

Analysis with the Pulsed Flame Photometric Detector (PFPD)

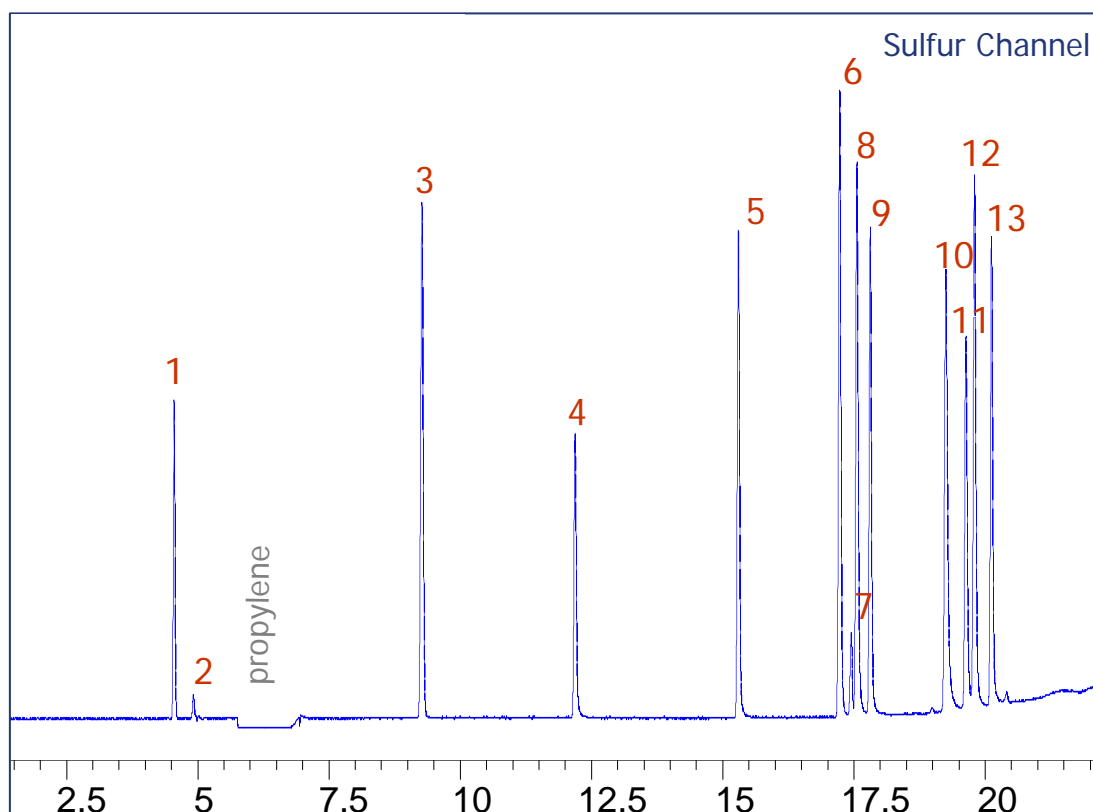
Sulfur in Petrochemical Matrices



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 are shown in the following slides.

Sulfur in Propylene

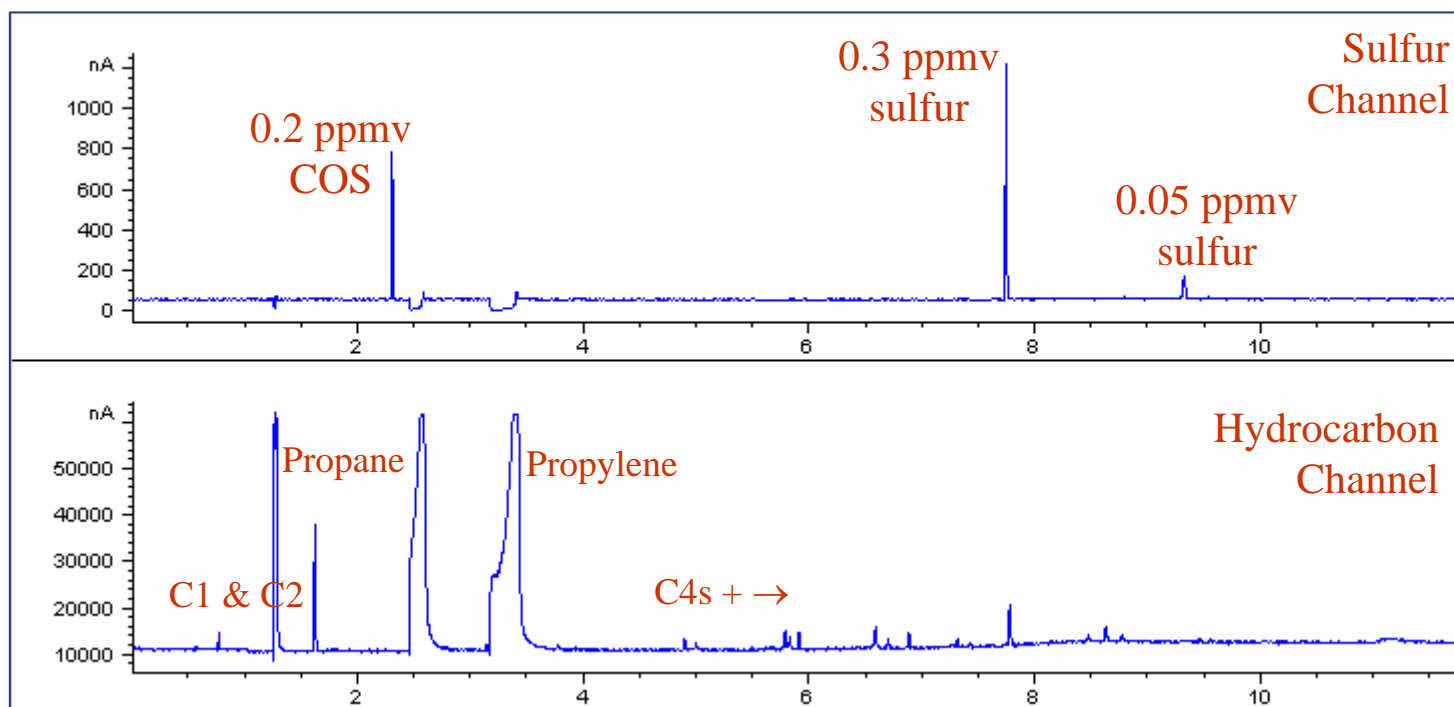


- 1 COS
- 2 H₂S
- 3 CS₂
- 4 Methylmercaptan
- 5 Ethylmercaptan
- 6 Thiophene
- 7 DMS
- 8 2-Propanethiol
- 9 1-Propanethiol
- 10 2-Methyl-2-propanethiol
- 11 2-Methyl-1-propanethiol
- 12 1-Methyl-1-propanethiol
- 13 1-Butanethiol

0.2-mL gas sampling loop; split 5:1.
Each compound (except H₂S) present in this
propylene standard at approximately 1 ppm.

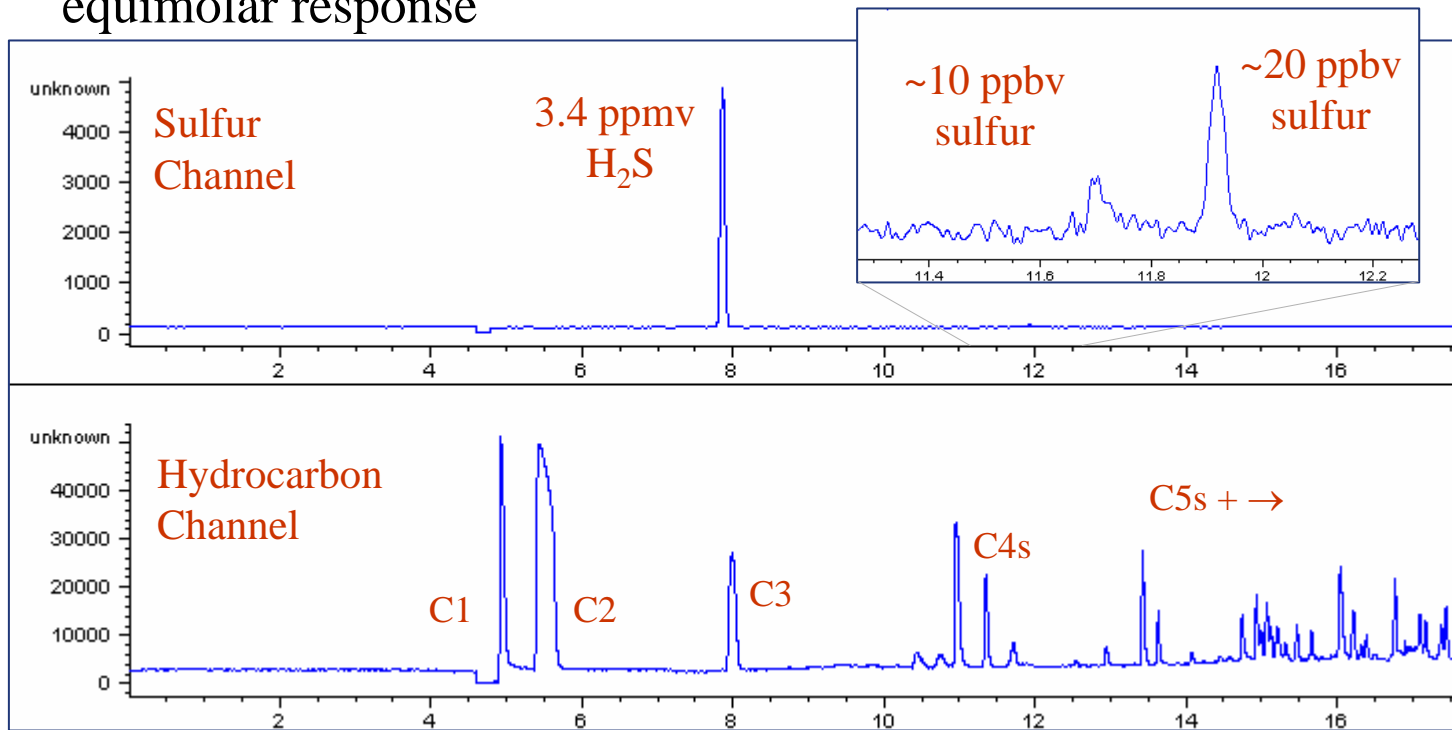
Sulfur in Propane-Propylene Mix

- Acquired on the *OI Analytical S-PRO 3200 System*
- 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

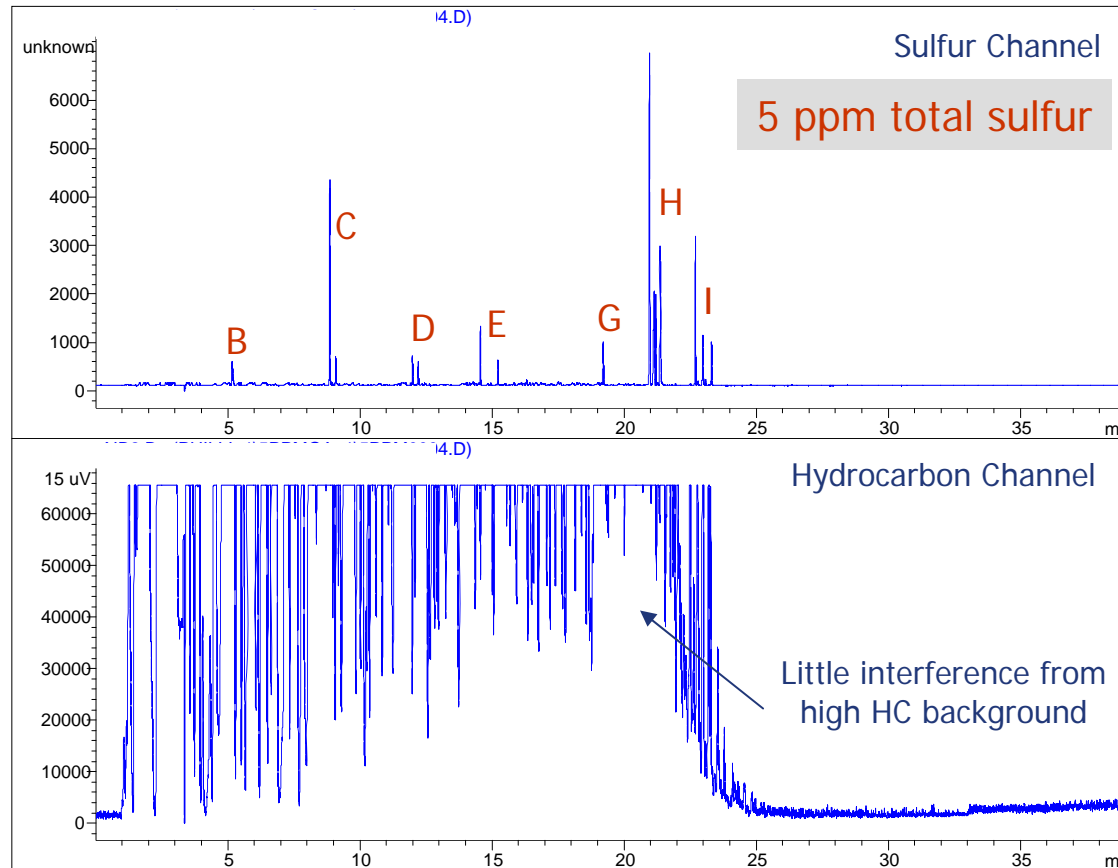


Sulfur in Pipeline Natural Gas

- Acquired on the *OI Analytical S-PRO 3200 System*
- 0.5-mL gas loop, 9:1 split, GasPro column, isothermal oven
- [H₂S] determined with H₂S permeation wafer device
- Unknown [S] determined with COS permeation device and equimolar response



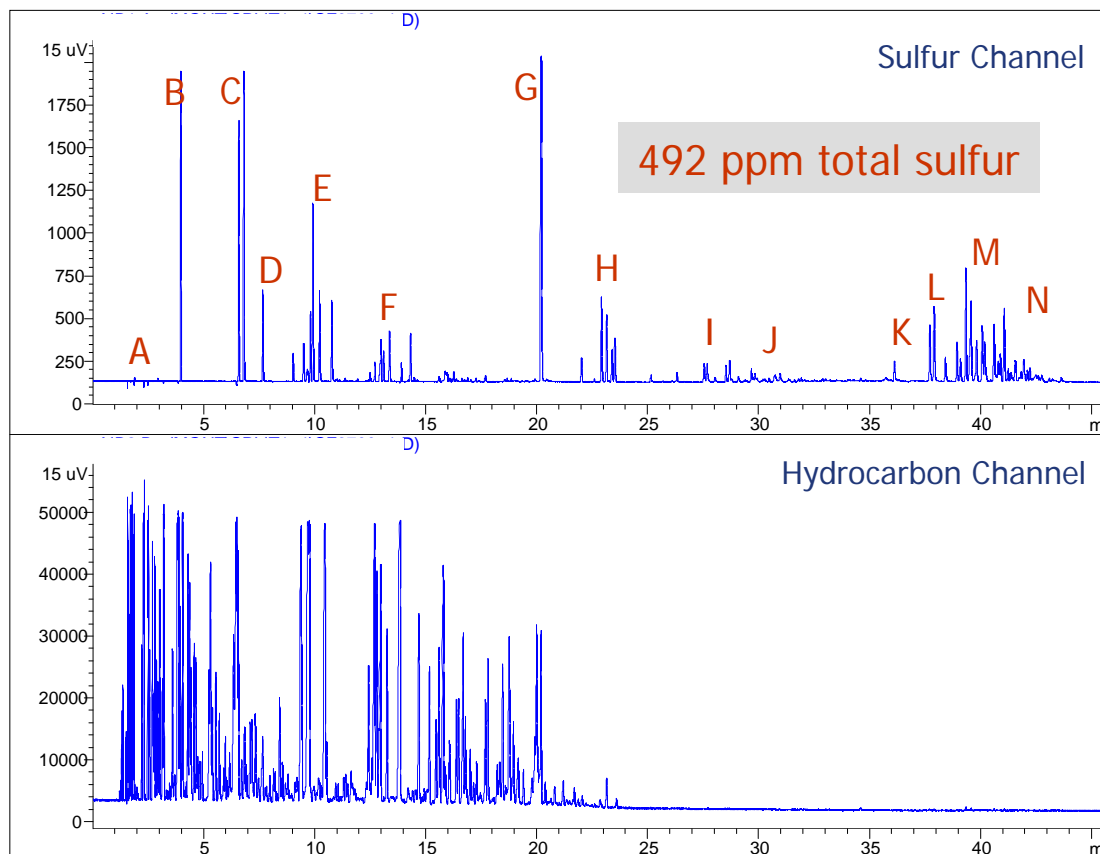
Low-Level Sulfur in Gasoline



- 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- μ L injection; split 10:1.
Concentration reported by client as 5 ppm.

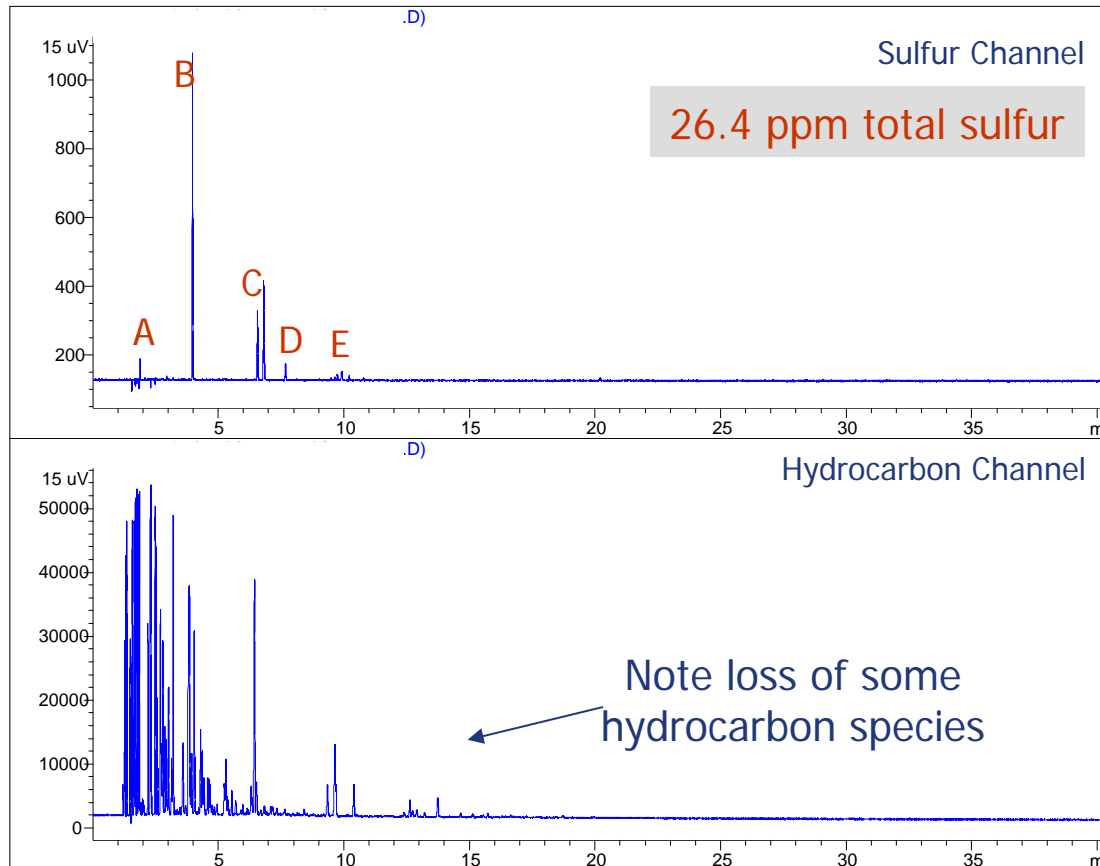
Gasoline Before Sulfur Treatment



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

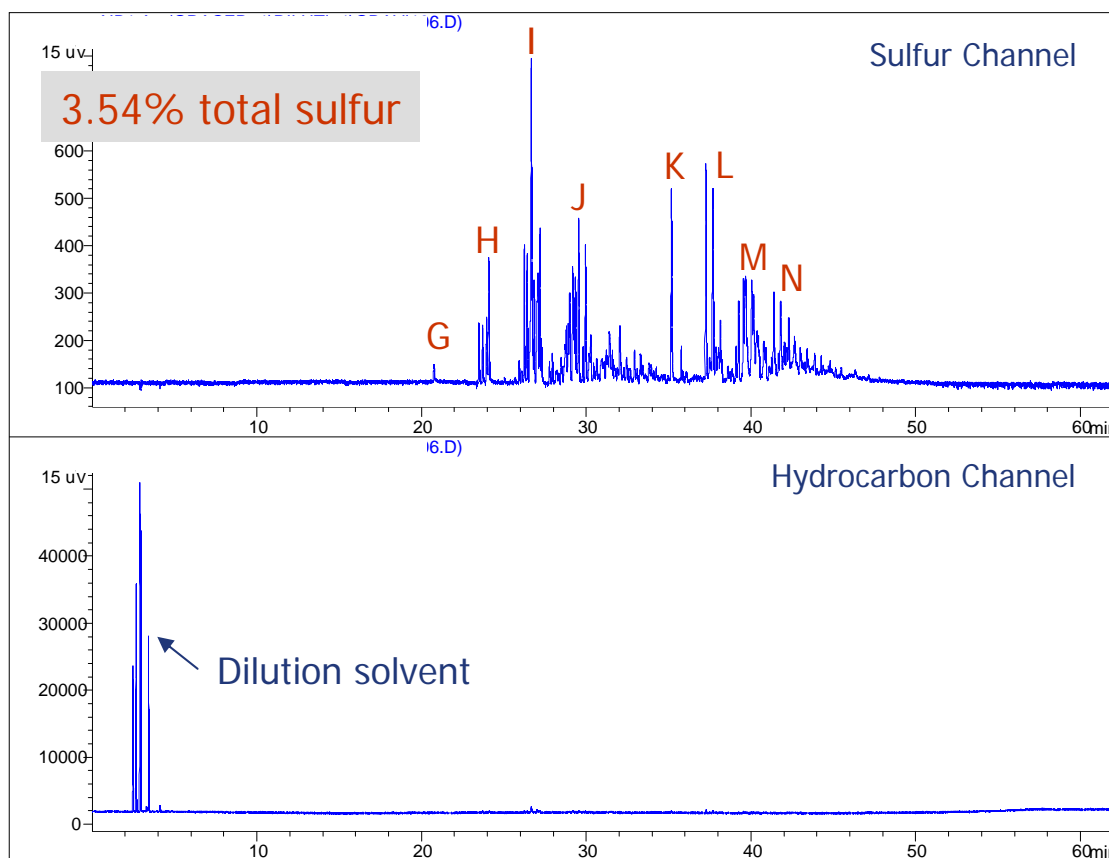
Gasoline After Sulfur Treatment



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

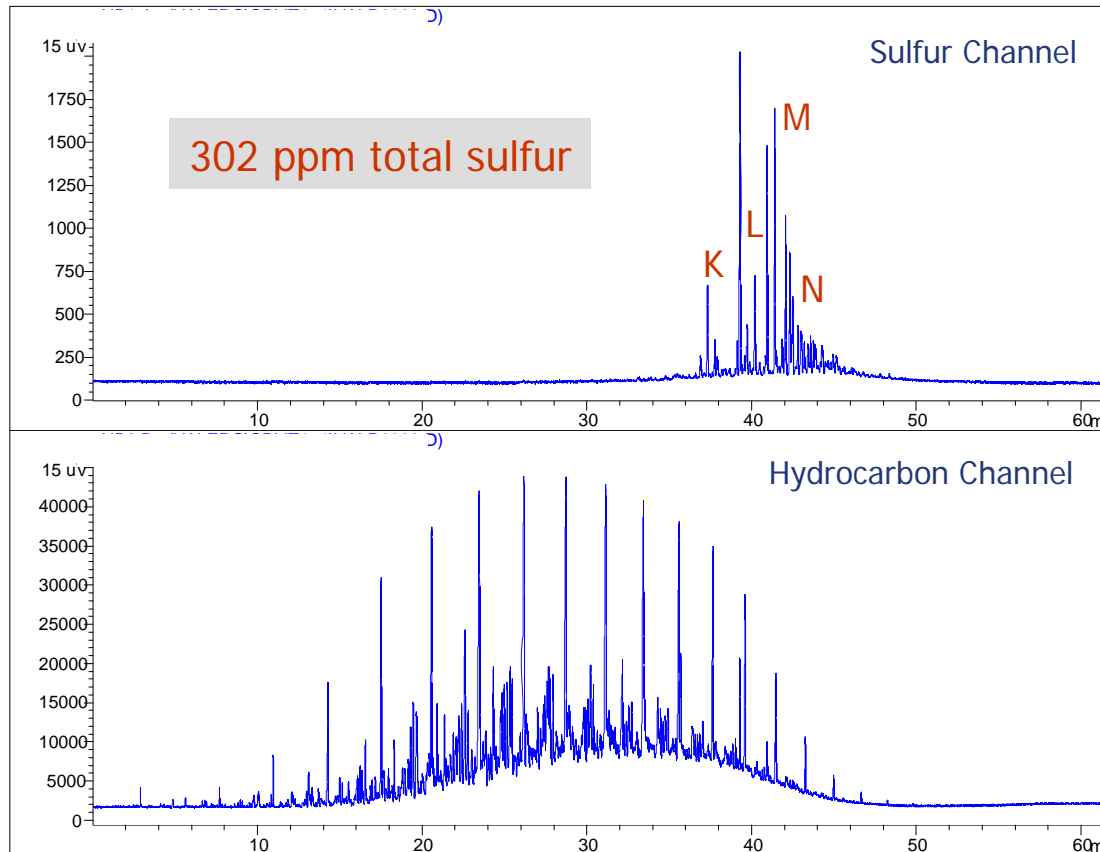
High-Level Total Sulfur in Diesel



- 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.

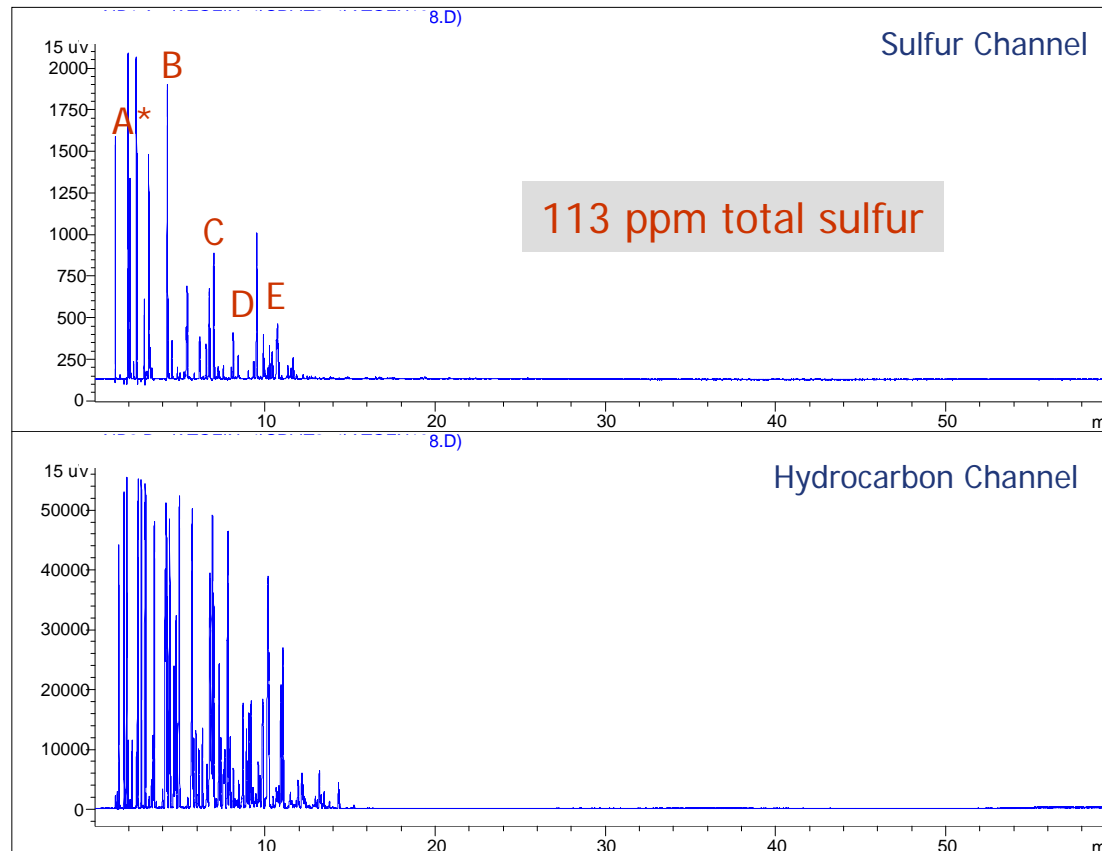
Mid-Range Total Sulfur in Diesel



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

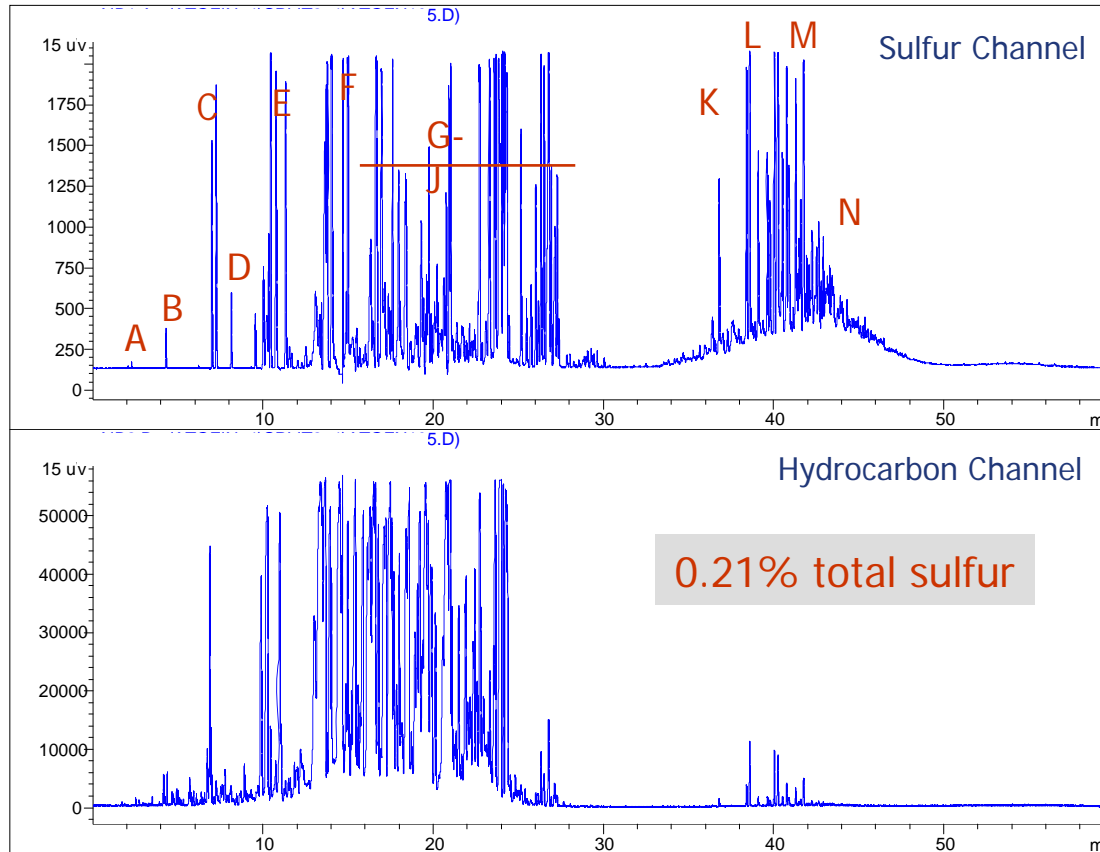
Sulfur in Naptha Stabilizer Bottoms



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

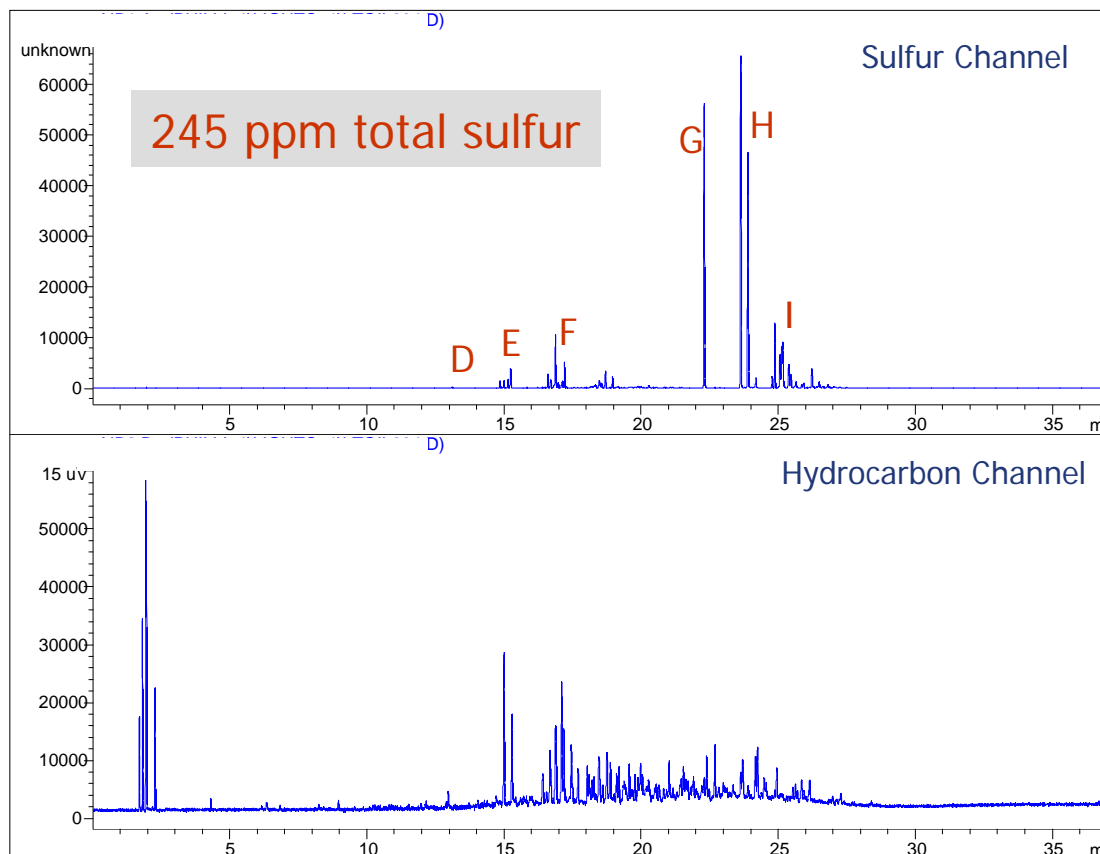
Sulfur in Heavy Catalytic Naptha



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

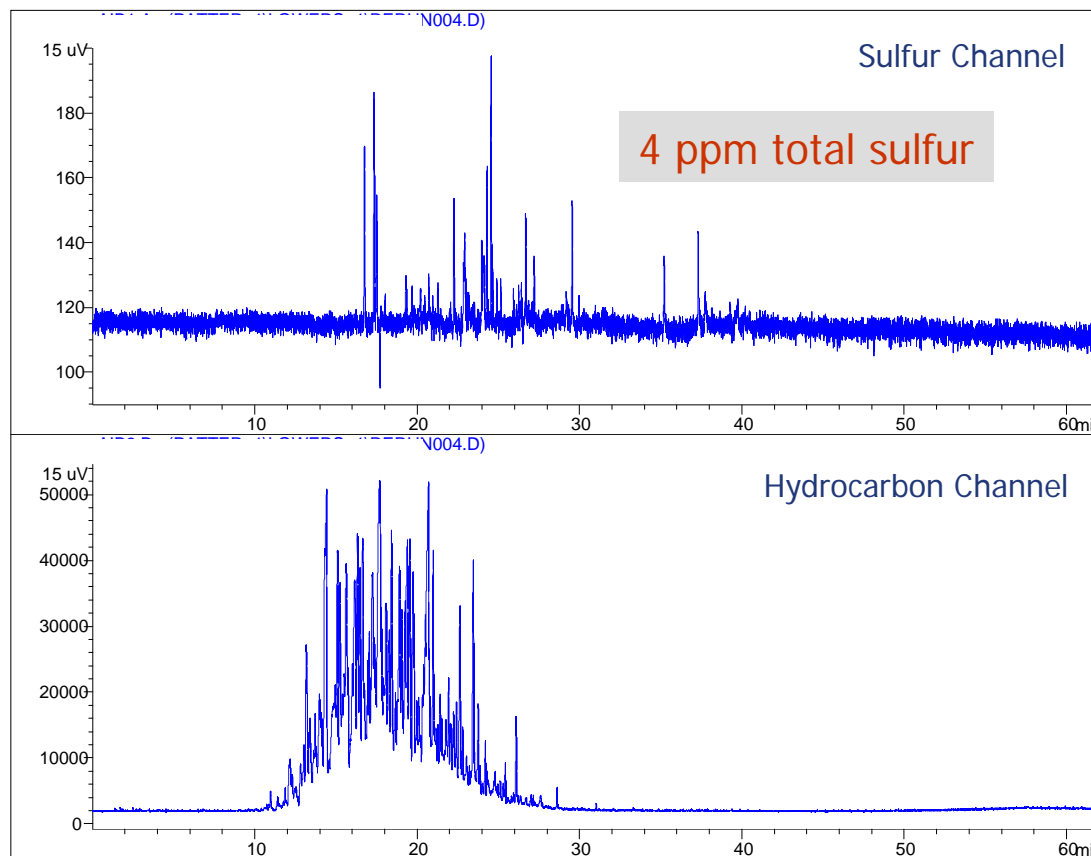
Total Sulfur in LCO



- 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

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

Low-Level Sulfur in Jet Fuel

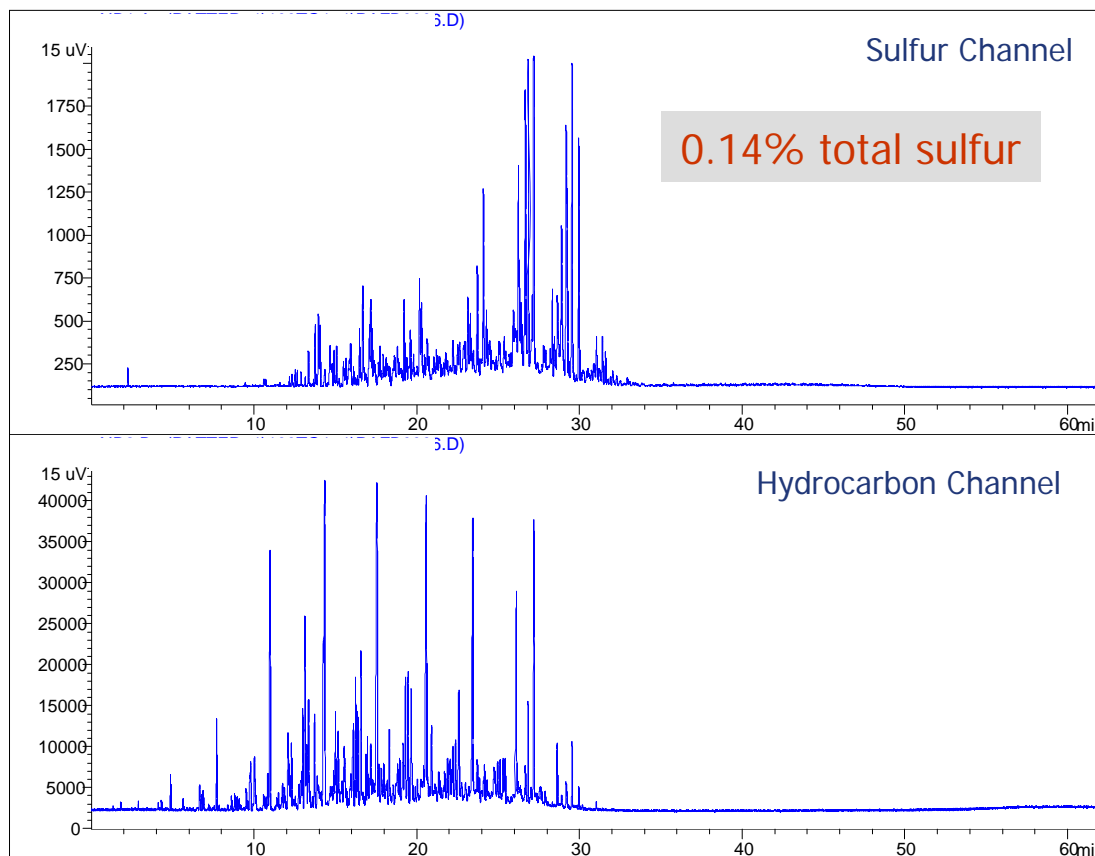


- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O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

1- μ L injection; split 10:1.

No reference was available for identification of sulfur peak groupings in jet fuel.

High-Level Sulfur in Jet Fuel

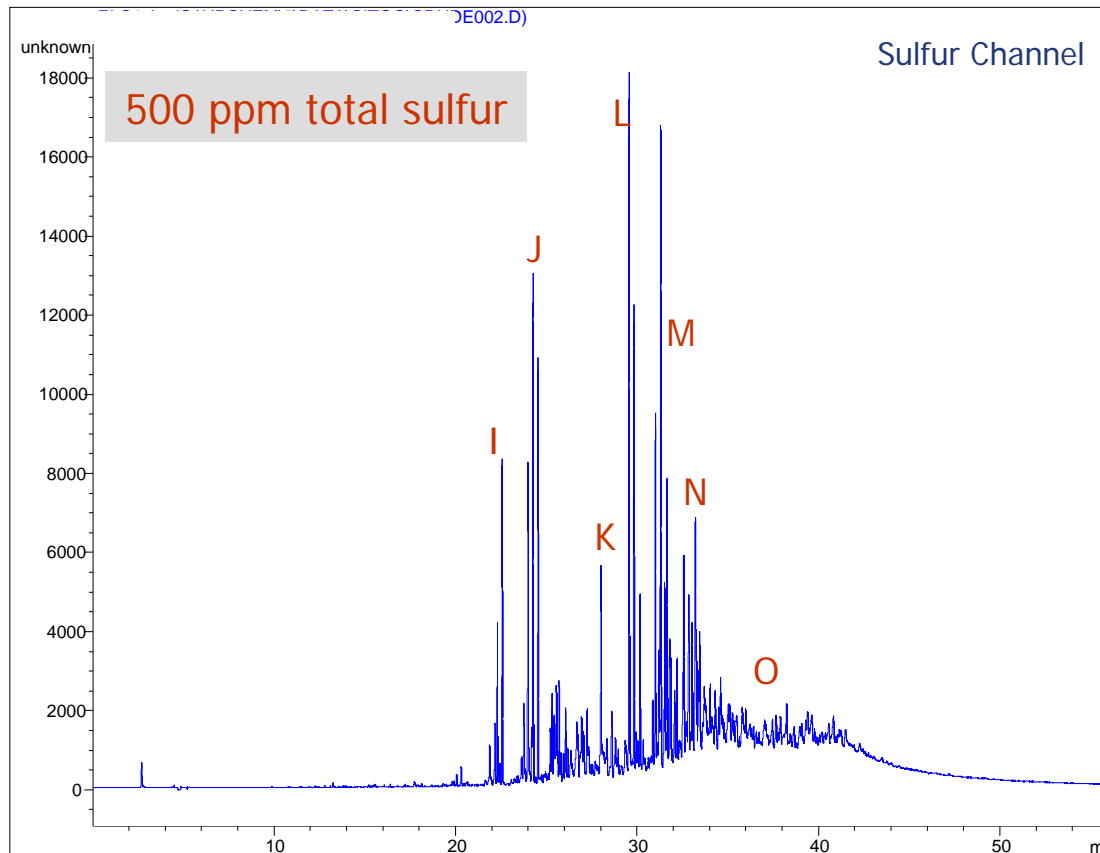


- A Methyl mercaptan
- B Thiophene
- C C1-Thiophenes
- D Tetrahydrothiophene
- E C2-Thiophenes
- F C3-Thiophenes
- G Benzothiophene
- H C1-Benzothiophenes
- I C2-Benzothiophenes
- J C3-Benzothiophenes
- K Dibenzothiophene
- L C1-Dibenzothiophenes
- M C2-Dibenzothiophenes
- N C3-Dibenzothiophenes
- O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

1- μ L injection; split 100:1.

No reference was available for identification of sulfur peak groupings in jet fuel.

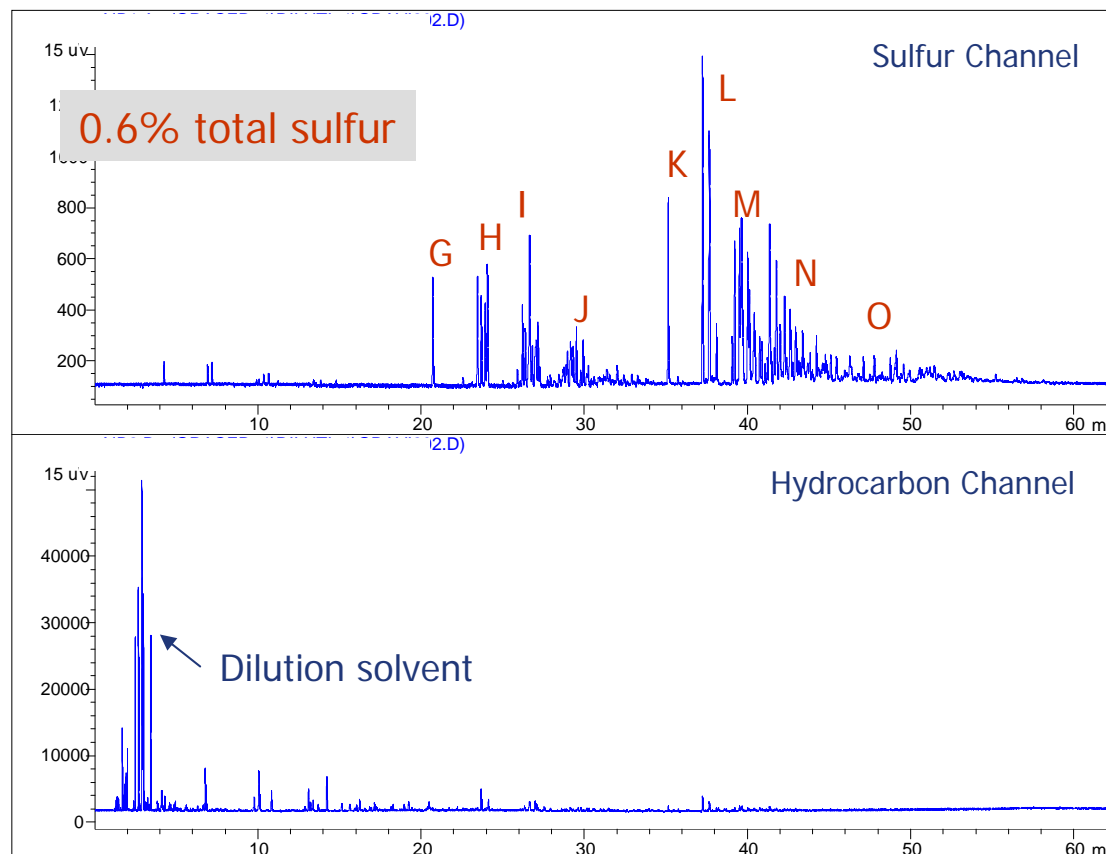
Total Sulfur in Crude Oil



- 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- μ L injection; split 25:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

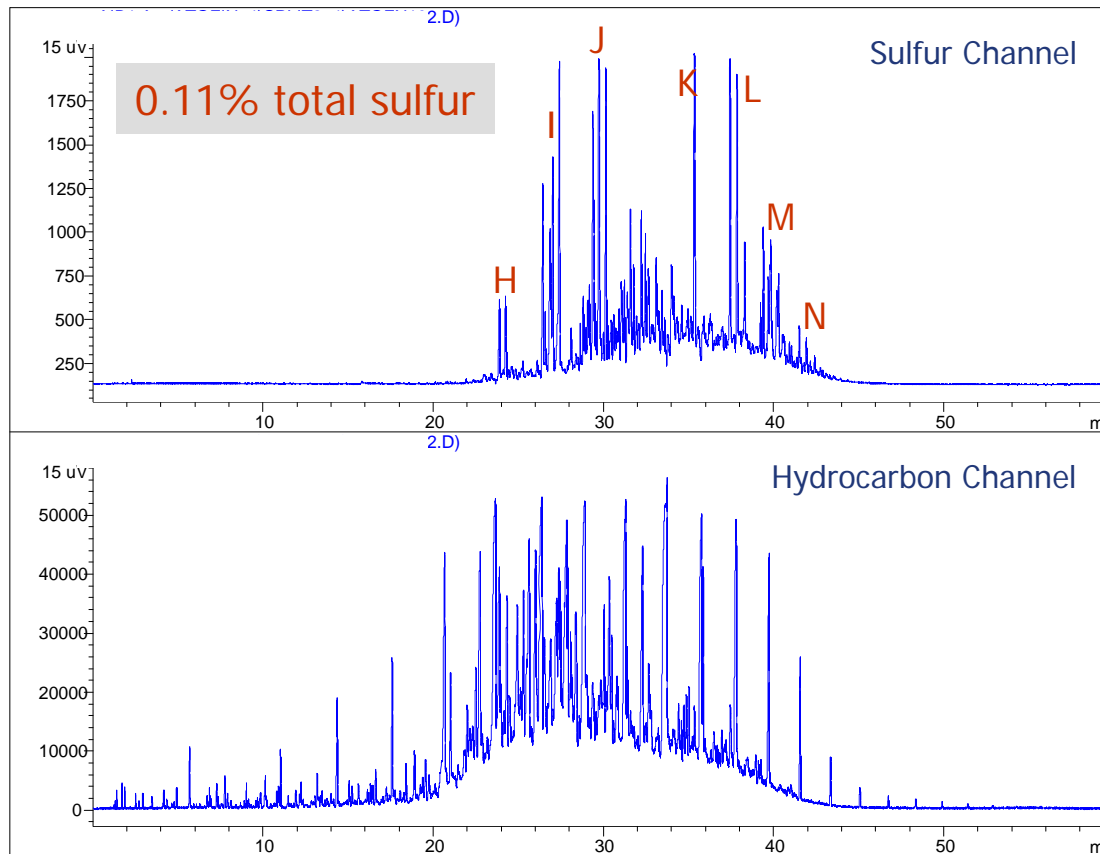
Sulfur in Synthetic Crude



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

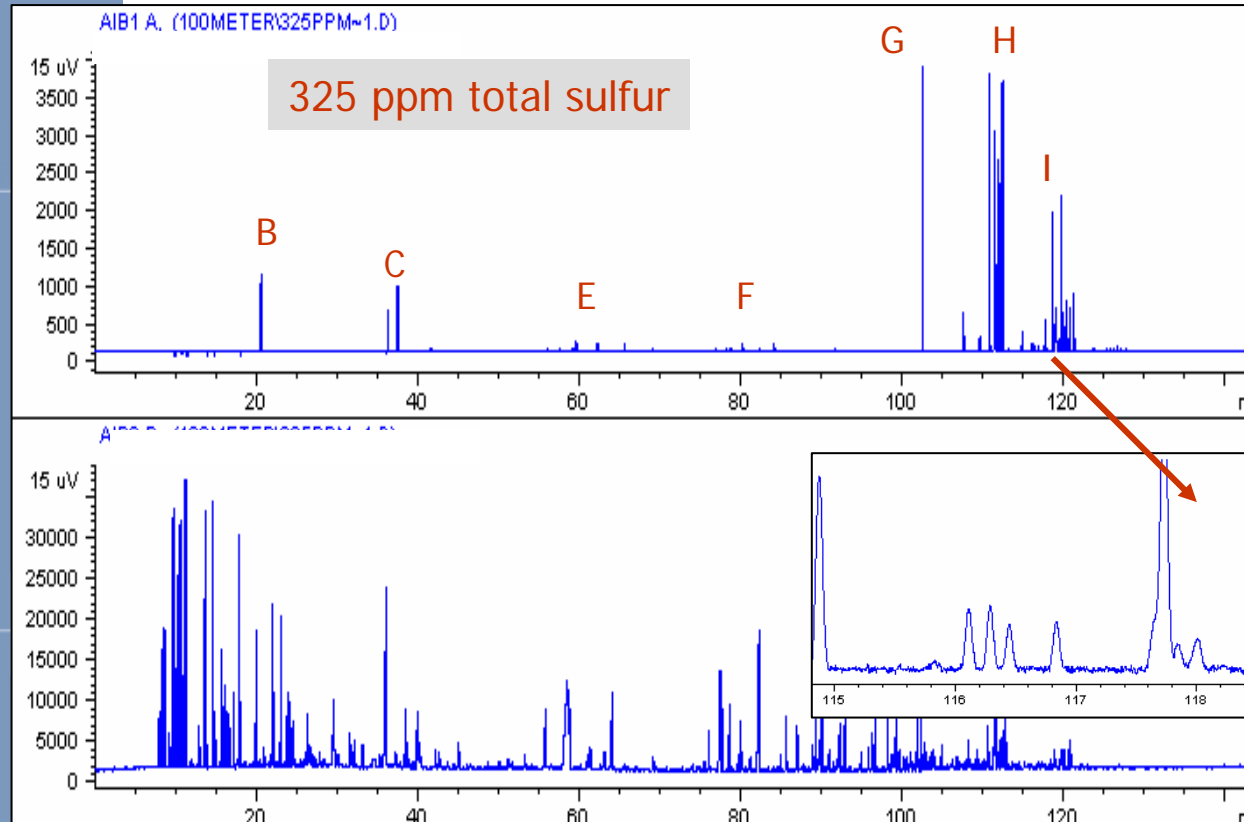
High-Level Sulfur in Furnace Oil



- 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

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

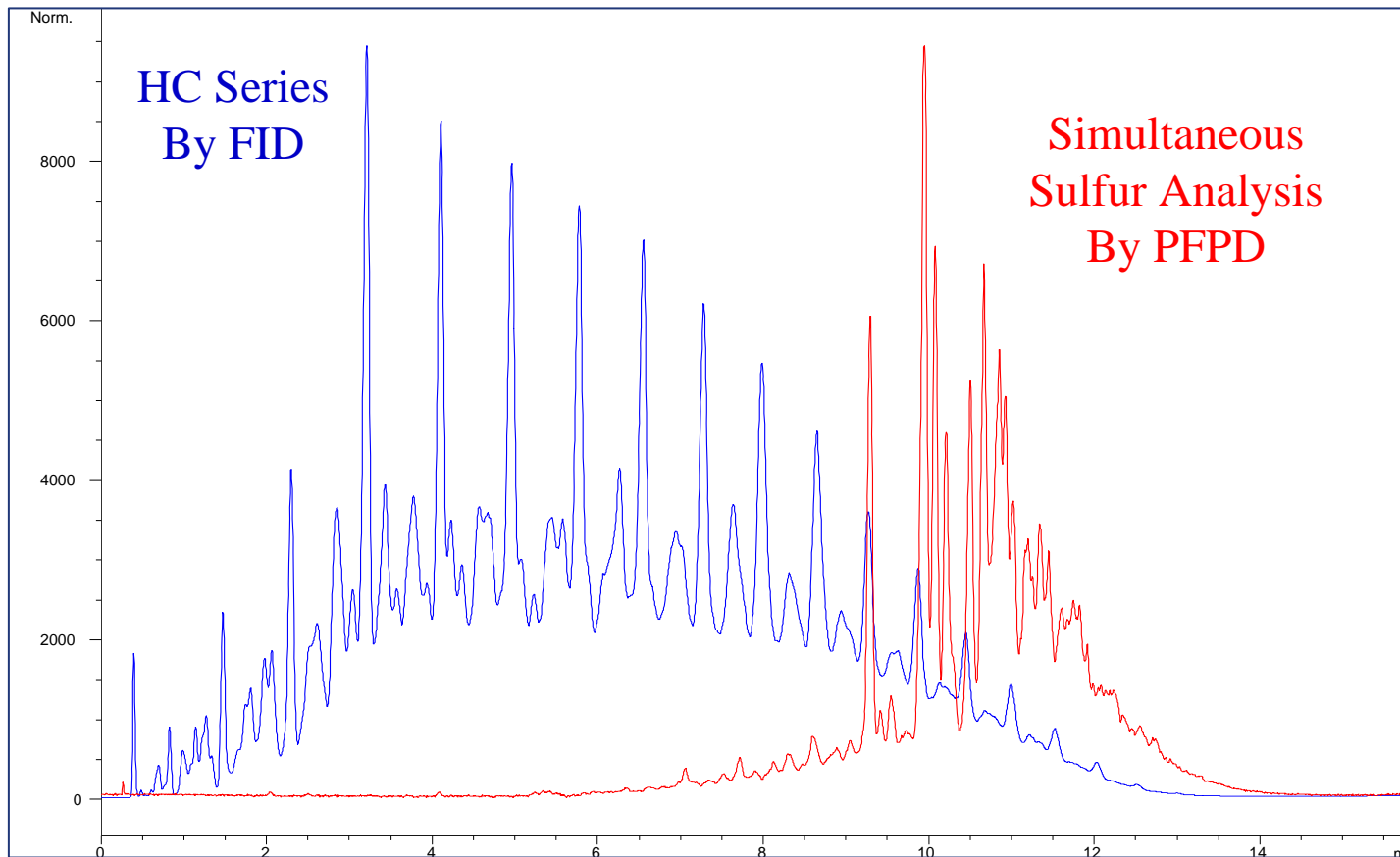
"DHA-Type" Sulfur Analysis



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

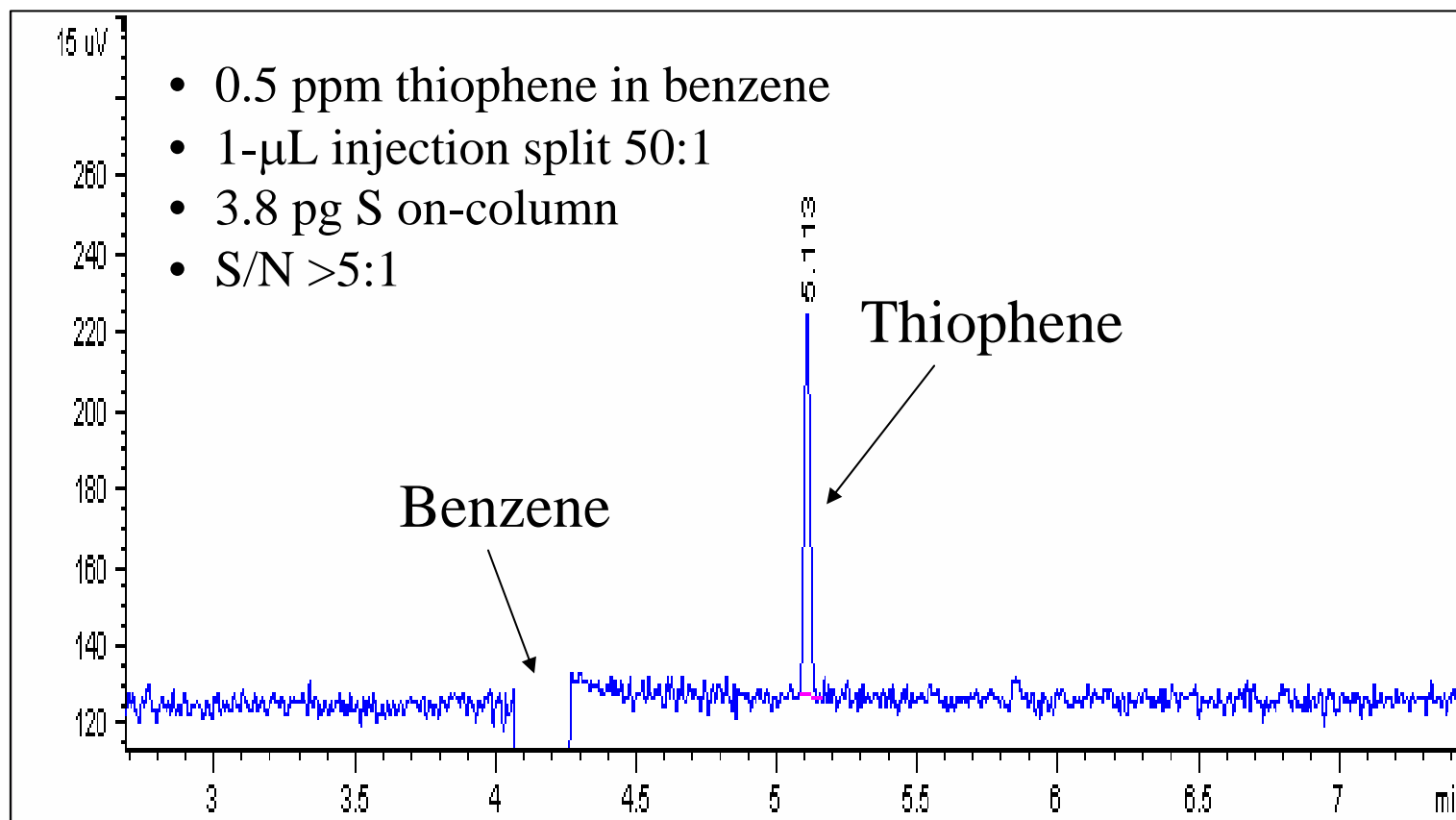
1- μ L injection; split 50:1.
Quantified using thiophene as an external standard.

Sulfur by Simulated Distillation

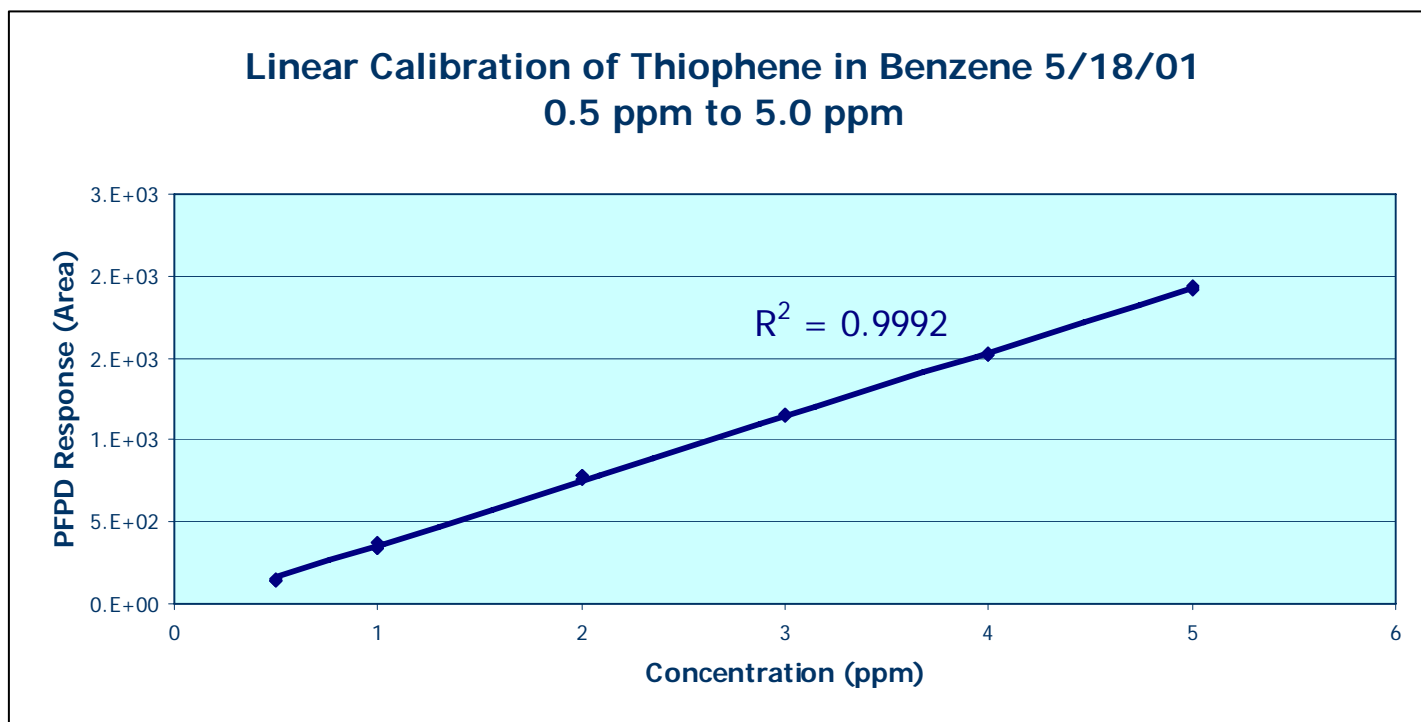


Reference standard for ASTM Method D2887-02
used as a calibration standard for simulated distillation.

0.5 ppm Thiophene in Benzene

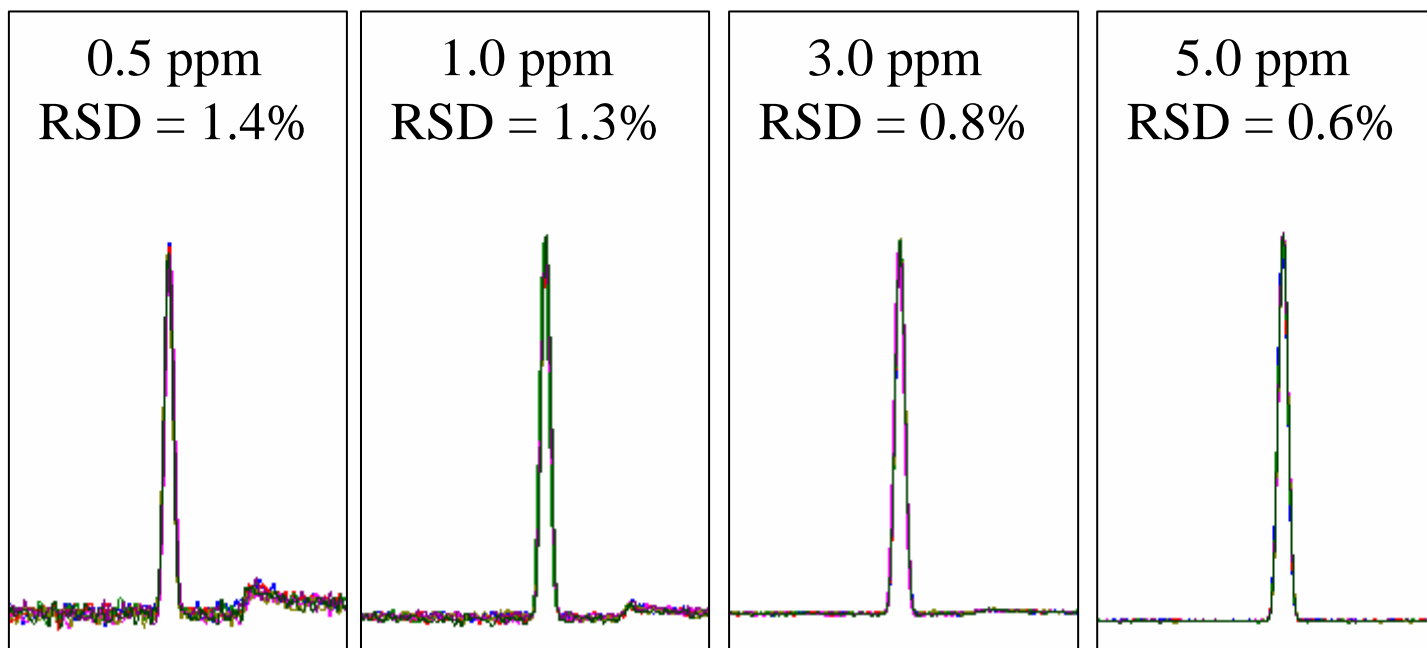


Thiophene Linear Calibration Plot



Thiophene Precision on the PFPD

- Overlaid chromatograms
- 4 concentration levels
- 7 replicate analyses at each level over a 1-week time frame



Thiophene Sensitivity on the PFPD

