small, incorporated into GC
Price	About 2x the PFPD Higher maintenance costs	Low to moderate, depending on configuration chosen

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PFPD Performance Specifications

Specification	Criteria
Detectivity	<1 pg S/second <100 fg P/second
Detection limit	Application dependent, low or single-digit ppb range for most applications
Selectivity	S/C > 10^6, adjustable to ∞ P/C > 10^6
Linear range	~10^3
Operating temperature	100–400 °C
Gas flows	10–15 mL/min H_2 20–25 mL/min air

Sulfur in Petrochemical Matrices Using the PFPD

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Sulfur in Petrochemical Matrices

- Sulfur is present in most petrochemical matrices at concentrations ranging from sub-ppb for single sulfur species up to weight % for total sulfur.
- Sulfur is measured in petrochemical matrices for two main reasons:
  - The total sulfur content is regulated in gasoline and diesel matrices.
  - Understanding the sulfur species present in a product is important for process adjustments.
- Examples of sulfur in a wide range of petrochemical samples using the PFPD are shown in the following slides.

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Sulfur in Petrochemical Matrices (cont.)

- Total sulfur concentrations reported here have been determined by either an internal standard or external standard quantitation technique.
- Identification assigned to selected individual sulfur species are approximate and based on a minimum of two references.
- In some cases the species identification may be preliminary.
- Full analytical conditions for most of these applications can be found in the “Notes” view.

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Sulfur in
Gas Phase Matrices

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OI Analytical S-PRO 3200

- Turn-key system designed for detection and quantitation of low-level sulfur compounds in gas phase and LPG-type matrices
- Agilent 6890N platform with Agilent GS-GasPro® column
- Integrated permeation oven for automated generation of analytical standards
- Gas sampling loop available in a range of sizes
- OI Volatiles Interface, Sulfinert™ treated and capable of wide range of split ratios
- PFPD for low-level sulfur detection and quantitation
  - High selectivity and sensitivity
  - Low maintenance, long term stability
  - No coking or fouling of the detector

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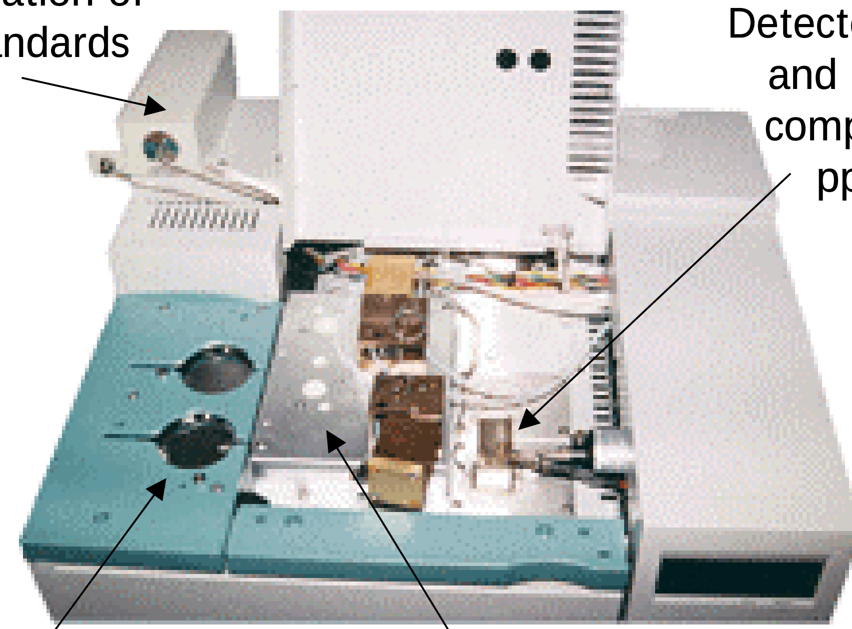
OI Analytical S-PRO 3200

Integrated permeation oven for generation of calibration standards

Pulsed Flame Photometric Detector (PFPD) for detection and quantitation of sulfur compounds at single-digit ppbv concentrations



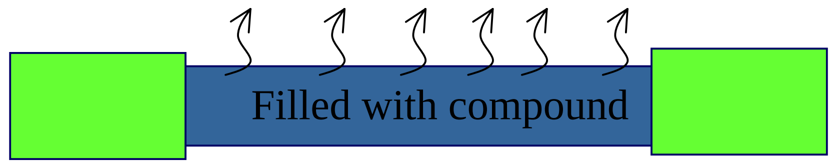
OI Volatiles Interface for introduction of gas phase matrices with split (Sulfinert treated)

Heated valve box with 6-port valve, gas sampling loop (optional LSV), and 4-port selection valve (all lines Sulfinert treated)

Theory of Permeation Oven

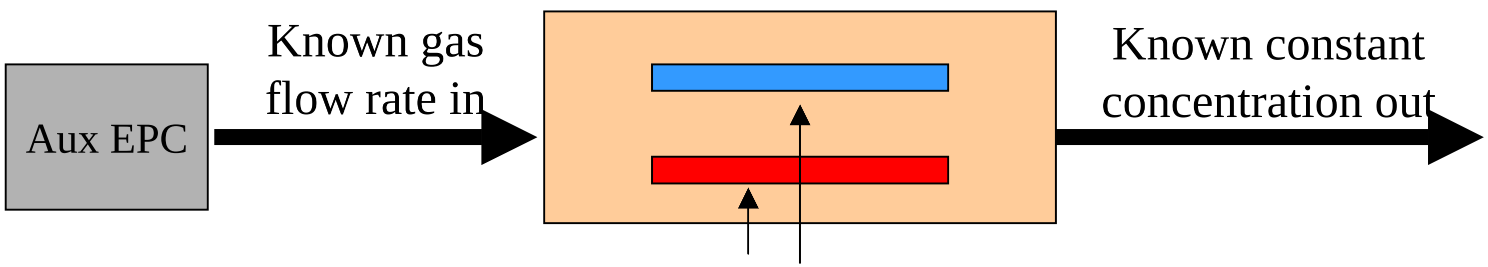
Compound diffuses across the membrane at a constant rate at a given temperature

R = ng/(min*cm)



Permeation device with permeable membrane

Permeation oven held at constant temperature ~ 30–35°C



Permeation devices with a known diffusion rate at given temperature

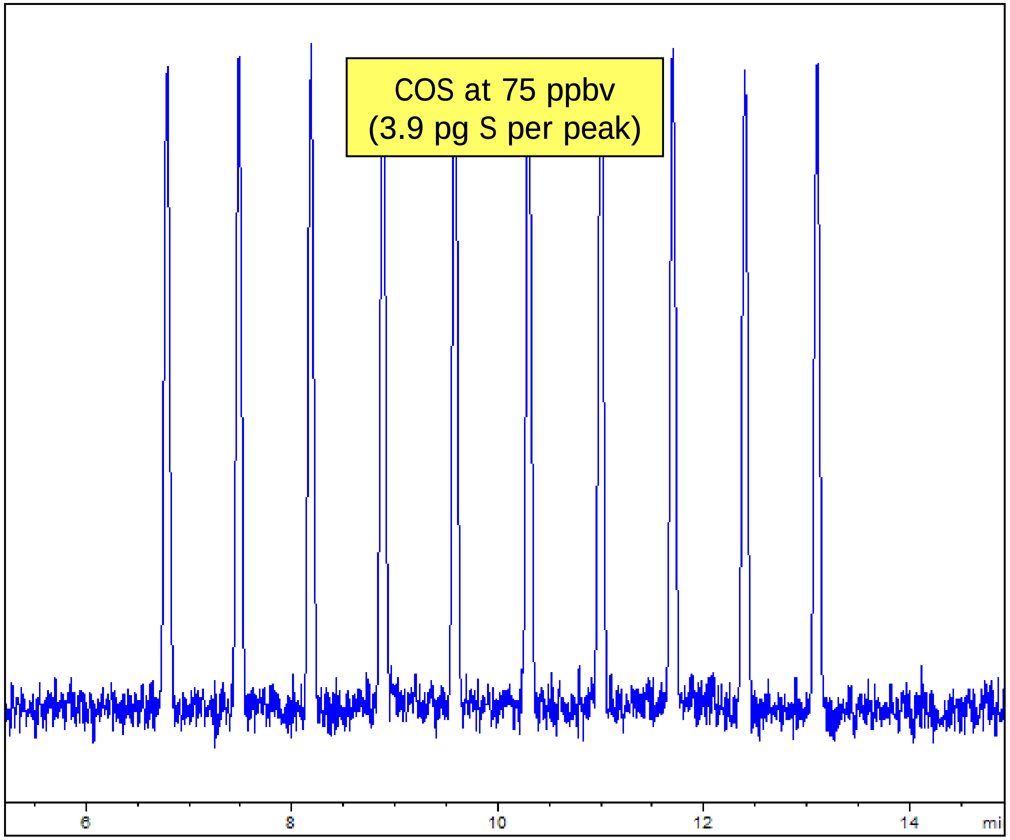
Generation of Analytical Gas Standard

- A COS gas-phase standard was generated using the S-PRO integrated permeation oven.
- For example:
  - COS permeation device, permeation rate of 91.5 ng/min at 30 °C
  - Permeation oven at 30 °C
  - 500 mL/min dilution gas (He)
  - 1-mL gas sample loop
  - 1 mL/min column flow (He)
  - Split ratio 15:1 (18.5 mL/min split flow)
  - Concentration of COS (and sulfur) eluting from permeation oven = 75 ppbv

COS Standard at 75 ppbv

10 replicate injections of COS from the permeation oven using the 1-mL gas sample loop and 6-port valve

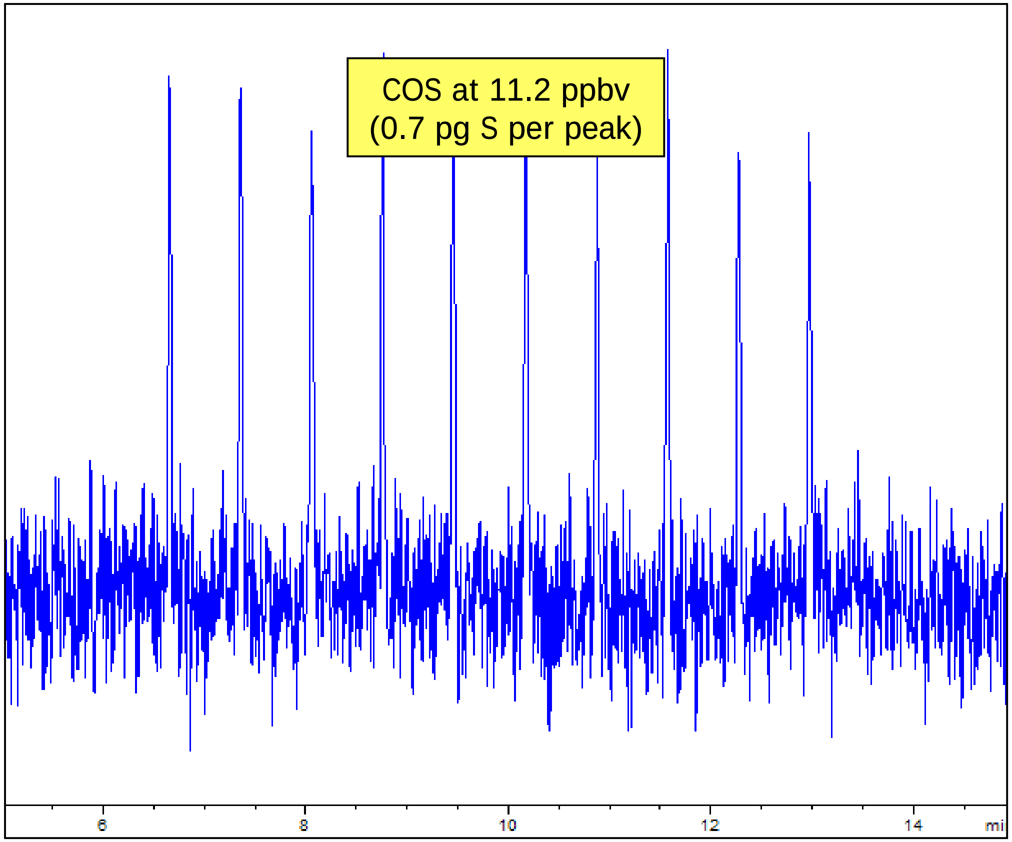
Peak Number	Area Counts
1	1148
2	1122
3	1157
4	1154
5	1156
6	1126
7	1173
8	1122
9	1162
10	1132
Average	***1145***
%RSD	***1.6%***



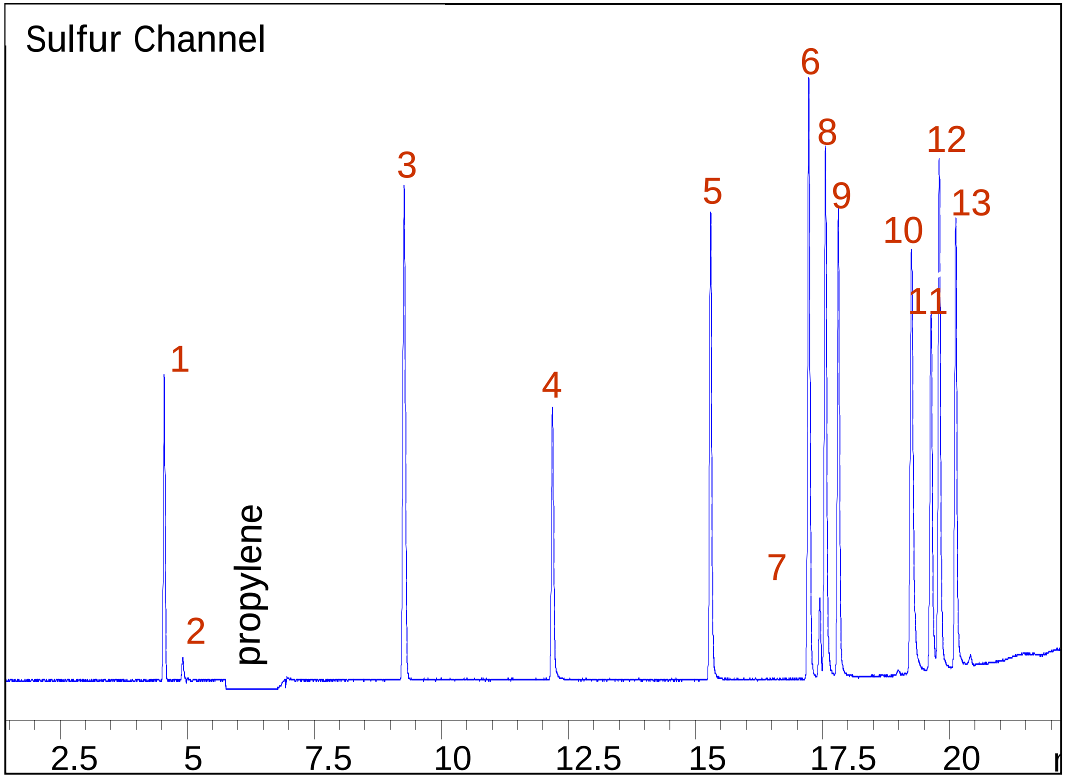
COS Standard at 11.2 ppbv

10 replicate injections of COS from the permeation oven using the 1-mL gas sample loop and 6-port valve

Peak Number	Area Counts
1	152
2	151
3	170
4	161
5	163
6	150
7	136
8	173
9	157
10	150
Average	***156.3***
%RSD	***6.9%***



13 Sulfur Compounds in Propylene



1 COS
2 H_2S
3 CS_2
4 Methylmercaptan
5 Ethylmercaptan
6 Thiophene
7 DMS
8 2-Propanethiol
9 1-Propanethiol
10 2-Methyl-2-propanethiol
11 2-Methyl-1-propanethiol
12 1-Methyl-1-propanethiol
13 1-Butanethiol

0.2 mL gas sampling loop; split 5:1.
Each compound present in this propylene standard at approximately 1 ppm (except H_2S).

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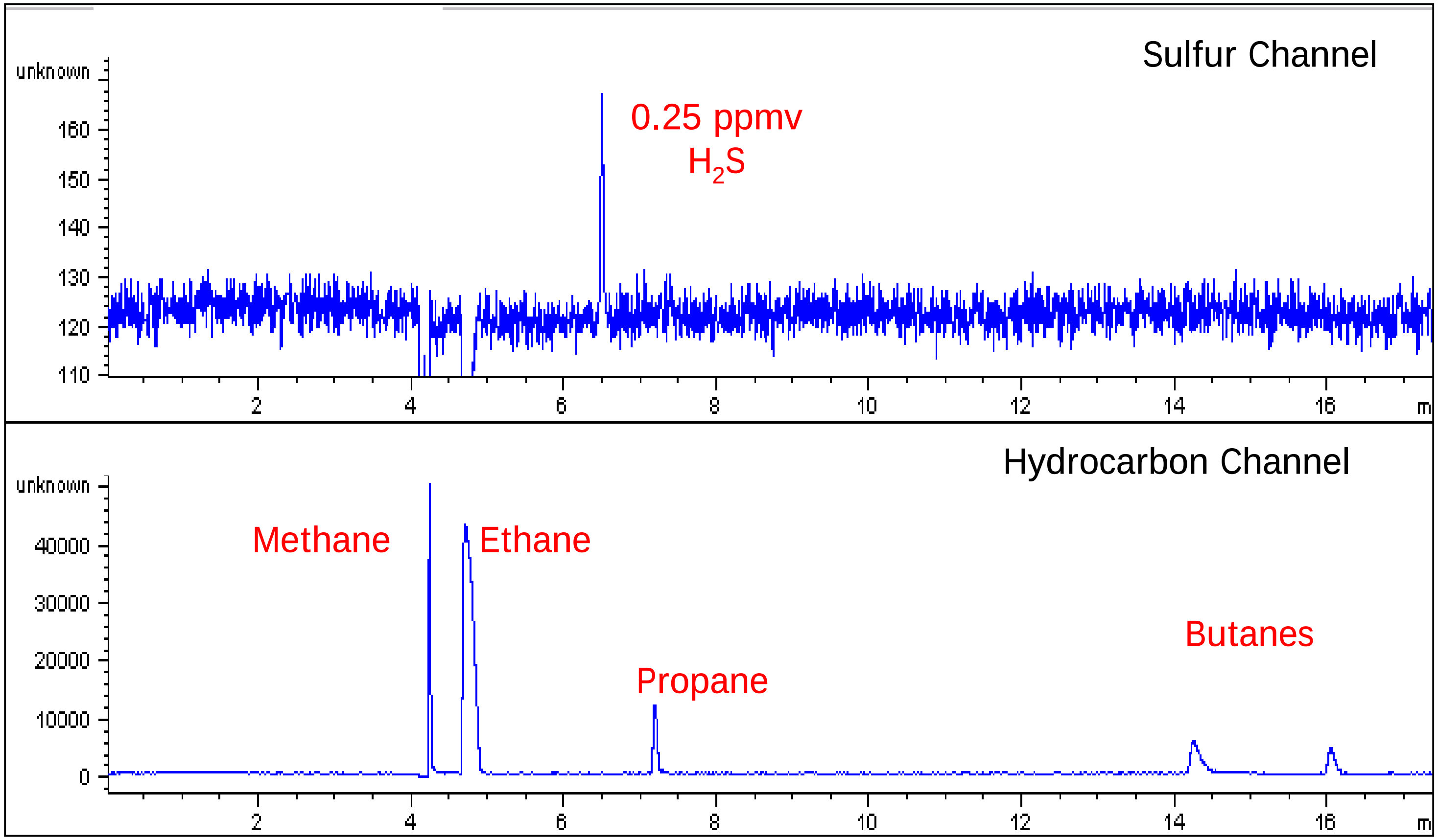
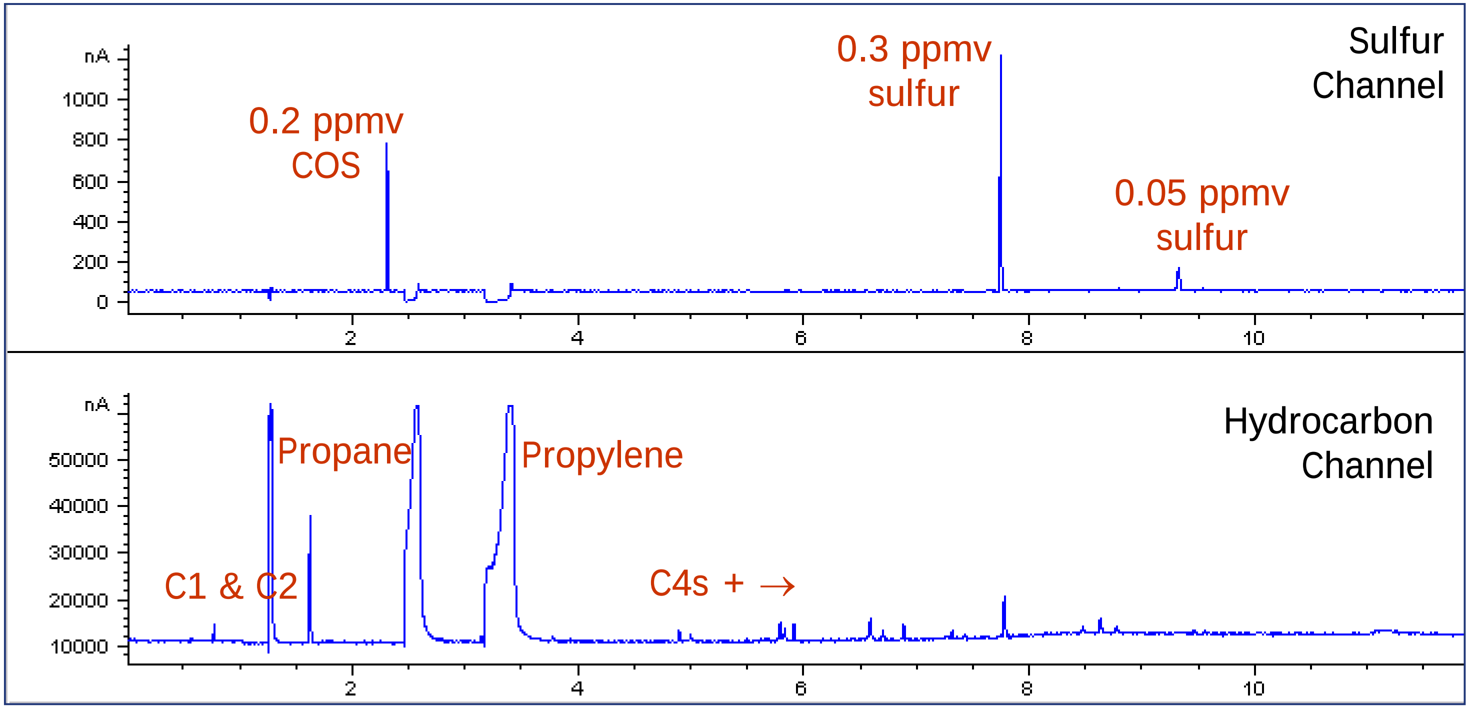
H_2S in Natural Gas on the S-PRO 3200



0.5 mL gas sampling loop; split 9:1.
Analyzed on the OI Analytical S-PRO 3200.

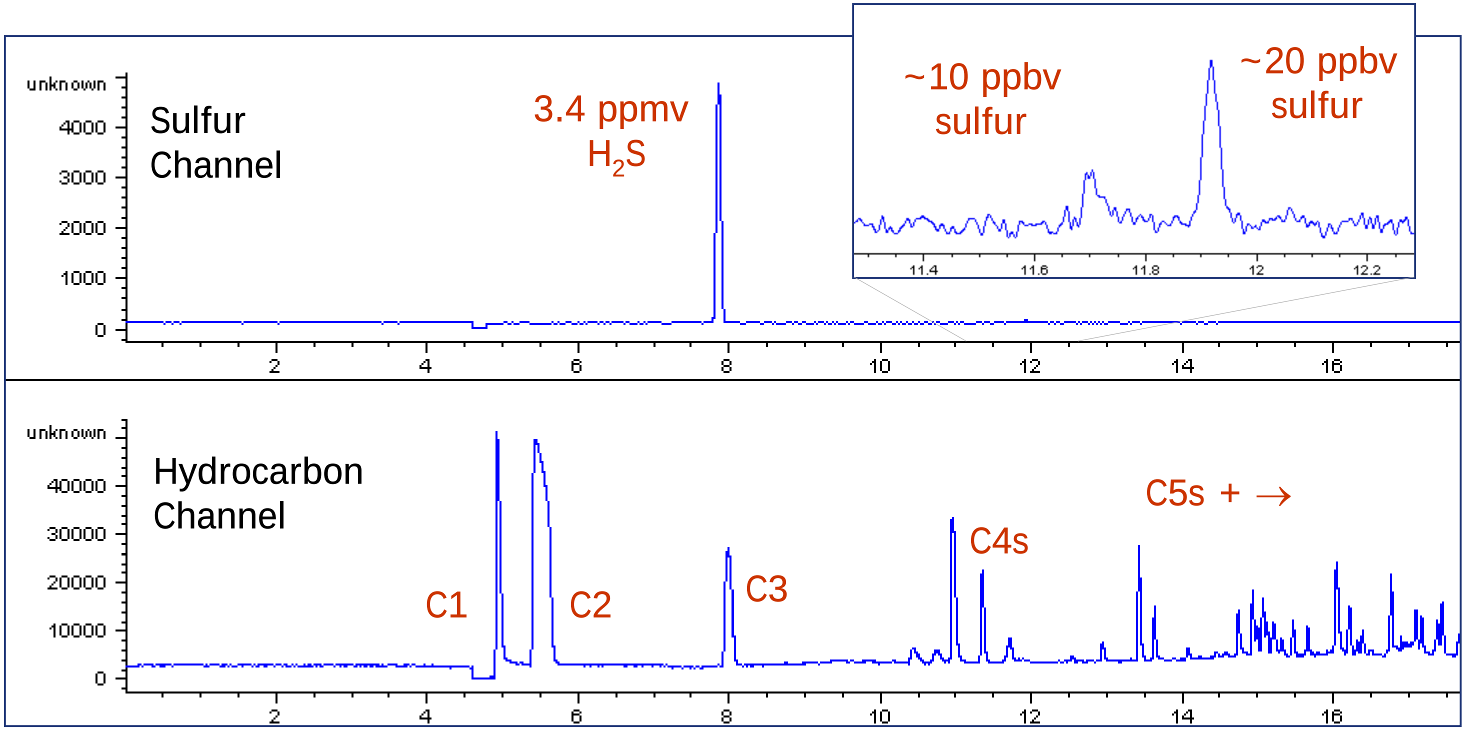
Sulfur in Propane-Propylene Mix

- Acquired on the *OI Analytical S-PRO 3200*
- 0.2-mL gas sample loop, 5:1 split, GasPro column, ramped oven
- [COS] & [S] determined with COS permeation wafer device and equimolar response of the PFPD

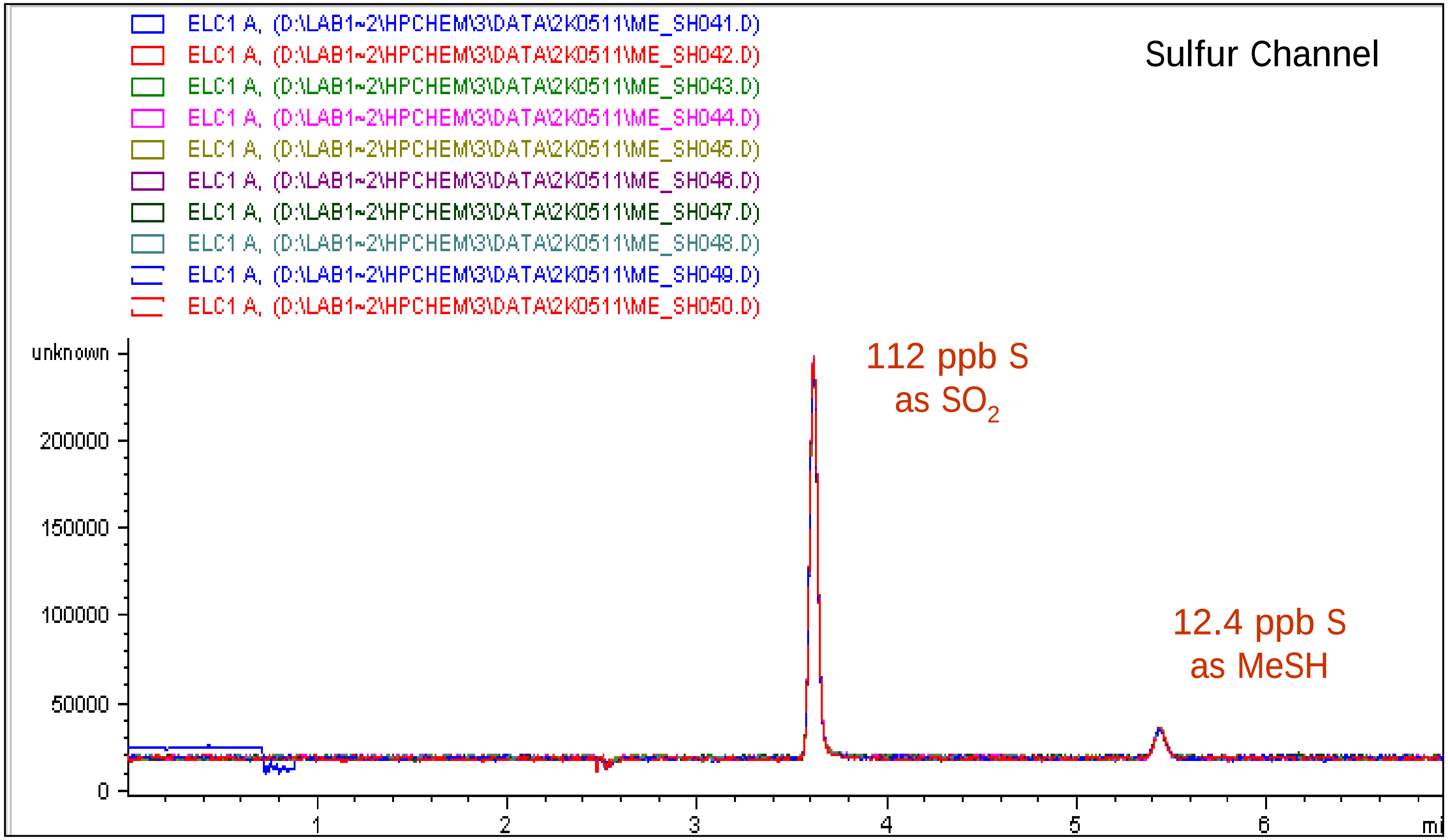


Sulfur in Pipeline Natural Gas

- Acquired on the *OI Analytical S-PRO 3200*
- 0.5-mL gas loop, 9:1 split, GasPro column, isothermal oven
- [H_2S] determined with H_2S permeation wafer device
- Unknown [S] determined with COS permeation device and equimolar response



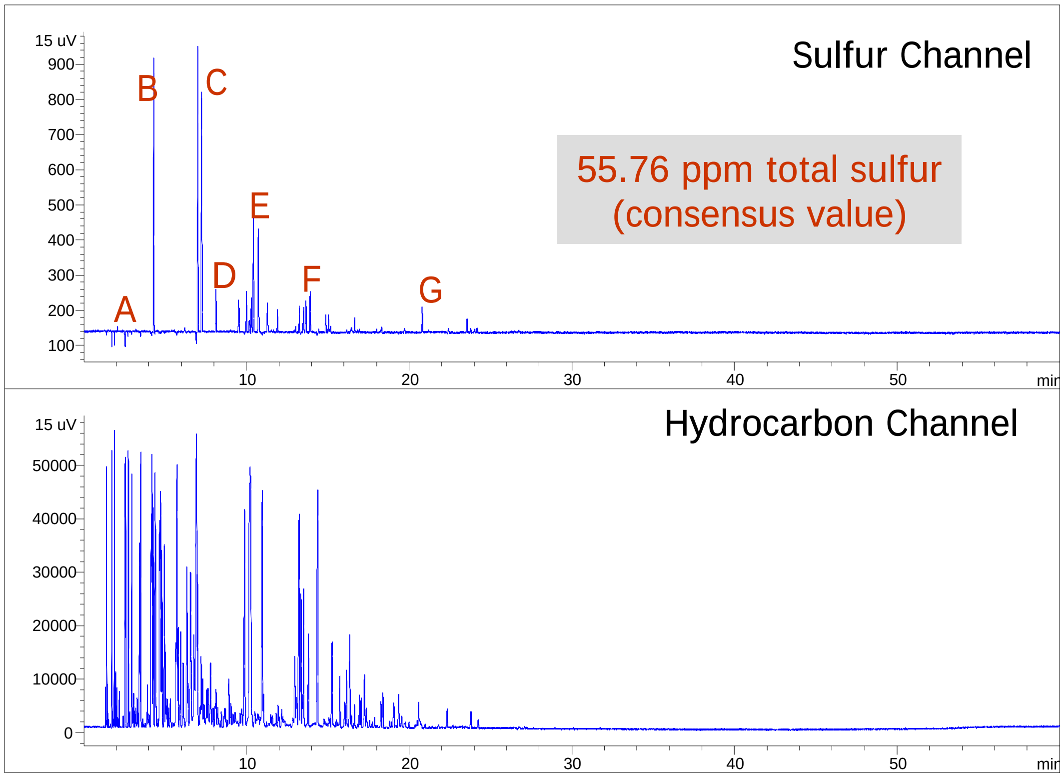
Sulfur Compounds in CO_2



0.5 mL gas sampling loop; slit 20:1.
10 replicate analyses on the S-PRO 3200.

Sulfur in Gasoline

ASTM Round Robin Gasoline #10



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
ASTM RR Gasoline #10 has a consensus value of 55.76 ppm total sulfur.

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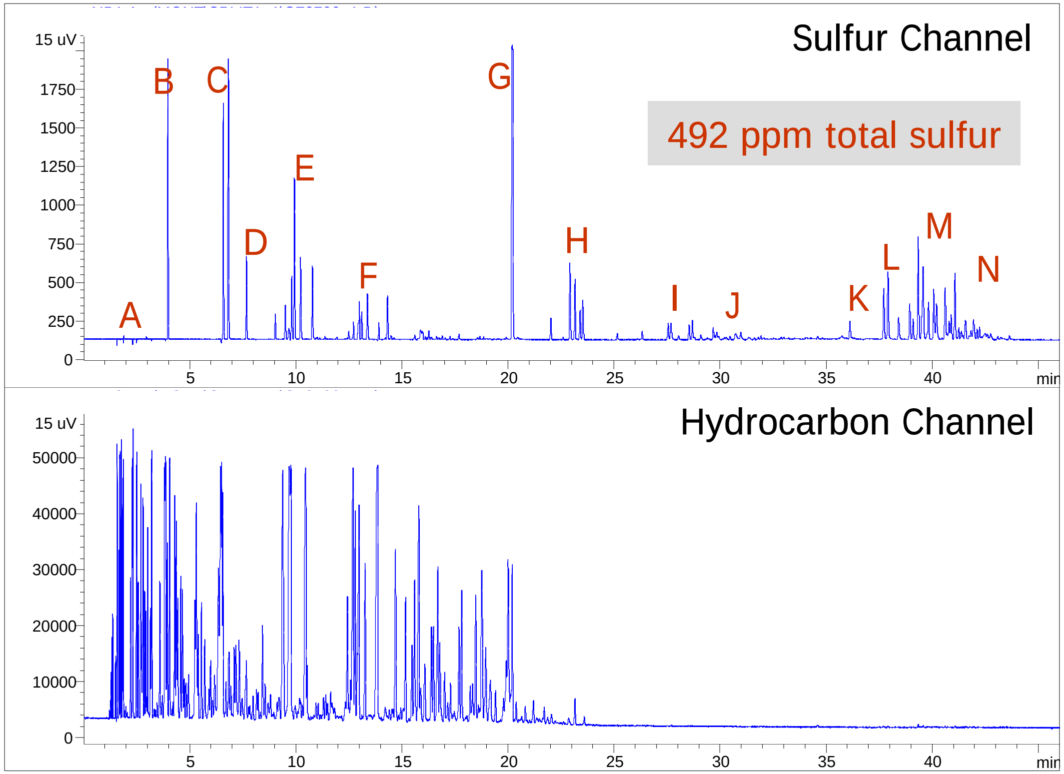
Gasoline "A" Before Sulfur Treatment



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F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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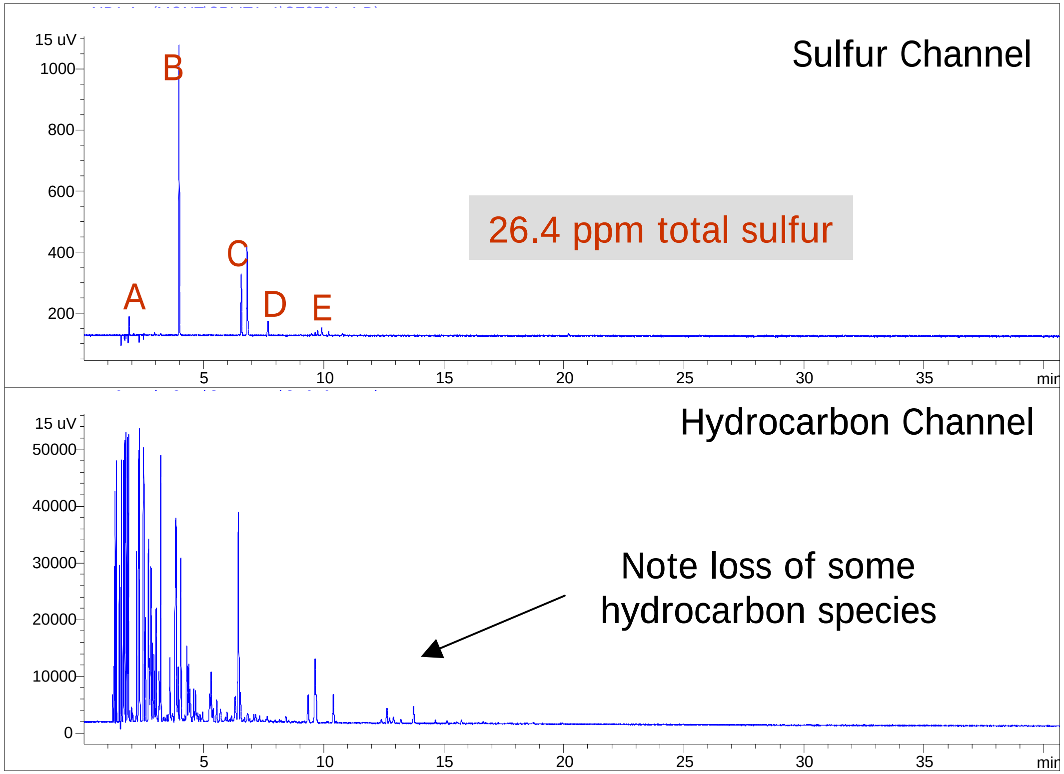
Gasoline "A" After Sulfur Treatment



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- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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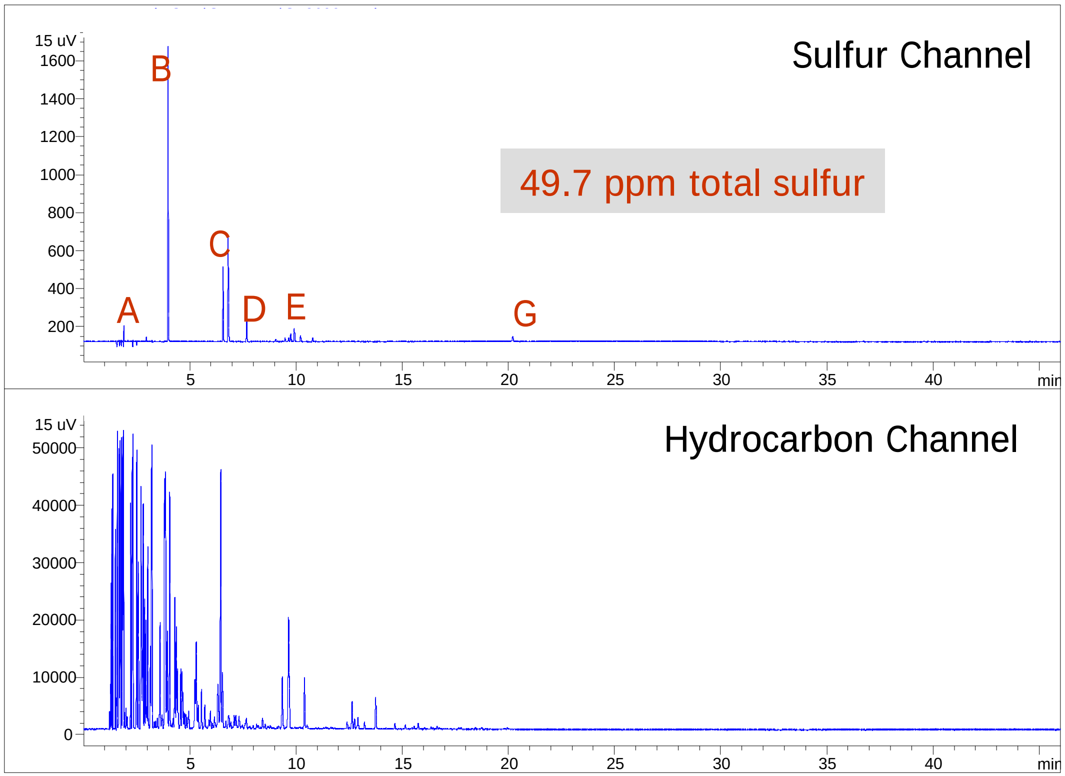
Gasoline “B” Before Sulfur Treatment



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F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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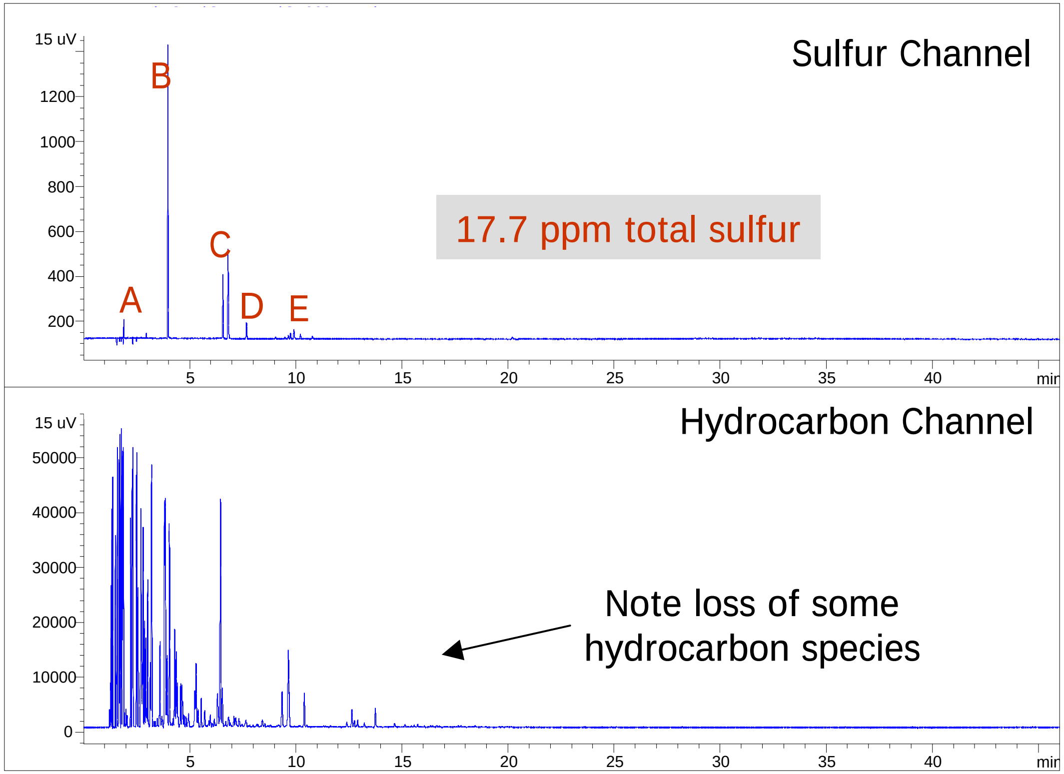
Gasoline "B" After Sulfur Treatment



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F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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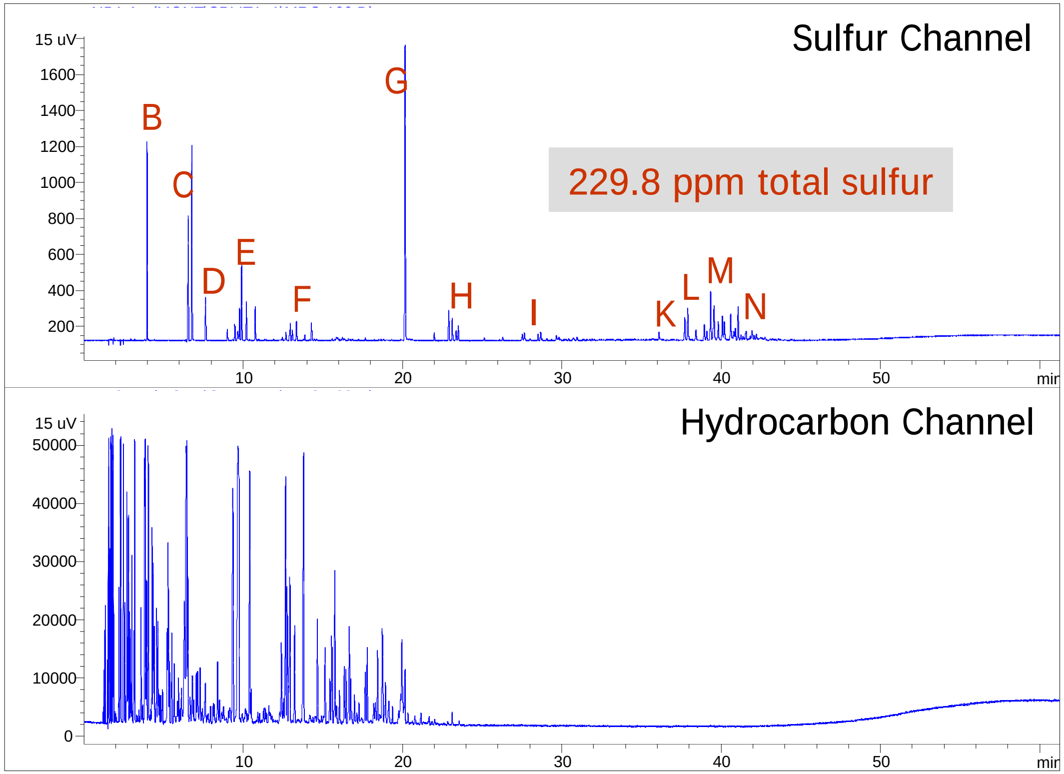
Gasoline "C", Unrefined



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I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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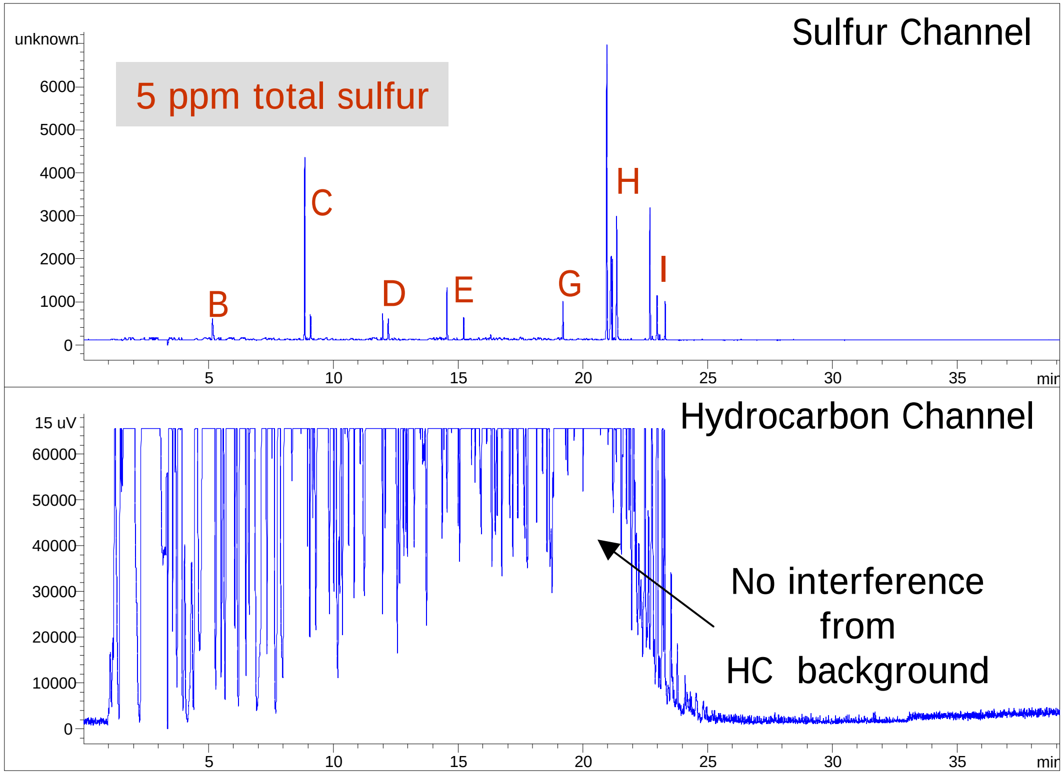
Gasoline "D", 5 ppm



A Methyl mercaptan
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F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 10:1.
Concentration reported by client as 5 ppm.

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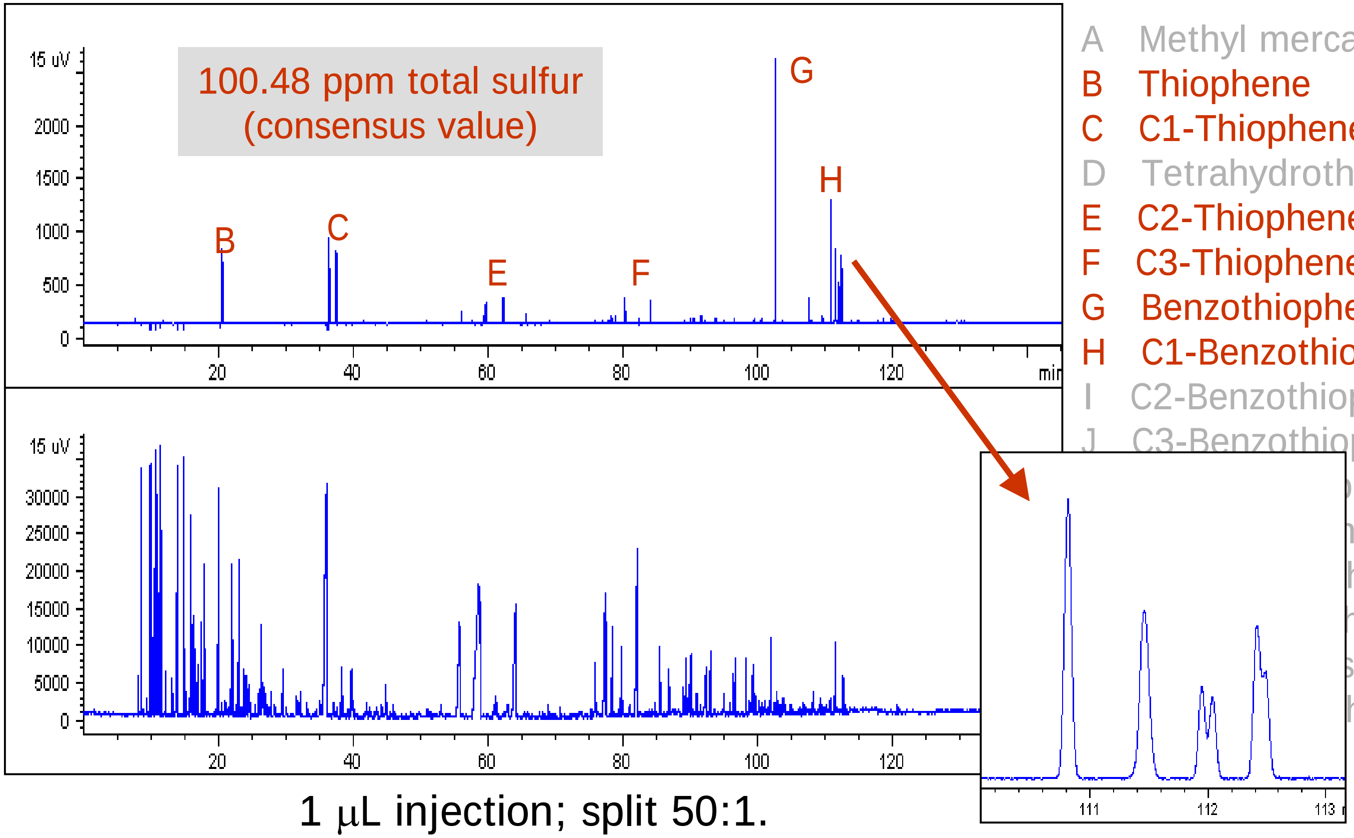
“DHA-Type” Analysis of RR Gas #13



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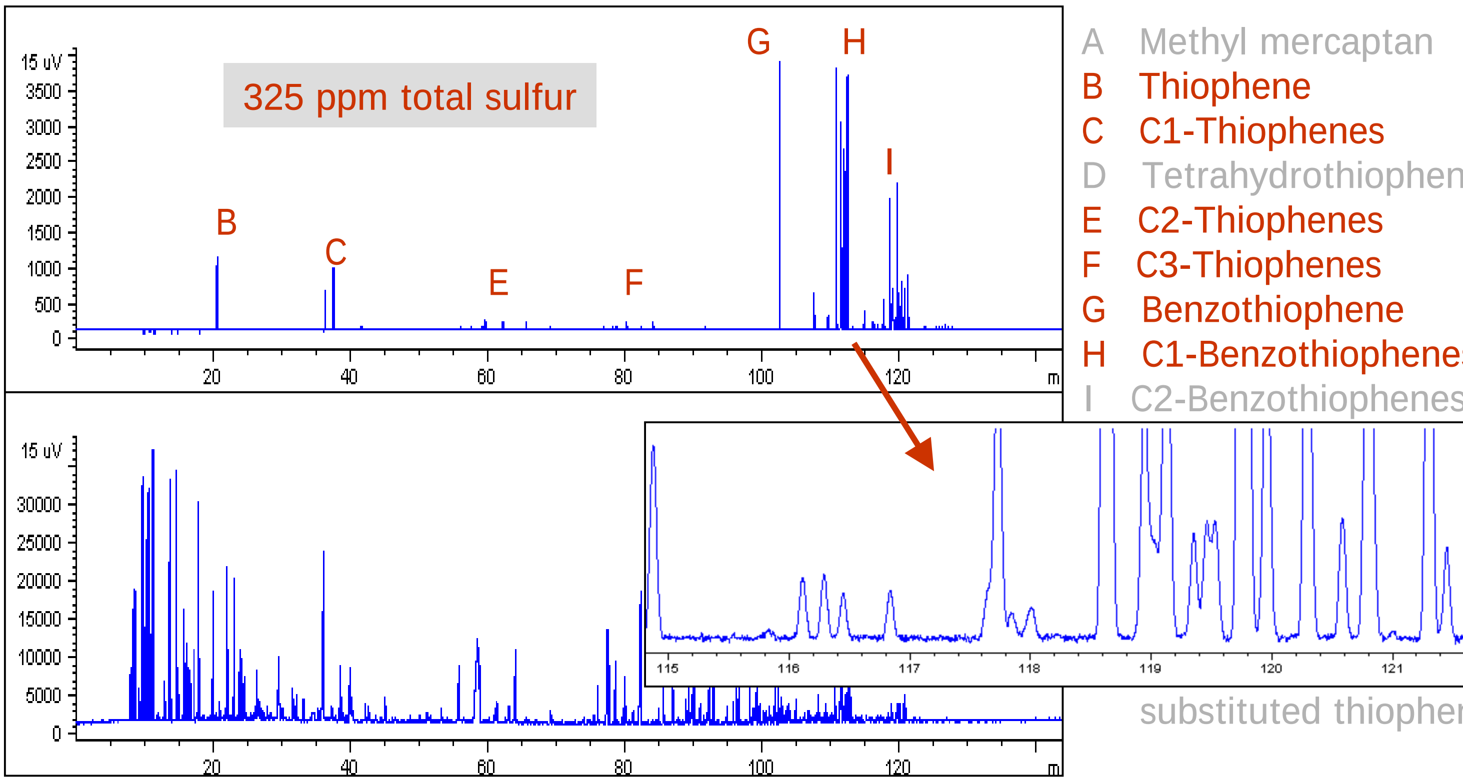
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes

1 µL injection; split 50:1.
ASTM RR Gasoline #13 has a consensus value of 100.48 ppm total sulfur

"DHA-Type" Analysis of Unknown Gas



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D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes

es
es
es
substituted thiophenes

1 µL injection; split 50:1.
Quantified using thiophene as an external standard.

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Sulfur in
Light Cycle Oil (LCO)

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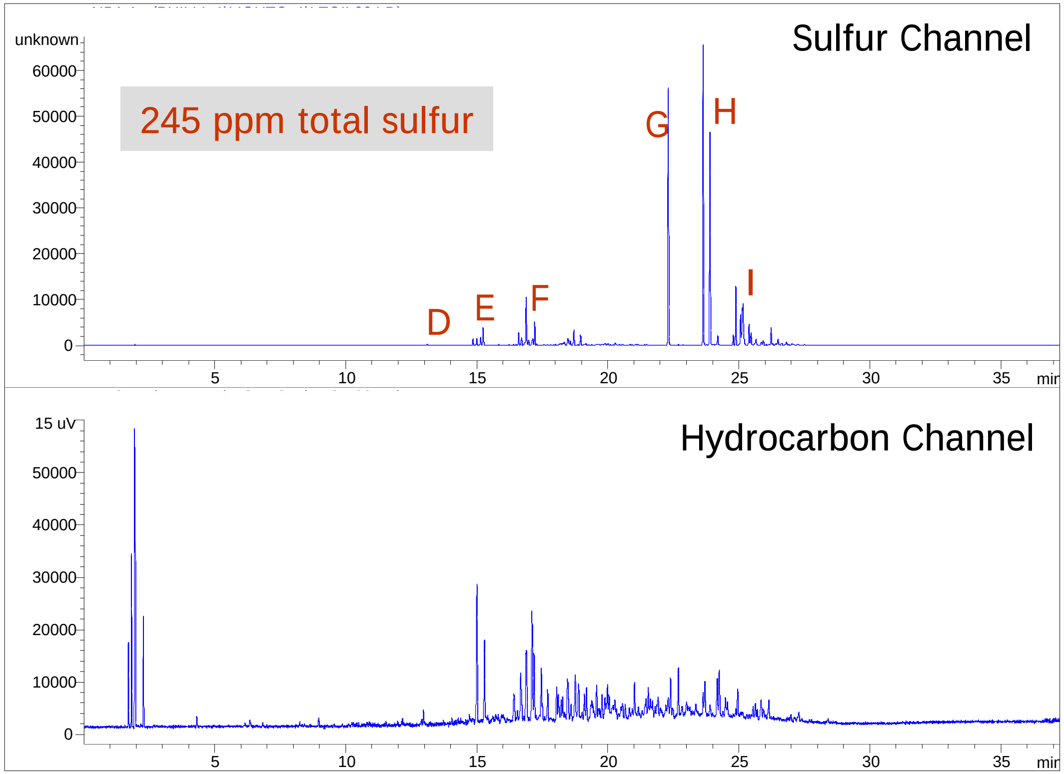
Light Cycle Oil “A”



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I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

0.2 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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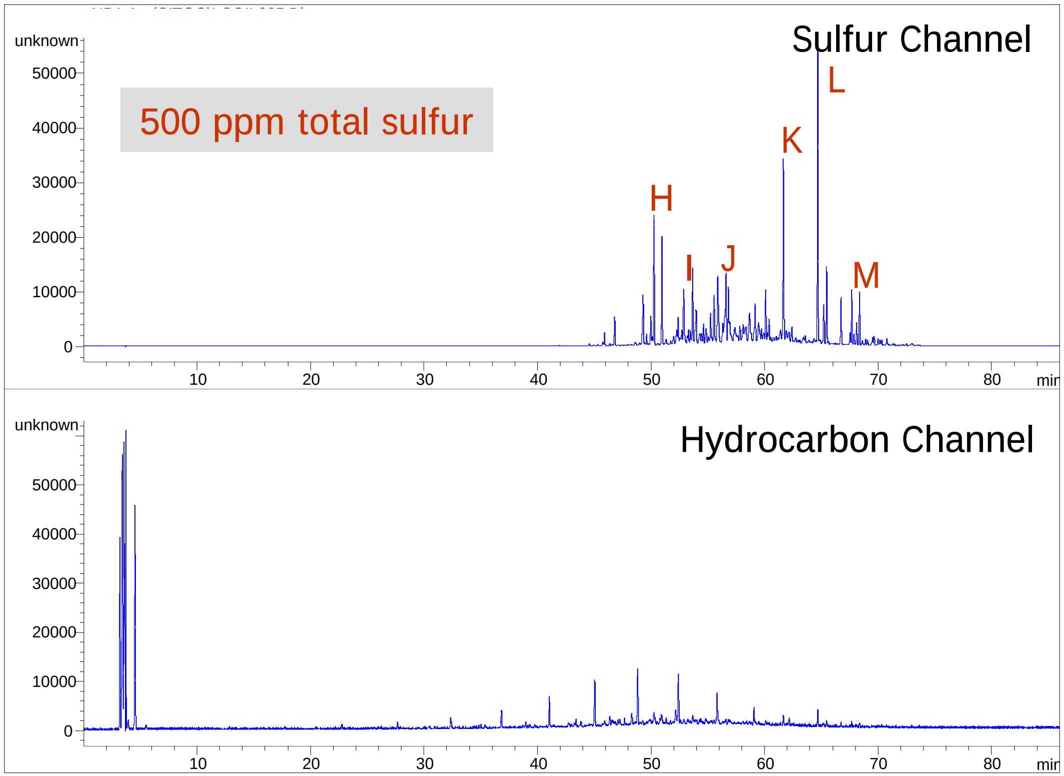
Light Cycle Oil “B”



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E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

Diluted 1:10 with hexane; 1 µL injection; split 50:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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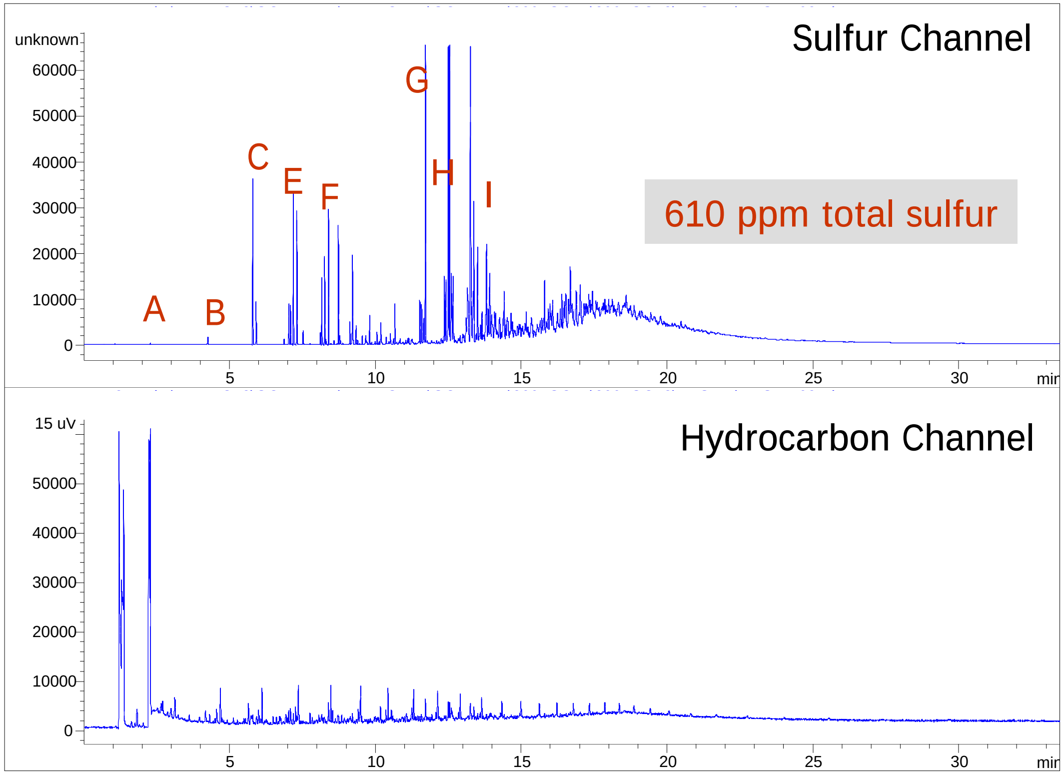
Light Cycle Oil "C"



A Methyl mercaptan
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E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

0.3 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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Sulfur in Diesel

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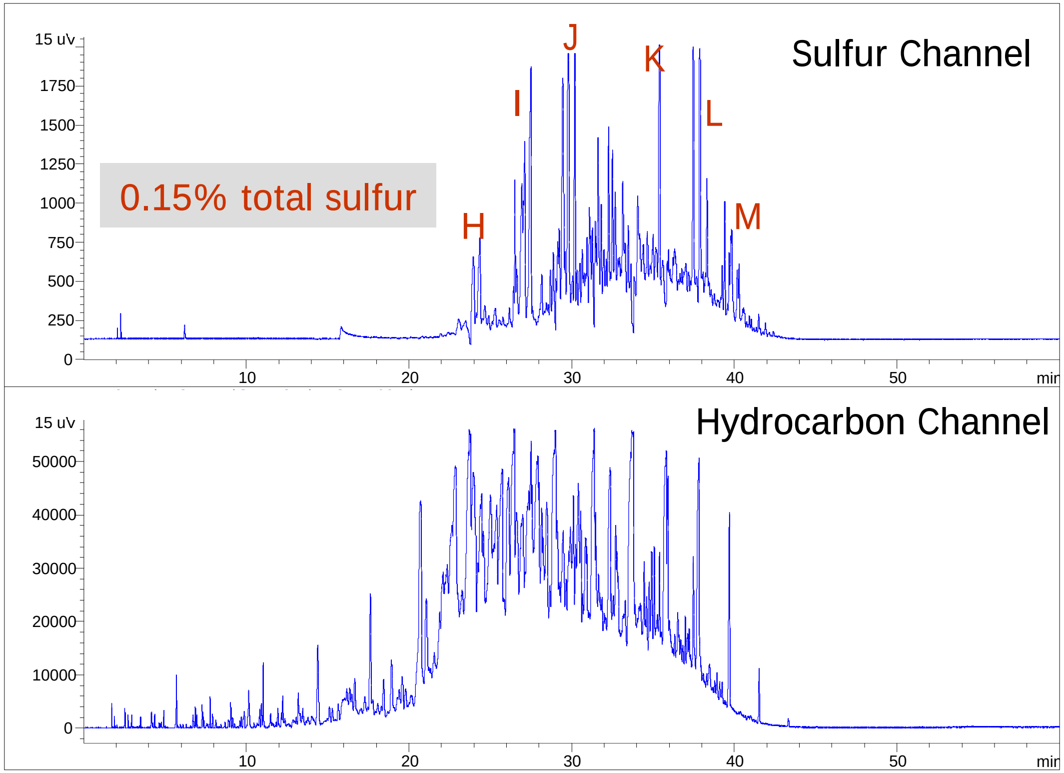
Diesel “A”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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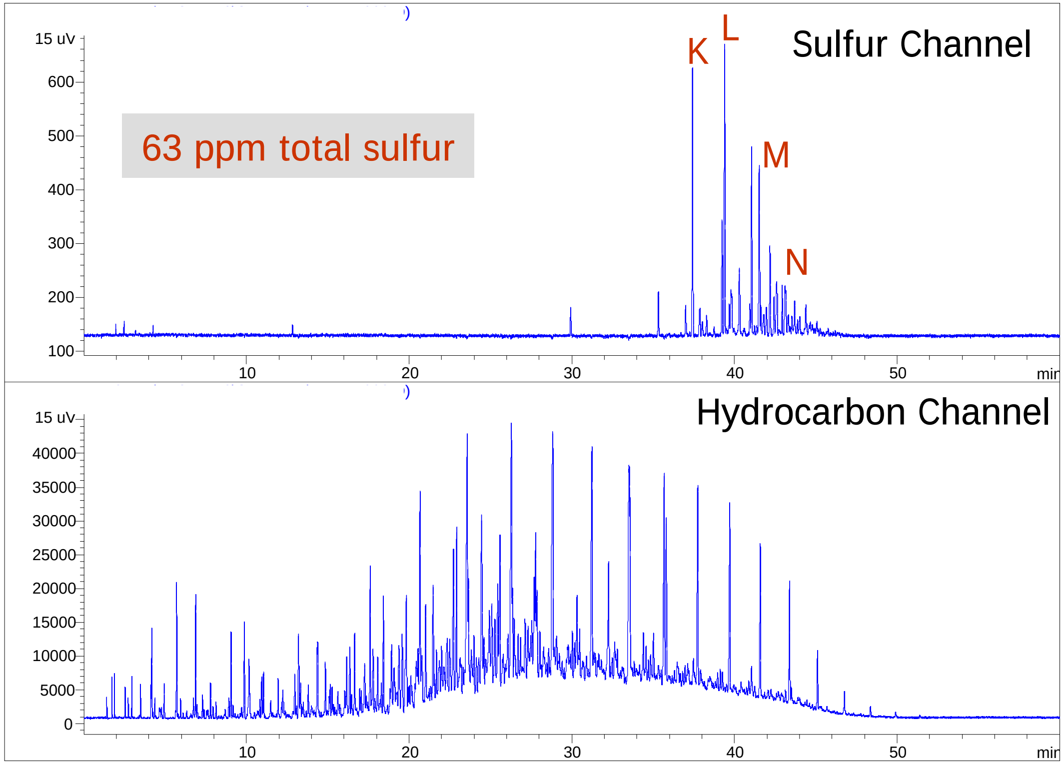
Diesel “B”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
Quantified by ASTM RR gasoline #10
as an external calibration standard.

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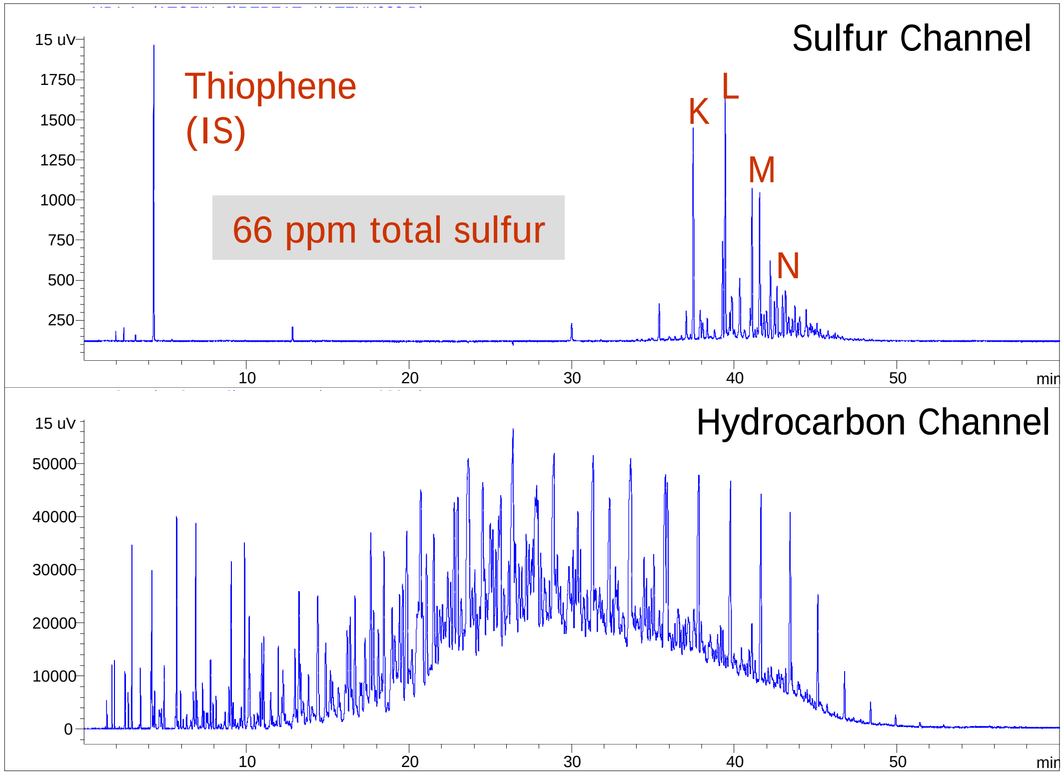
Diesel "B" Quantified by IS



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
Quantified using thiophene as an internal standard.

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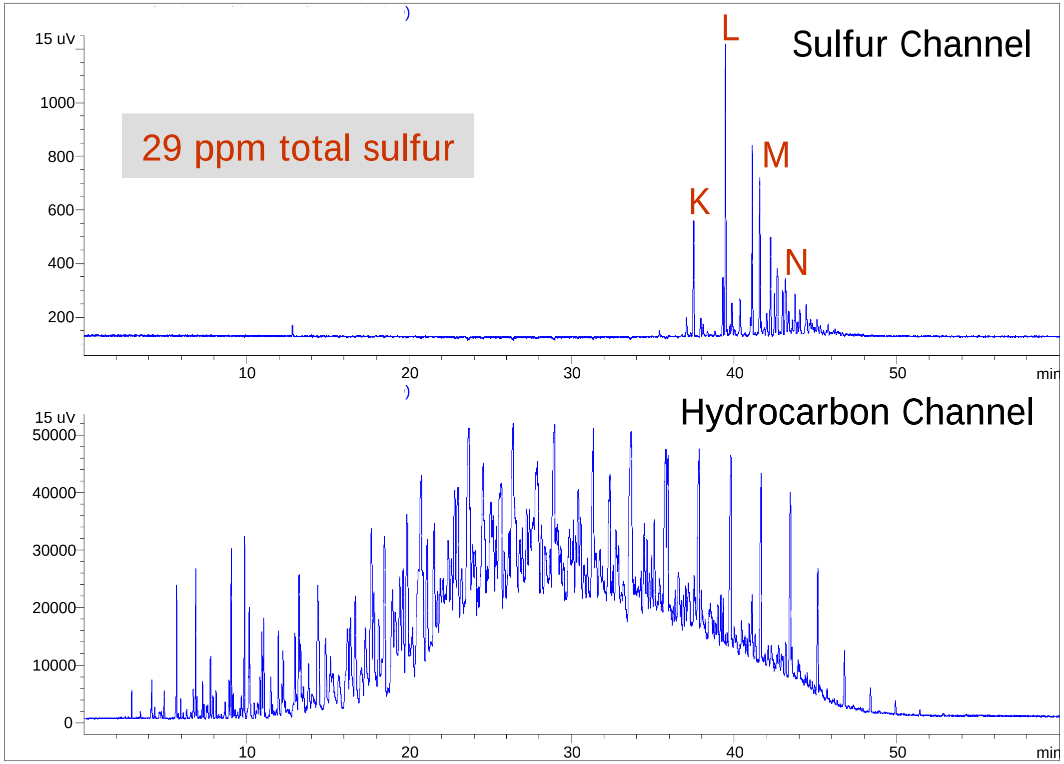
Diesel "C"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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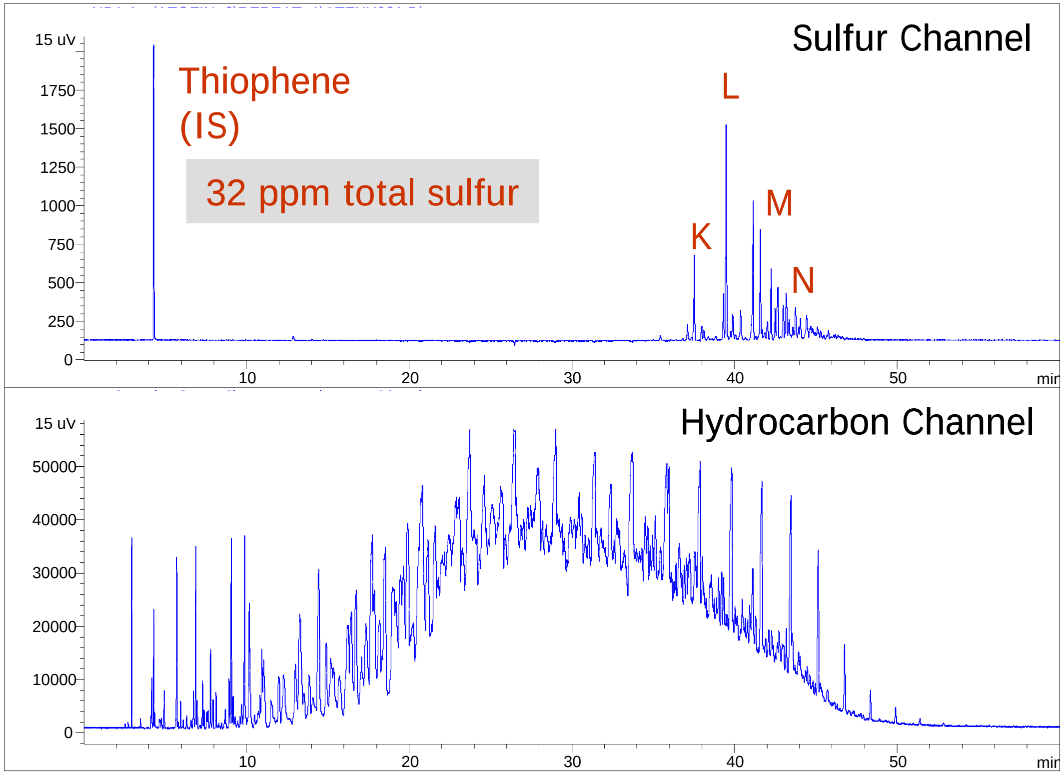
Diesel "C" Quantified by IS



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using thiophene as an internal standard.

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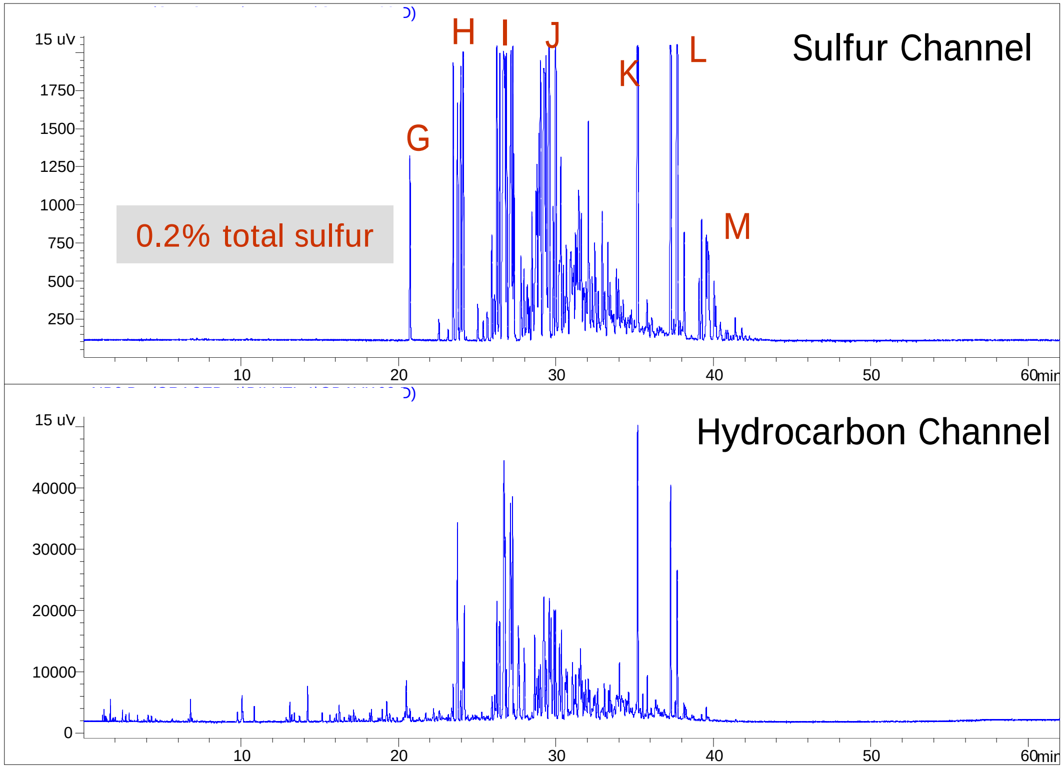
Diesel “D”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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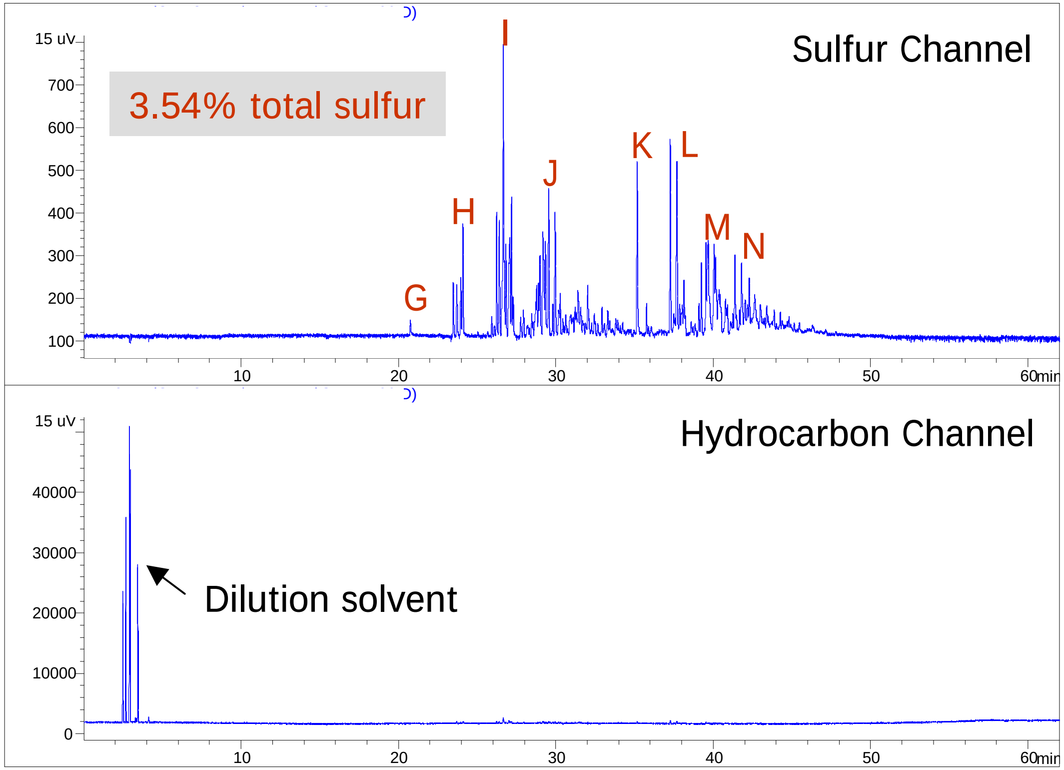
Diesel "E"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

Diluted 1:100 with hexane; 1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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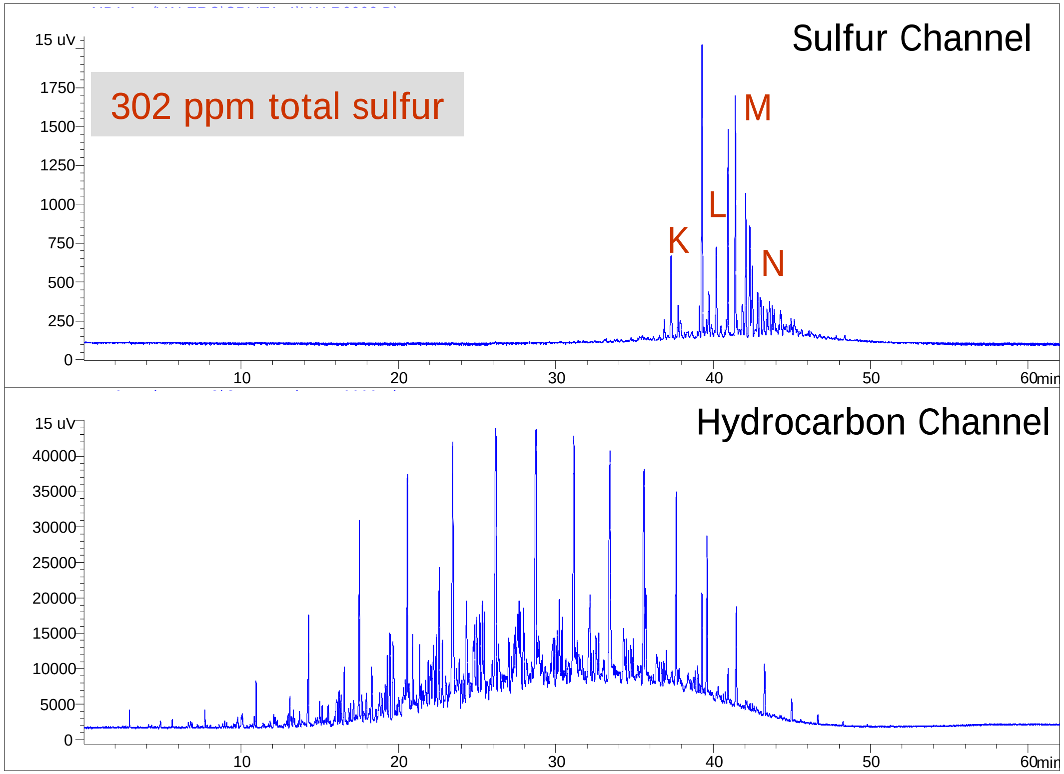
Diesel "F"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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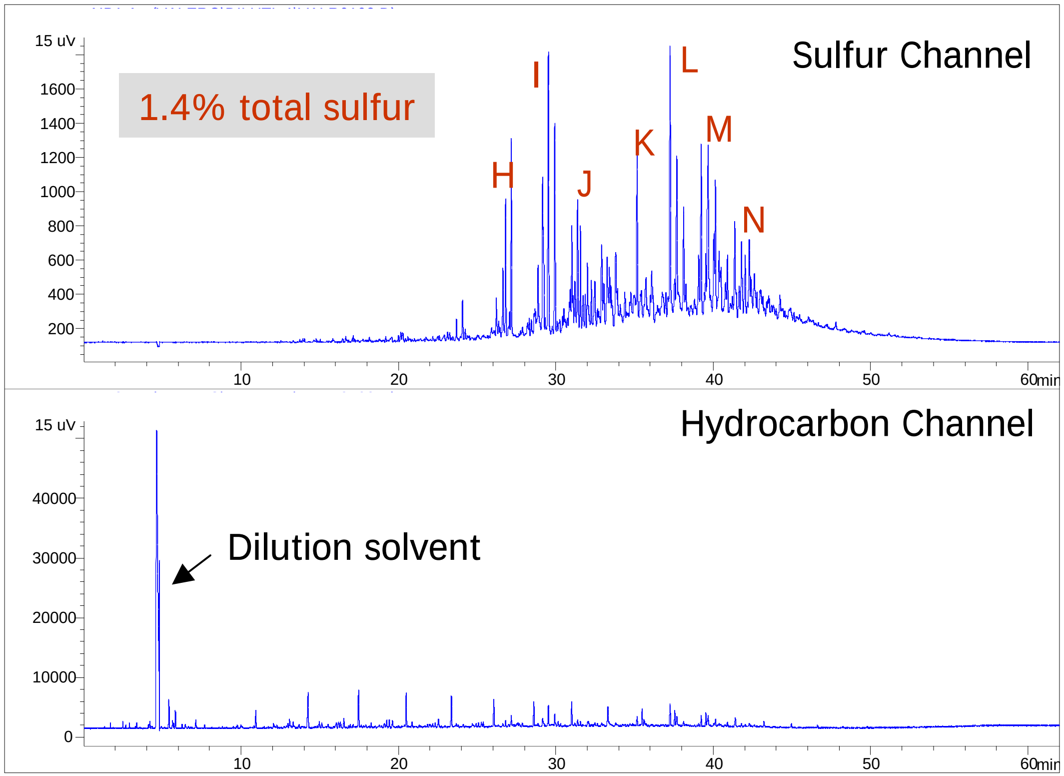
Diesel “G”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

Diluted 1:10 with isooctane; 1 μL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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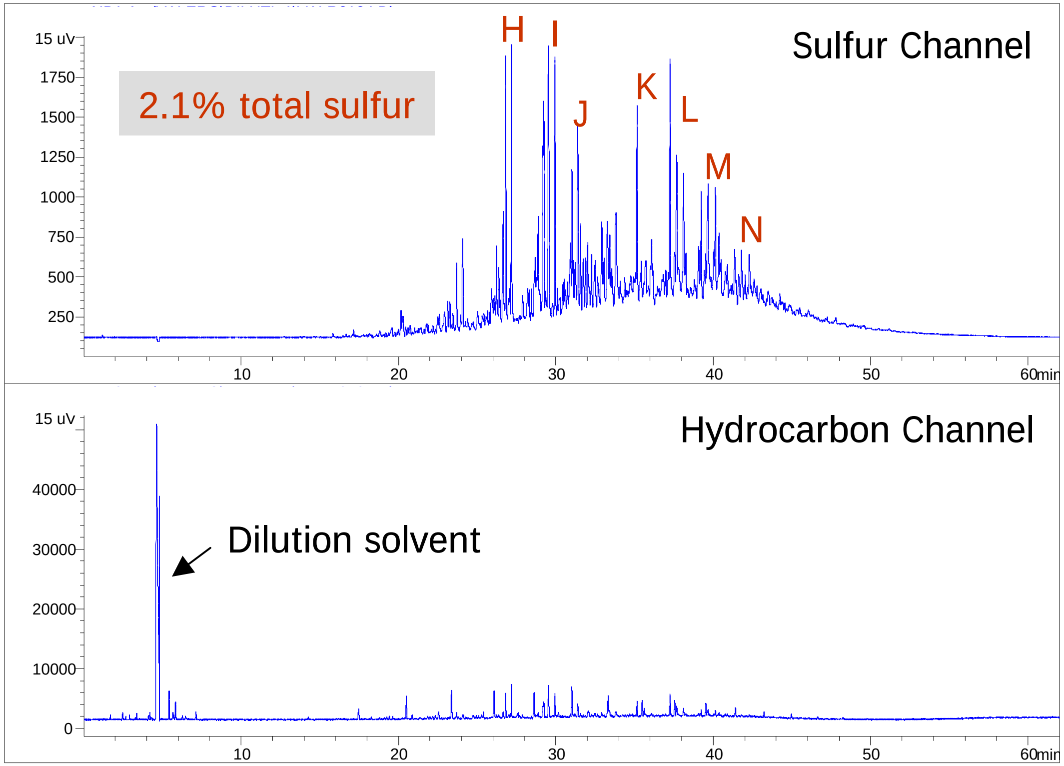
Diesel “H”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

Diluted 1:10 with isooctane; 1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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Sulfur in Naphtha

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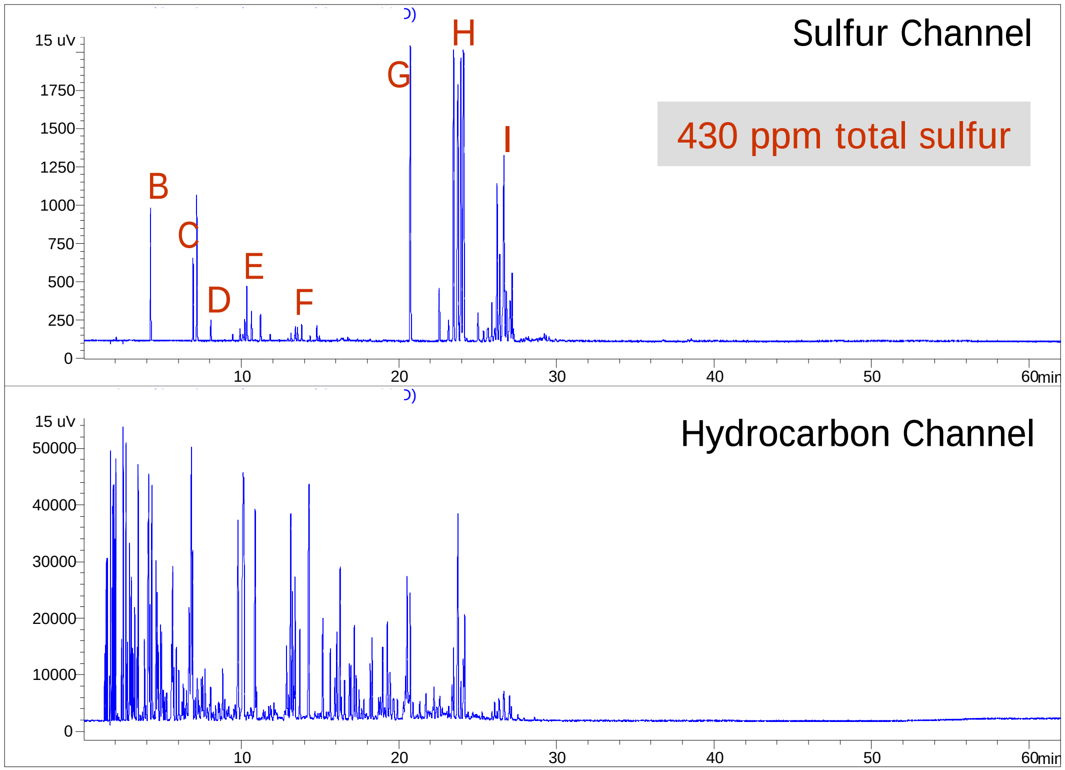
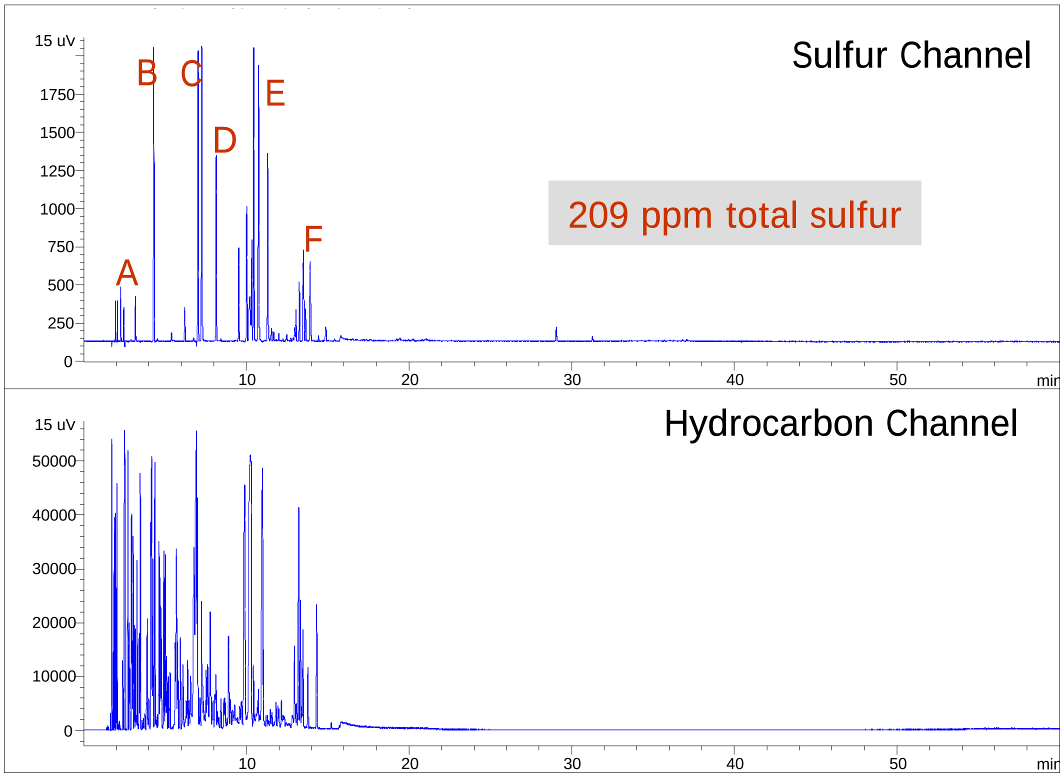
Naphtha “A”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard

Naphtha “B”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 250:1.
Quantified using ASTM RR gasoline #1
as an external calibration standard.

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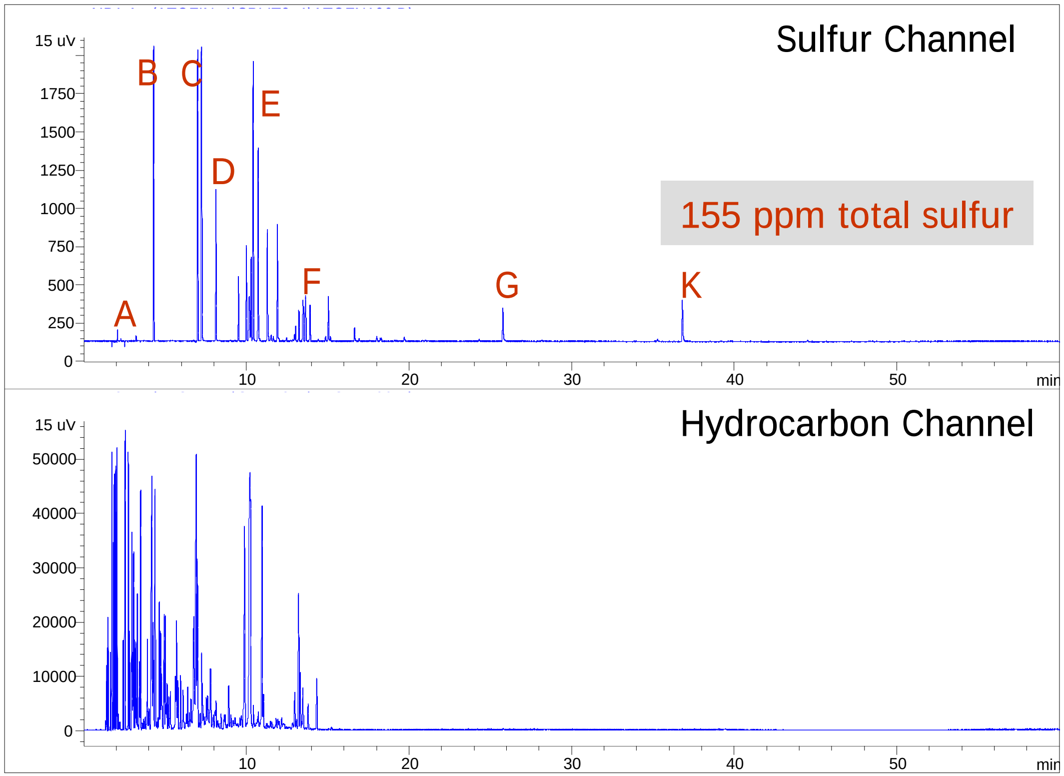
Naphtha “C”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 μL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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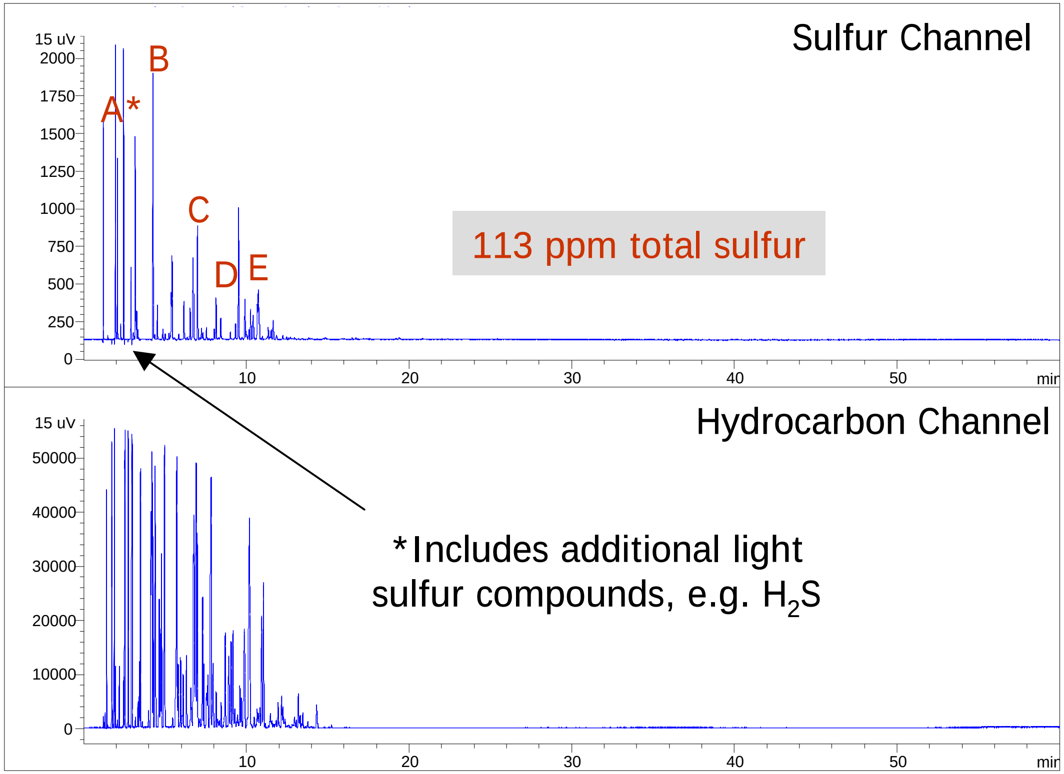
Naphtha "D"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 250:1.
Quantified using ASTM RR gasoline #10 as an external calibration standard.

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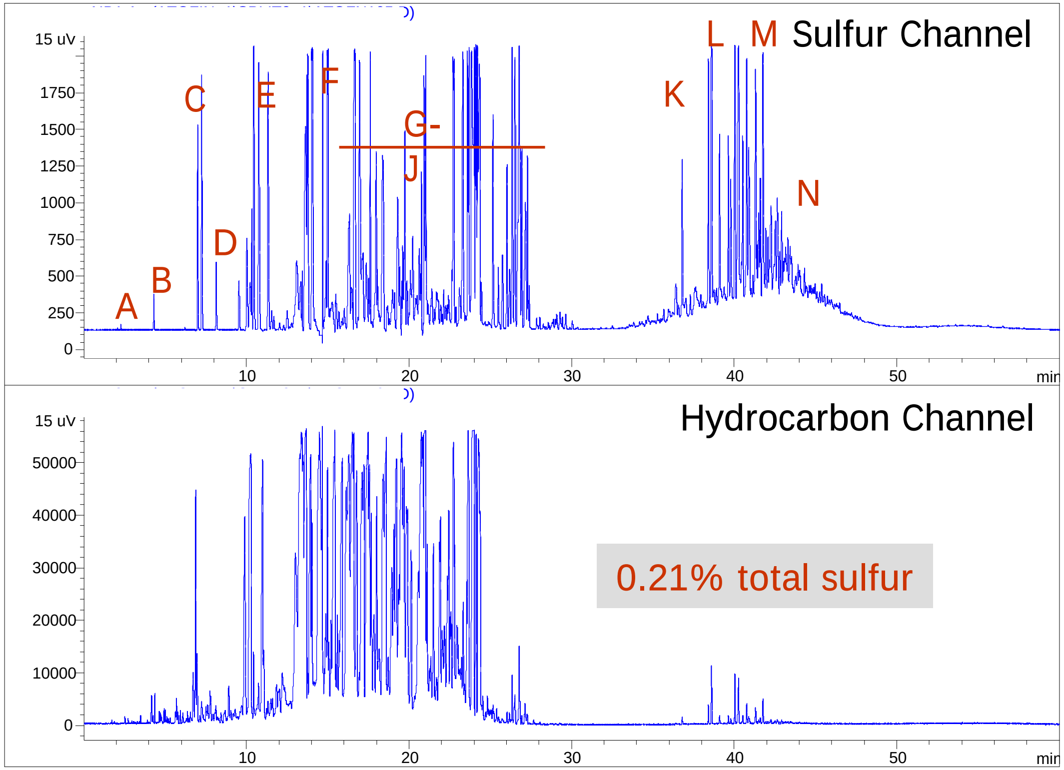
Naphtha “E”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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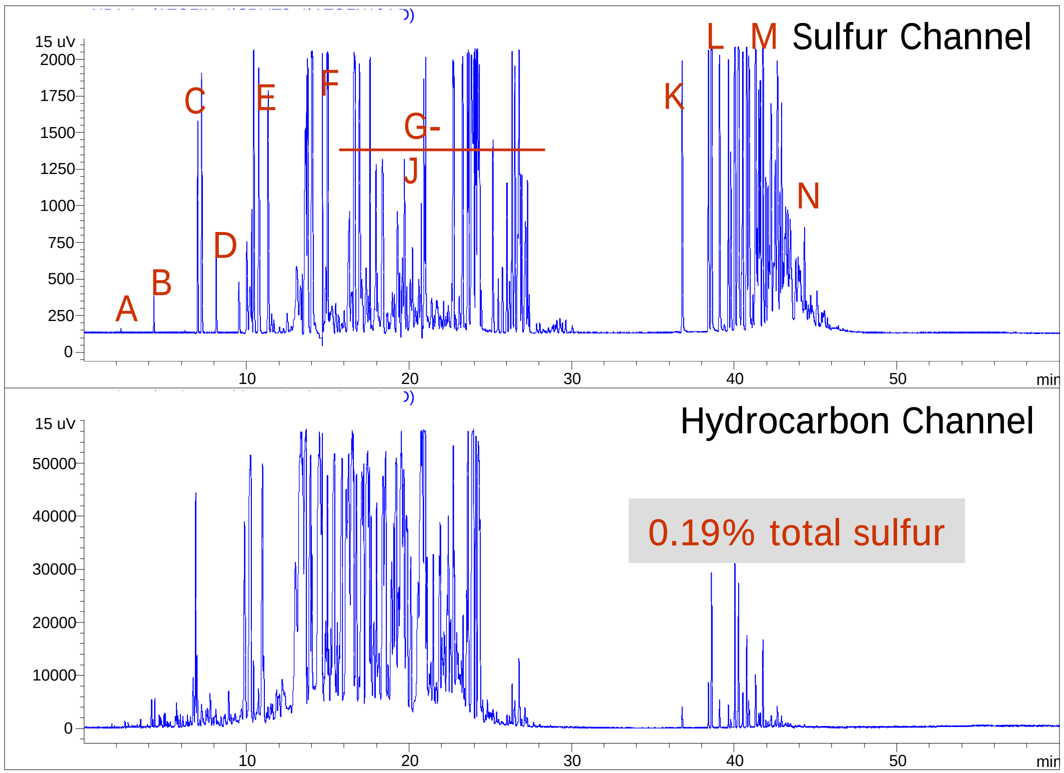
Naphtha “F”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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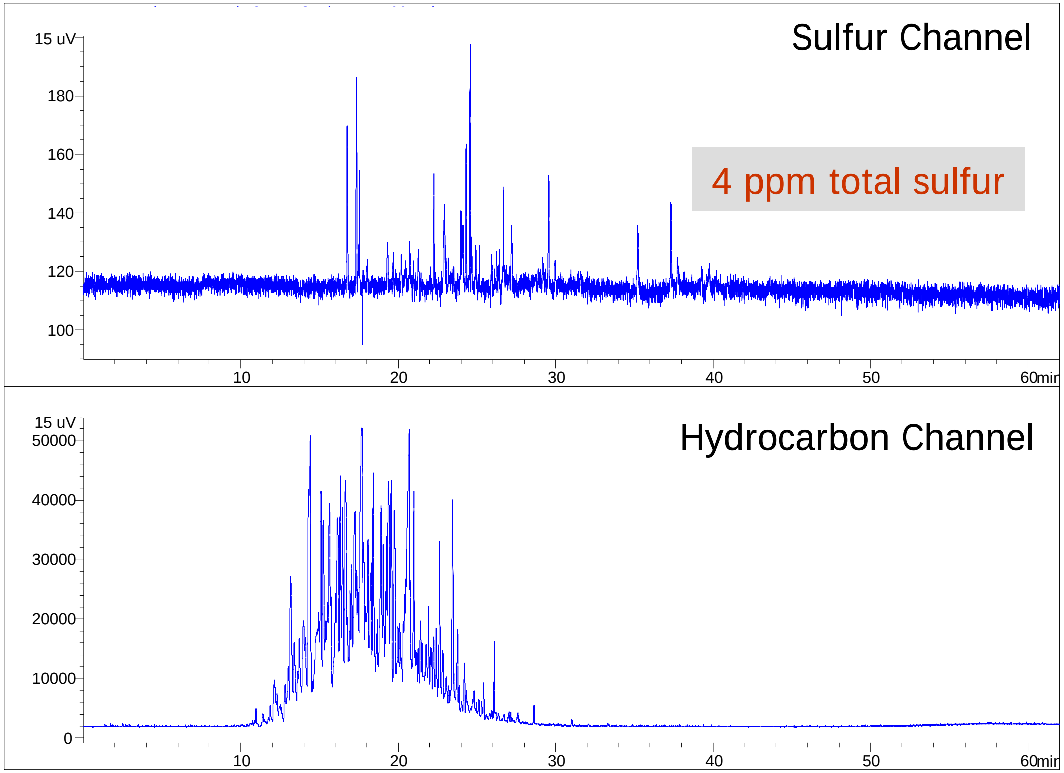
Sulfur in Jet Fuels

Jet Fuel “A”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 10:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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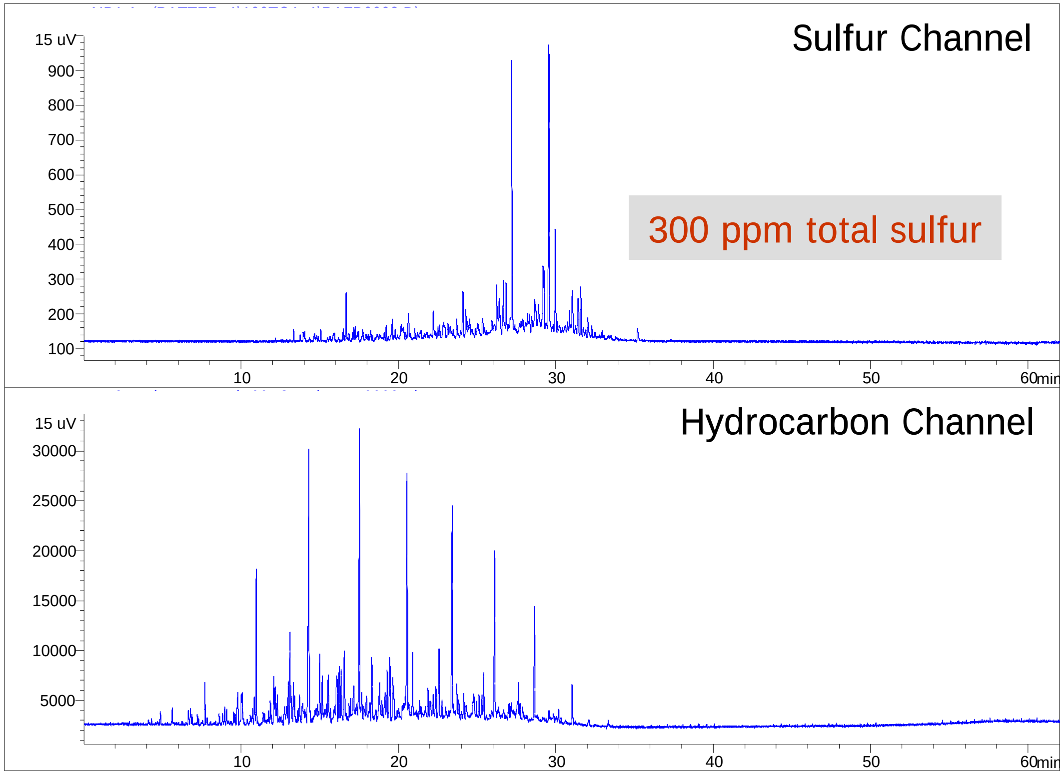
Jet Fuel “B”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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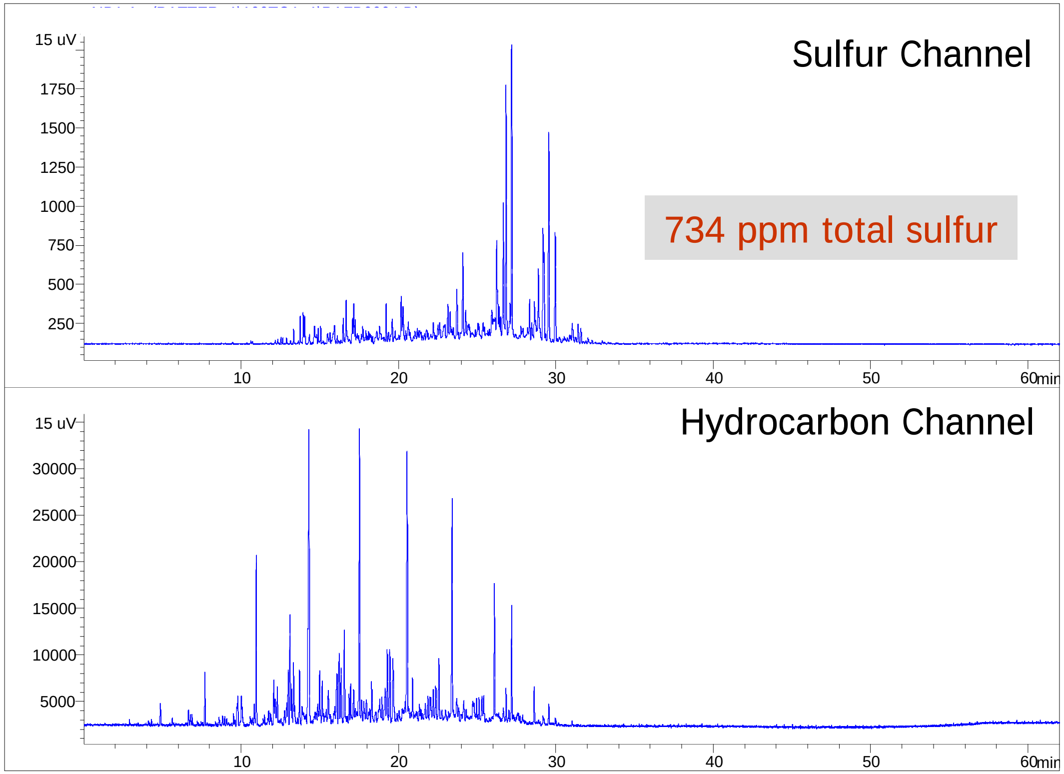
Jet Fuel "C"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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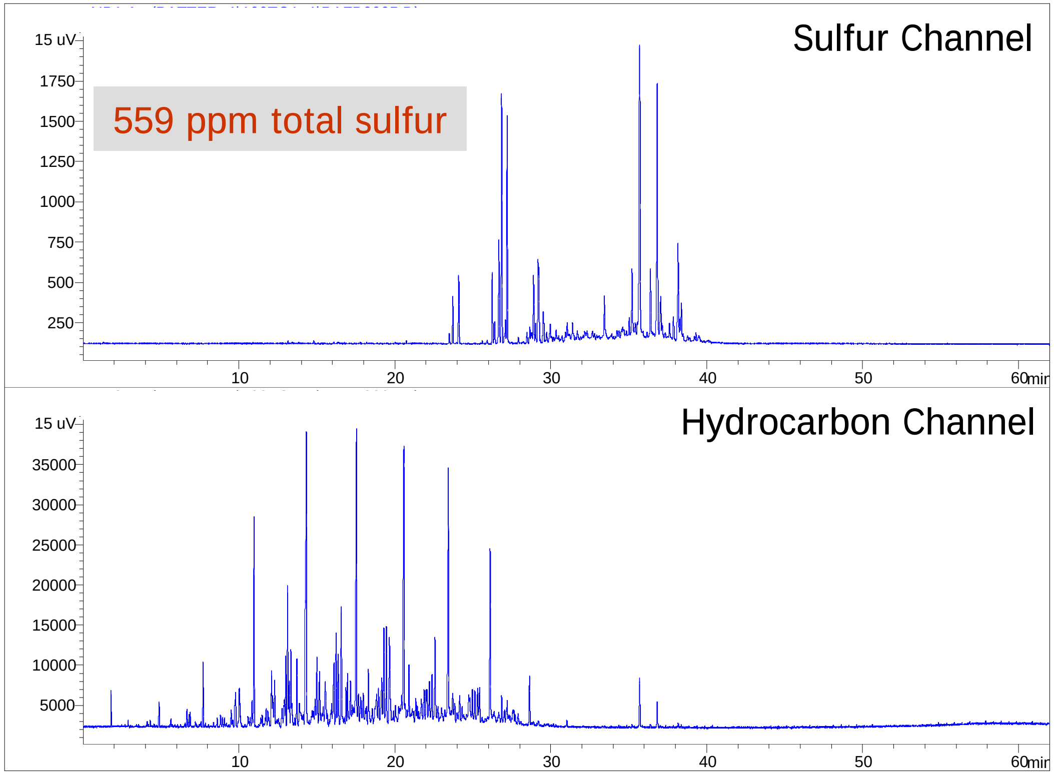
Jet Fuel “D”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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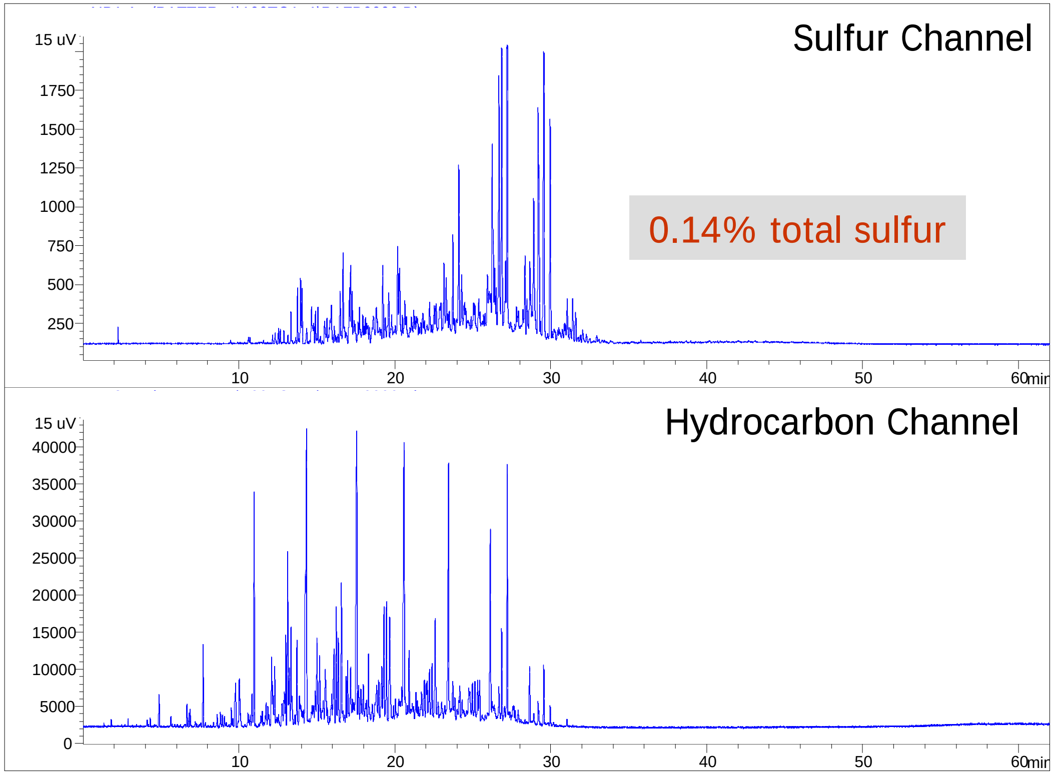
Jet Fuel "E"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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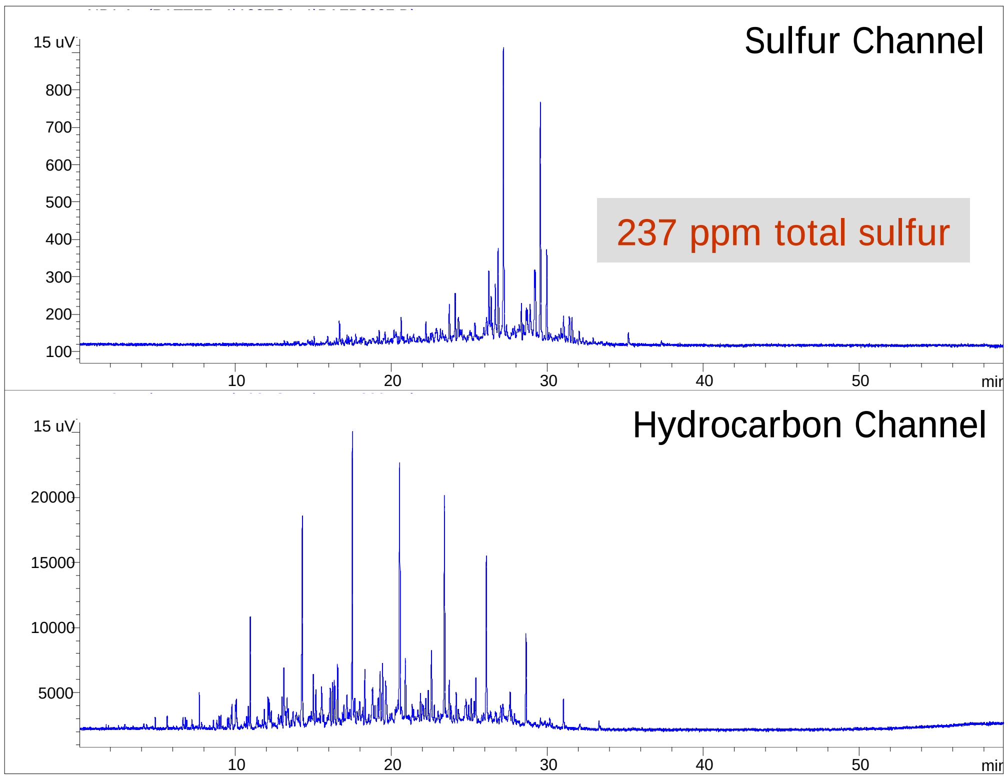
Jet Fuel “F”



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 μL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

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Sulfur in Specialty Applications and Methods

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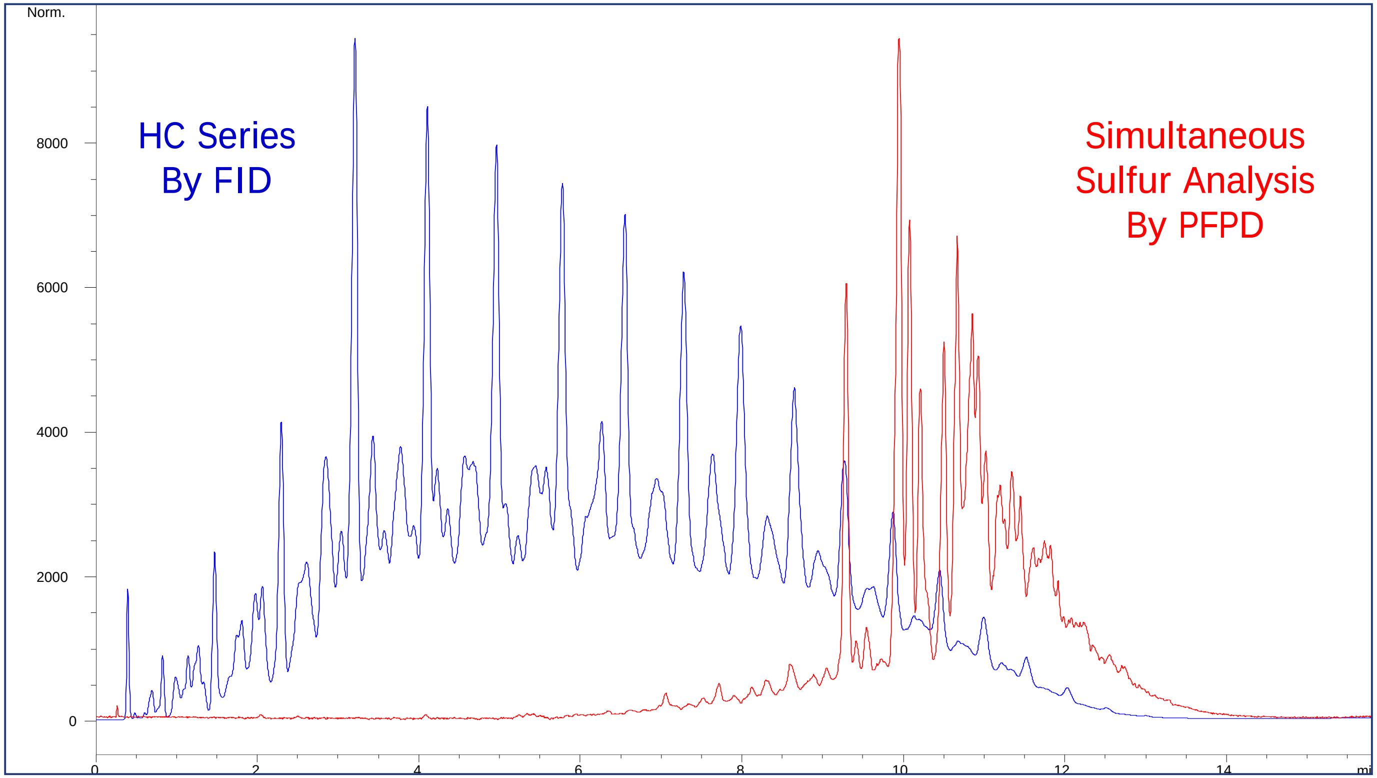
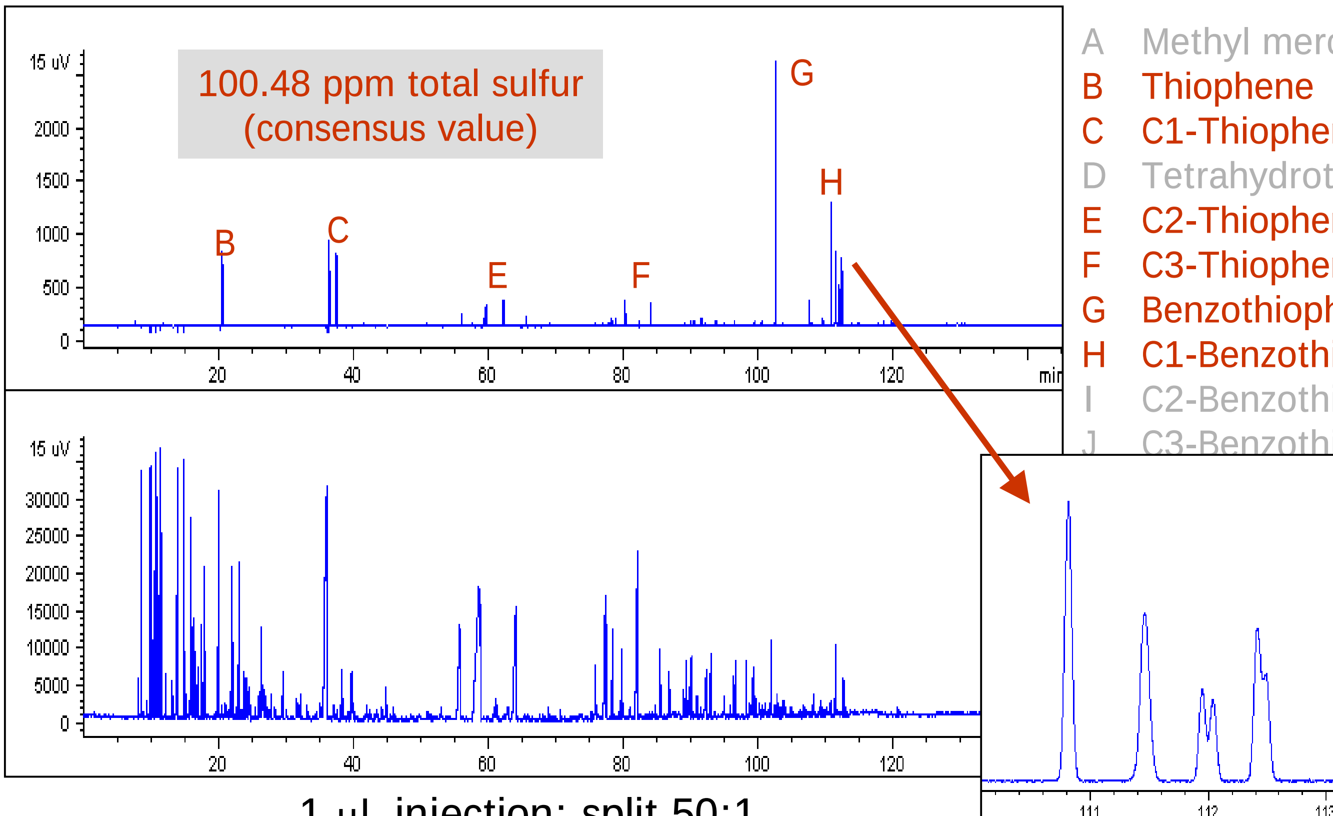
Simulated Distillation



Reference standard for ASTM Method D2887-02
used as a calibration standard for simulated distillation.

“DHA-Type” Analysis of RR Gas #13



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- phene
- hiophenes
- hiophenes
- hiophenes
- s &
- hiophenes

1 μL injection; split 50:1.
ASTM RR Gasoline #13 has a consensus value of 100.48 ppm total sulfur

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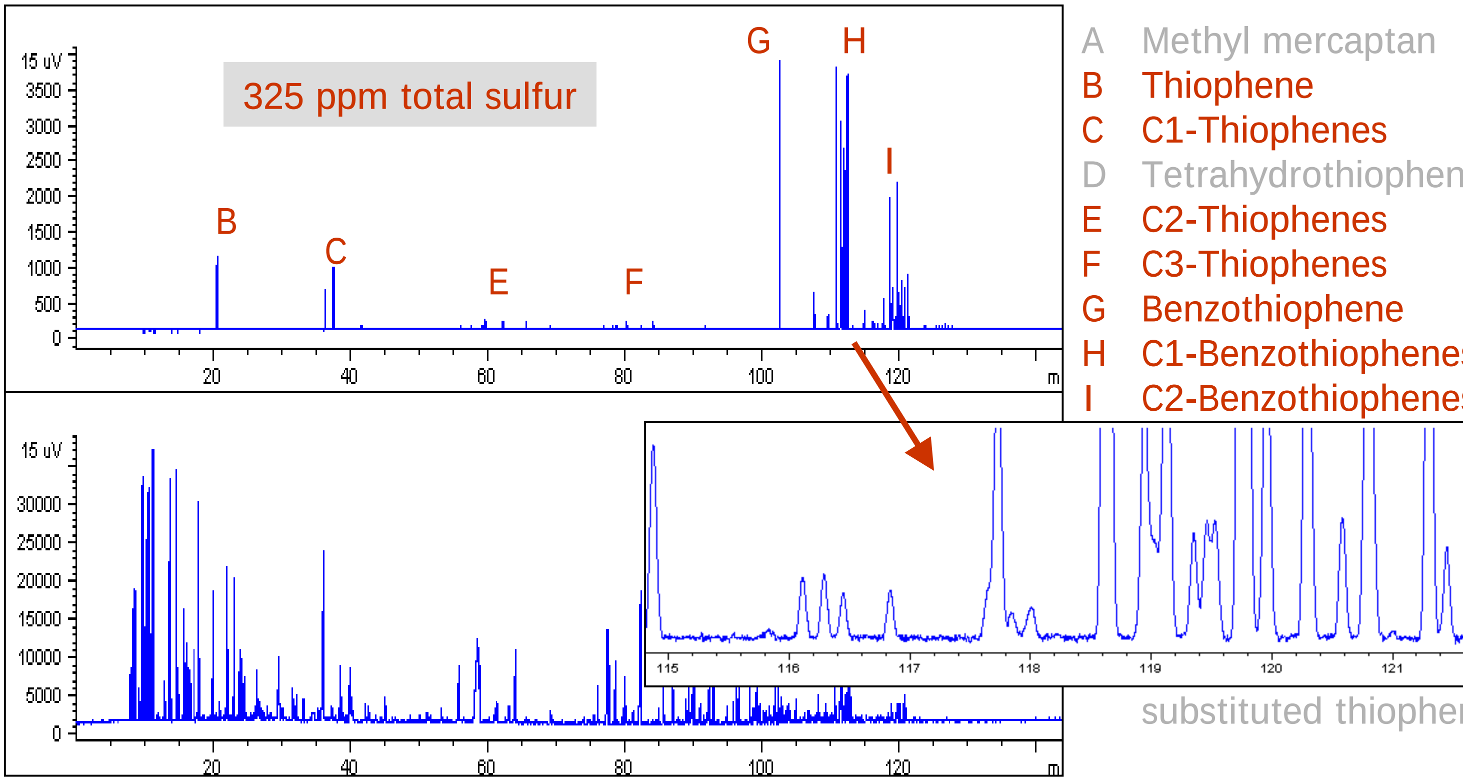
“DHA-Type” Analysis of Unknown Gas



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes

es
es
es
substituted thiophenes

1 µL injection; split 50:1.
Quantified using thiophene as an external standard.

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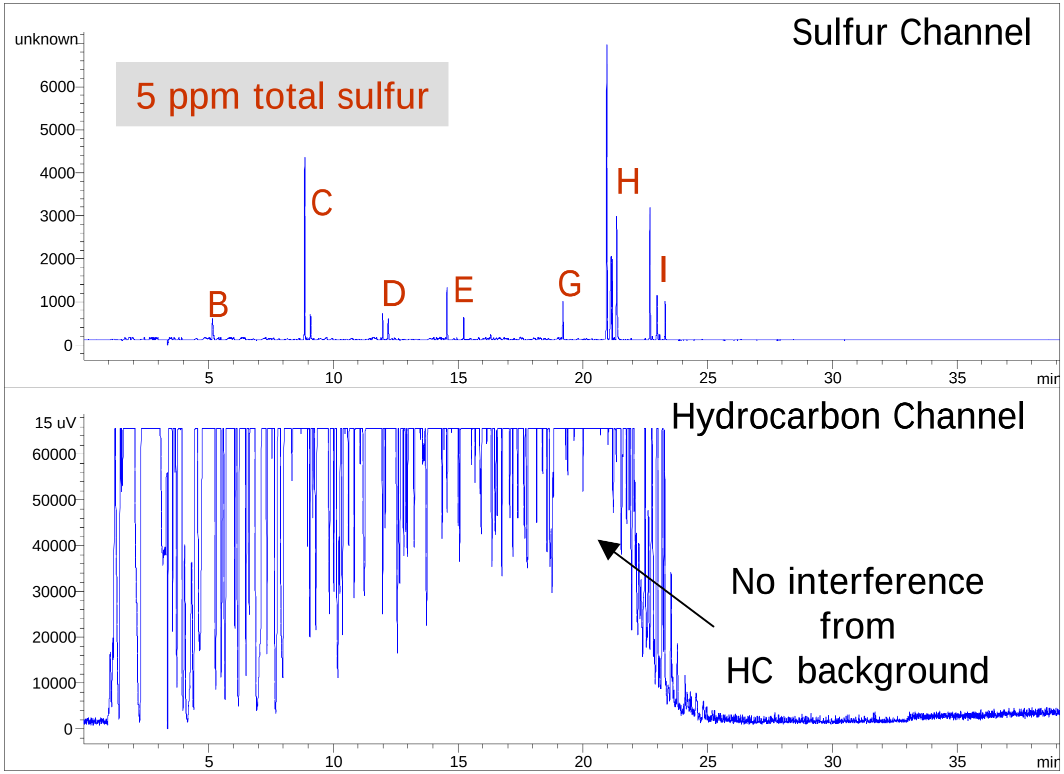
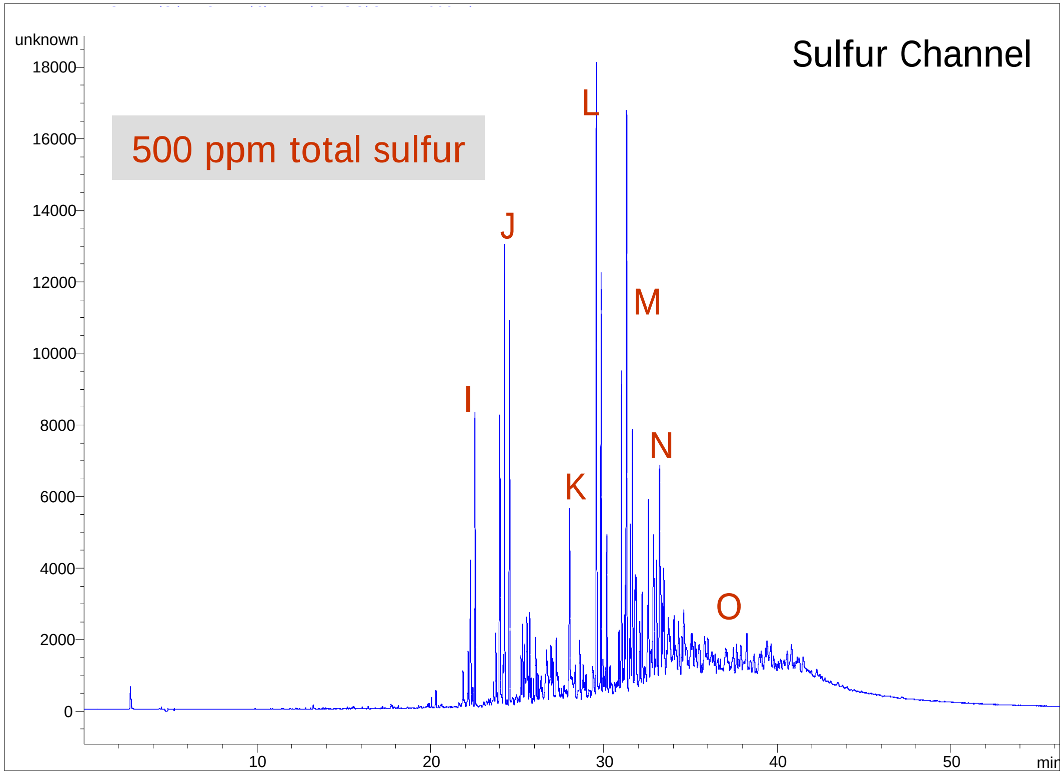
Gasoline "D", 5 ppm



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 10:1.
Concentration reported by client as 5 ppm.

Crude Oil



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

Diluted 1:10 with hexane; 1 μL injection; split 25:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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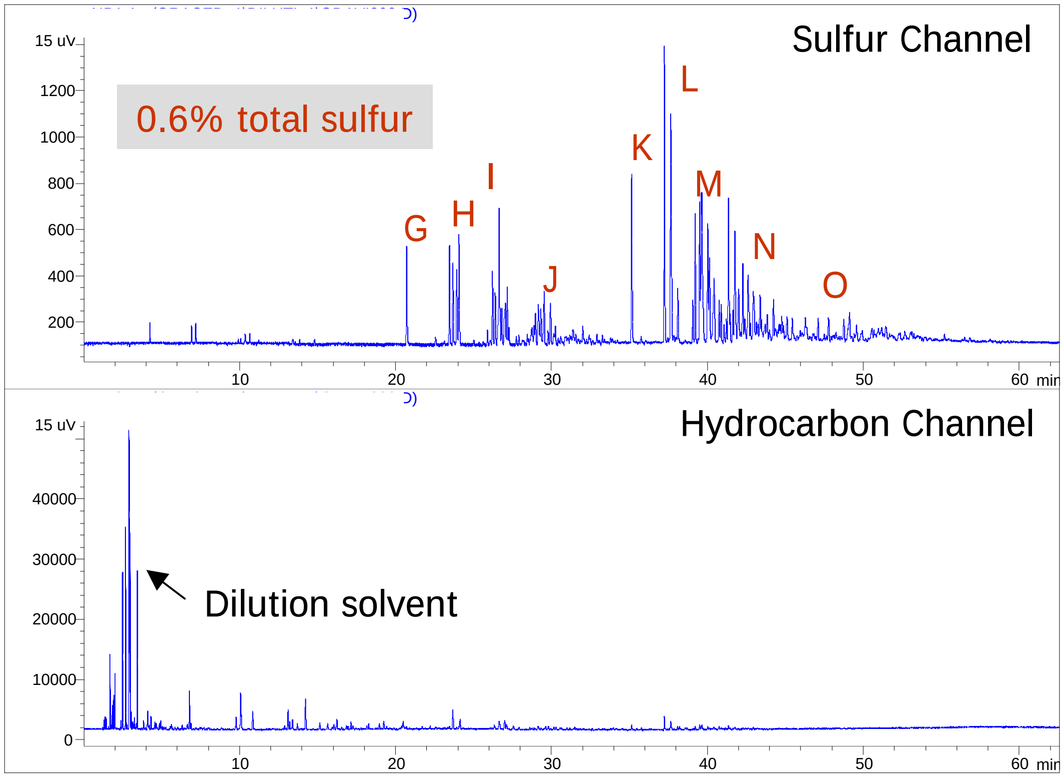
Synthetic Crude



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

Diluted 1:10 with hexane; 1 μL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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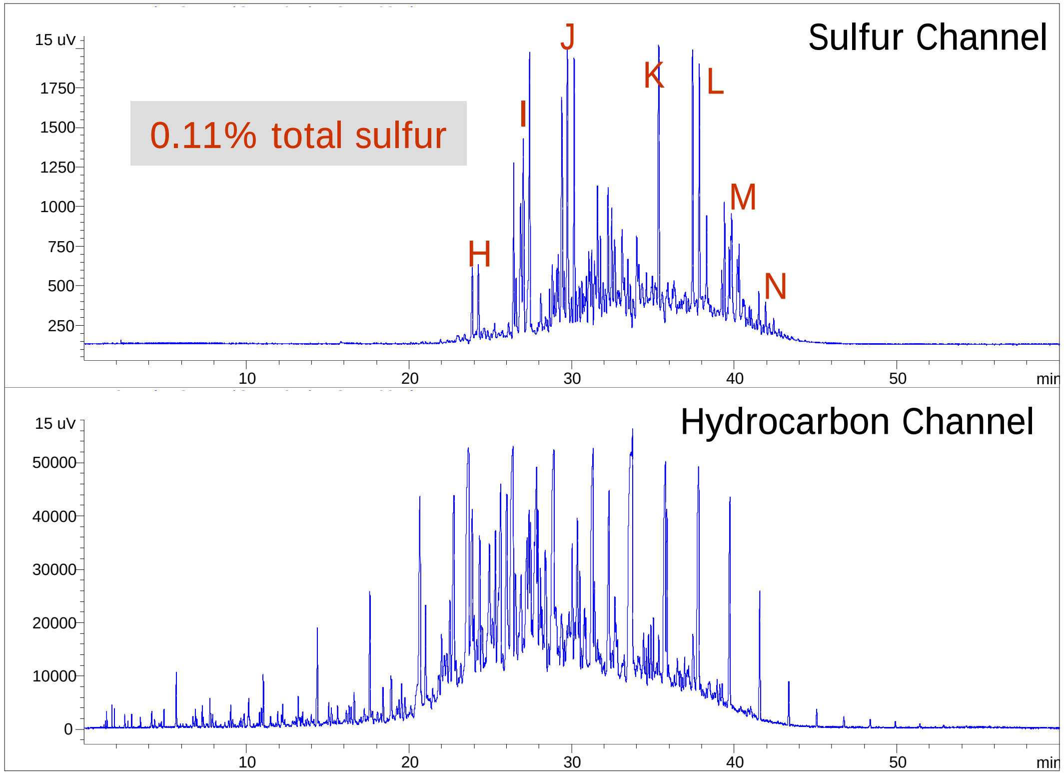
Furnace Oil "A"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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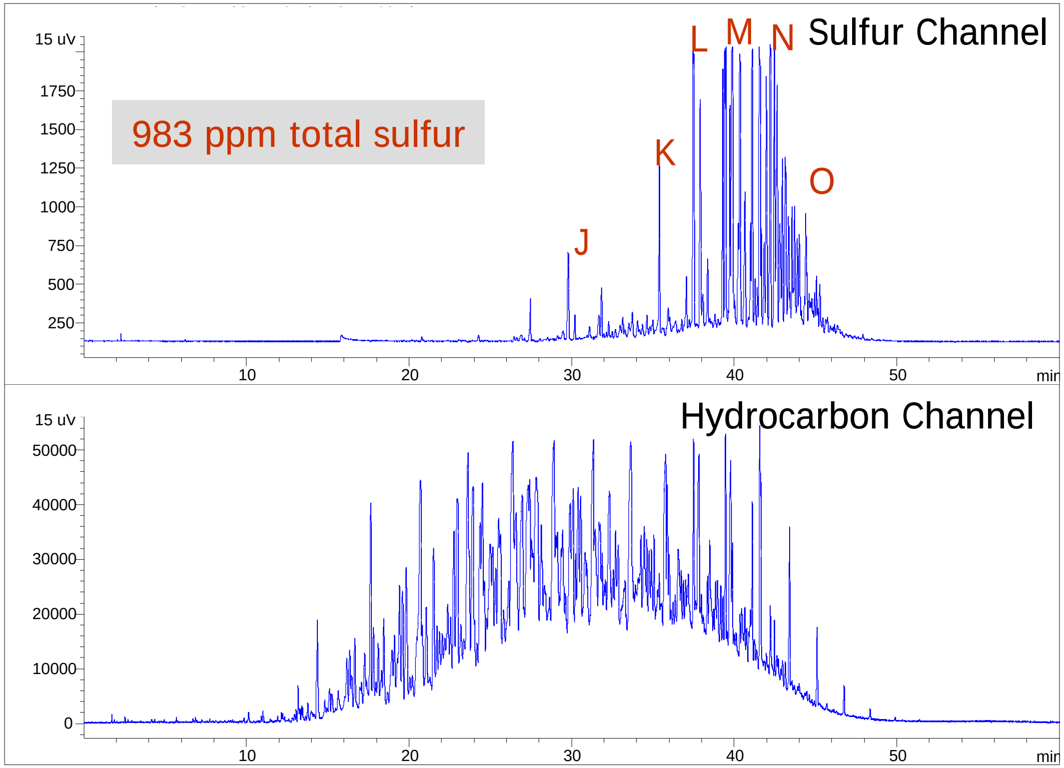
Furnace Oil "B"



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

1 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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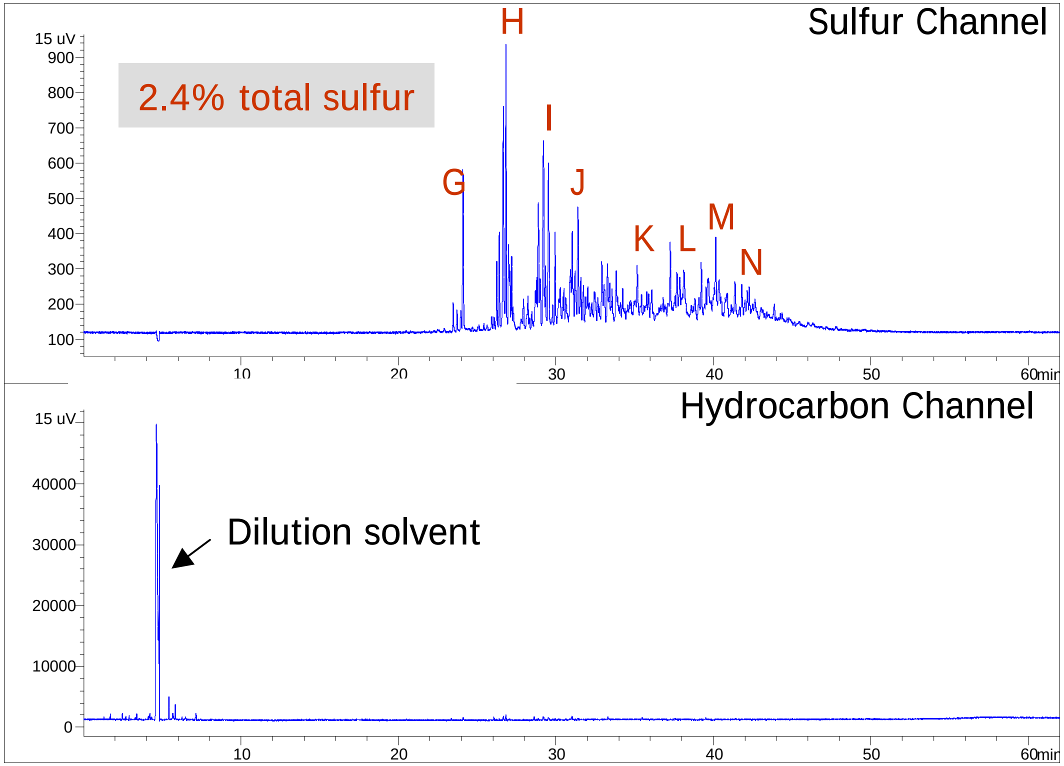
Coker Light Gas Oil



A Methyl mercaptan
B Thiophene
C C1-Thiophenes
D Tetrahydrothiophene
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

Diluted 1:50 with isooctane; 1 μL injection; split 100:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

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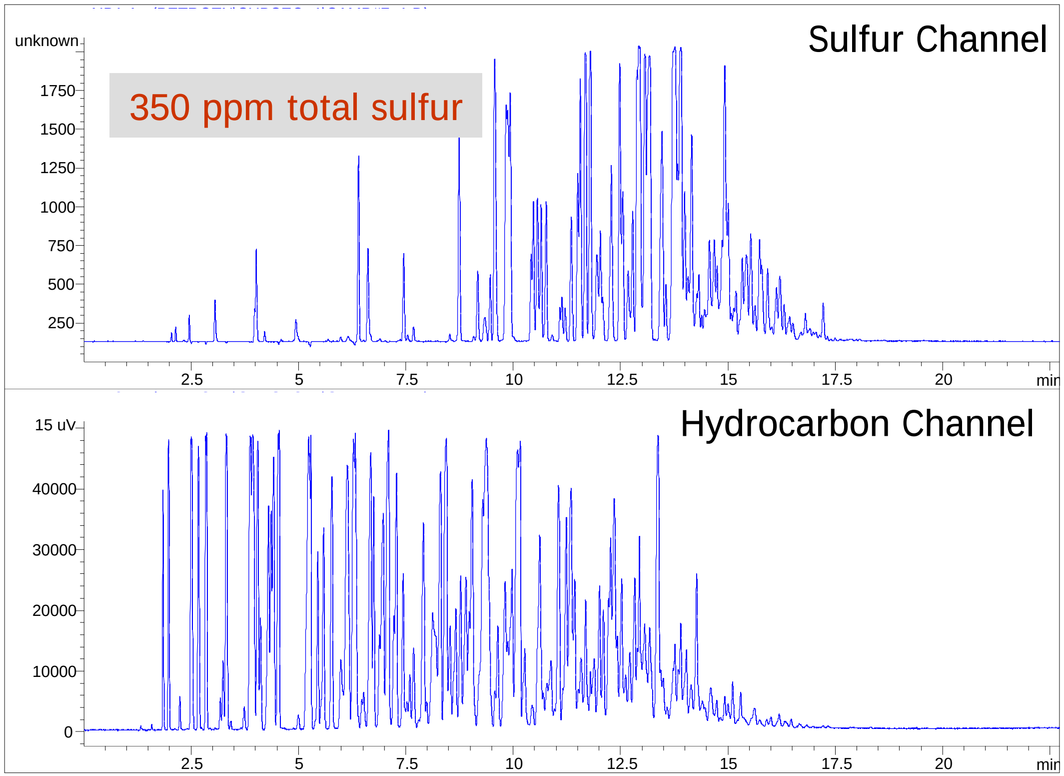
“Unifier Charge”



- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

1 µL injection; split 75:1.
No reference was available for identification of sulfur peak groupings in this sample.

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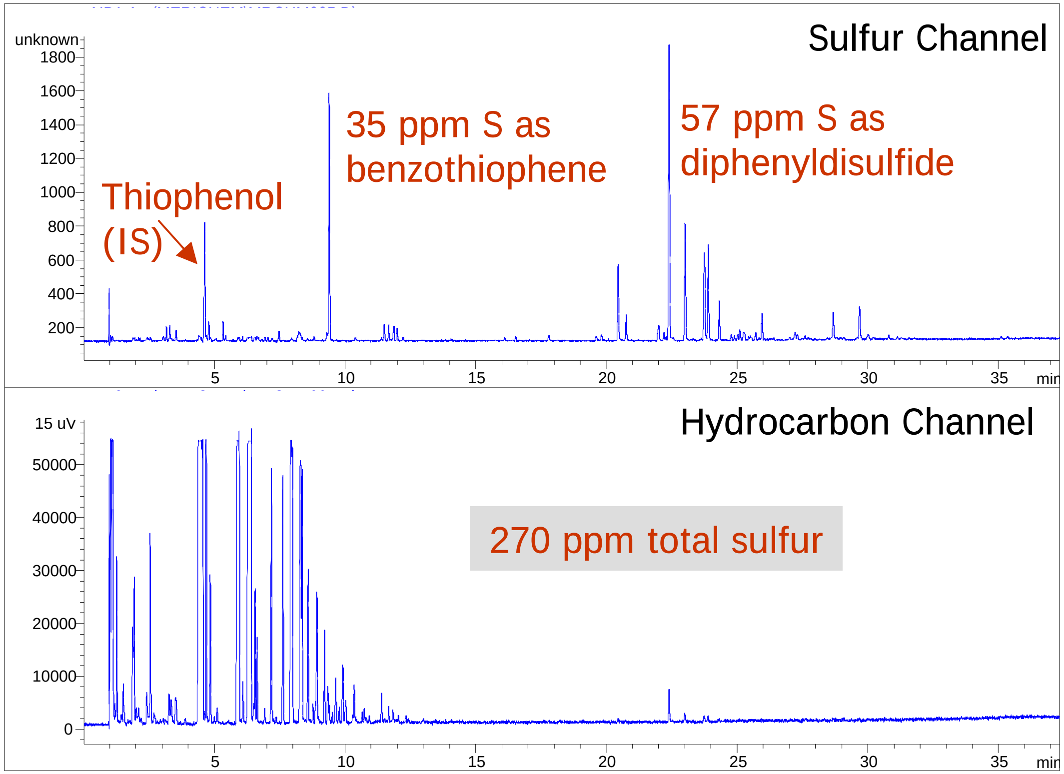
Crude Cresylic Acid



0.2 µL injection; split 50:1.
Two individual peaks plus total sulfur quantified using thiophenol as an internal standard (29 ppm S).

- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O Alkyl sulfides & substituted thiophenes

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Thiophene in Benzene by PFPD using ASTM Method D4735-02

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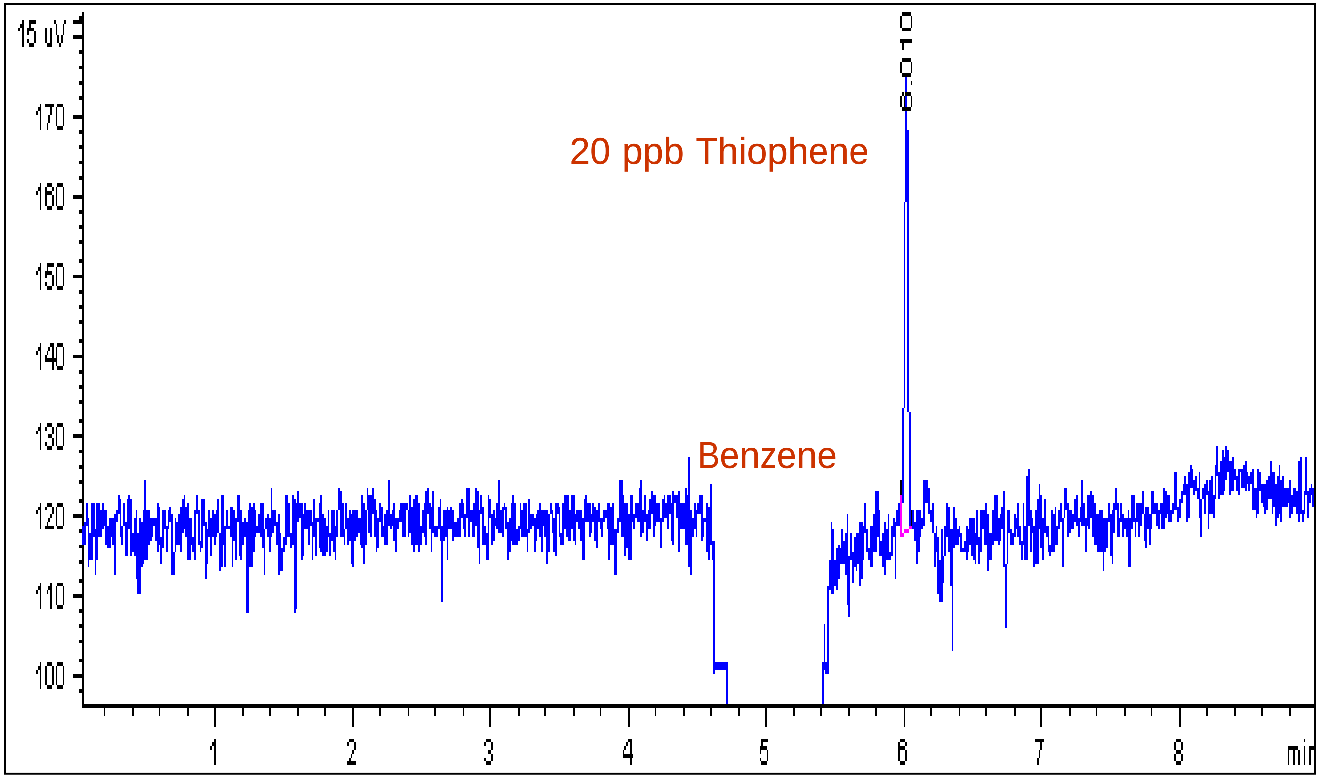
Low Level Thiophene in Benzene



1 µL injection, split 3:1
DB-WAX column

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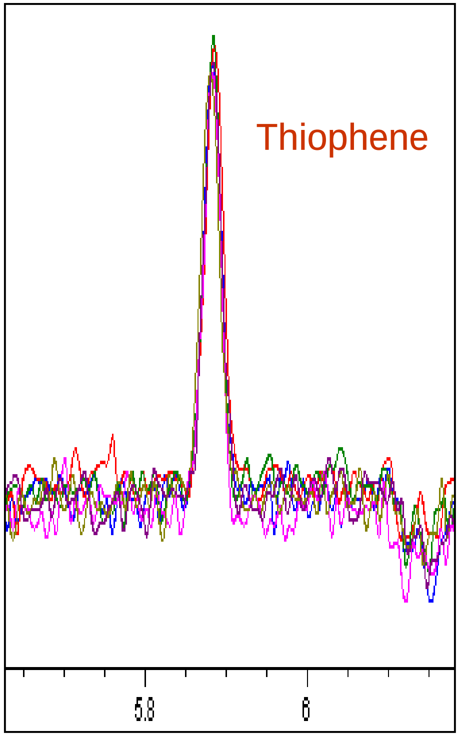
Thiophene Precision and Accuracy



	Area Counts	Calculated Conc. (ppb)	% Recy
Vial 1	221.6	47.7	90
	210.3	45.9	87
	202.9	44.8	85
Vial 2	210.4	46.0	87
	209.7	45.9	87
	207.6	45.5	86
Avg.	***210.4***	***46.0***	***87***
%RSD	***2.9***	***2.1***	***1.9***

1 µL injection, split 3:1
DB-WAX column

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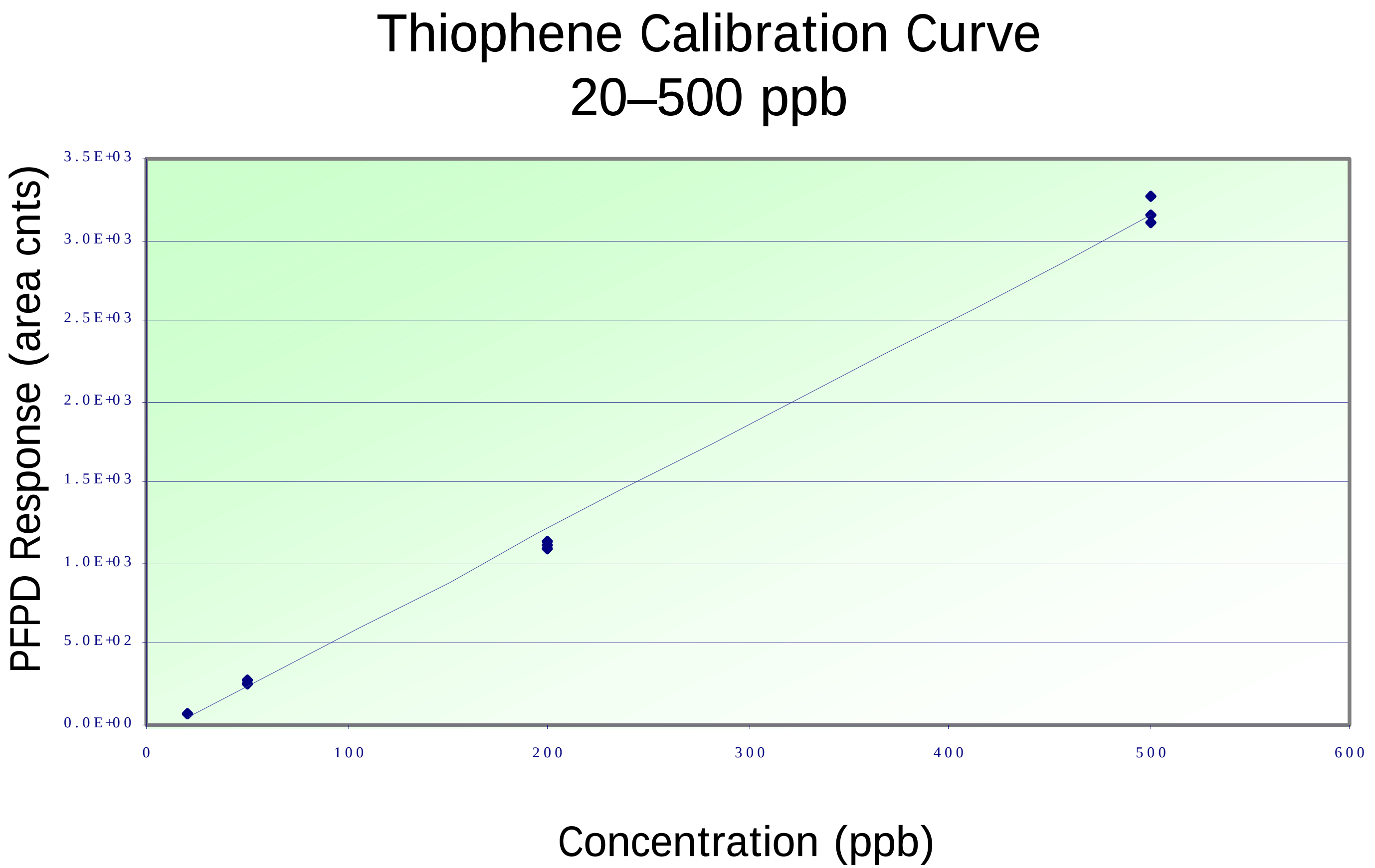
Linear Calibration $R^2 = 0.9997$



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Summary

- The Pulsed FPD has many significant advantages over the static FPD or the SCD, including:
  - Dual-element capability for ½ the cost of the static FPD dual mode
  - ½ the cost of an SCD
  - Low cost of operation
  - Simultaneous, mutually selective chromatograms for S/C
  - Ease of use and long-term stability
- Please check the OI web site for more information on the OI Analytical PFPD and a complete list of application notes.

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