The Pulsed Flame Photometric Detector: A Rugged and Versatile Selective Detector For a Wide Range of Applications

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Presentation Outline

- Introduction to the PFPD
- Comparison of FPD, Agilent Enhanced FPD, and Pulsed FPD (PFPD)
- PFPD applications
  - Sulfur in petrochemical matrices
  - Organophosphorus pesticides
  - Carbamate pesticides
  - Flavor and fragrance
  - Food and beverage
  - Other applications
- Summary

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
  - Minimal maintenance

Introduction (cont.)

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

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

Comparison of FPD, Agilent Enhanced FPD, and Pulsed FPD (PFPD)

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PFPD Advantages

- 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/P and S/C chromatograms
  - Linear, equimolar response
  - Wider range of applications and methods
  - Long-term stability
  - Lower cost of ownership and less gas usage
- A detailed comparison is shown in the tables on the following slides.

Comparison of FPDs: Sulfur Mode

	FPD	Agilent 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 and remains stable. • Infinite S/C selectivity. • Simultaneous, mutually selective S and C chromatograms from a single detector.

Comparison of FPDs: Phosphorus Mode

	FPD	Agilent 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 OP pesticides with excellent peak shape. • Analyze for P and S simultaneously with mutually selective chromatograms.

Comparison of FPDs: General

	FPD	Agilent Enhanced FPD	Pulsed FPD
Cost	Single $10K Dual $20K	Single $10K Dual $20K	Single $15K Dual $15K + cable
Simultaneous S and 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
Nitrogen mode?	Unknown	Unknown	Yes
Tin mode?	Yes, limited sensitivity	Unknown	Yes, 100-fold improvement in sensitivity for organotins
Other elements?	Not easily	Not easily	• As, Se, Si • 28 total elements
Cost of operation	High, gas usage	High, gas usage	• Low gas usage • Low maintenance

PFPD Applications

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PFPD Applications

- The unique operation of the Pulsed FPD allows it to be easily configured for many applications that are beyond the capability and scope of static FPDs.
- Examples of the principle applications are shown in the following slides and include:
  - Petrochemical applications
  - Pesticide applications
  - Flavor/fragrance and food/beverage applications
  - Pulp mill effluent
  - Arsenic, tin, and selenium applications
  - Chemical warfare agent monitoring

Sulfur in Petrochemical Matrices

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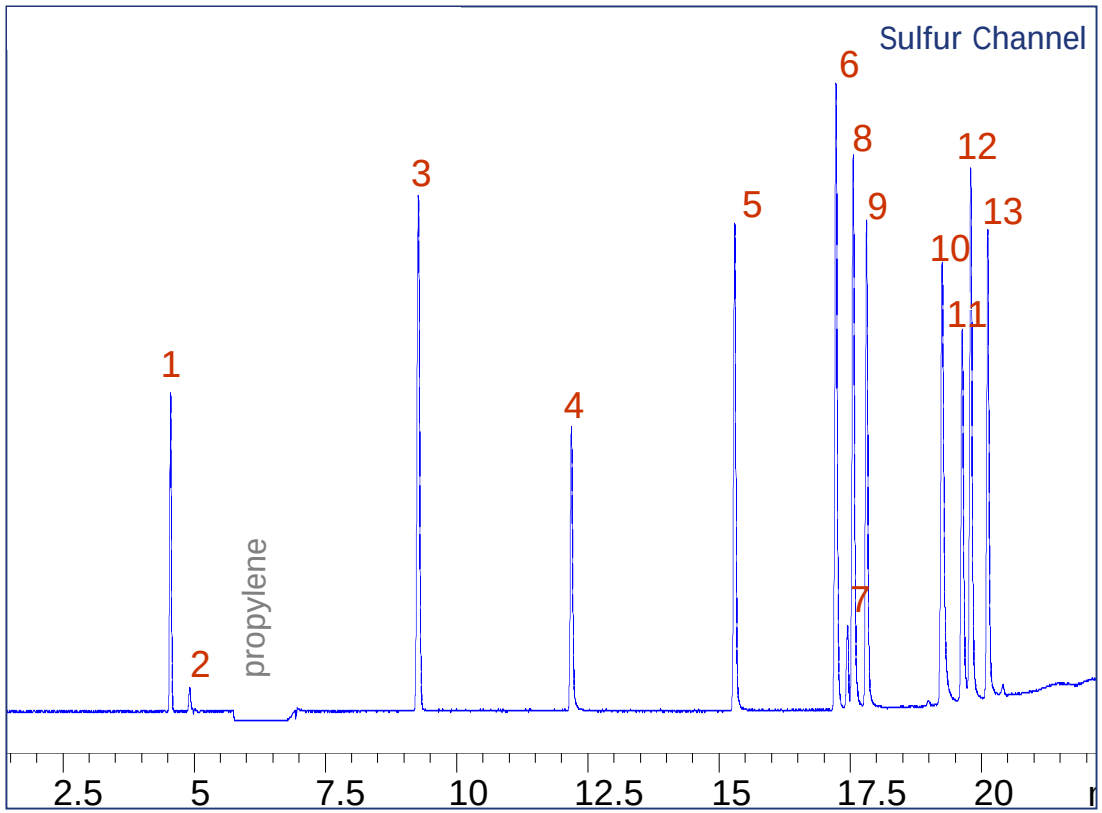
Sulfur in Petrochemical Matrices

- 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 are shown in the following slides.

Sulfur in Propylene

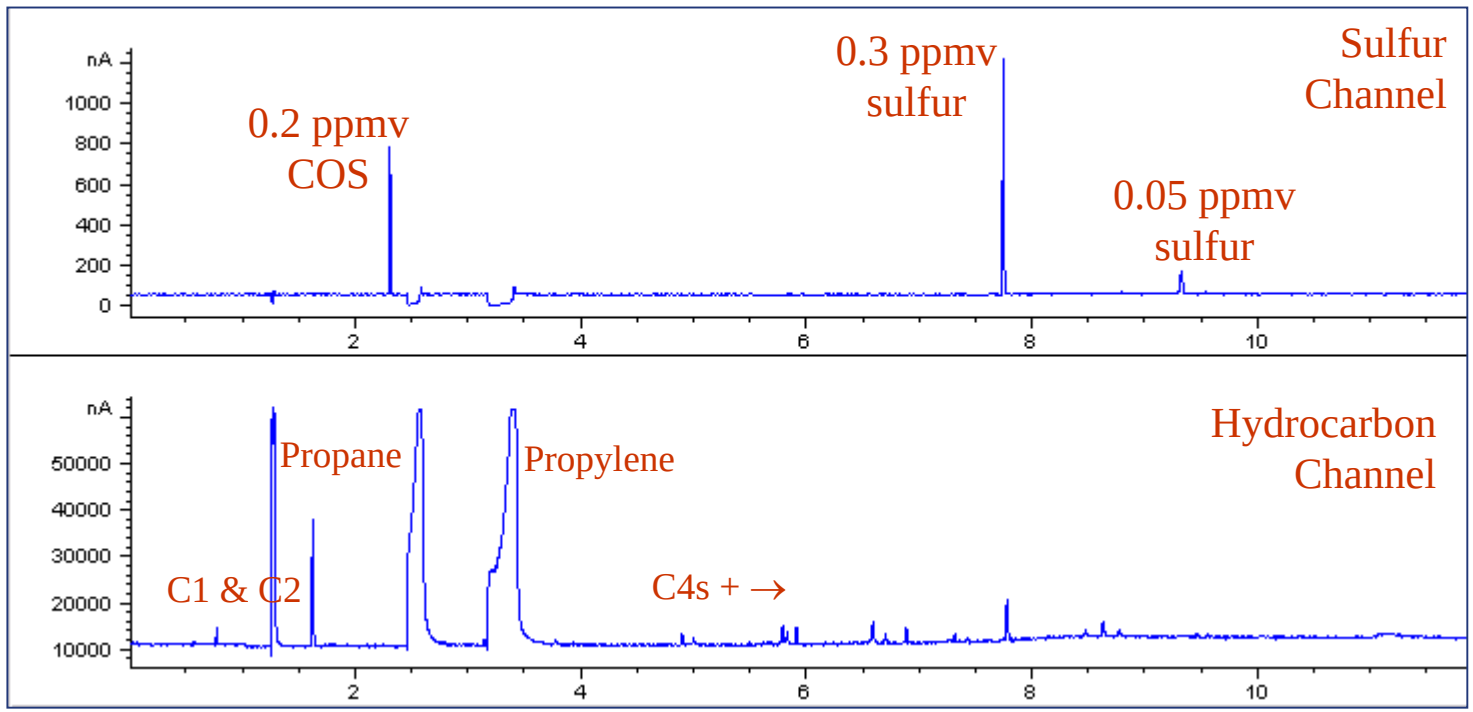


1 COS
2 H_2S
3 CS_2
4 Methylmercaptan
5 Ethylmercaptan
6 Thiophene
7 DMS
8 2-Propanethiol
9 1-Propanethiol
10 2-Methyl-2-propanethiol
11 2-Methyl-1-propanethiol
12 1-Methyl-1-propanethiol
13 1-Butanethiol

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

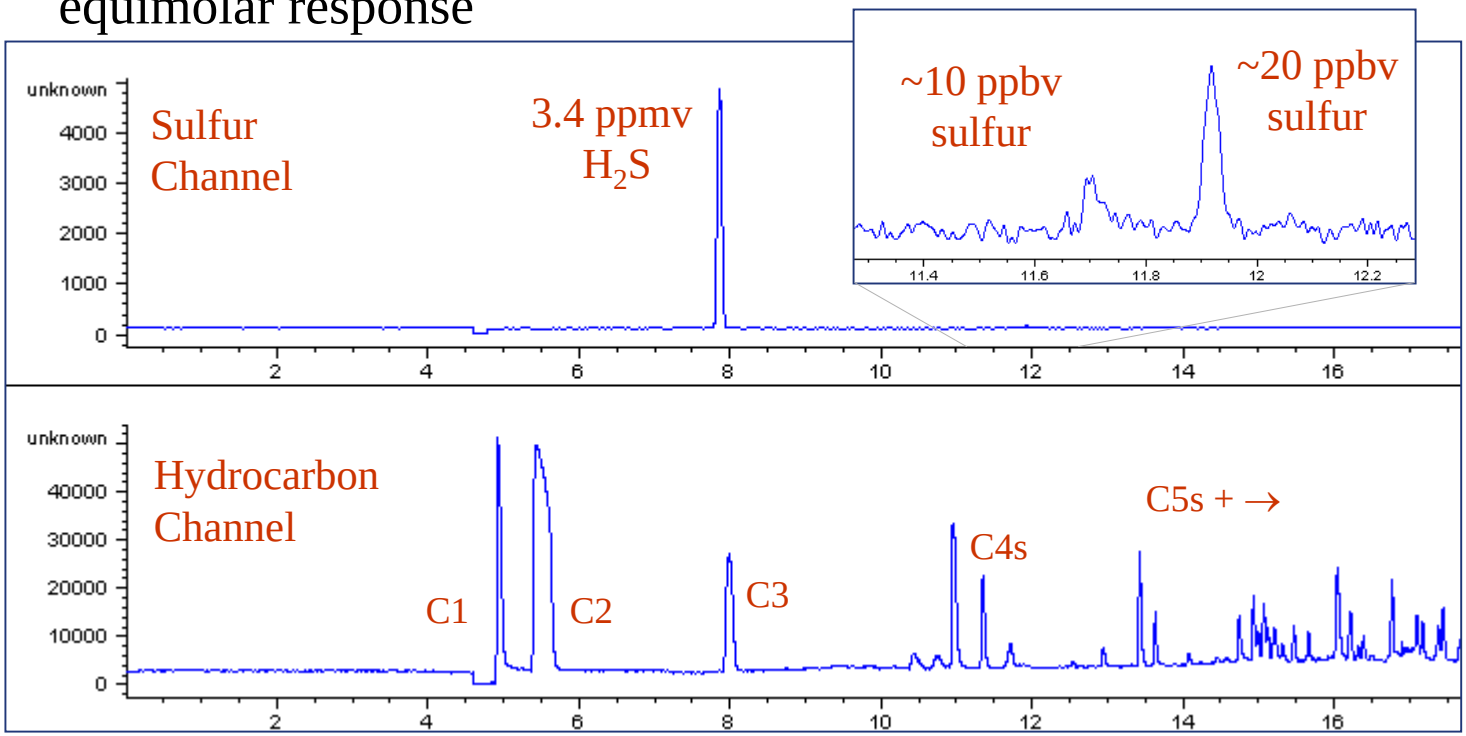
Sulfur in Propane-Propylene Mix

- 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

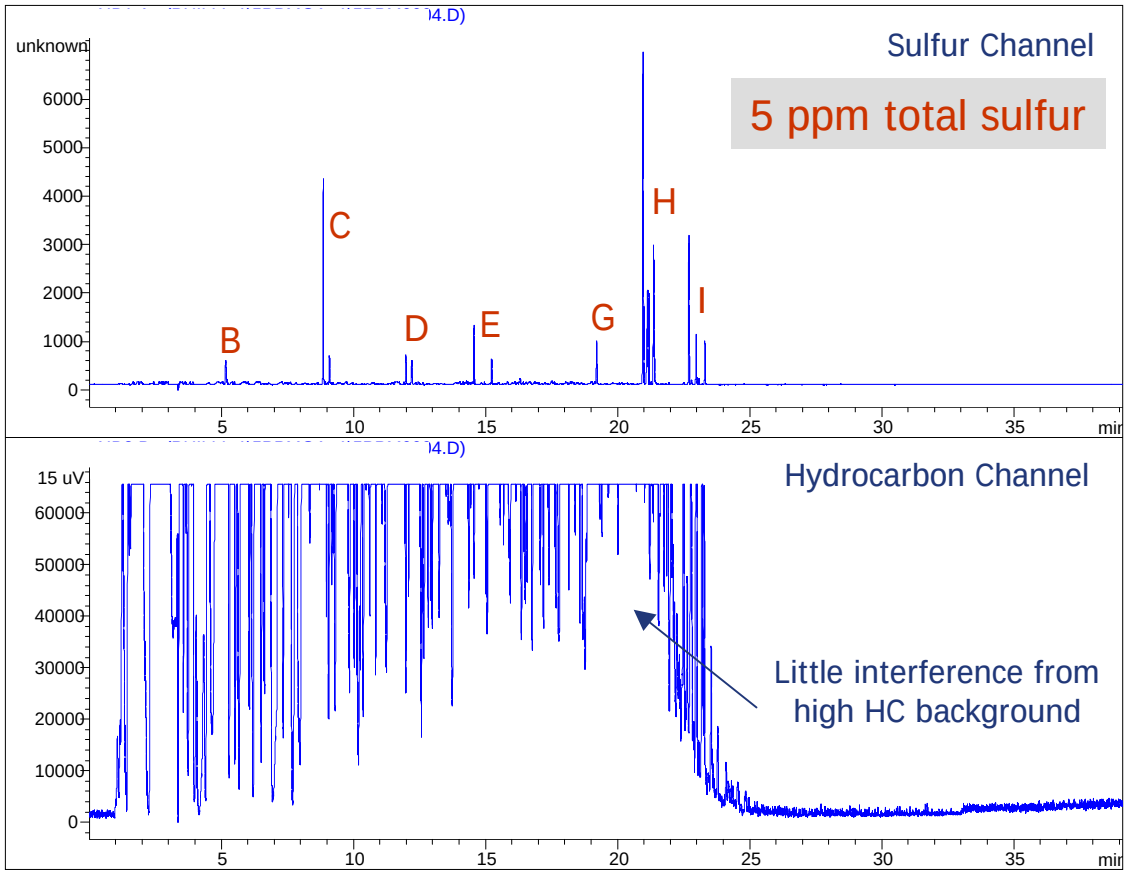


Sulfur in Pipeline Natural Gas

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



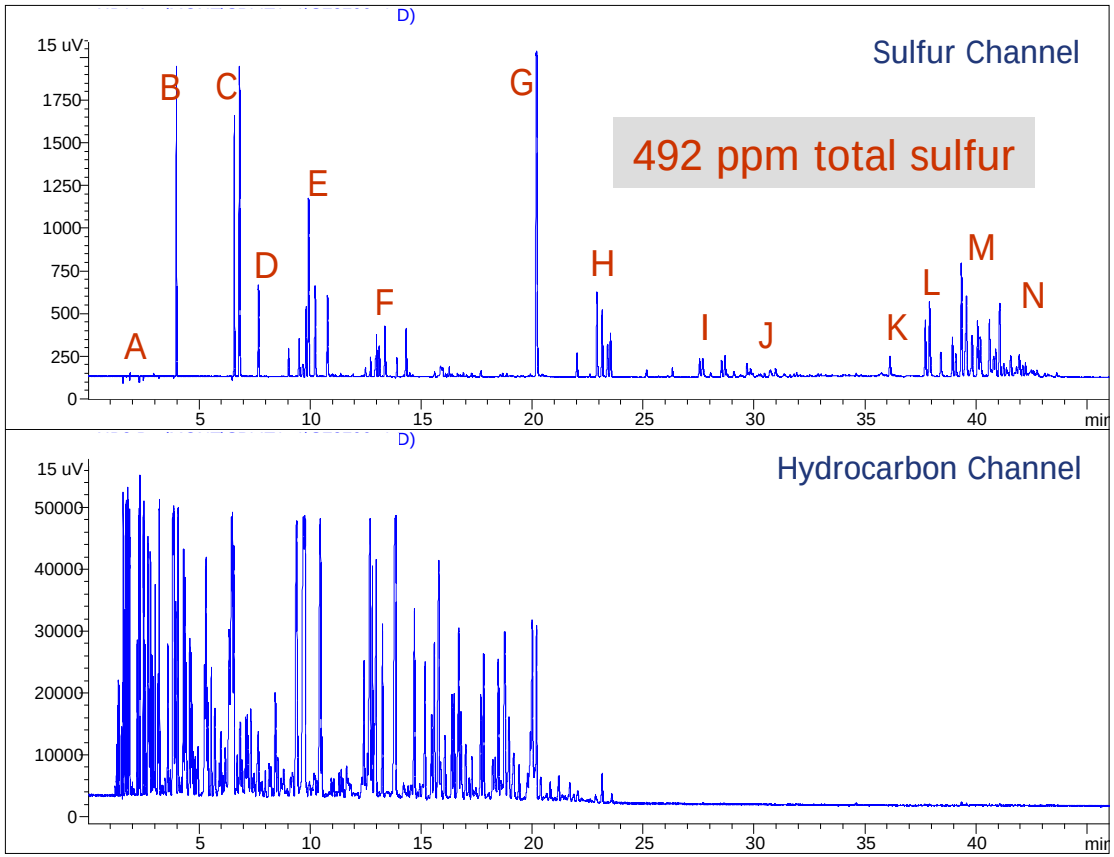
Low-Level Sulfur in Gasoline



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

Gasoline Before Sulfur Treatment



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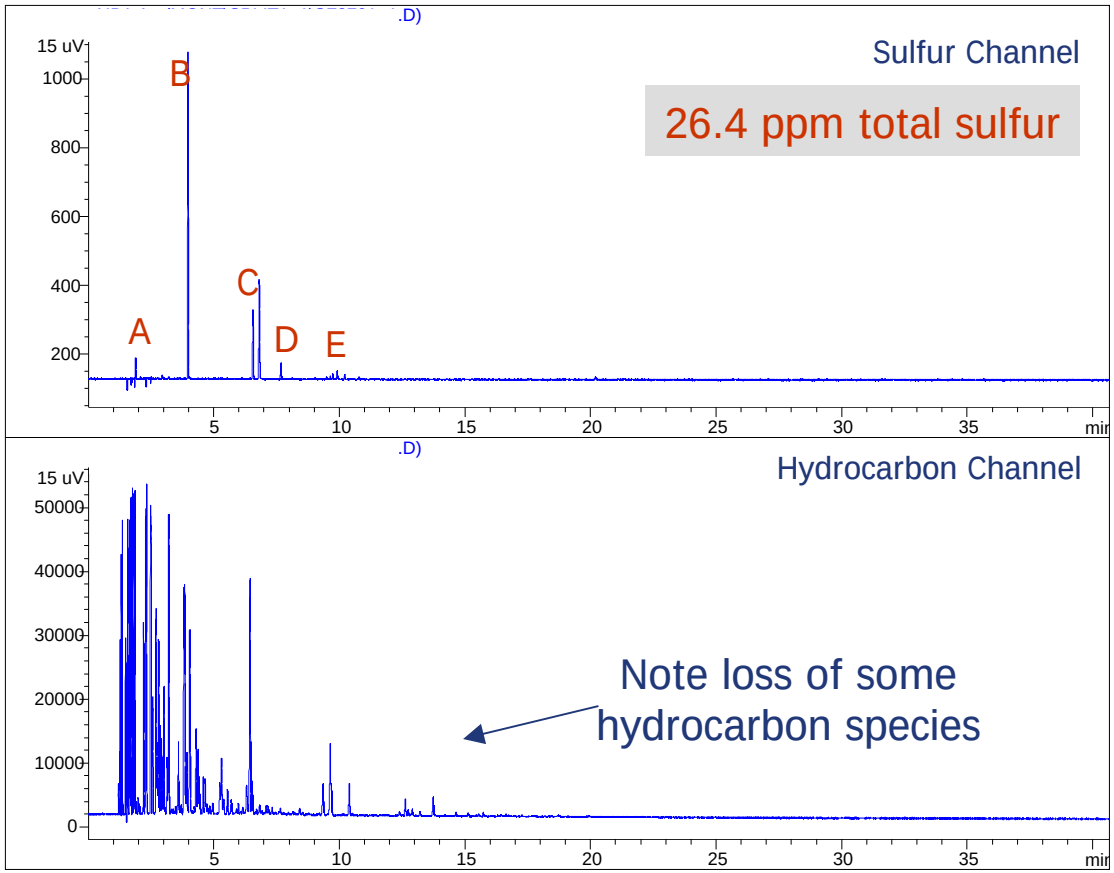
O Alkyl sulfides & substituted thiophenes

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

Gasoline After Sulfur Treatment



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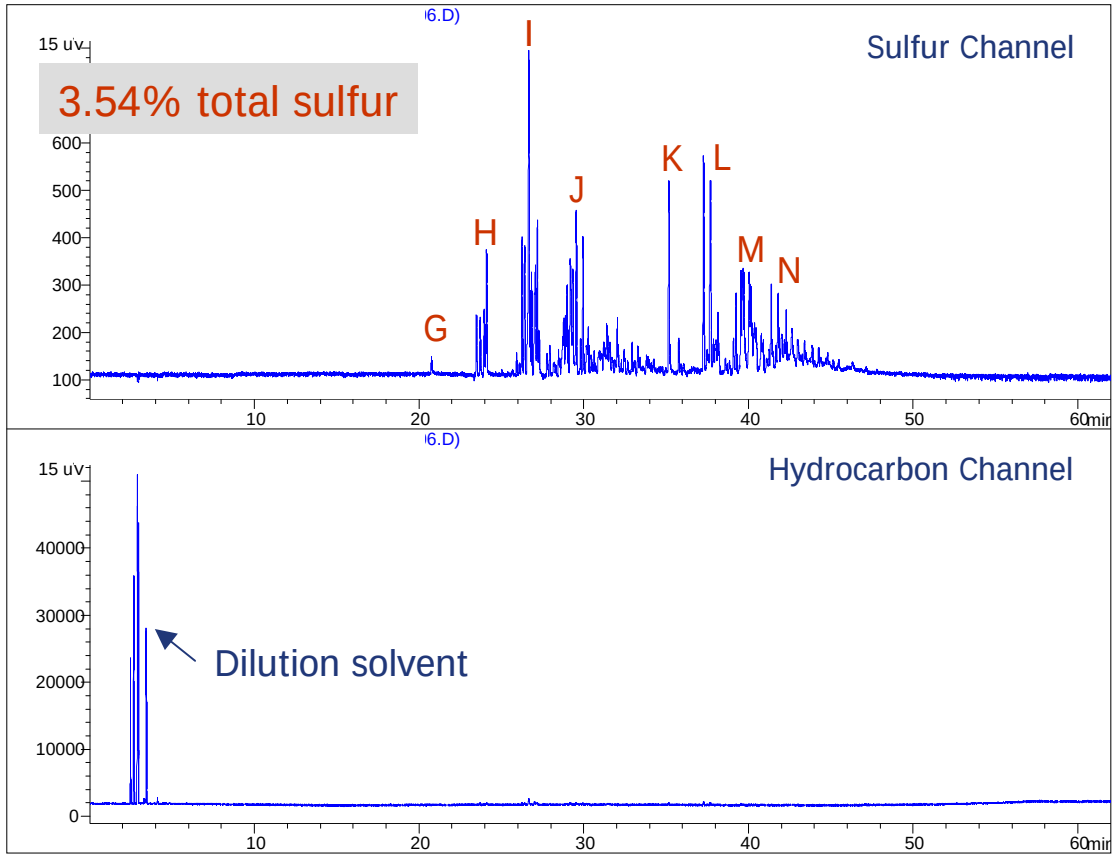
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

High-Level Total Sulfur in Diesel



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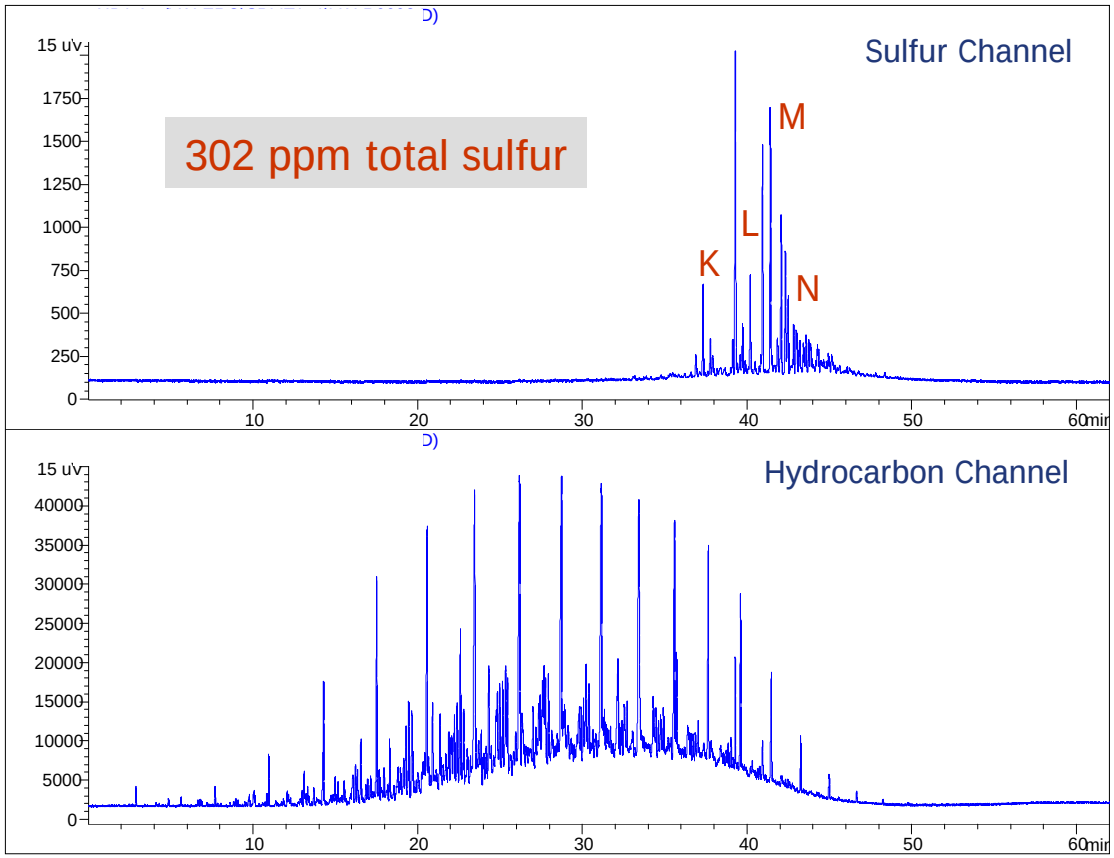
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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



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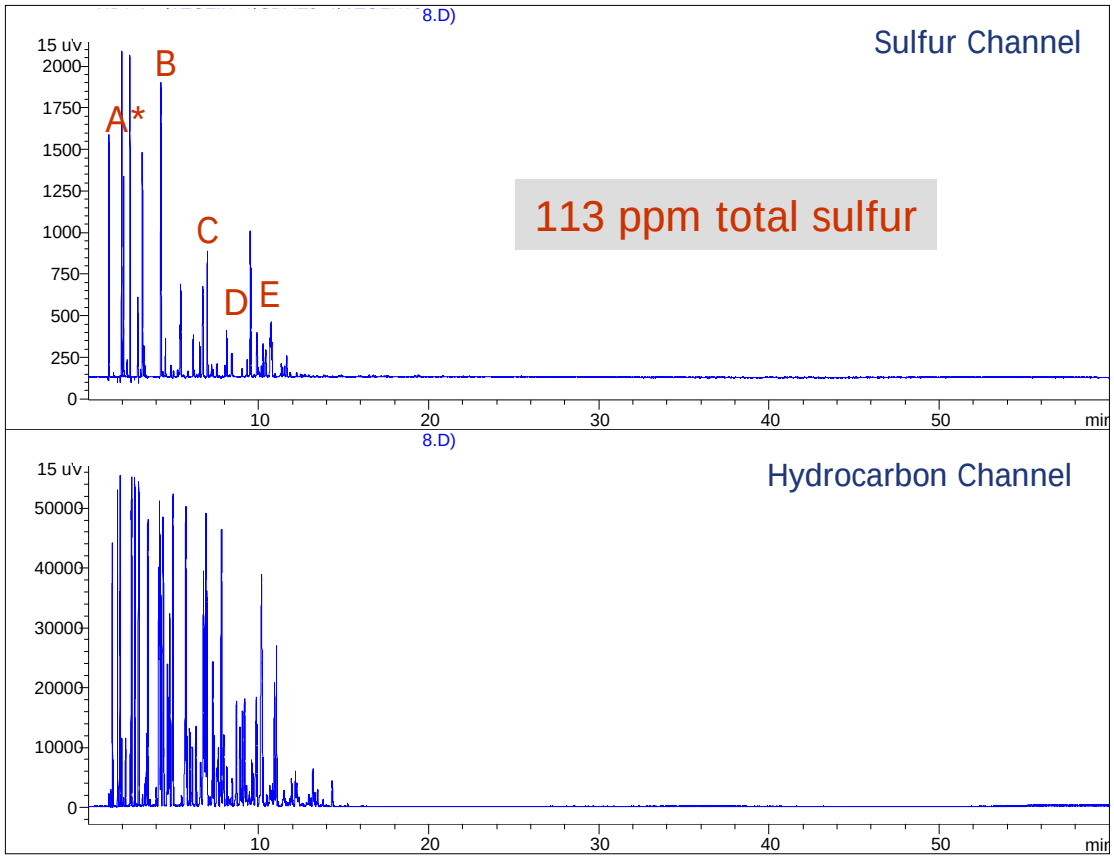
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Sulfur in Naptha Stabilizer Bottoms



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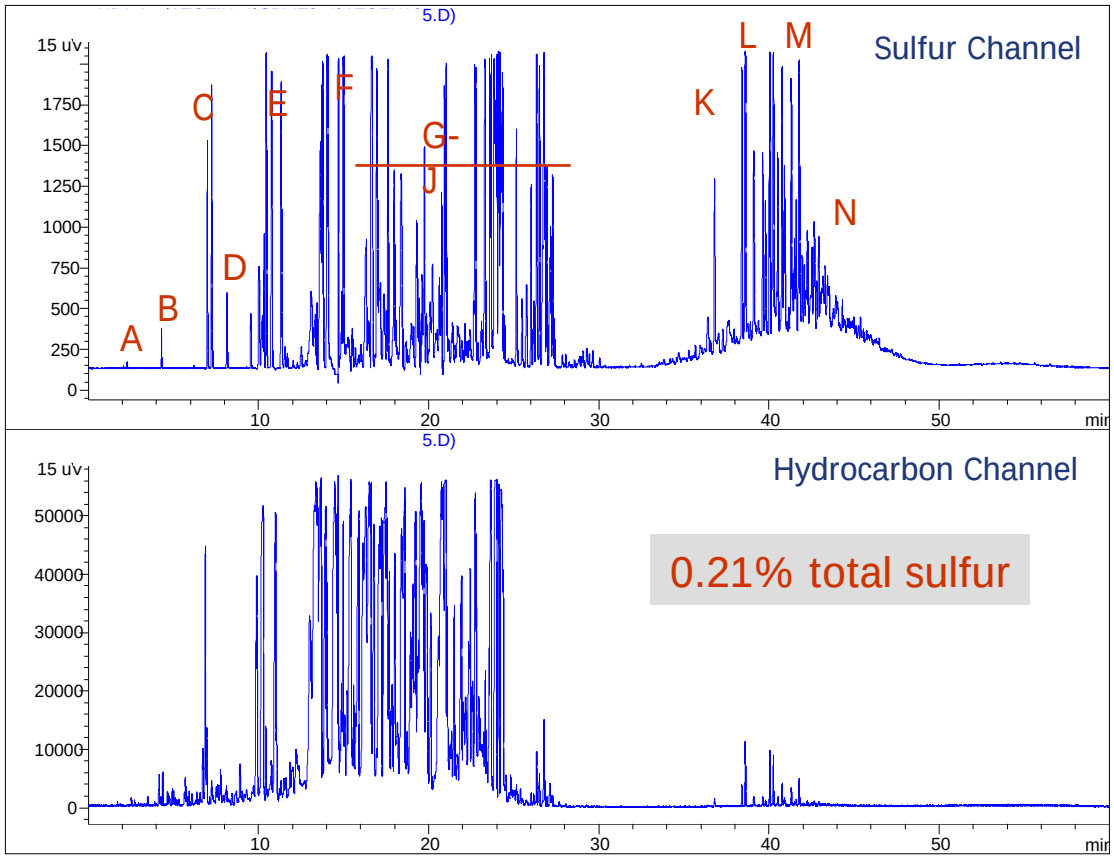
O Alkyl sulfides & substituted thiophenes

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

Sulfur in Heavy Catalytic Naptha



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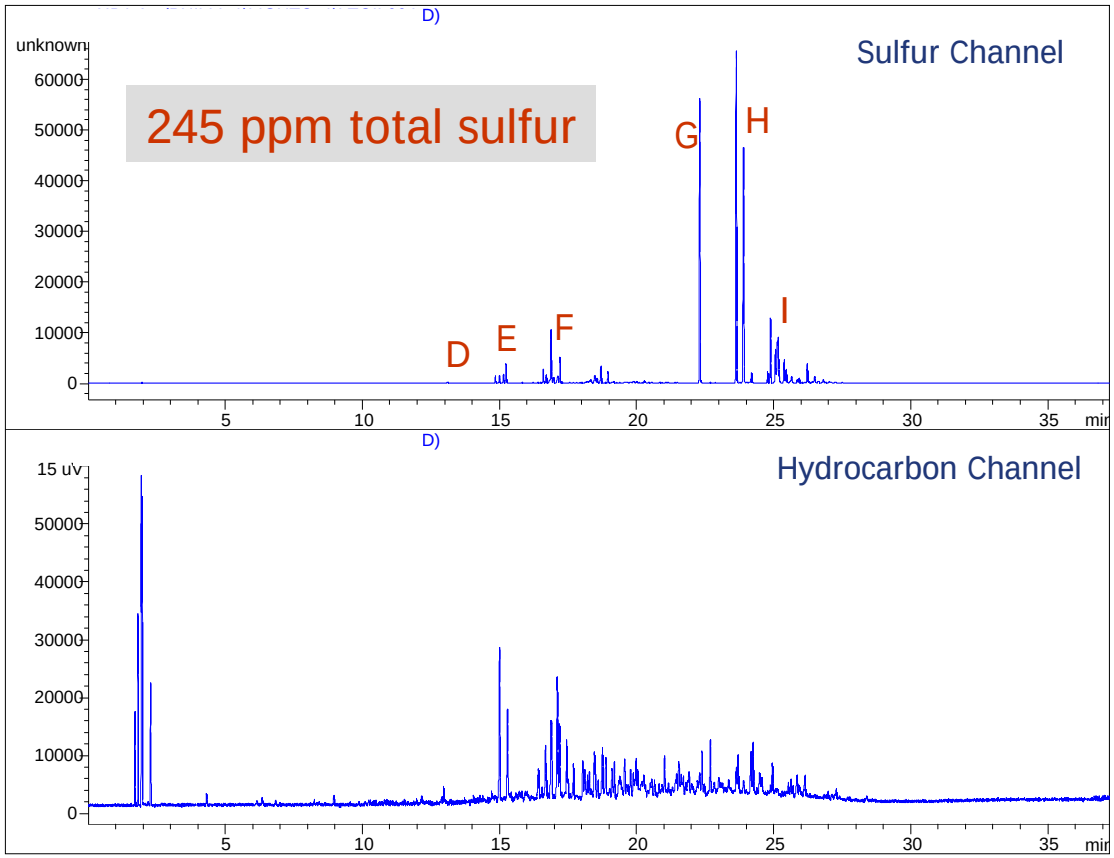
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Total Sulfur in LCO



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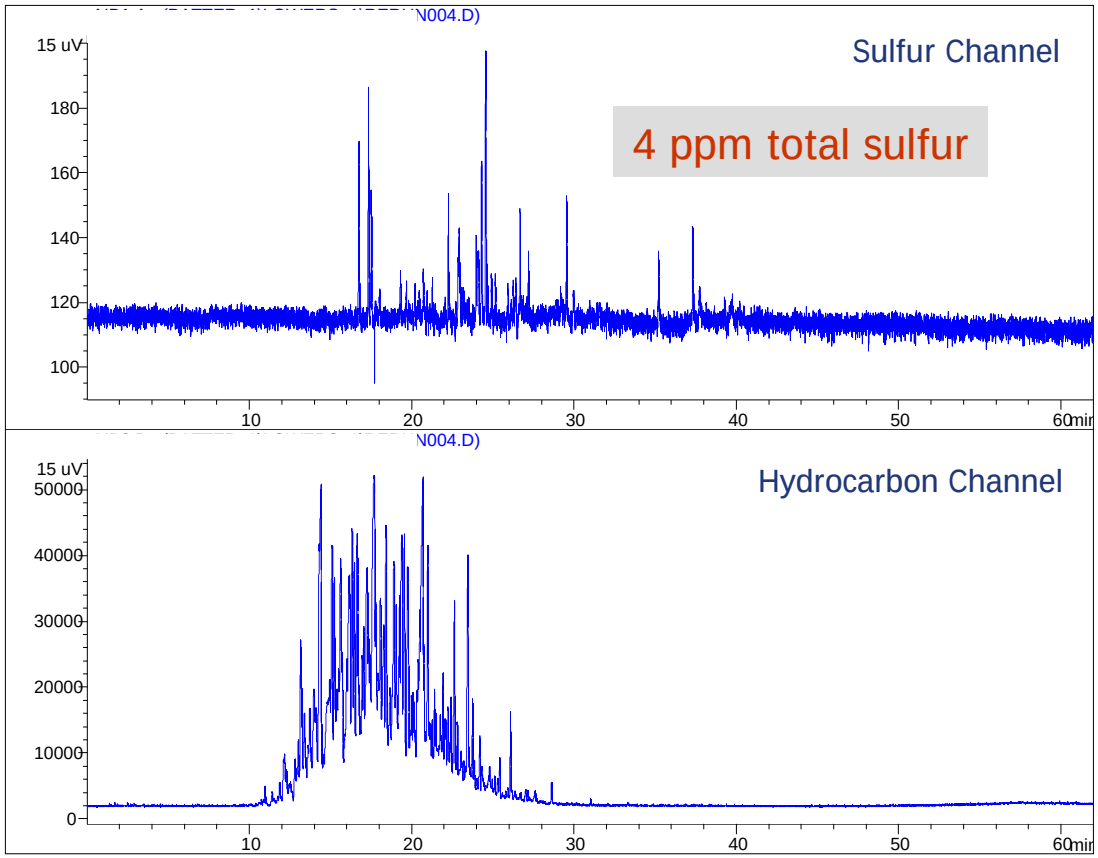
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Low-Level Sulfur in Jet Fuel



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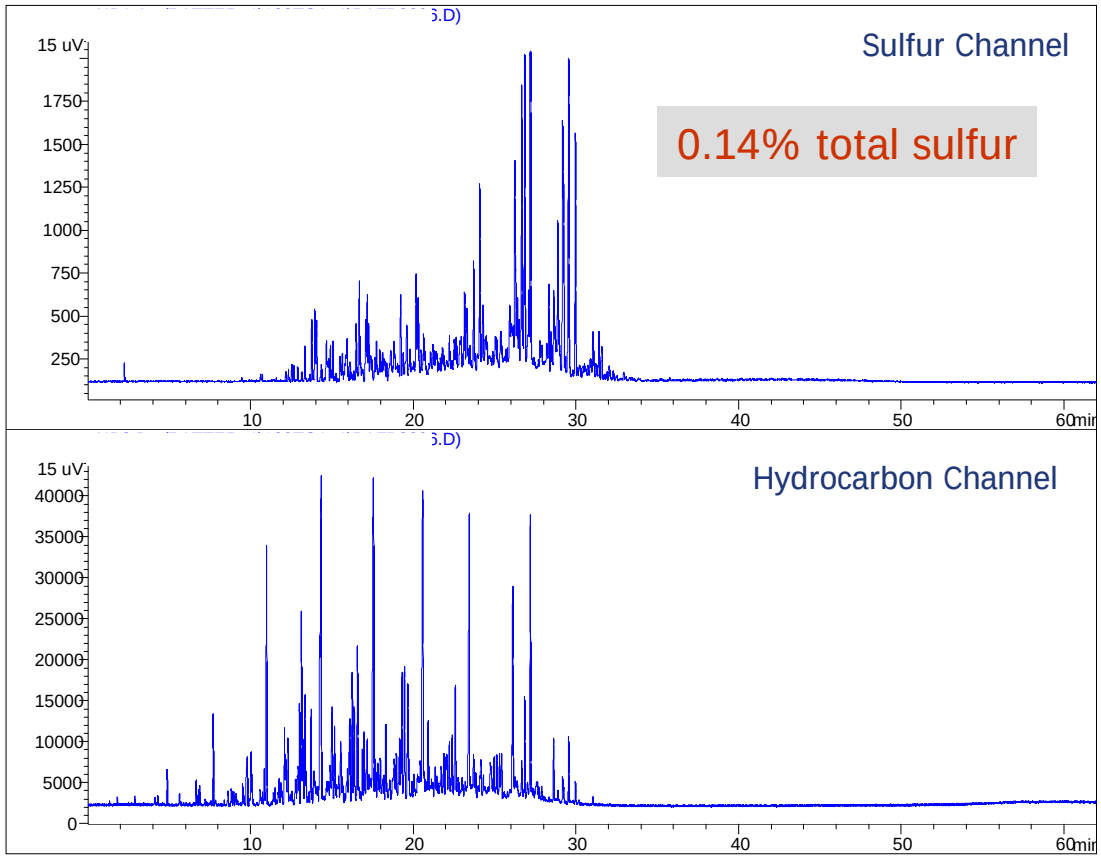
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

High-Level Sulfur in Jet Fuel



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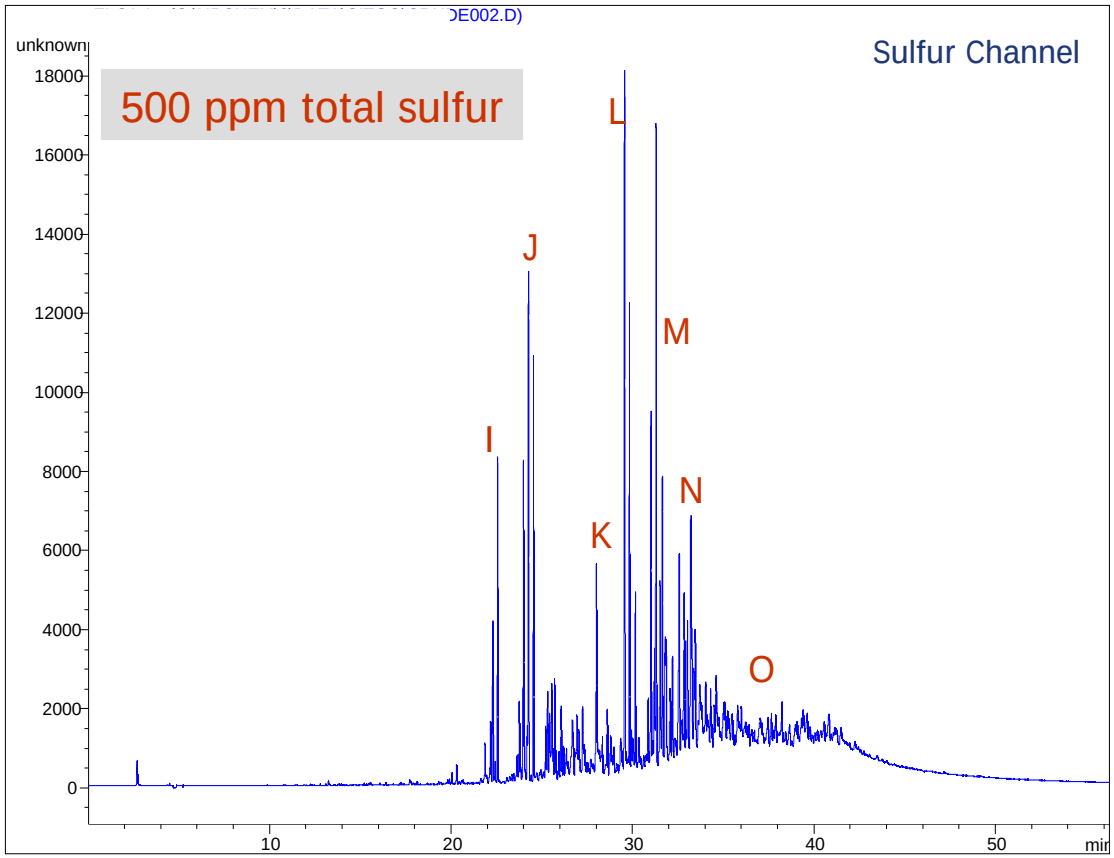
O Alkyl sulfides & substituted thiophenes

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

Total Sulfur in Crude Oil



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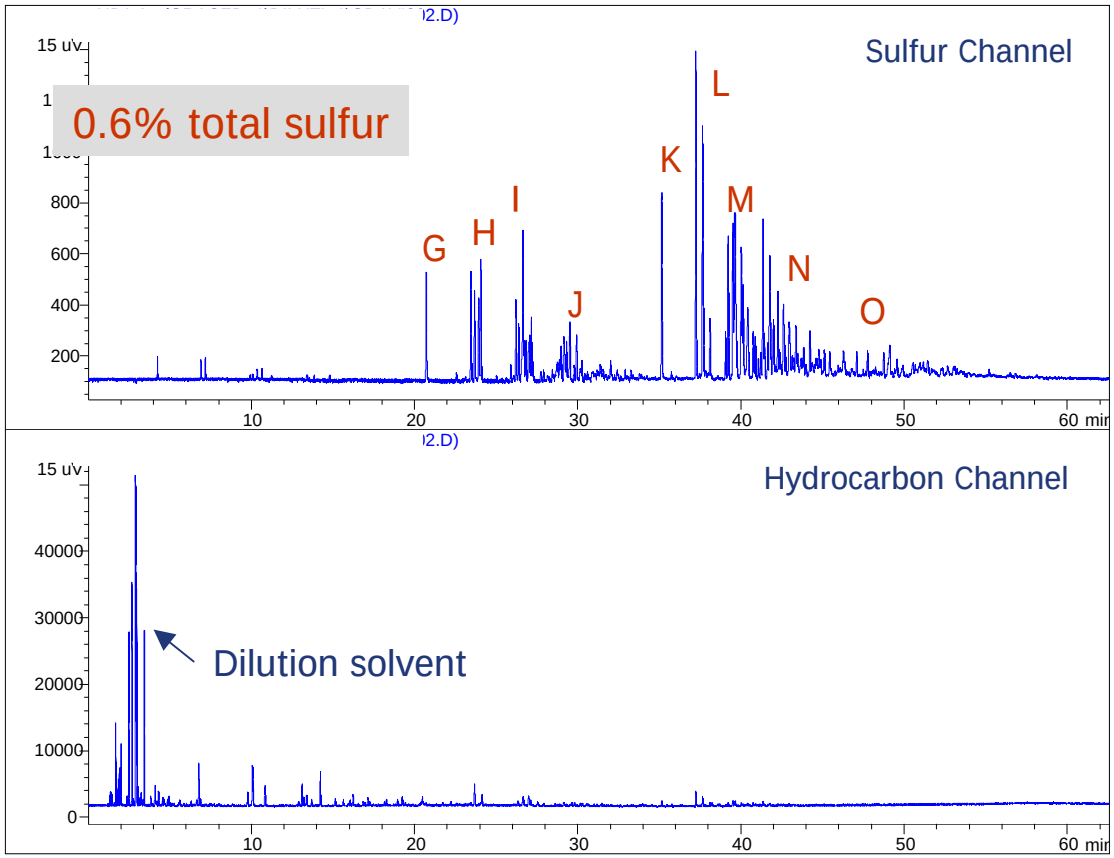
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Sulfur in Synthetic Crude



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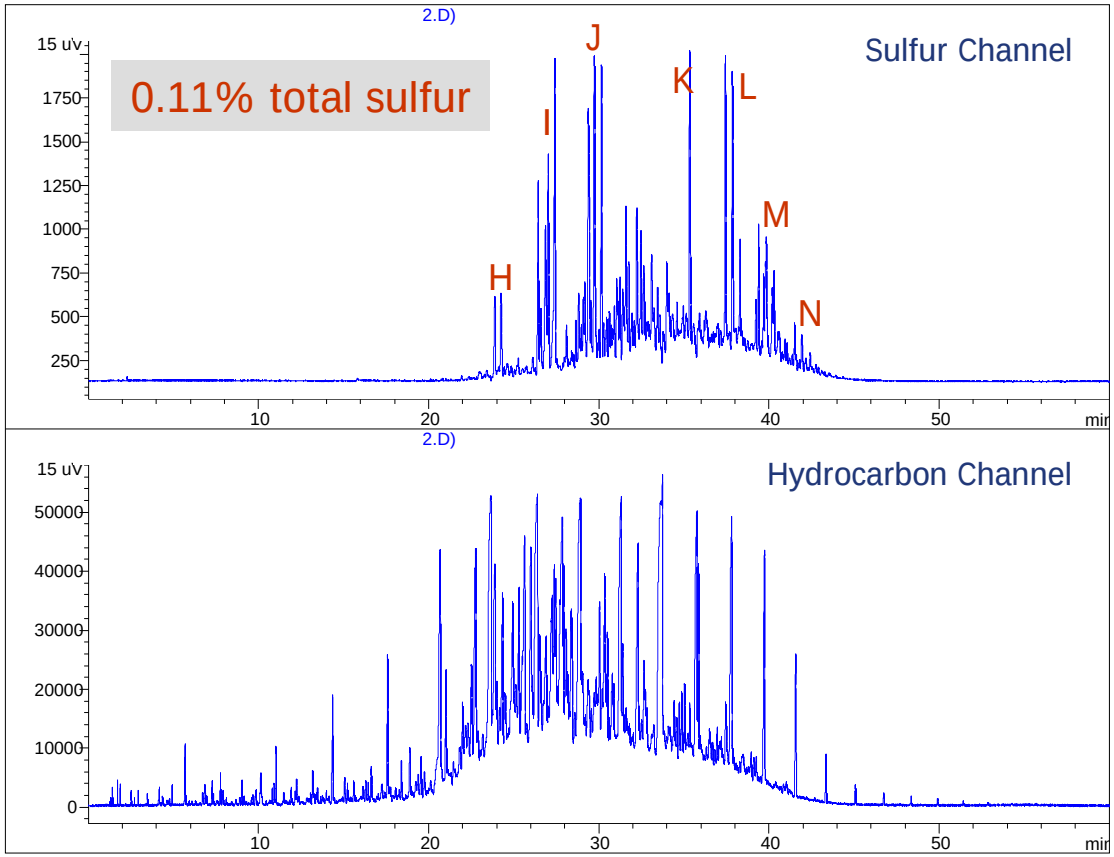
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

High-Level Sulfur in Furnace Oil



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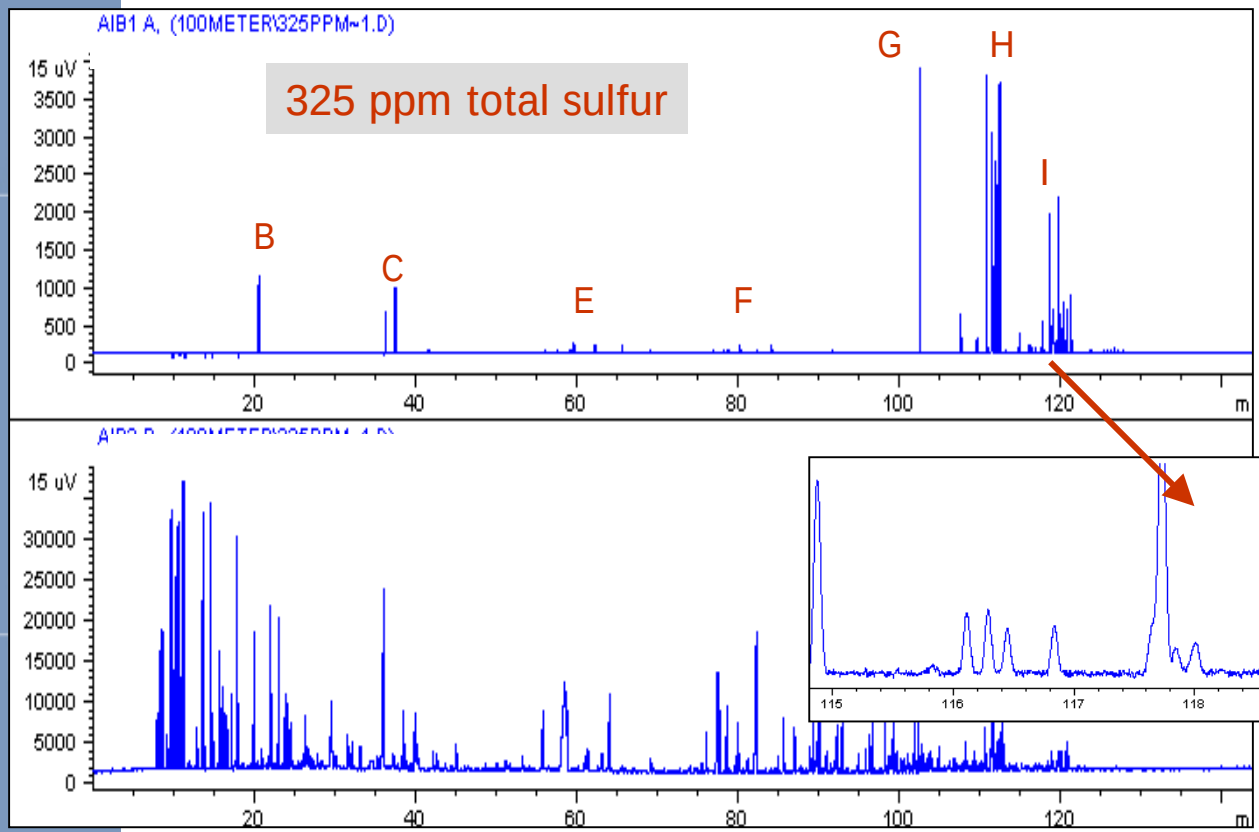
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

“DHA-Type” Sulfur Analysis



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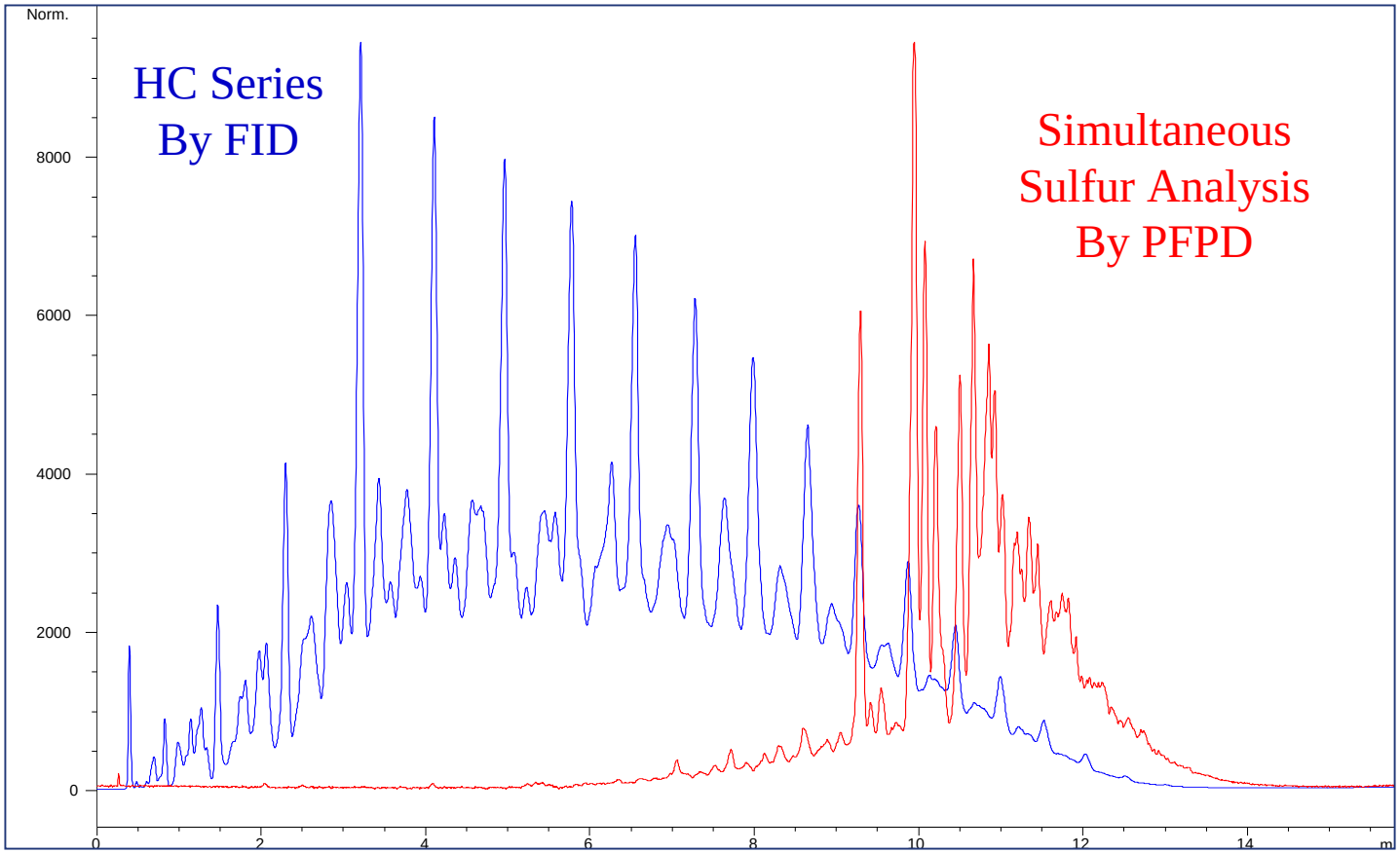
H C1-Benzothiophenes
I C2-Benzothiophenes

substituted thiophenes

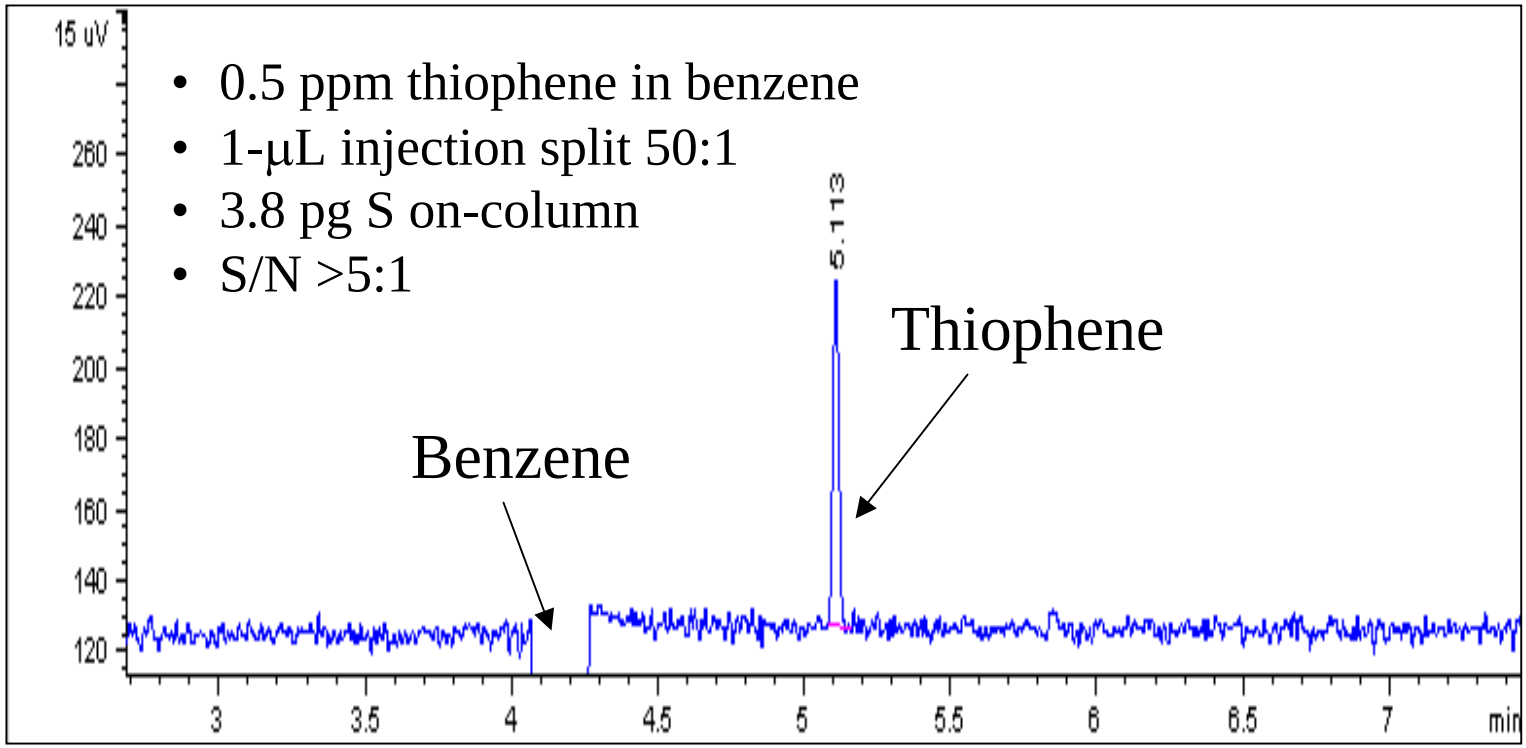
1-µL injection; split 50:1.
Quantified using thiophene as an external standard.

Sulfur by Simulated Distillation



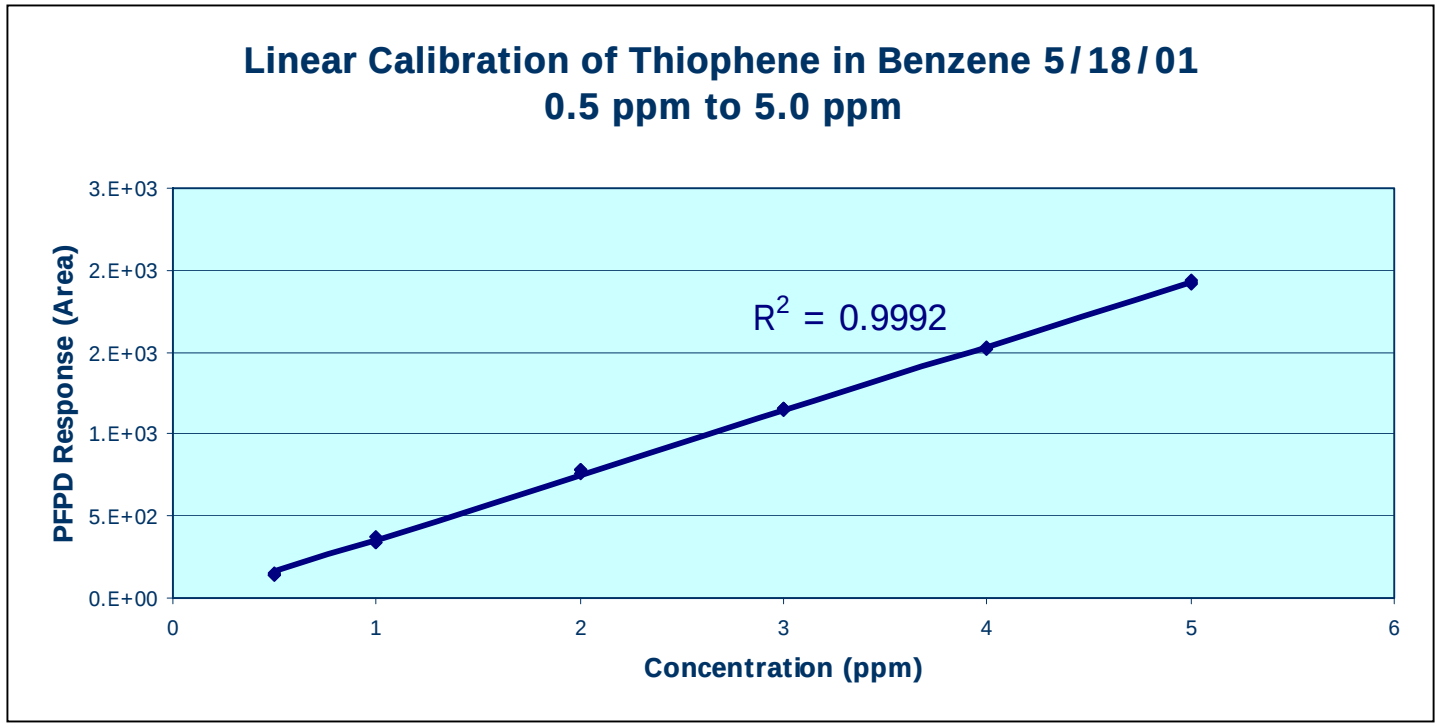
Reference standard for ASTM Method D2887-02
used as a calibration standard for simulated distillation.

0.5 ppm Thiophene in Benzene



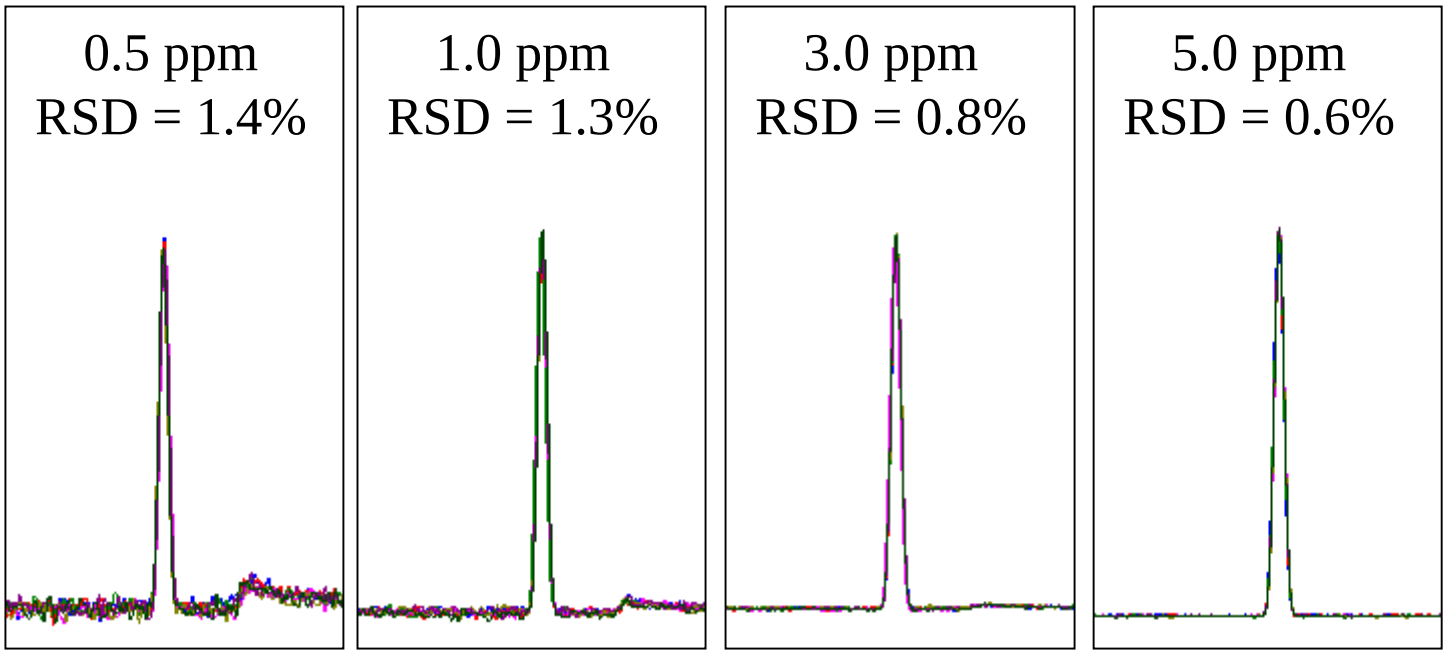
- 0.5 ppm thiophene in benzene
- 1-µL injection split 50:1
- 3.8 pg S on-column
- S/N >5:1

Thiophene Linear Calibration Plot

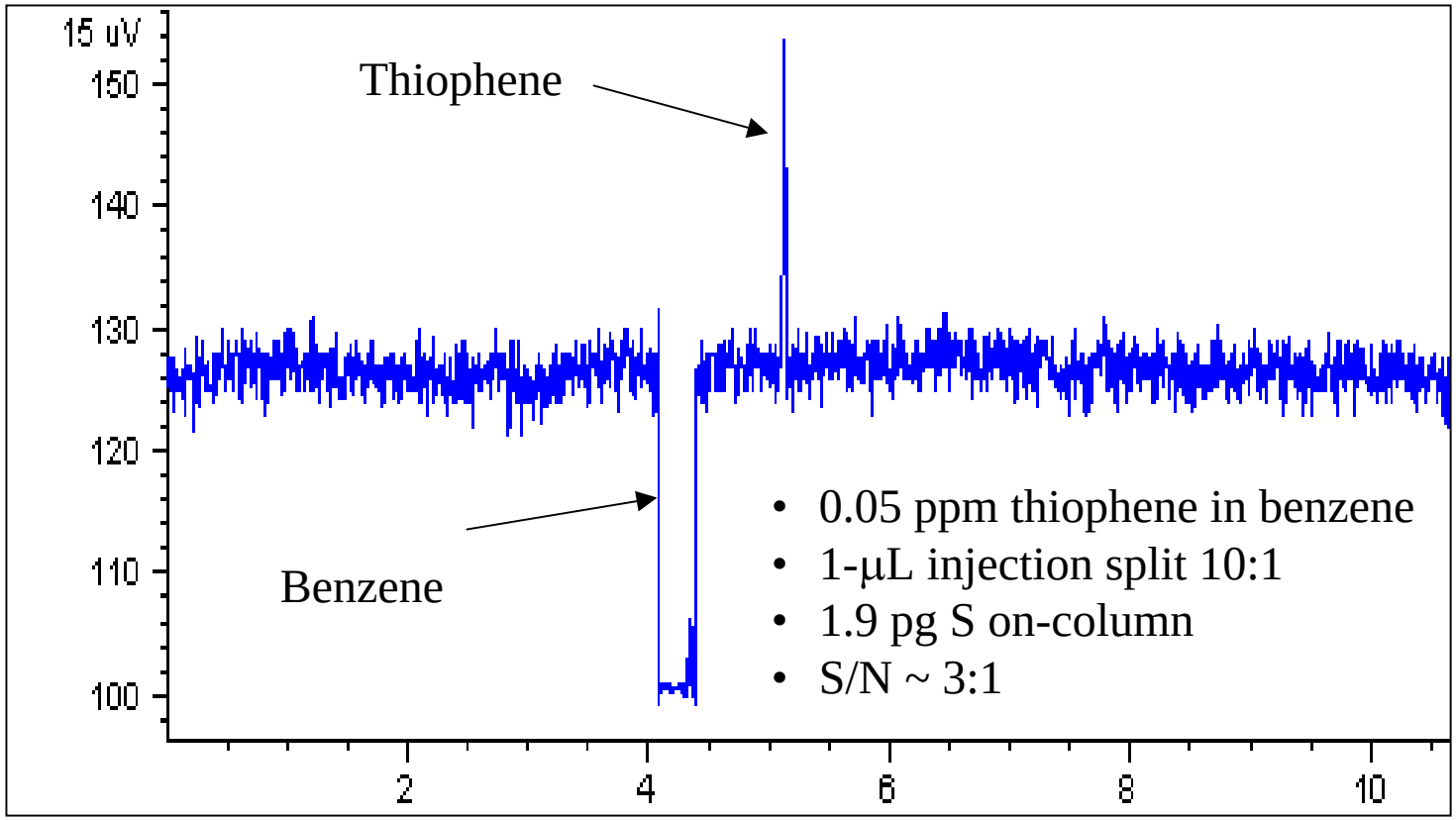


Thiophene Precision on the PFPD

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



Thiophene Sensitivity on the PFPD



Organophosphorus Pesticides

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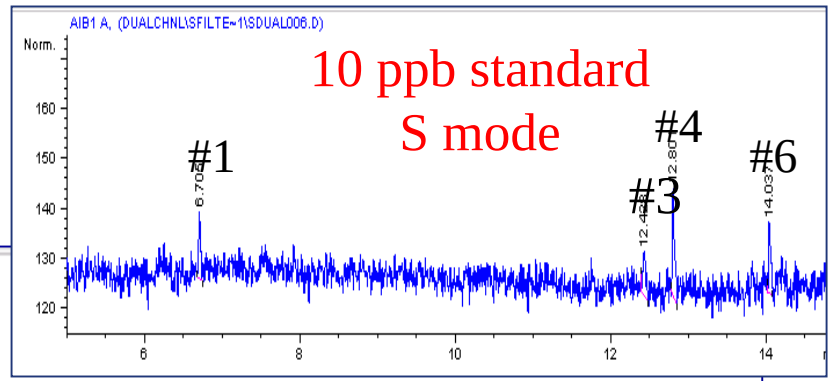
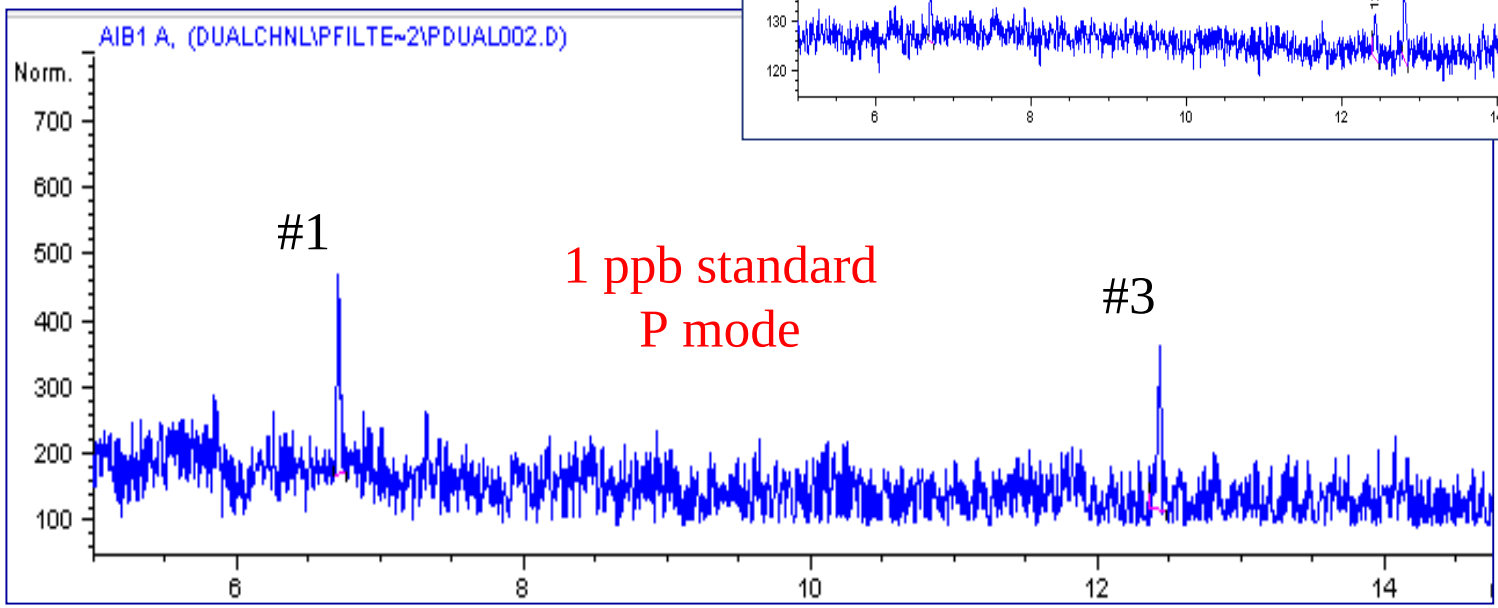
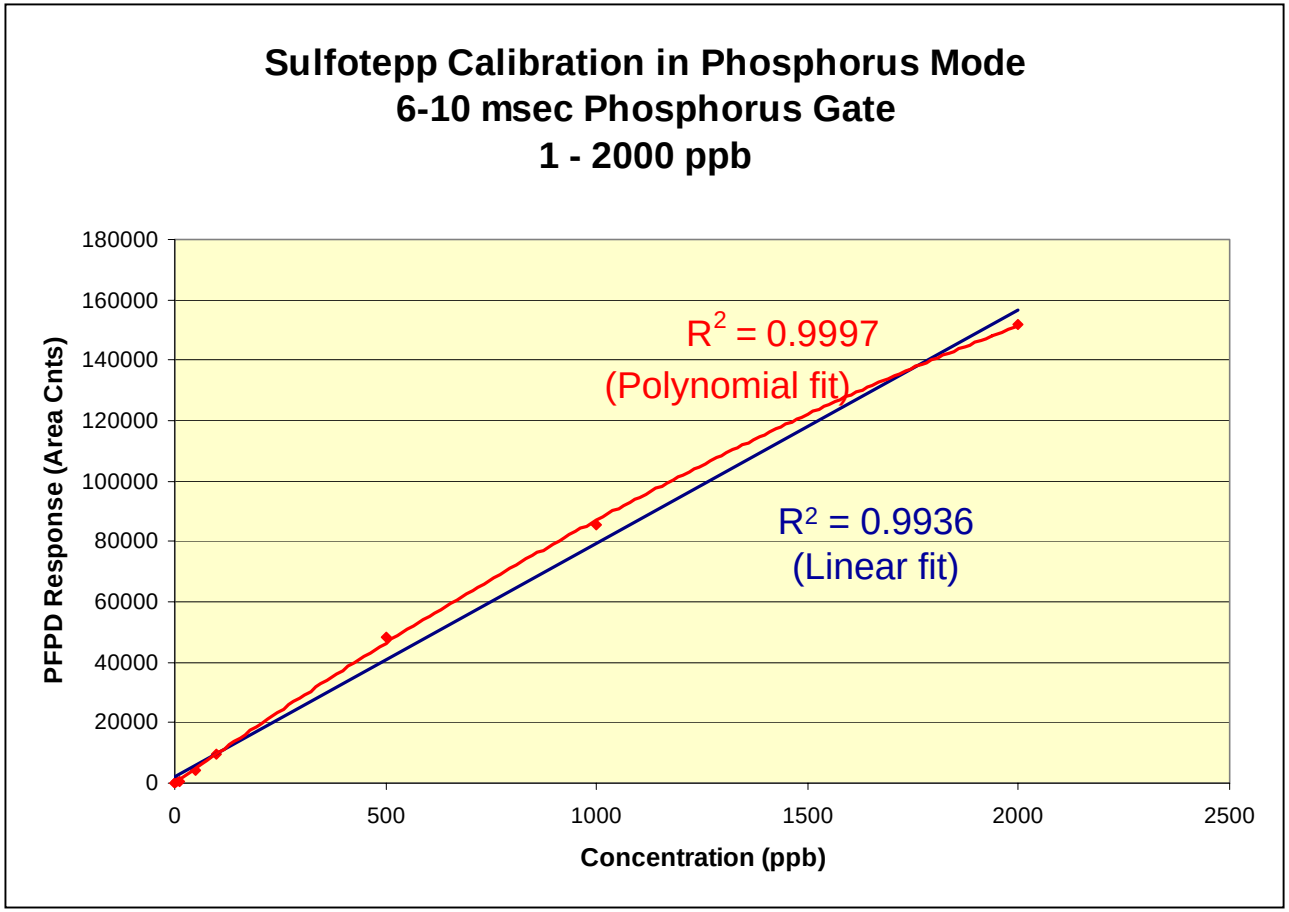
OP Pesticide Detection Limits

- Two compounds detected at 1 ppb
- #1 with one P atom
- #3 with two P atoms
- Compare to 10 ppb in S mode

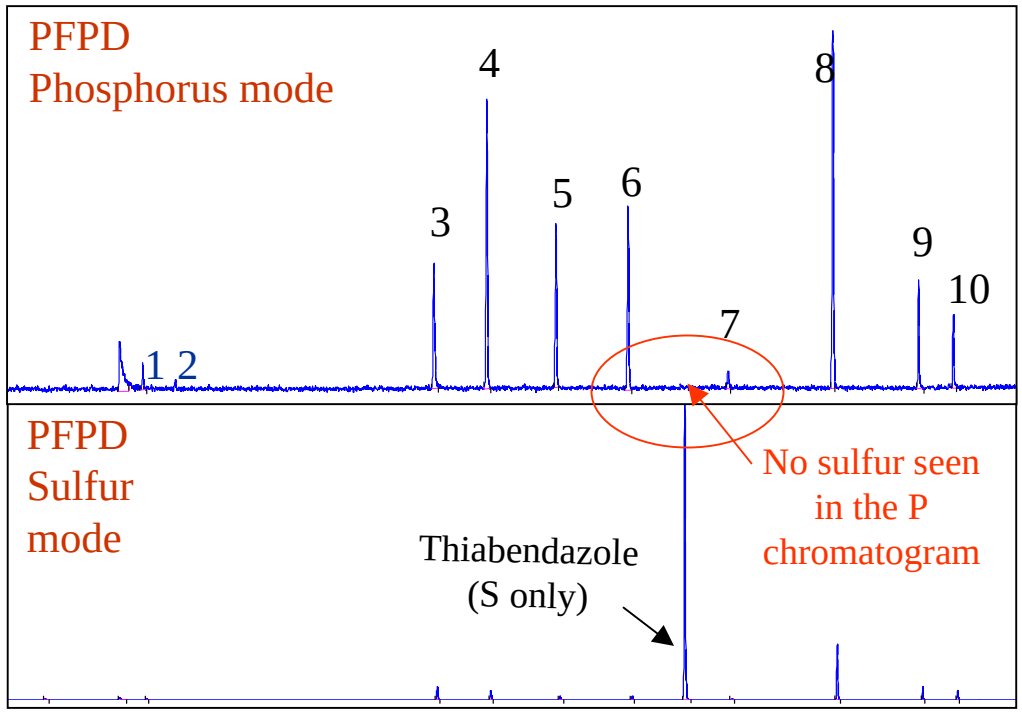




OP Pesticide Calibration Range



Simultaneous Phosphorus & Sulfur



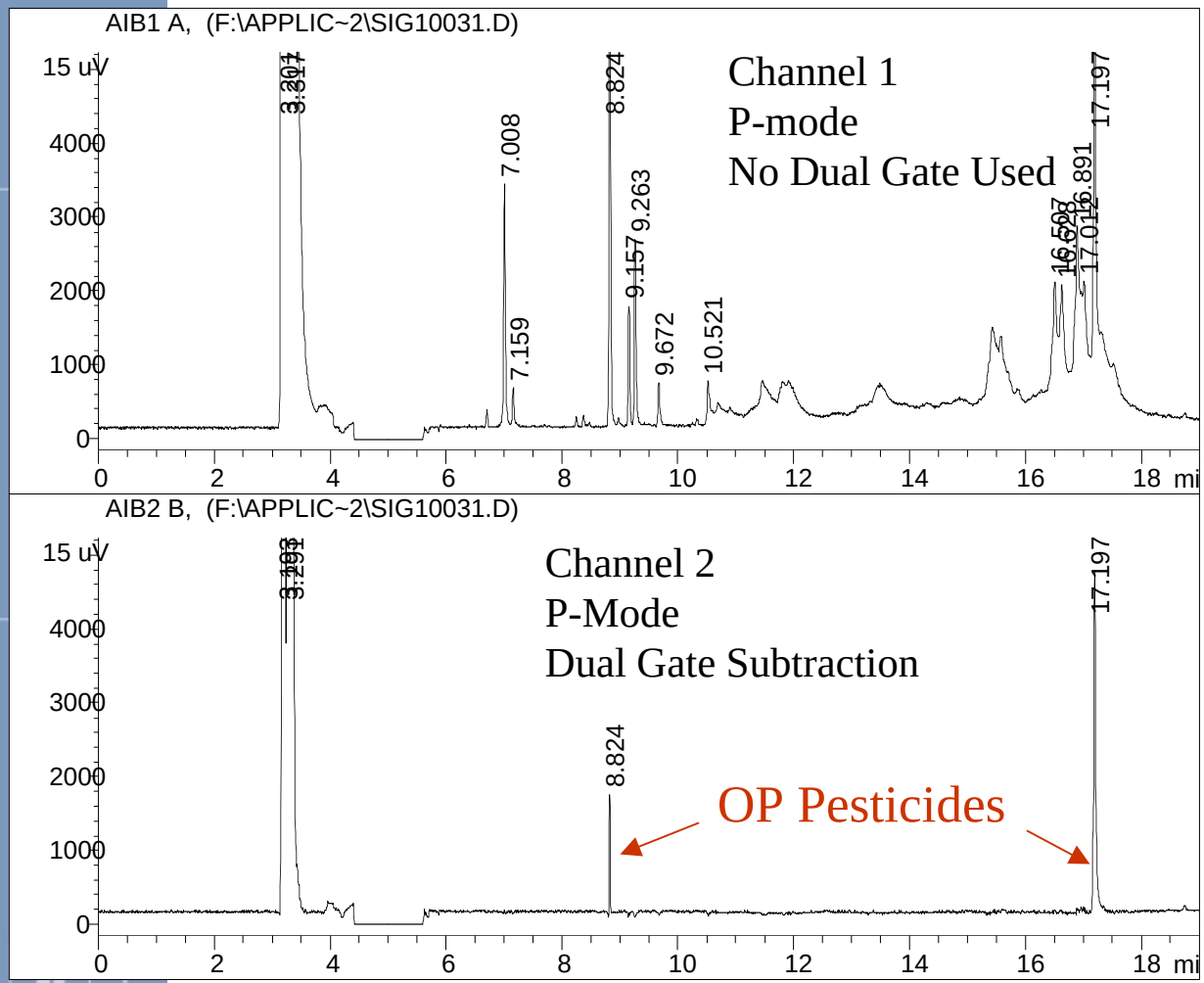
- Compounds 1–10 contain both P and S
- Thiabendazole contains only S
- PFPD produces simultaneous, mutually selective phosphorus and sulfur chromatograms using Dual Gate Subtraction

	Compound	ppb
1	Methamidophos	100
2	Acephate	60
3	Dimethoate	60
4	Diazinon	60
5	Chlorpyrifos-Me	50
6	Chlorpyrifos	50
7	Disulfoton sulfone	50
8	Ethiohn	60
9	Phosmet	100
10	Azinphos-Me	150

Plus

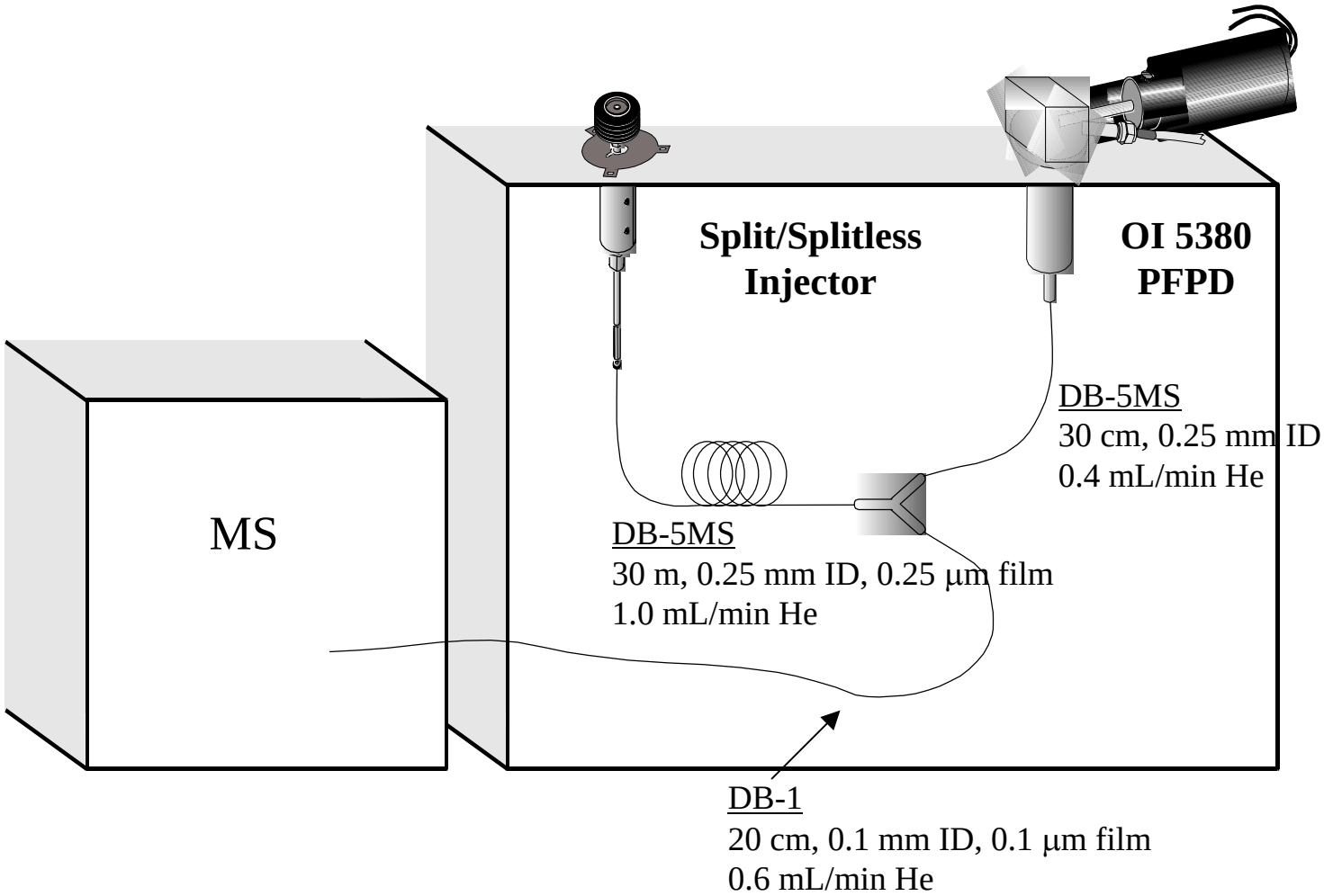
Thiabendazole ~ 1 ppm (sulfur only)

Dual Gate Subtraction



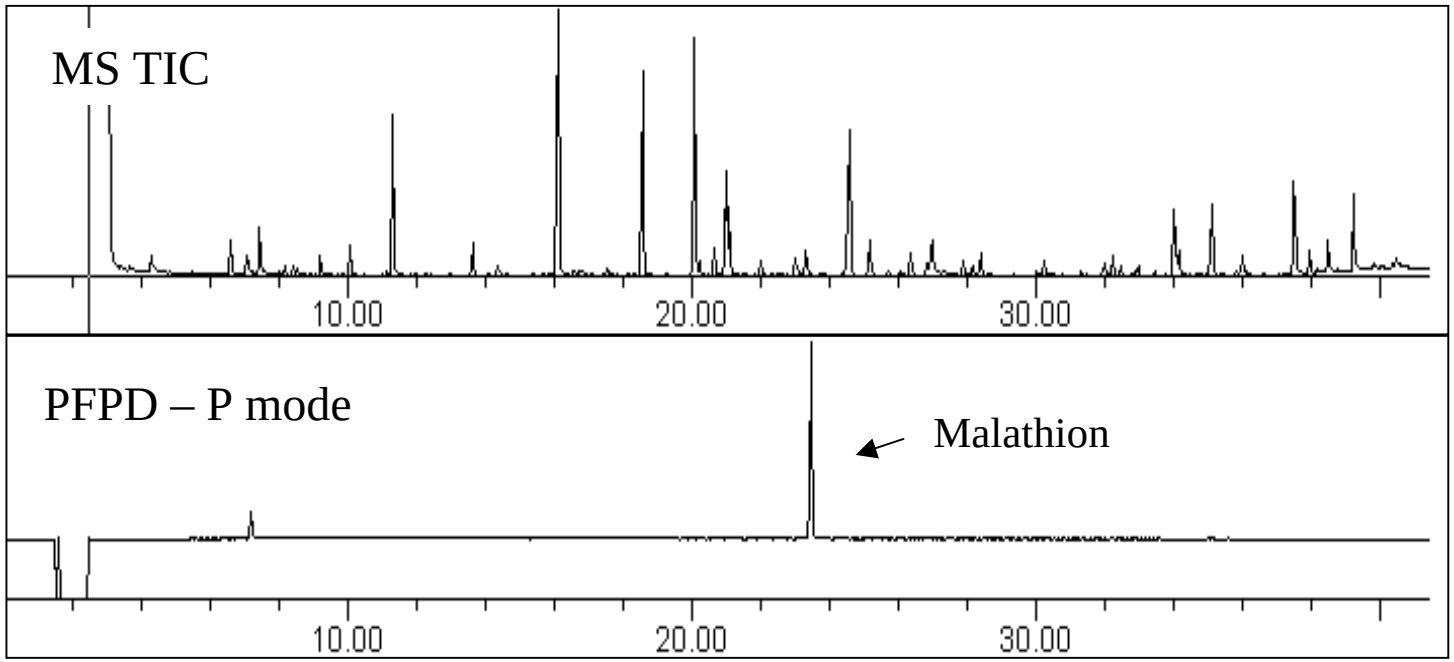
- Onion extract; no clean-up
- Large interfering sulfur background
- Ch1 – No subtraction
- Ch2 – Sulfur background subtracted using PFPDView & Dual Gate Subtraction

PFPD-MS Tandem Configuration



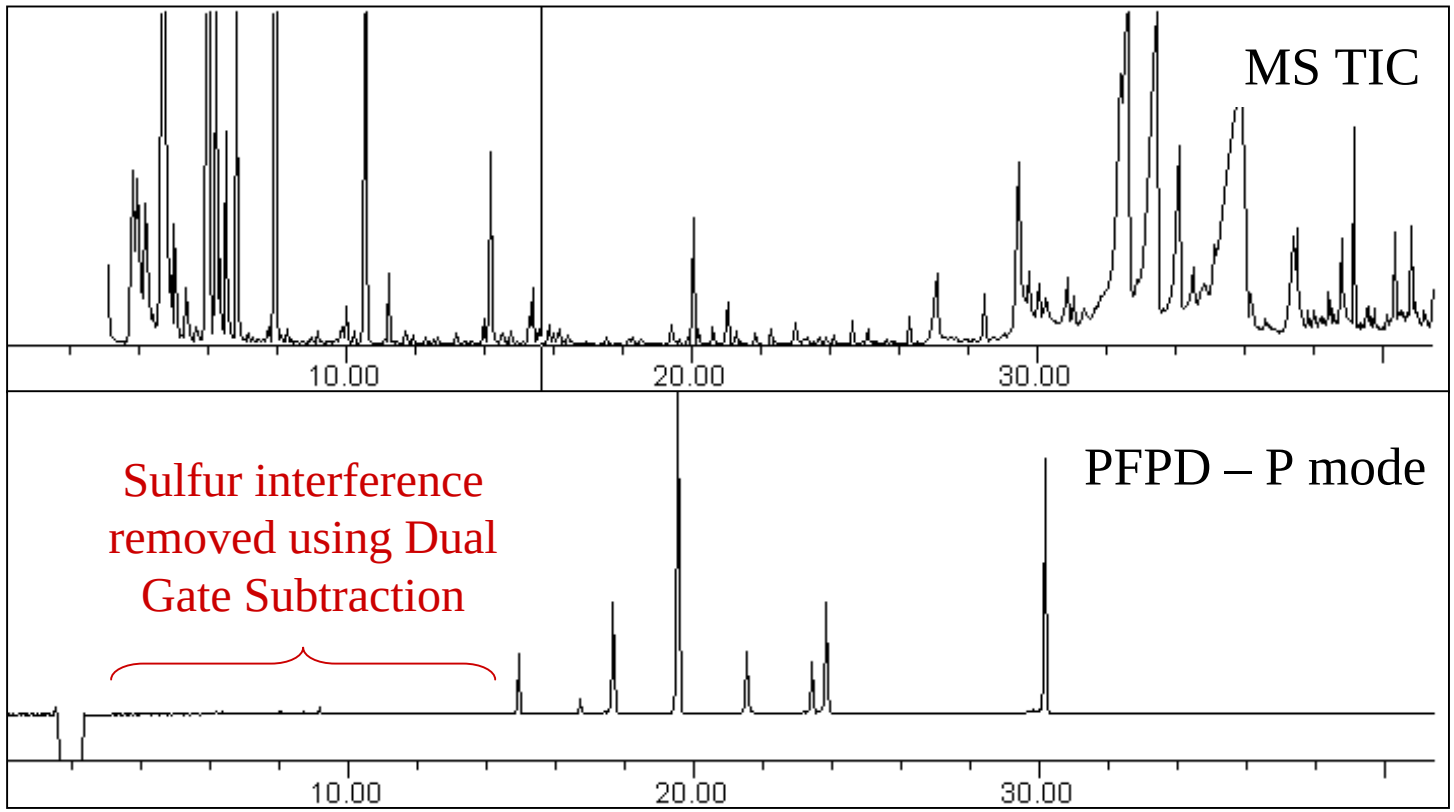
Coriander Spiked with 1-ppm Malathion

The PFPD is used in parallel with the MS to identify RT of OP pesticides in the presence of complex background.

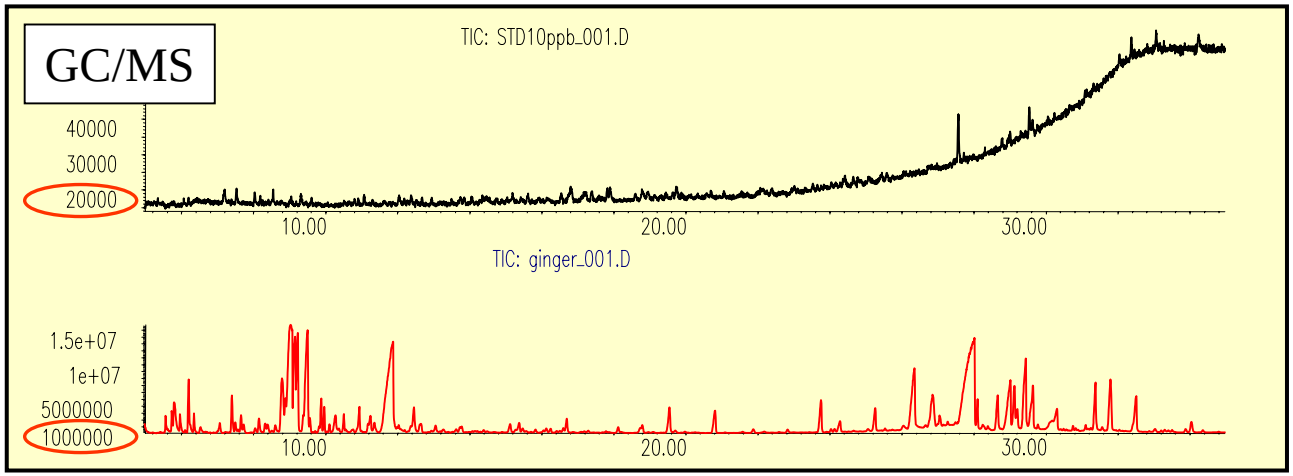


Broccoli Spiked with Method 614 Mix

Dual Gate Subtraction can also be used to remove interferences.

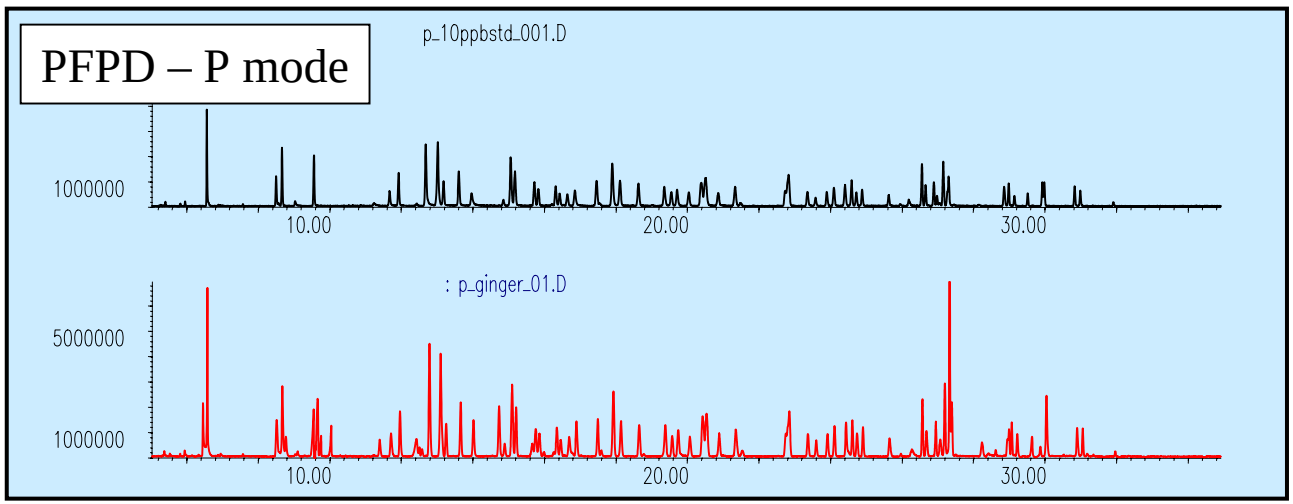


Ginger Extract With 10-ppb OP Pesticides



Stnd Mix
307 compounds
10 ppb

Ginger extract +
307 compounds
10 ppb

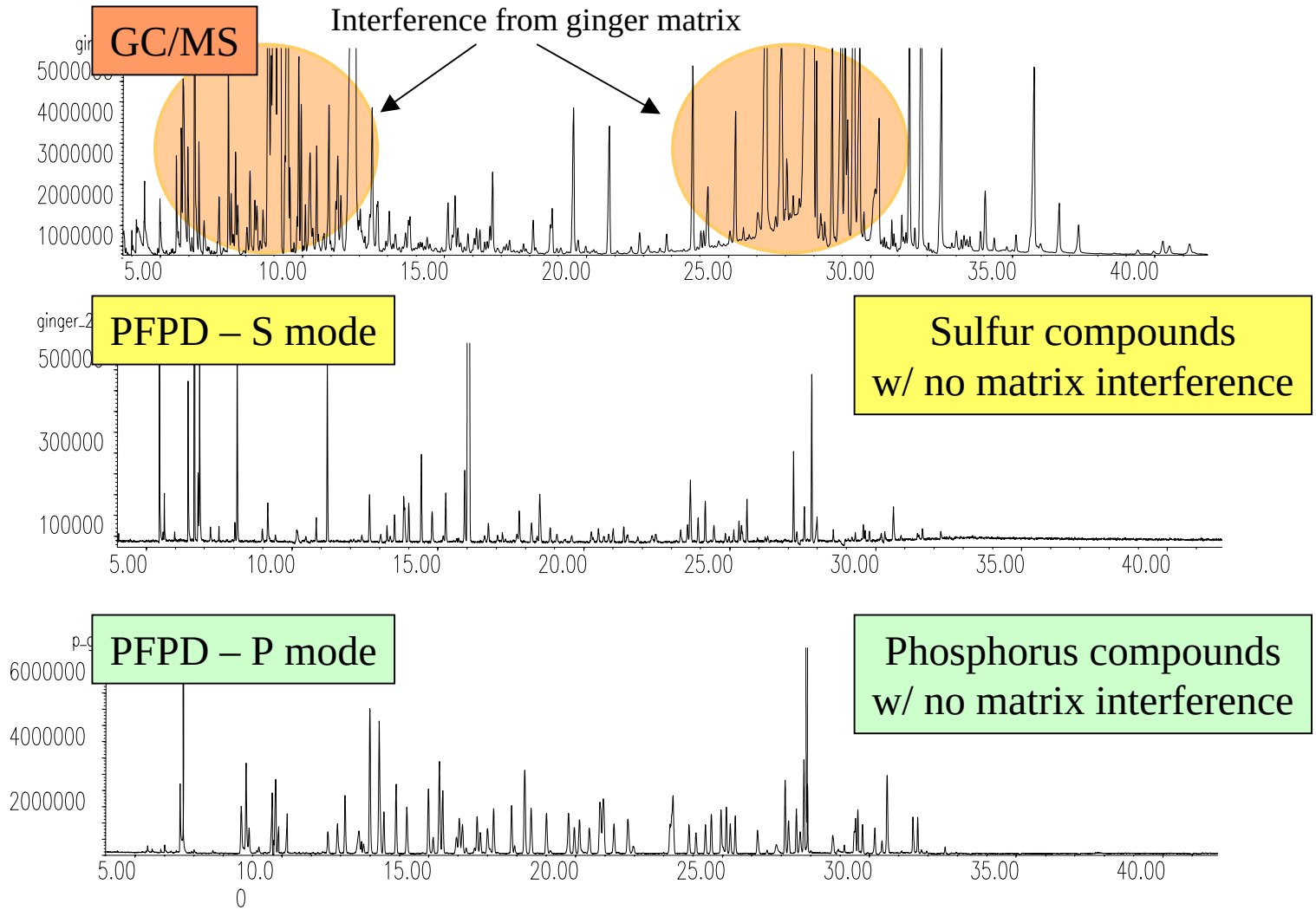


Stnd Mix
307 compounds
10 ppb

Ginger extract +
307 compounds
10 ppb

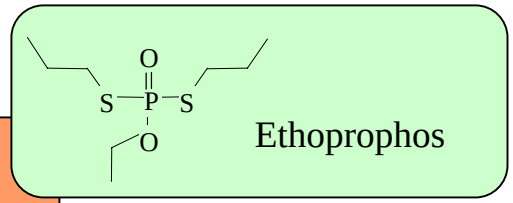
Courtesy of Kinryo Electric, Japan

Ginger Extract With 10-ppb OP Pesticides

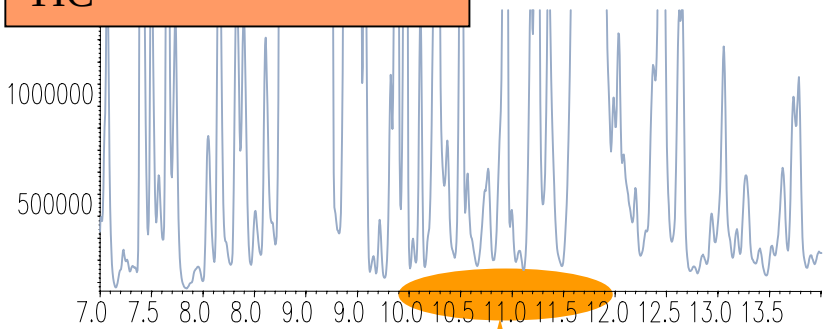


Courtesy of Kinryo Electric, Japan

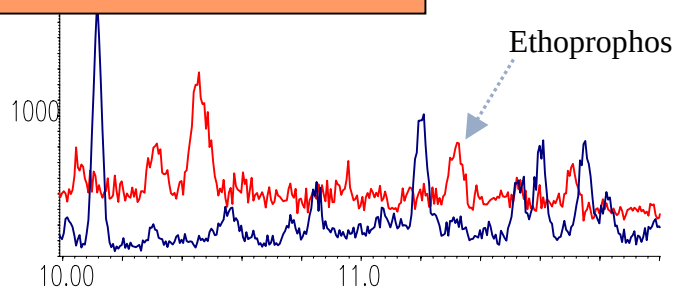
Ginger Extract With 10-ppb OP Pesticides



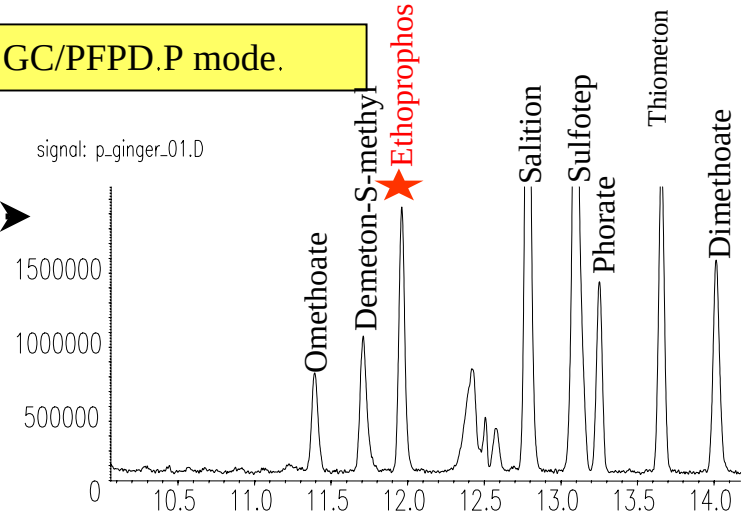
GC/MS (scan mode.
TIC



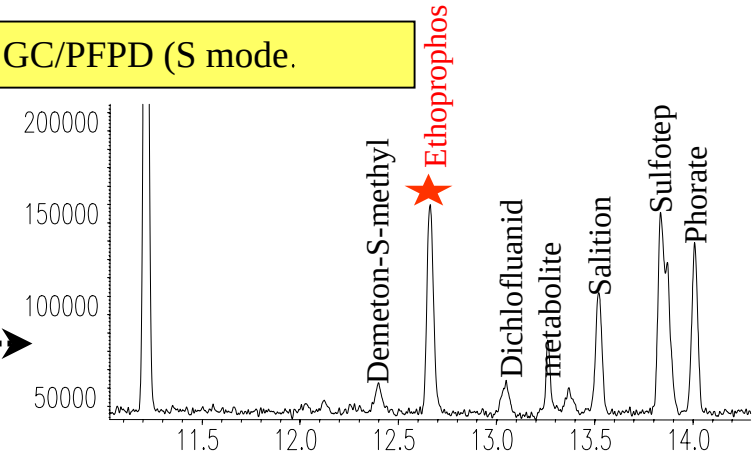
GC/MS (scan mode.
EICP m/z 158 and 200



GC/PFPD.P mode.



GC/PFPD (S mode.



No matrix interference with PFPD

Carbamate Pesticides

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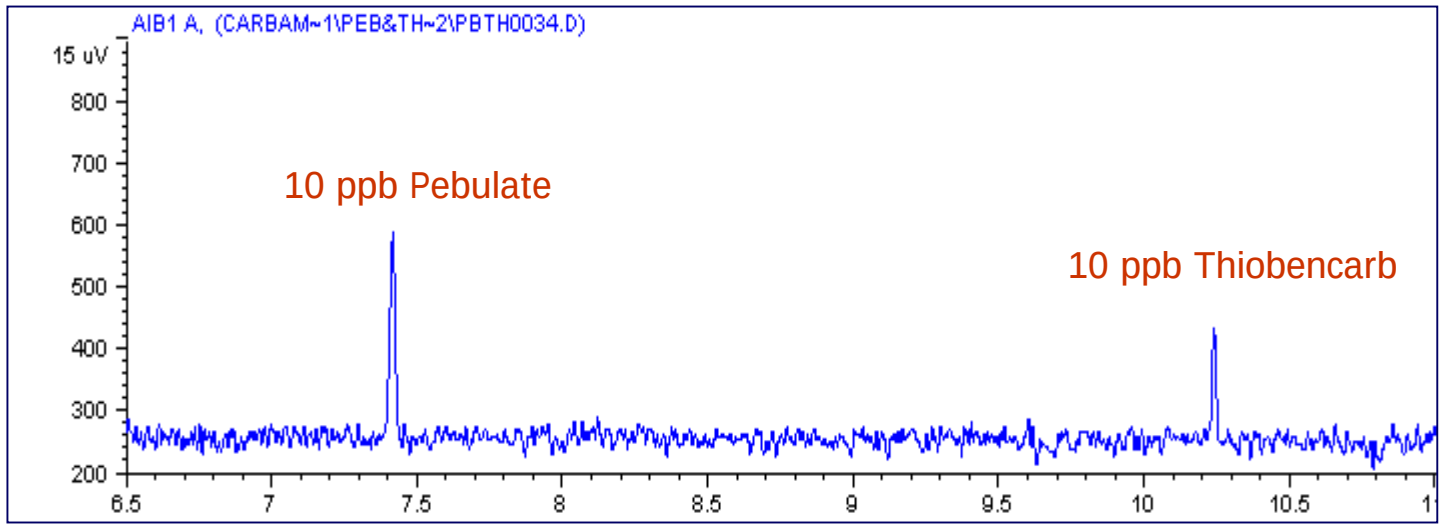
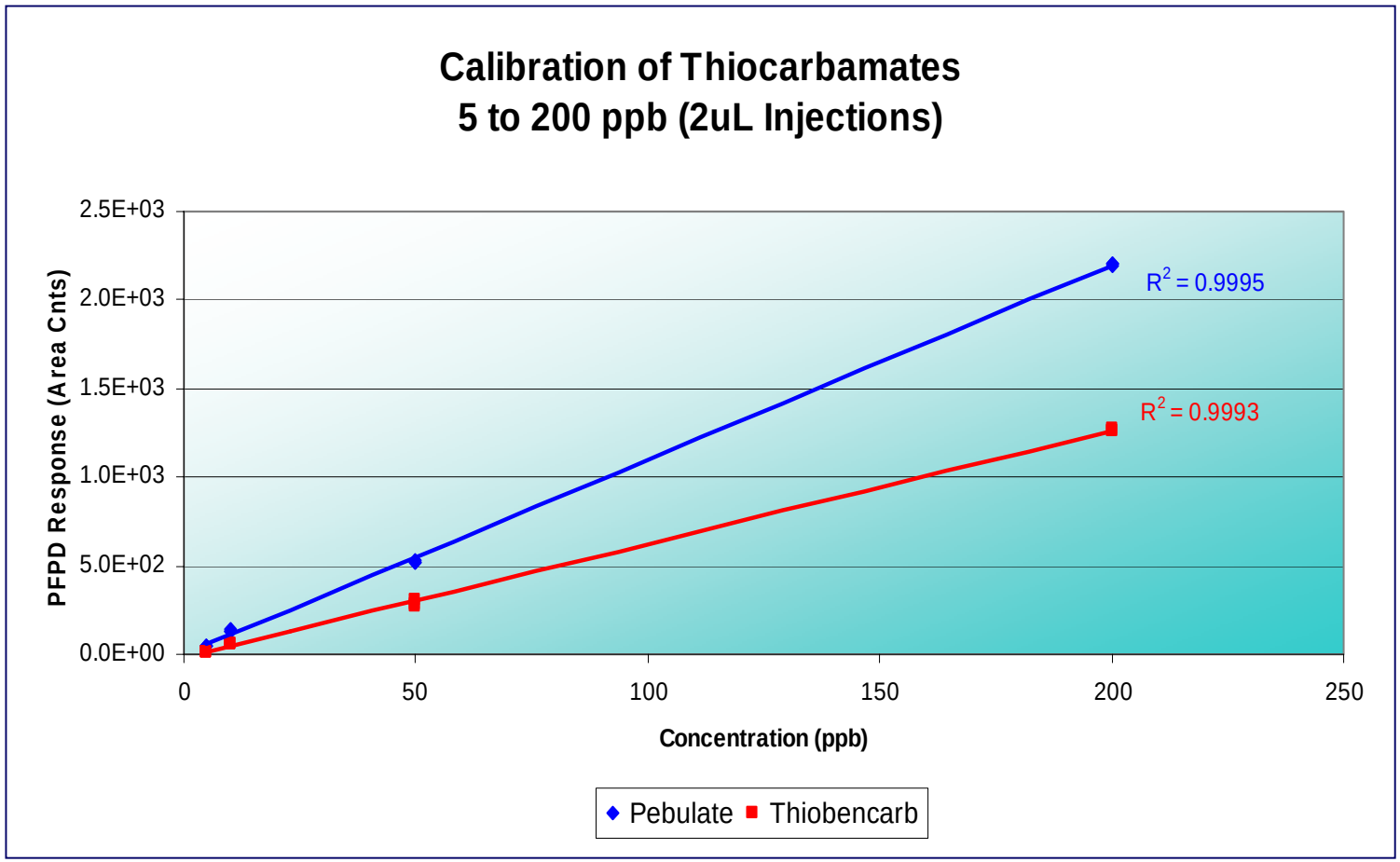
10-ppb Pebulate & Thiobencarb

- 2-µL injection; pulsed splitless mode
- Injector temperature 250 °C
- HP-5 column, 30-m x 0.32-mm ID x 0.25-µm film
- 60 °C for 1 minute, 20 °C/min to 300 °C, hold 1 minute

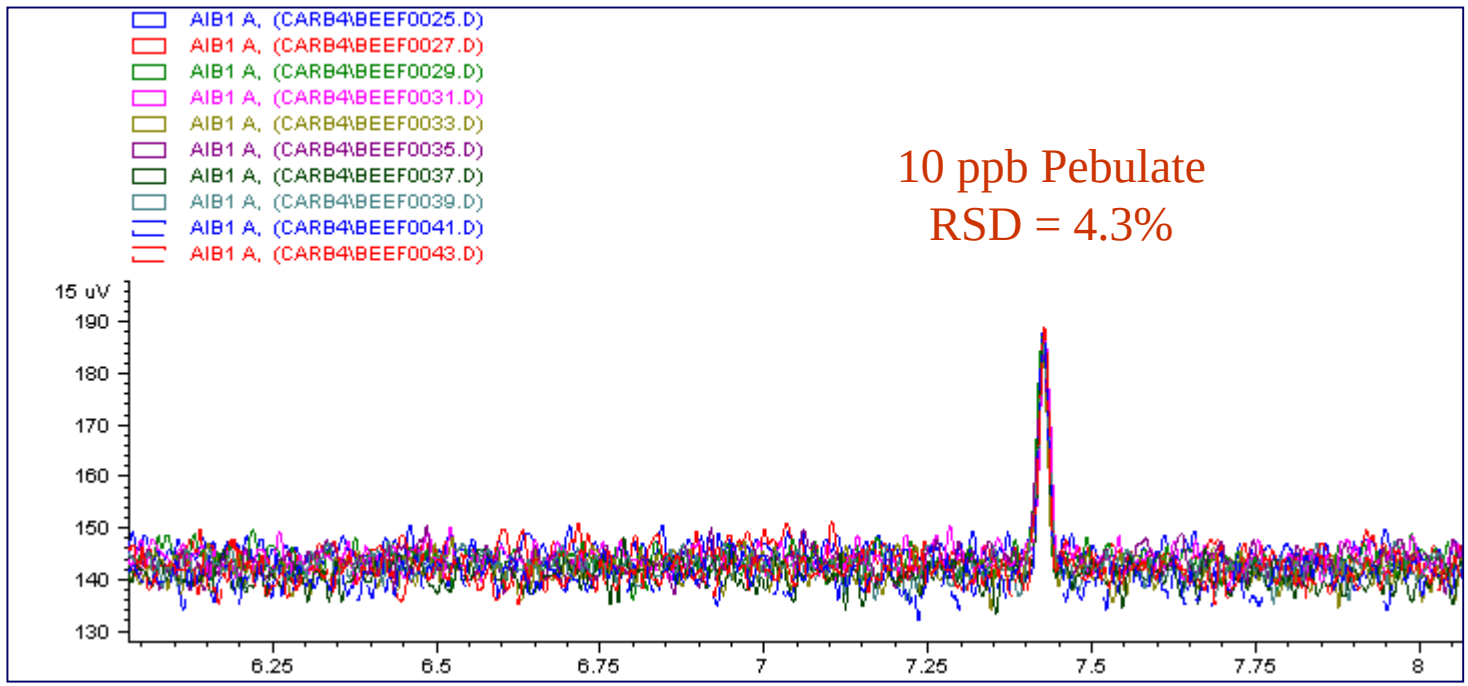


Calibration Curves 5 - 200 ppb



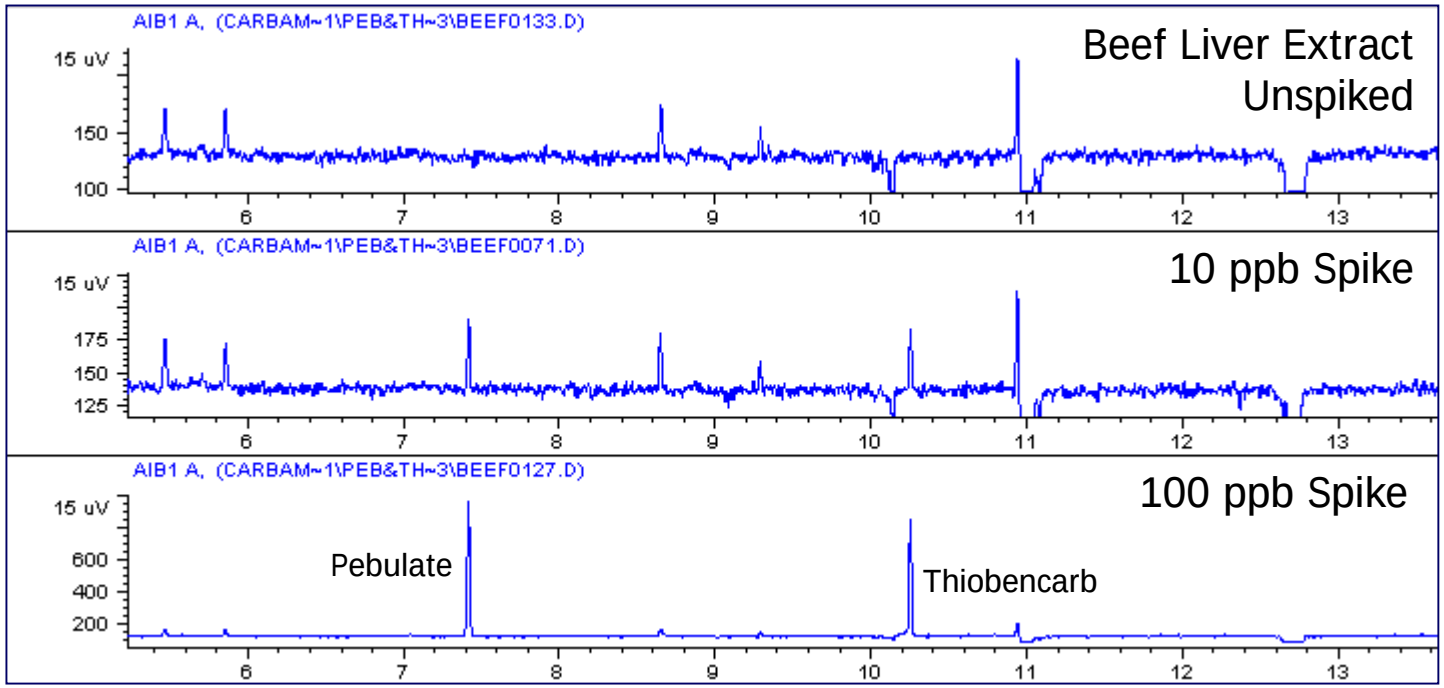
Repeatability at 10 ppb

- 10 ppb pebulate RSD = 4.3% (n=10)
- 10 ppb thiobencarb RSD = 6.9% (n=10)



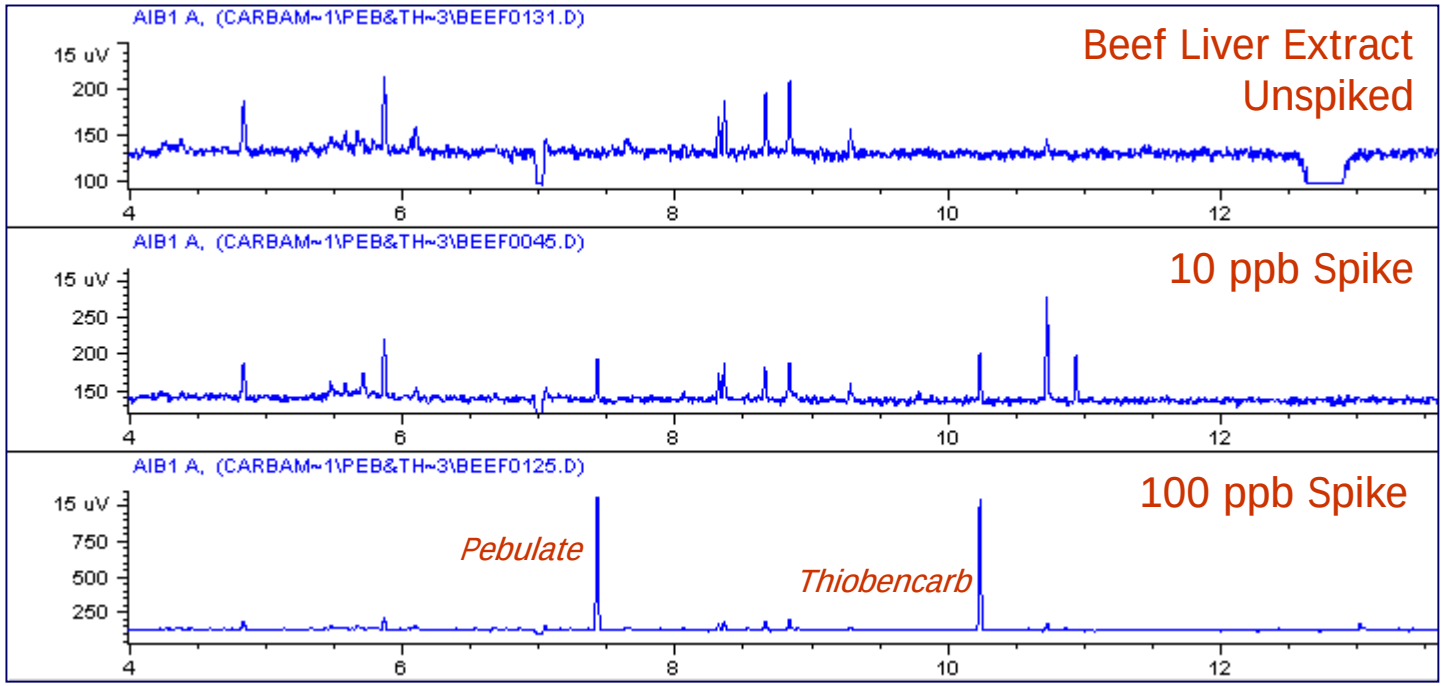
Carbamates in Beef Fat

- 2-µL splitless injection – GC – PFPD
- Pebulate & Thiobencarb at 10 ppb or less



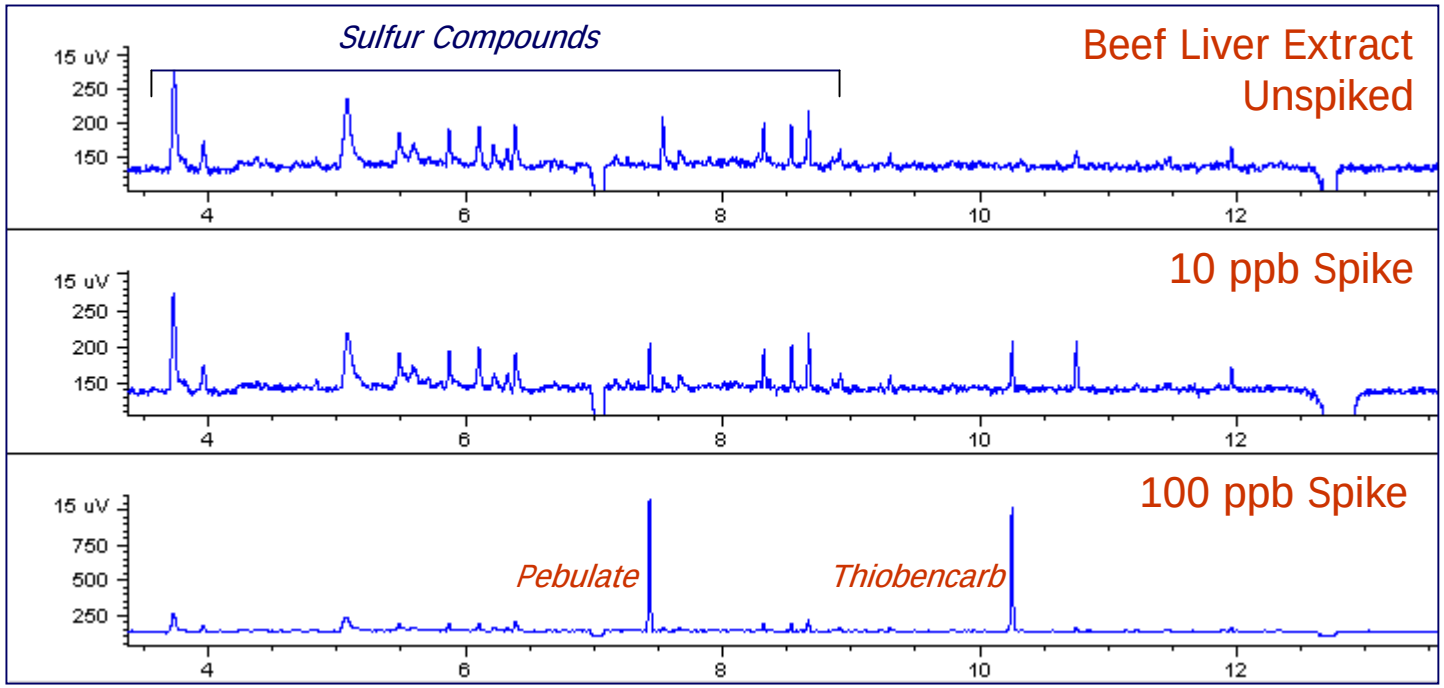
Carbamates in Beef Muscle

- 2-µL splitless injection – GC – PFPD
- Pebulate & Thiobencarb at 10 ppb or less



Carbamates in Beef Liver

- 2-µL splitless injection – GC – PFPD
- Pebulate & Thiobencarb at 10 ppb or less



Flavor and Fragrance

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Introduction

- Sulfur compounds are an important component of flavor and fragrance analyses.
- They are responsible for specific and distinctive flavors in many foods & beverages.
- Sulfur compounds can be difficult to analyze and identify because they are present at trace levels in a complex matrix.
- MS or FID commonly used, but not sensitive enough to detect sulfur compounds at trace levels.
- The PFPD can be used in parallel with MS to identify RT of trace level sulfur compounds.

GC Configuration MS/FID/PFPD

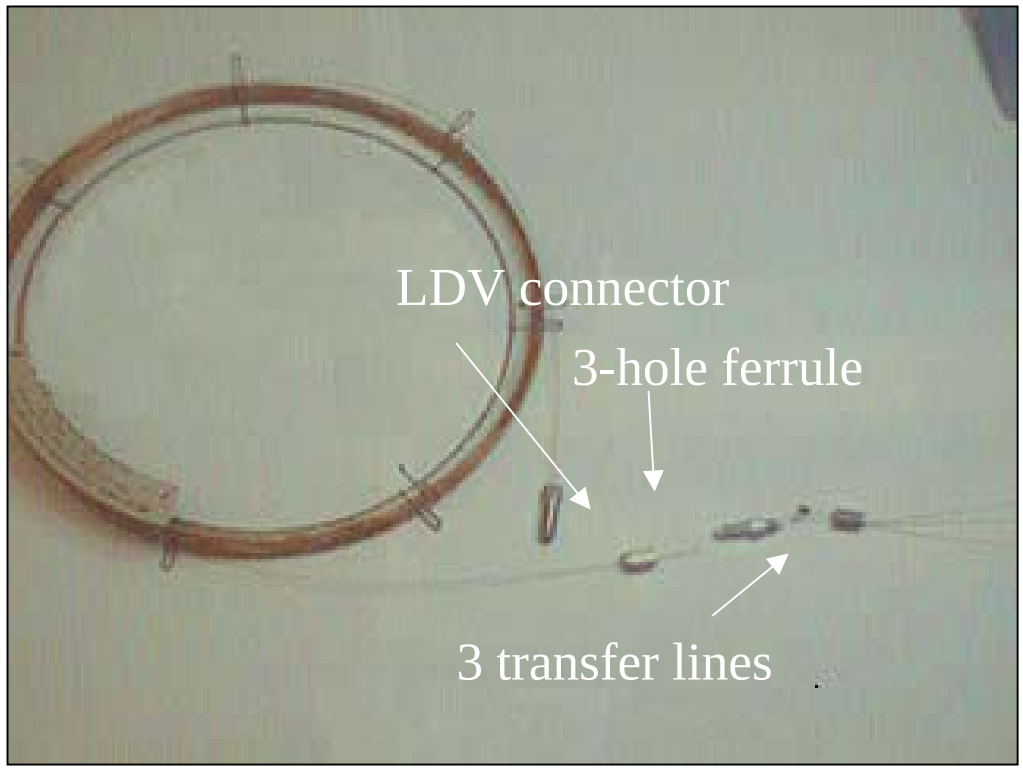
6890N GC with
5973N MS

Agilent FID in Front
for Sulfur Quantitation

OI Analytical PFPD in Back
for Identification and RT Marking

Column Configuration for 3 Detectors

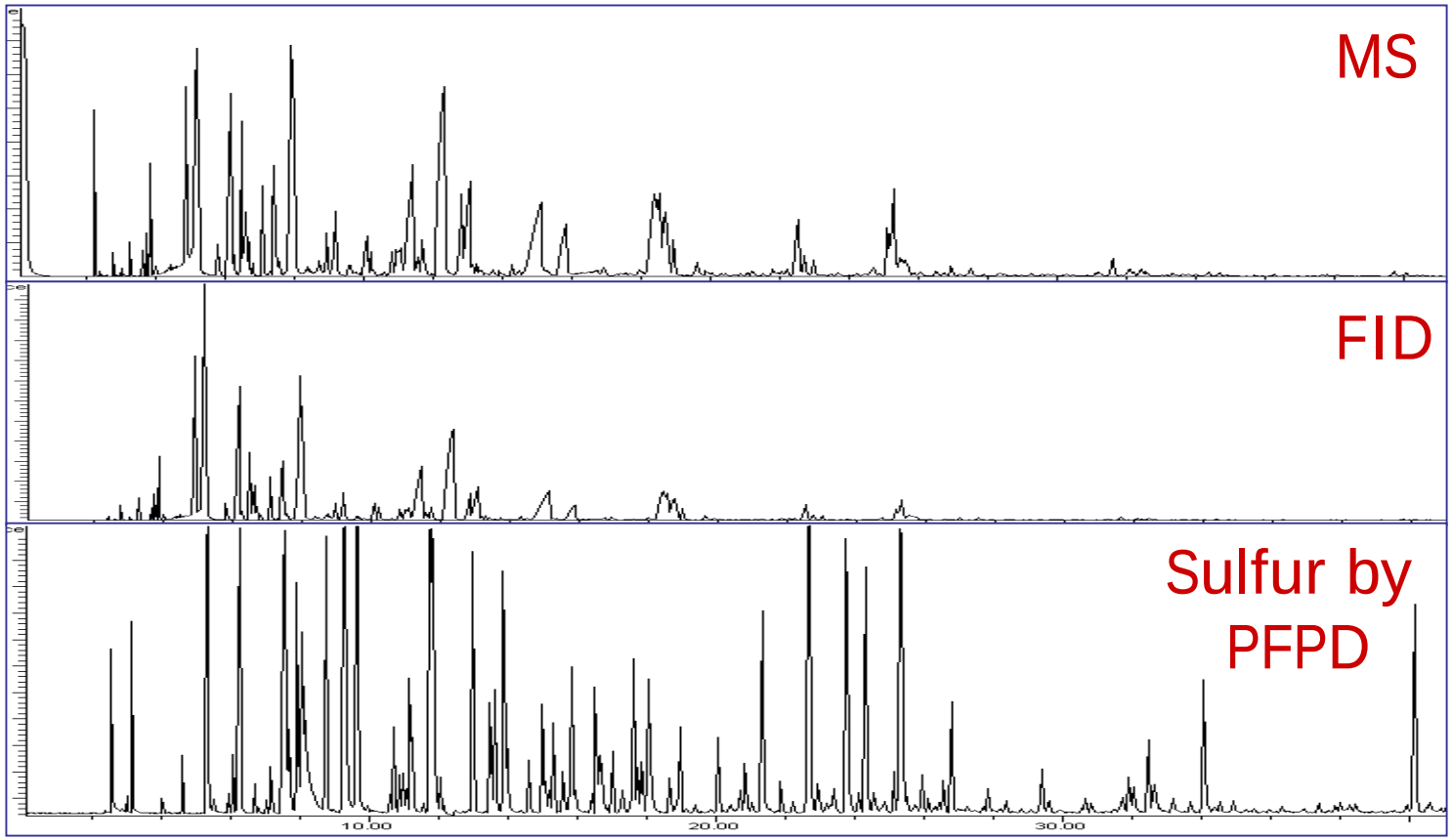
Standard installation of the column at the injection port



Detector end of the column is split using low-dead-volume (LDV) connector and a 3-hole ferrule

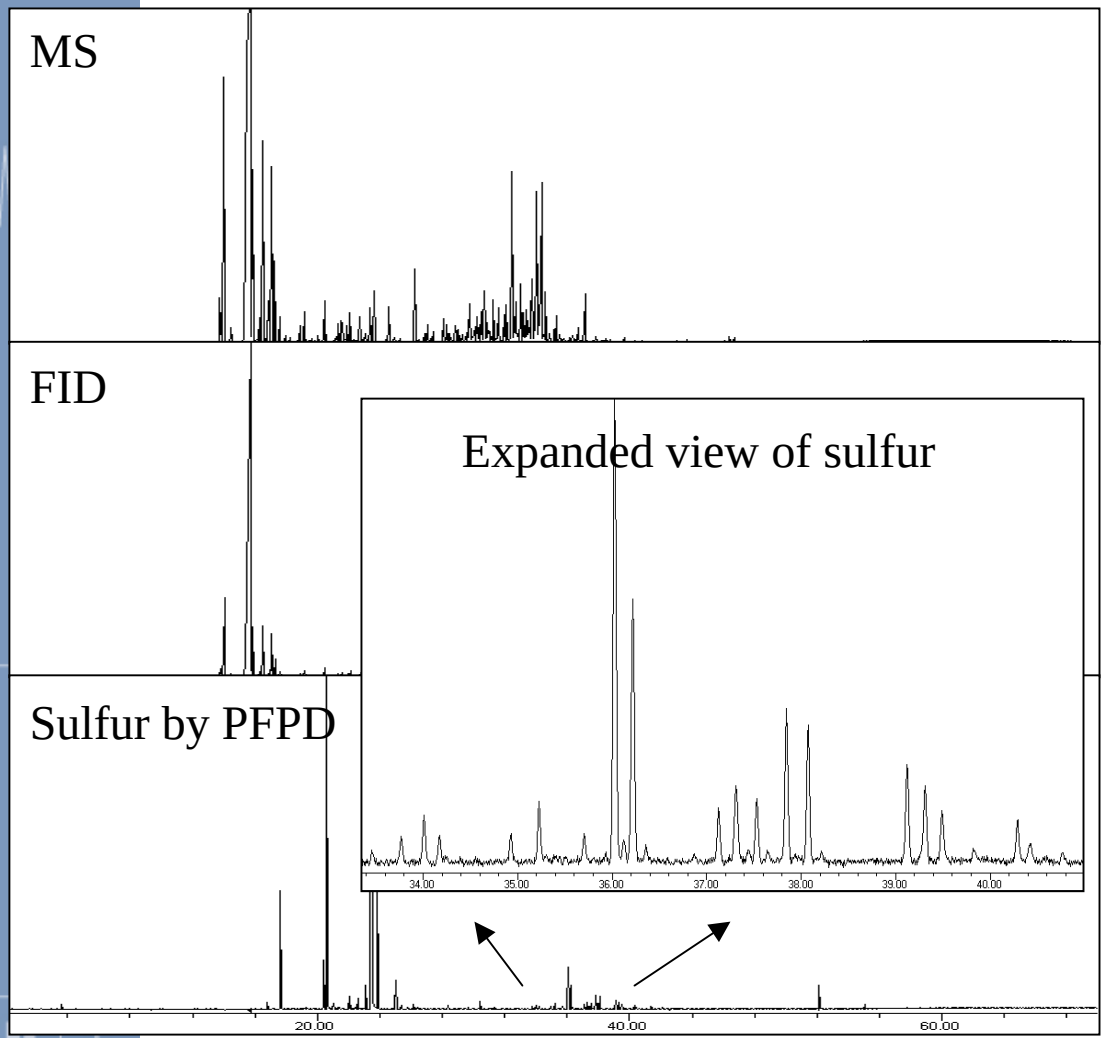
Sulfur in Coffee by MS/FID/PFPD

3 Simultaneous Chromatograms From Coffee “A”



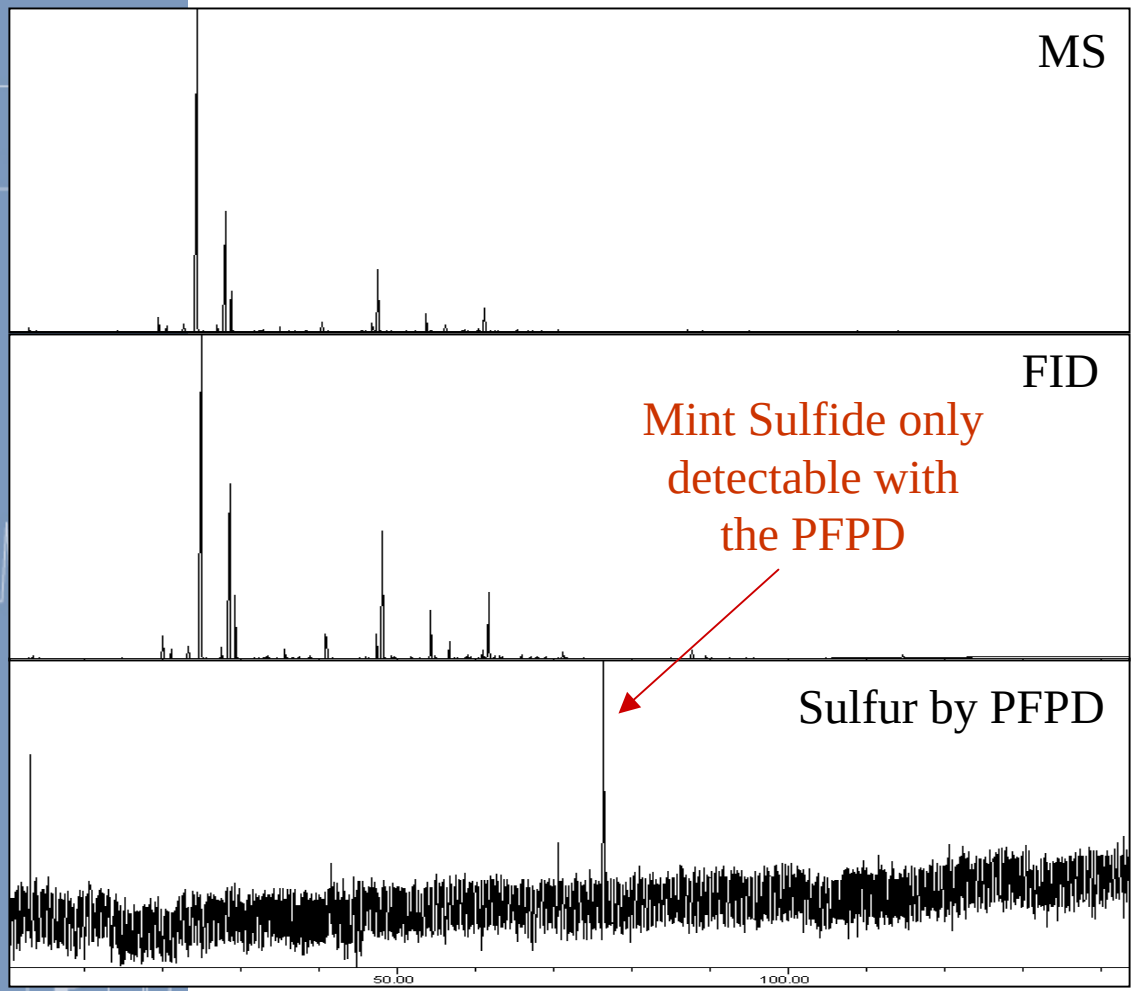
Over 200 sulfur peaks detected

Sulfur in Galbanum Oil



- Essential oil distilled from the galbanum plant
- Green, fresh leafy odor, dry woody undertones, pine highlights
- Used in production of fragrances
- Using an FPD, only 4 sulfur peaks were detected

Sulfur in Fishwort Oil



- Essential oil distilled from the fishwort, or “Chinese Lizard Tail”, plant (2 varieties)
- Corriander aroma or lemon/orange odor
- Used in production of flavors
- Using an FPD, no sulfur peaks were detected

Food and Beverage

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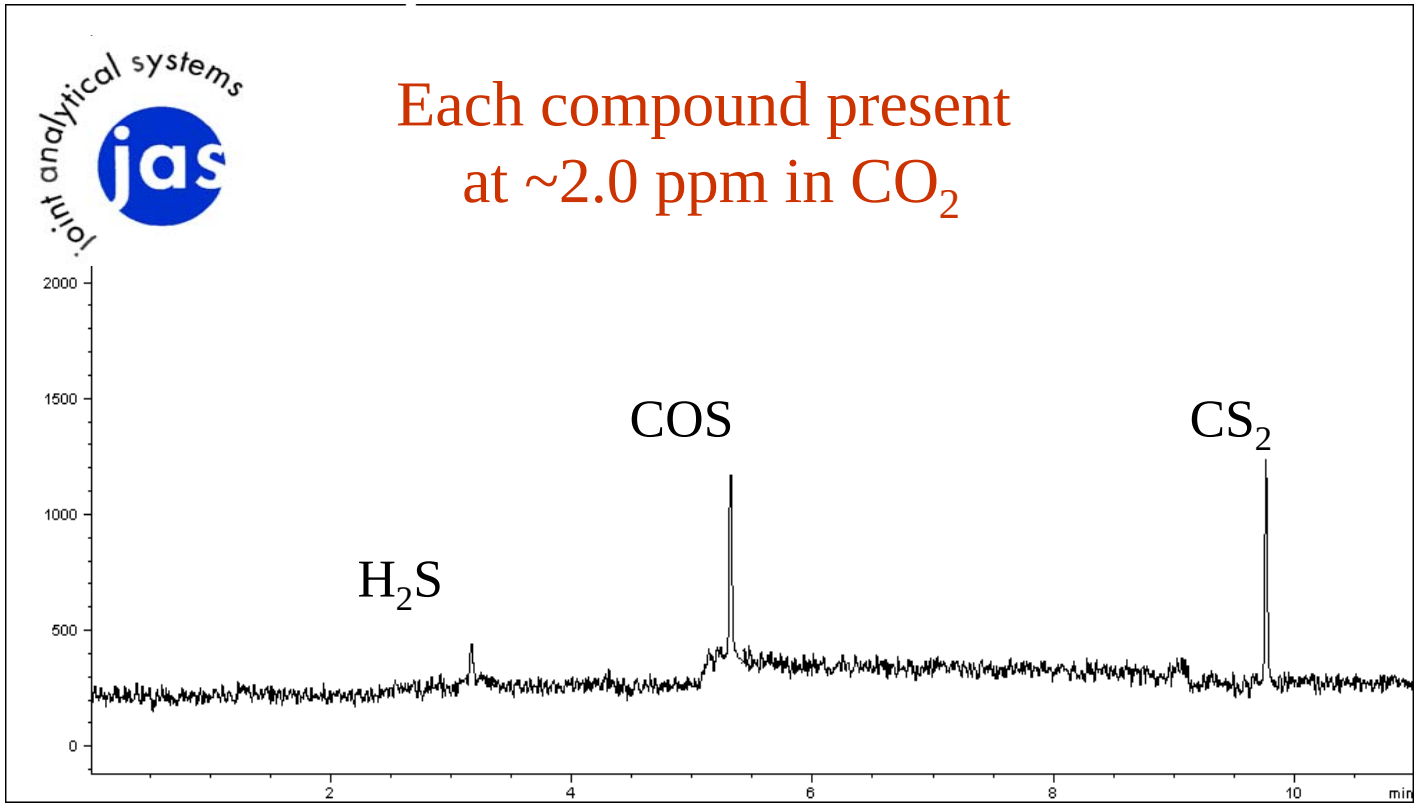
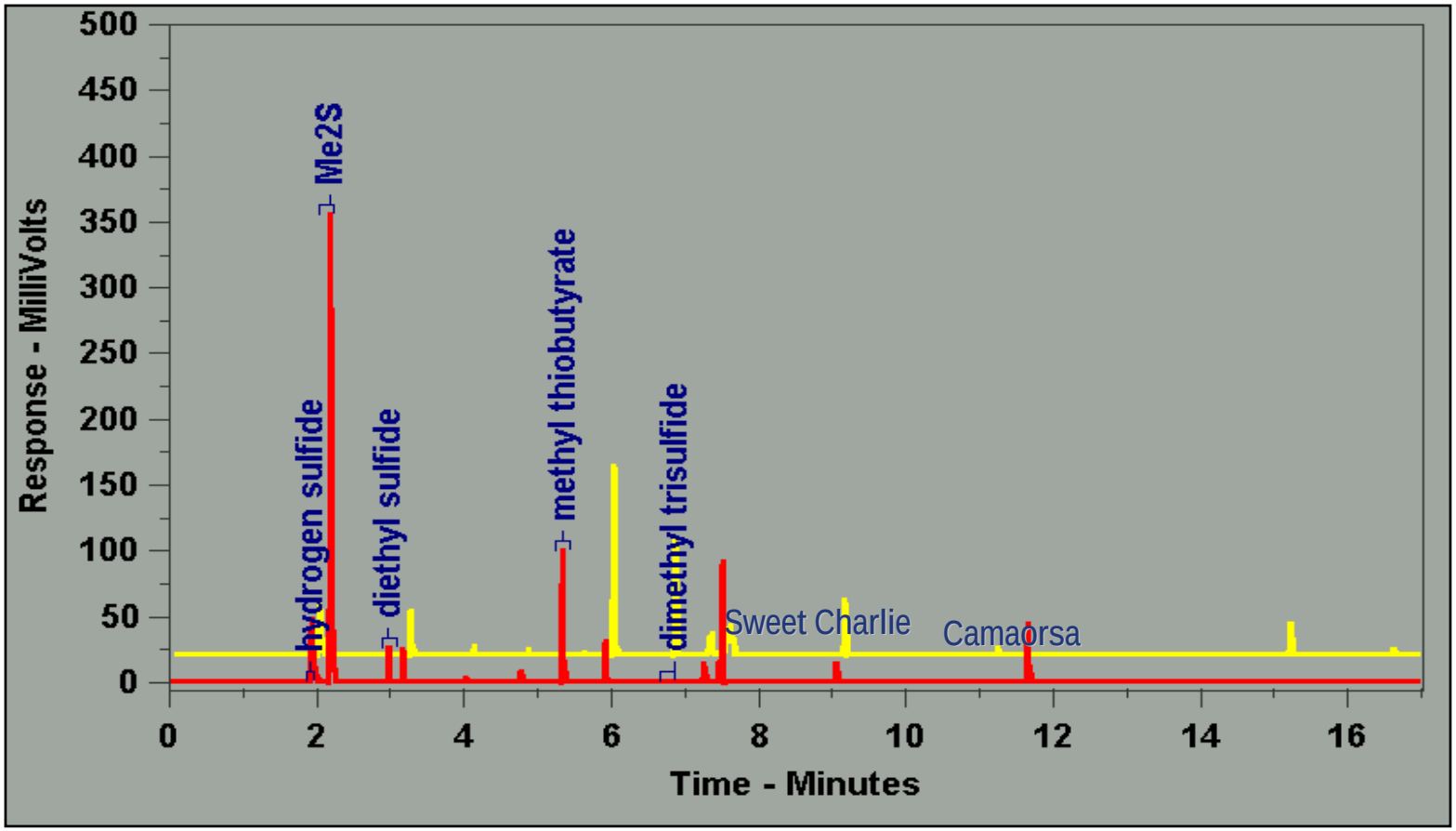
Sulfur in Beverage Grade CO_2



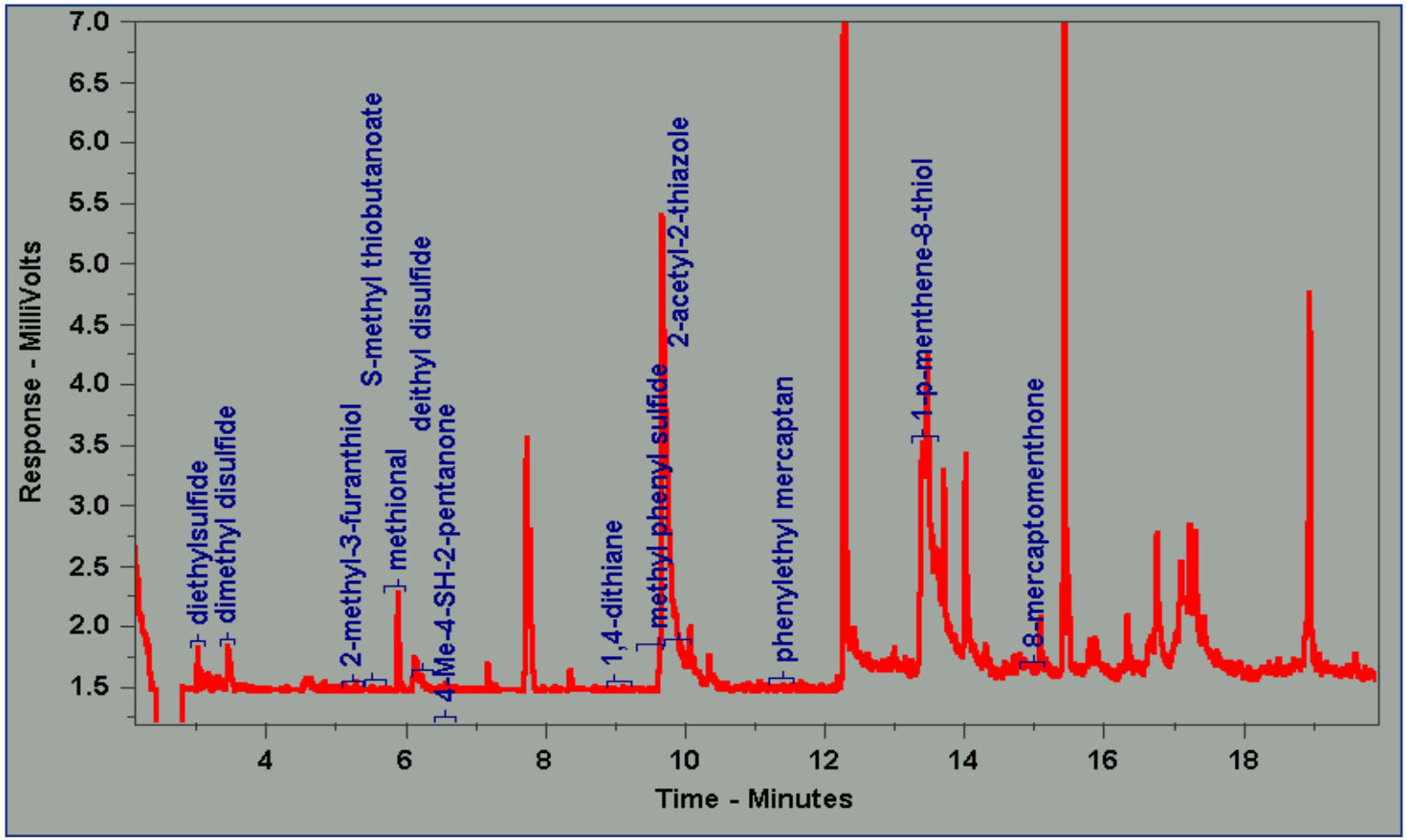
Chromatogram courtesy of JAS

Sulfur in Strawberry



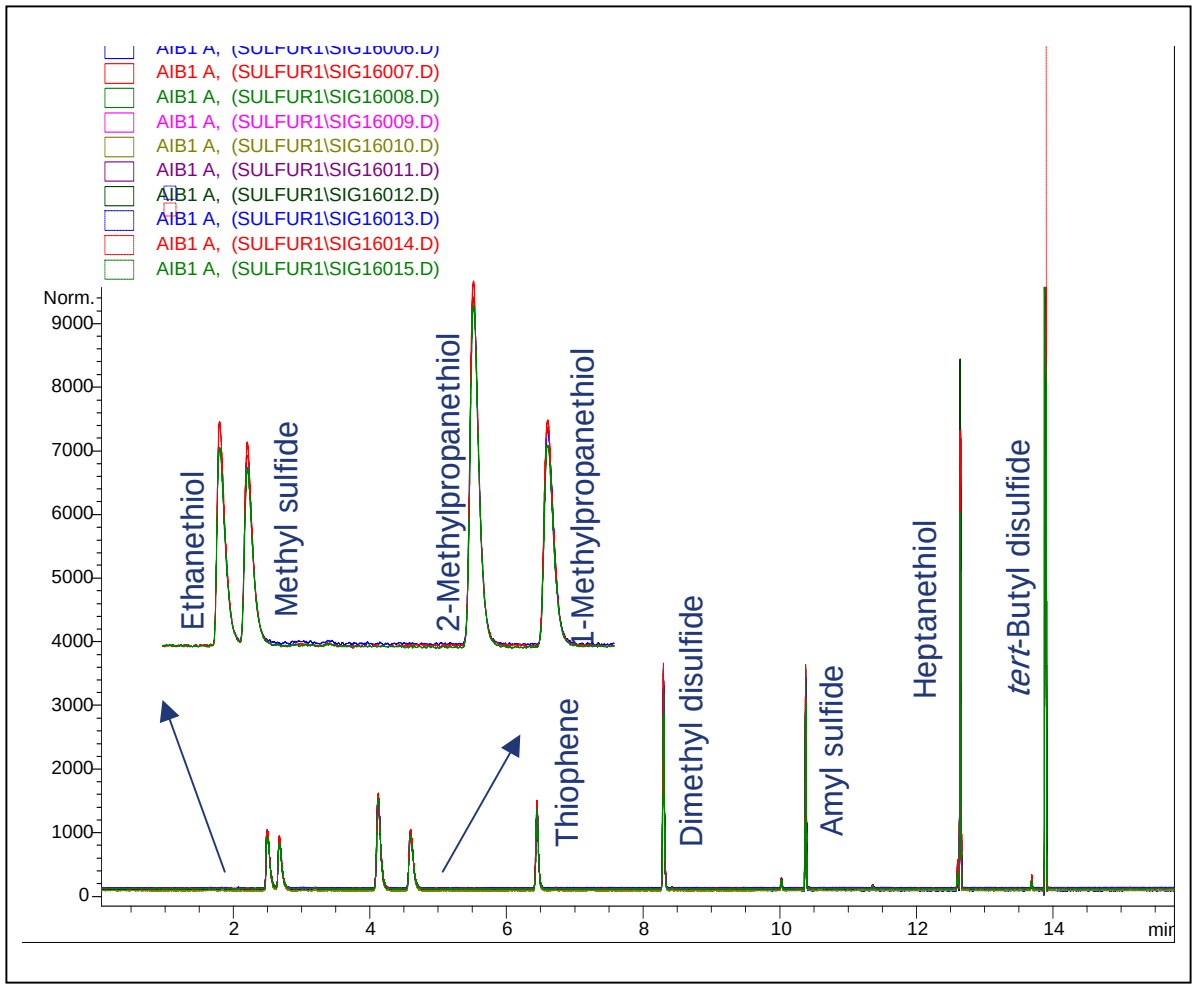
Chromatogram courtesy of Russell Rouseff, PhD, at University of Florida

Sulfur in Grapefruit



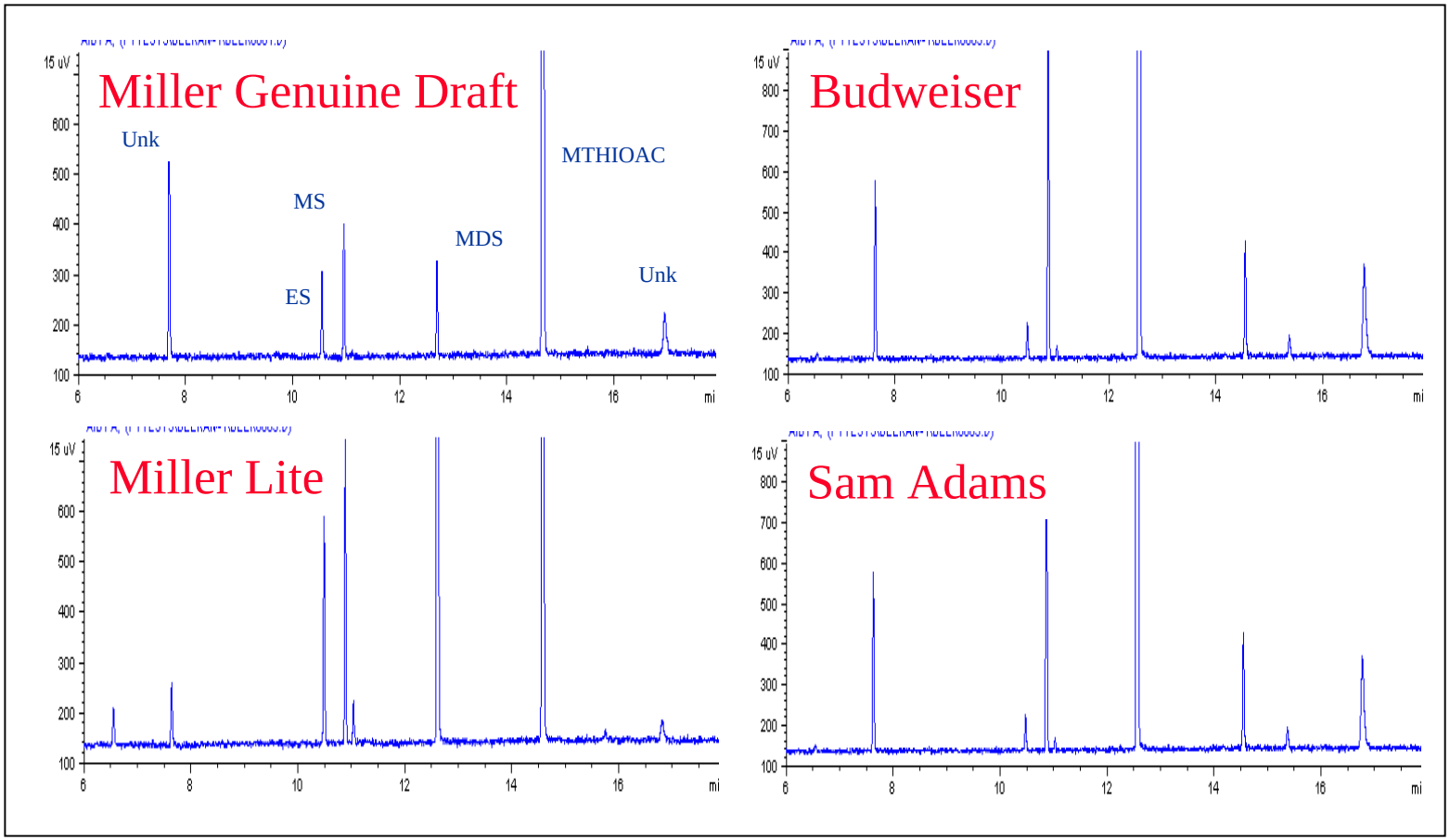
Chromatogram courtesy of Russell Rouseff, PhD, at University of Florida

Sulfur in Beer



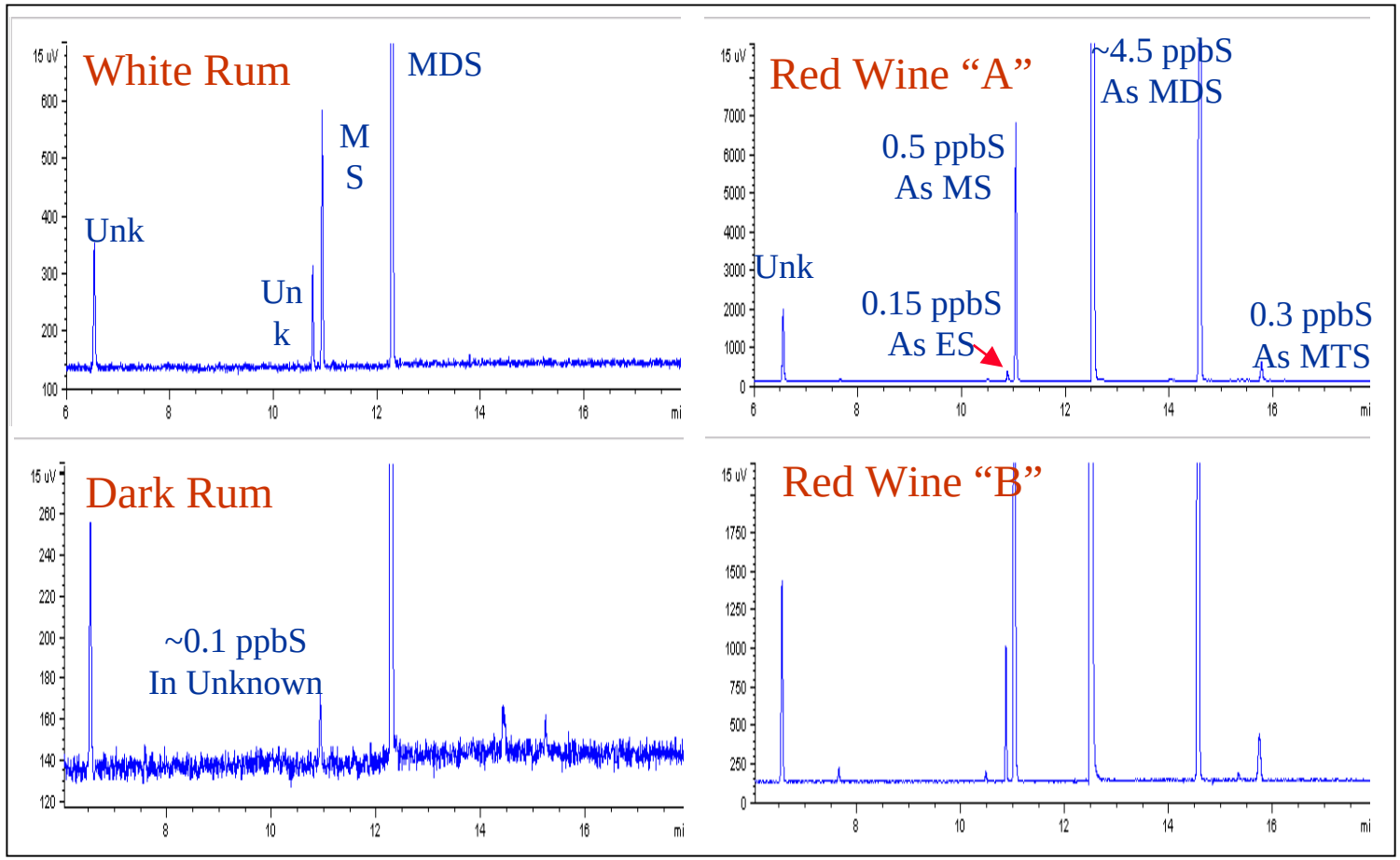
PFPD repeatability at 10 ppb better than 10%

Sulfur in Beer

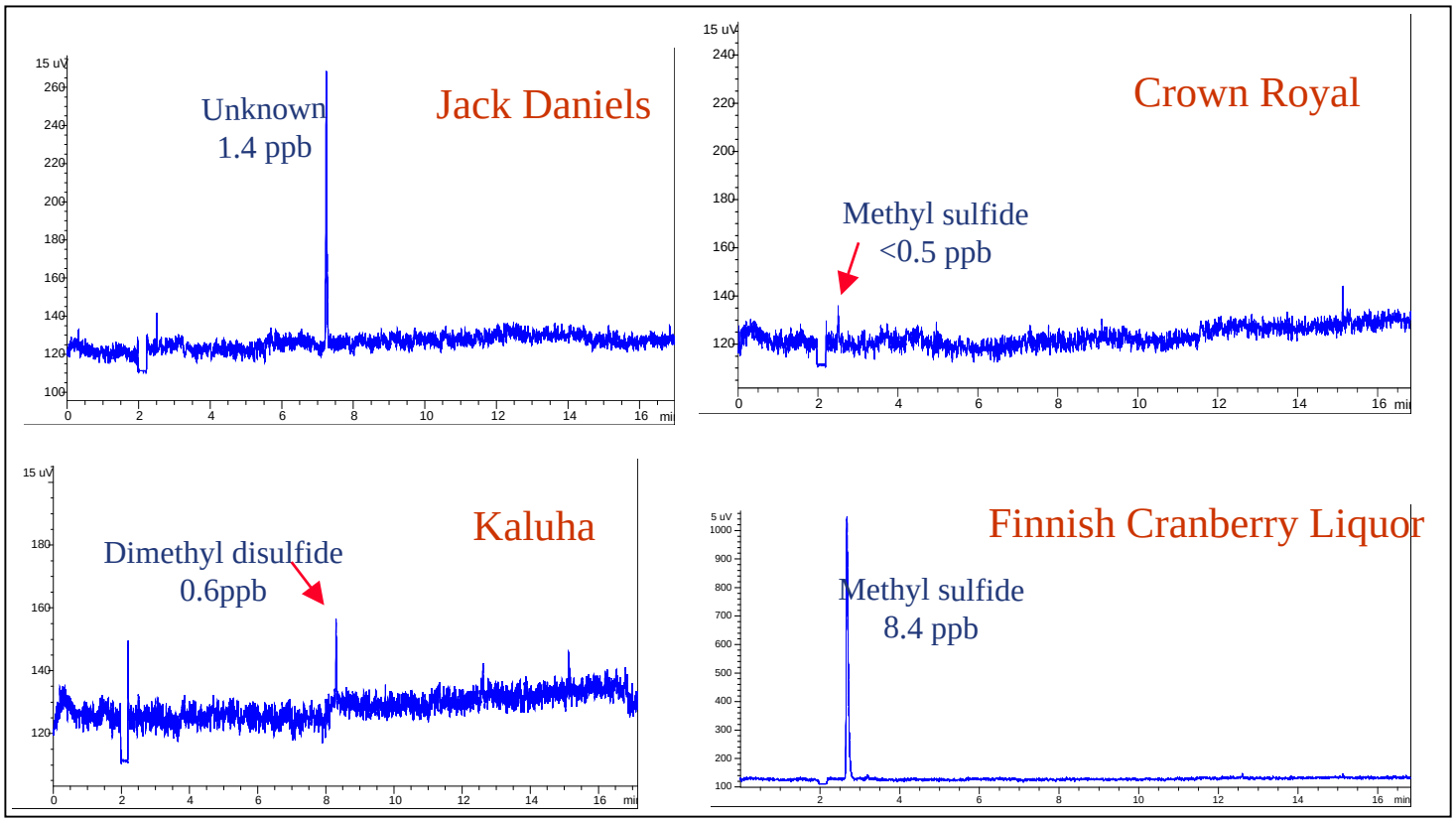


Sulfur concentrations in beers tested ranged from 0.1 ppb S to ~4 ppb S

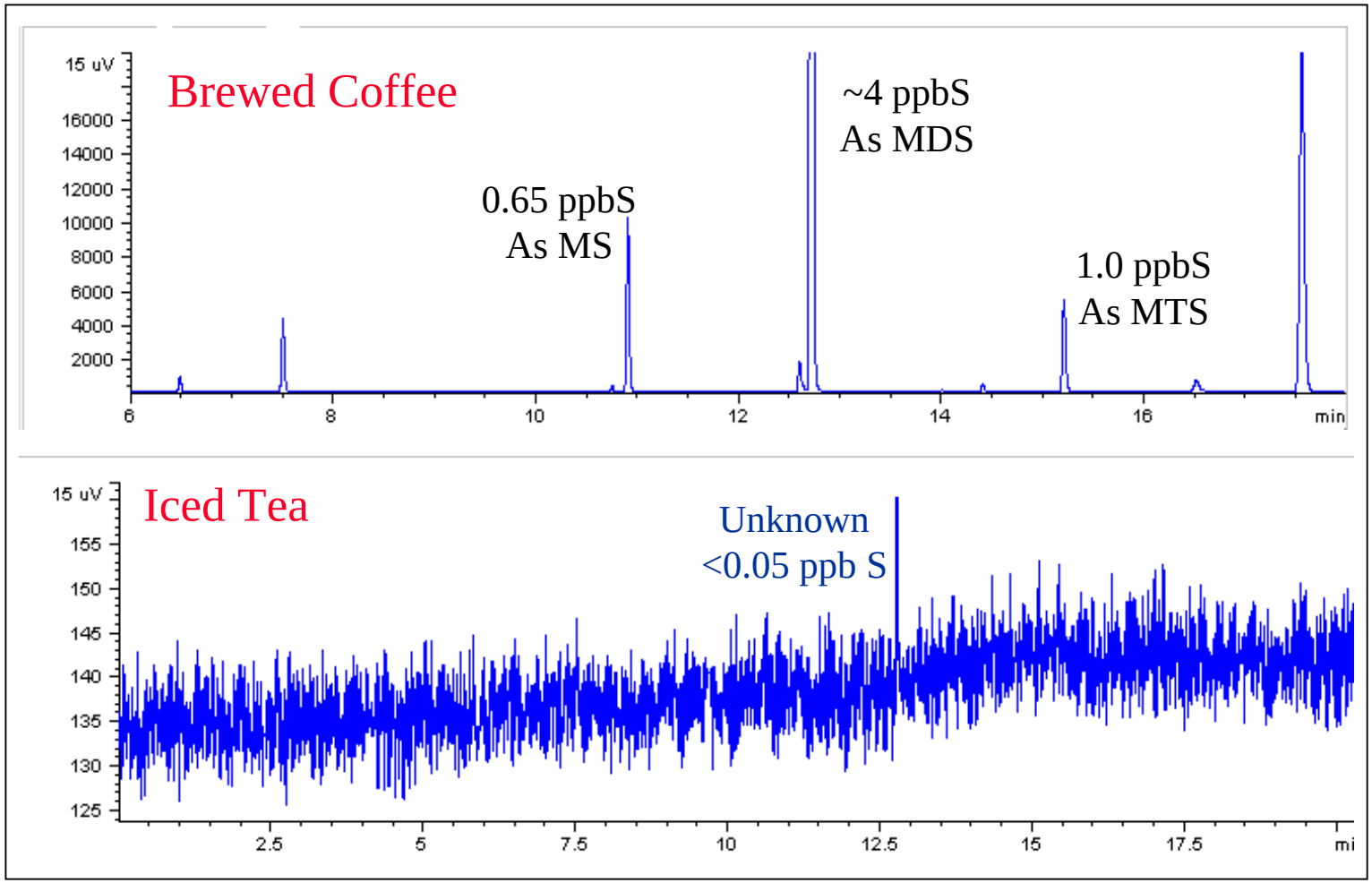
Sulfur in Wine and Rum



Sulfur in Liquors



Sulfur in Coffee & Tea



Other Applications

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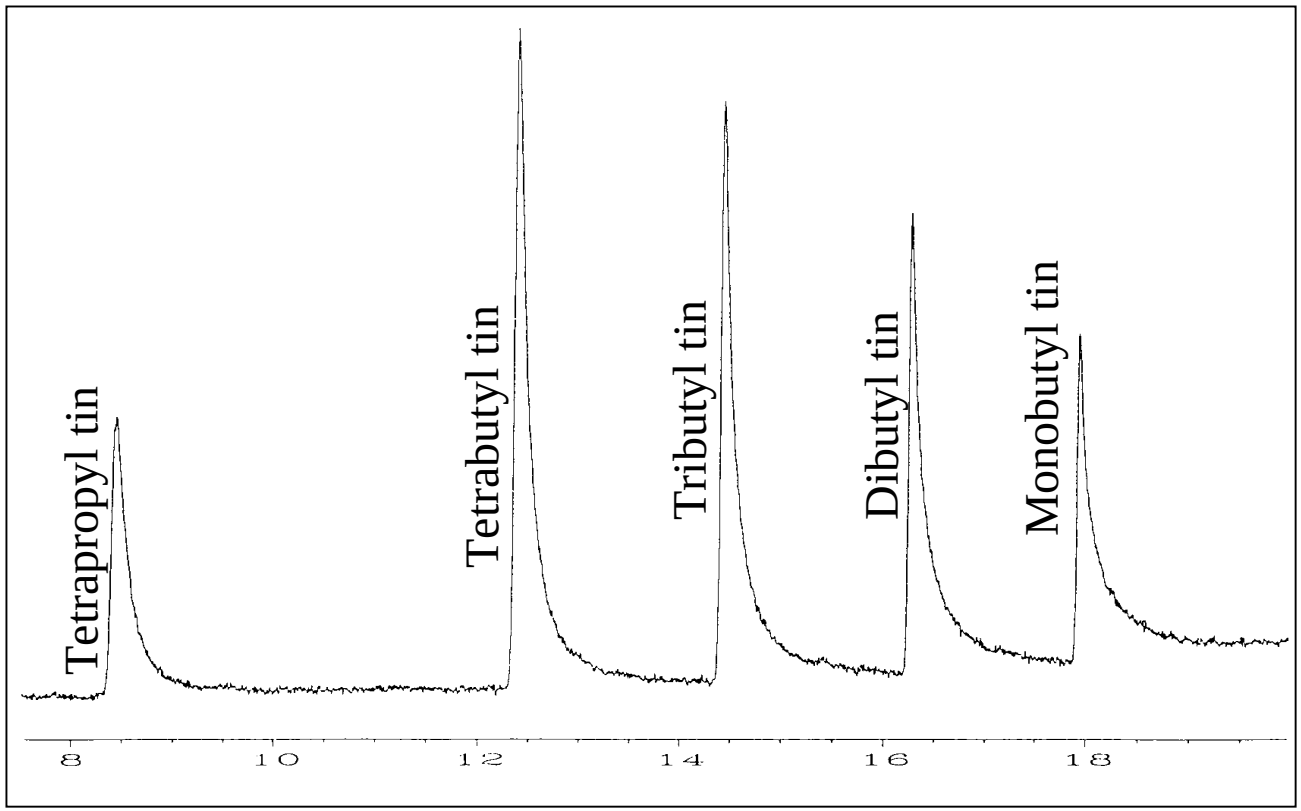
Organo-tin Standard

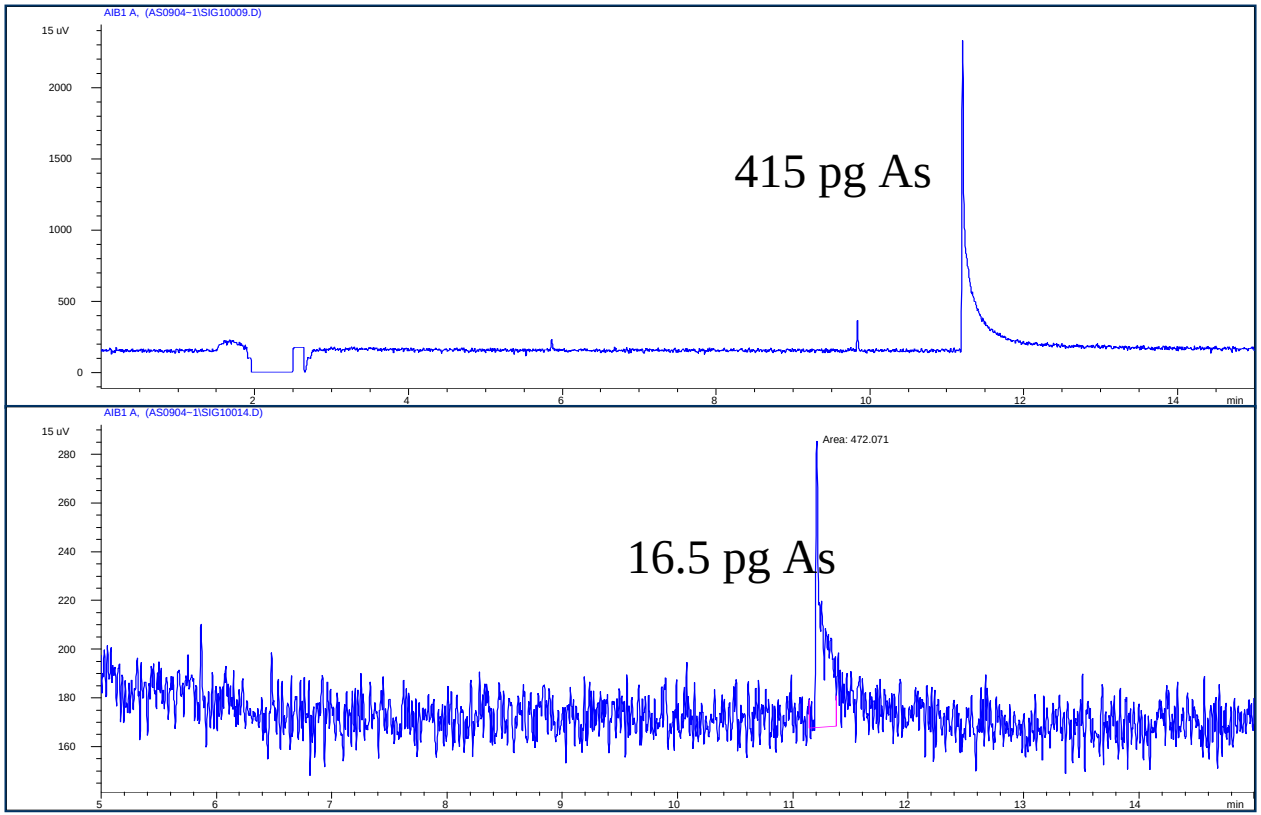
- Rtx-35 column, ramped oven program
- 5.0 pg Sn on column



Chromatogram courtesy of Restek

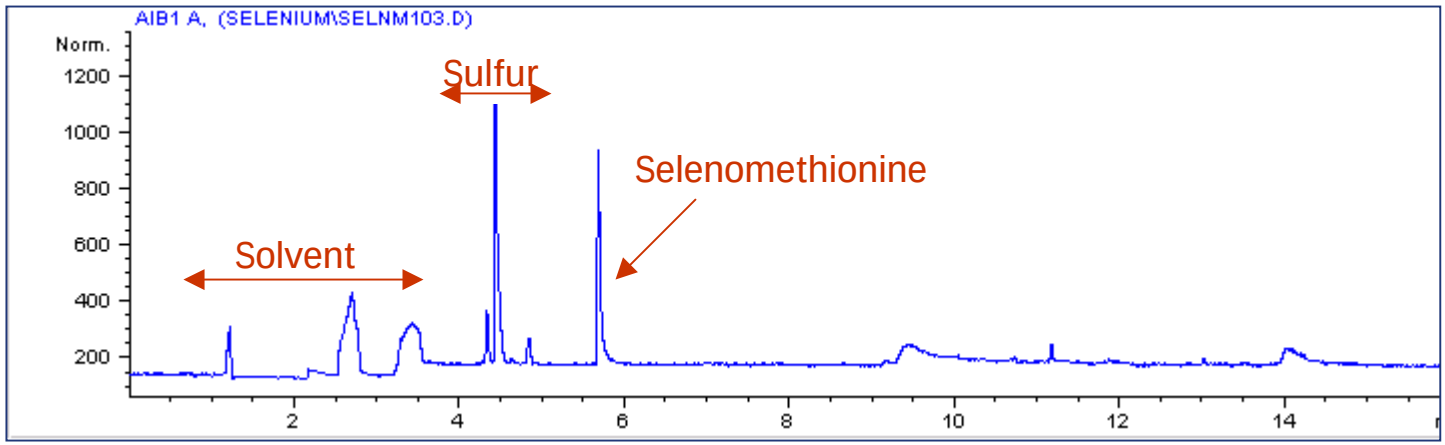
Arsenic Standard

- 1-μL injection of triphenylarsine
- WG-345 optical filter in PFPD
- 300 °C detector temperature



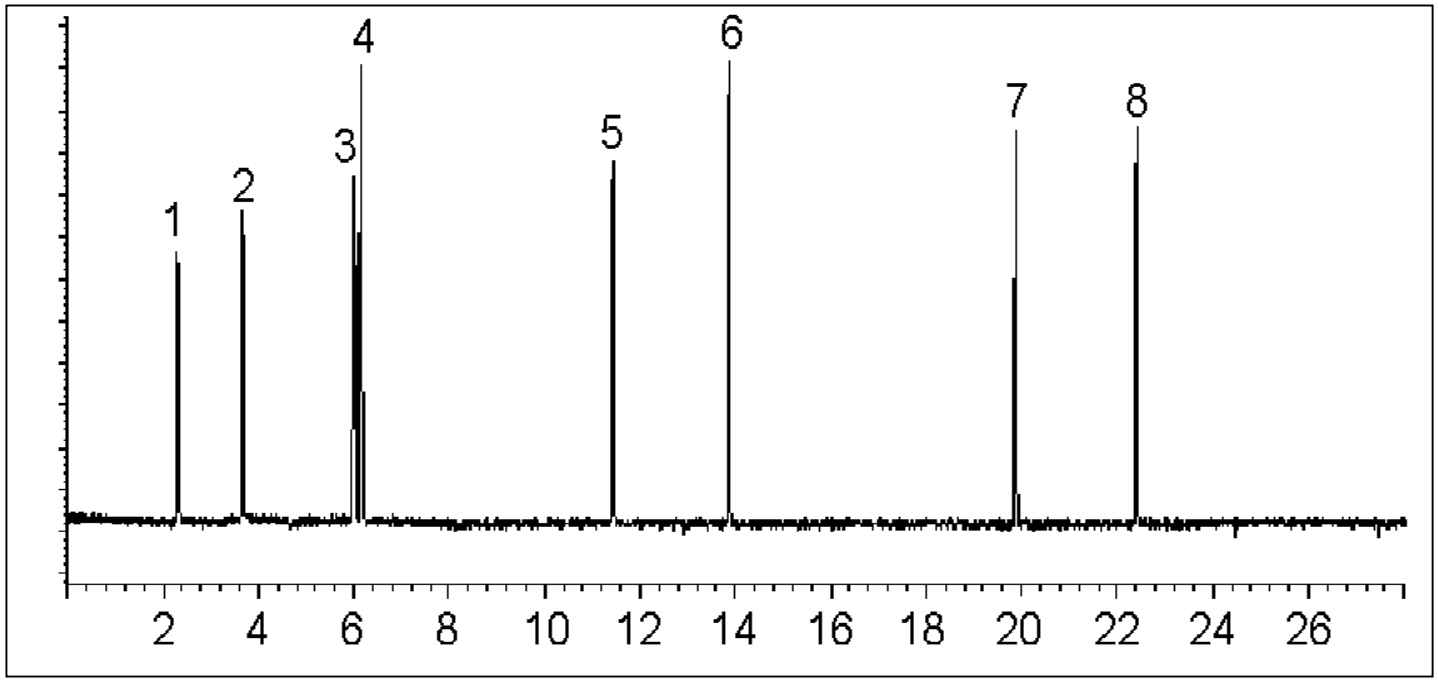
Selenium Standard

- 4 ppm Se as selenomethionine in chloroform
- 1-µL splitless injection
- DB-5MS column; ramped oven program



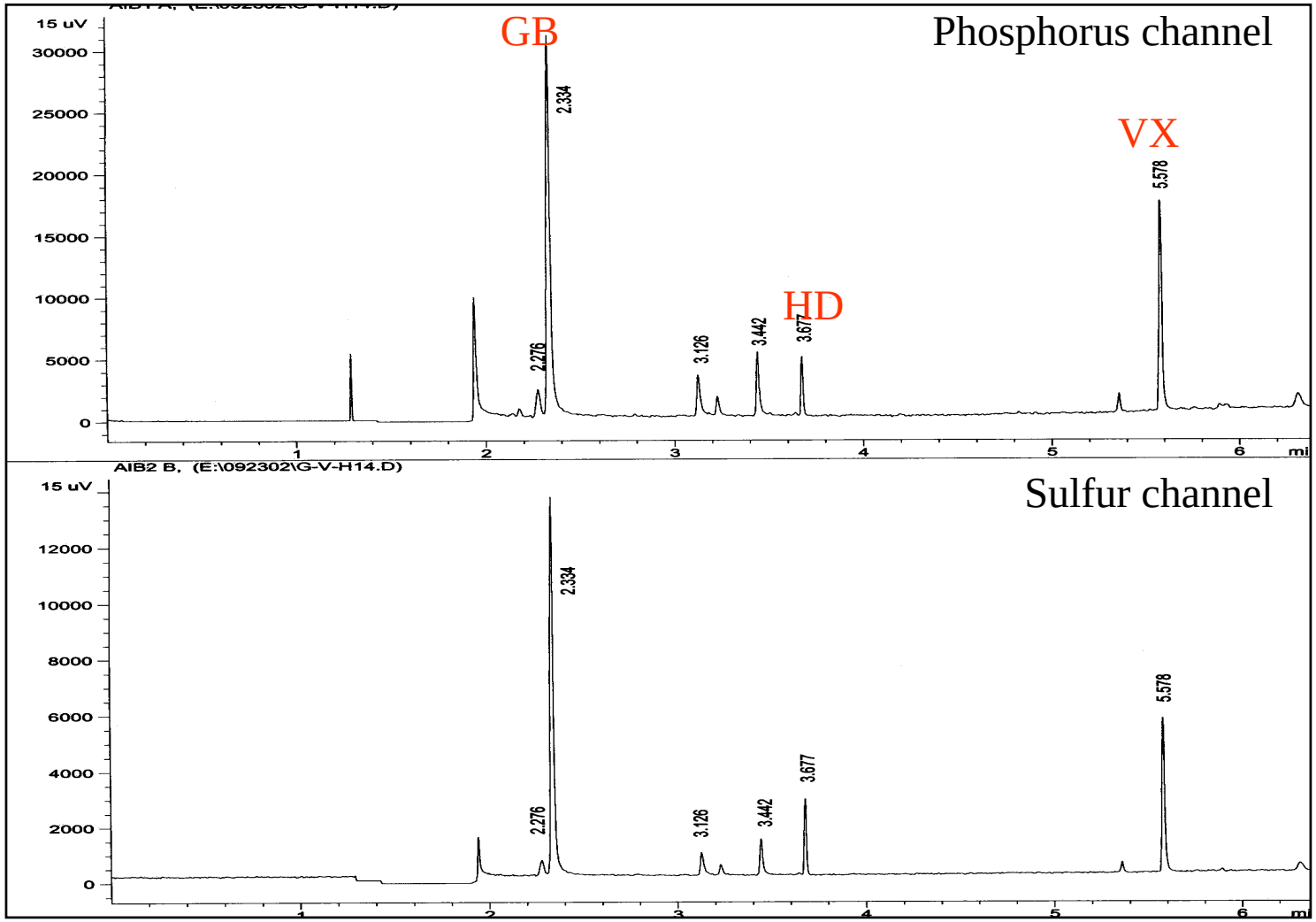
Reduced Sulfur in Pulp Mill Effluent

200 μg S/L aqueous standard



Chromatogram courtesy of NCASI

CW Agent Detection with PFPD



Summary

- The Pulsed FPD has many significant advantages over the traditional static FPD, including:
  - Dual-element capability for ½ the cost of the static FPD dual mode
  - Low cost of operation and long-term stability
  - Simultaneous, mutually selective chromatograms for S/C, S/P, and S/N
  - Wide range of applications not possible with the static FPD
- Please check the OI website for more information on the OI Analytical PFPD and a complete listing of application notes.

Contact Information

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