PFPD Training Course – Part 5
Applications

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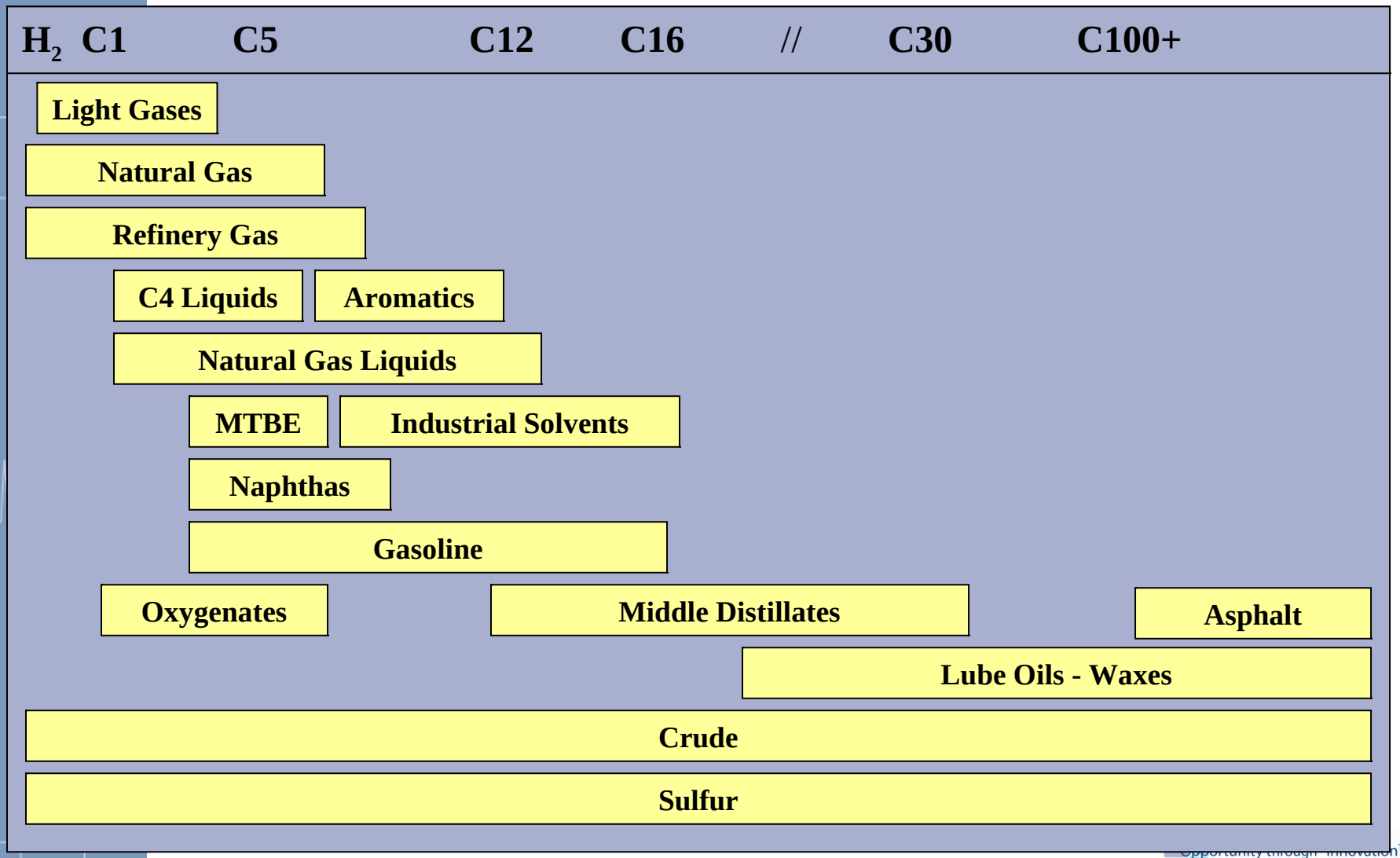
O·I·Analytical

Sulfur in Petrochemical Matrices by PFPD

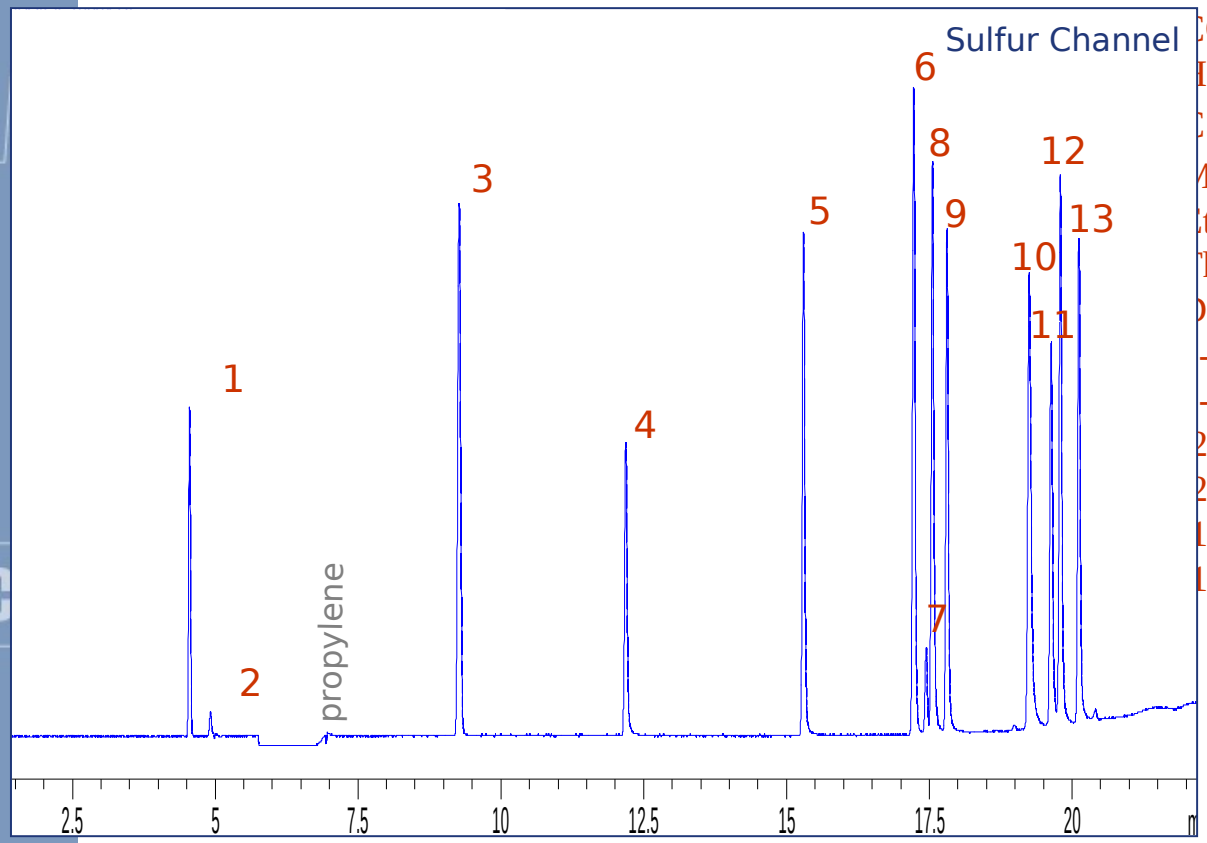
Hydrocarbons: C1 – C100+



Sulfur in Petrochem Matrices

- Sulfur is present in most petrochemical matrices
- Wide range of concentrations, from sub-ppb up to % of total weight
- Total sulfur content regulated
- Sulfur speciation important for process adjustments
- Unknowns quantified using equimolar response of PFPD

Sulfur Standards in Propylene

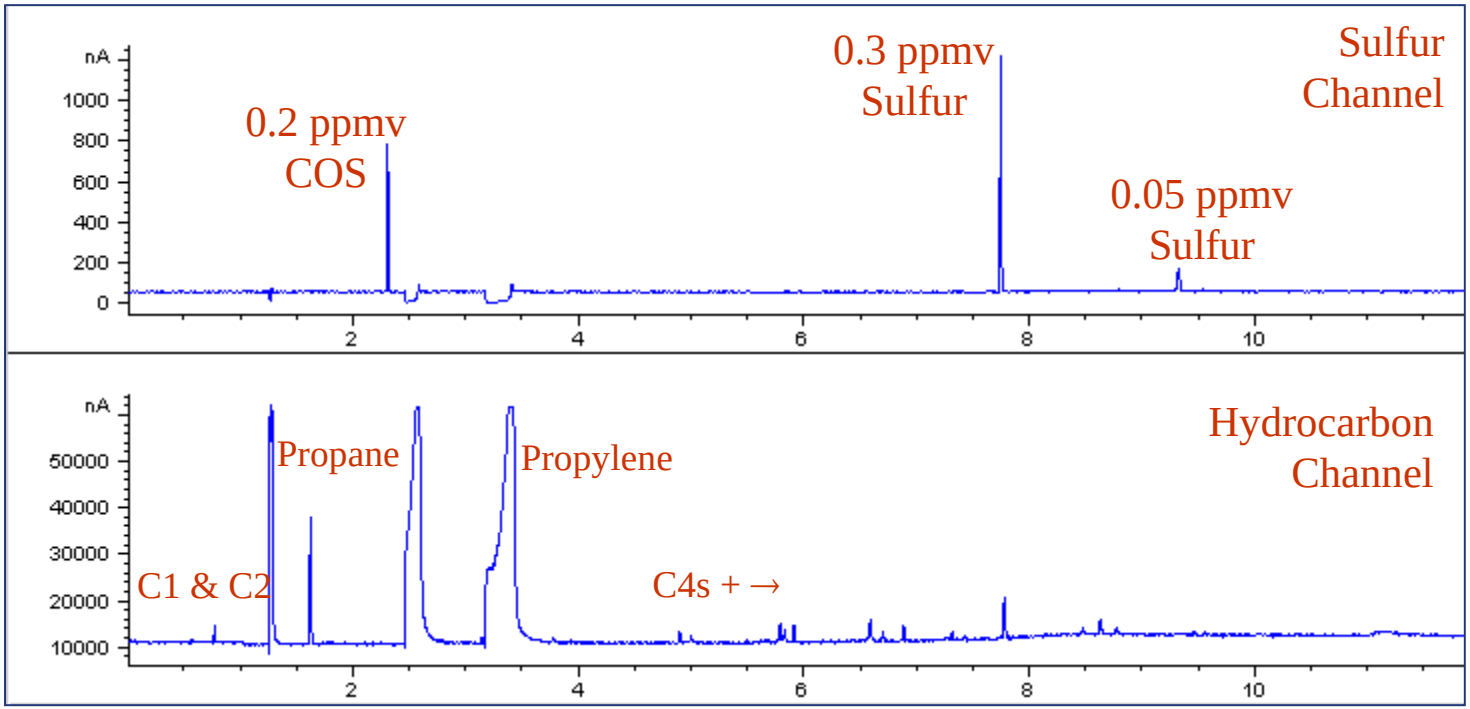


COS
H_2S
CS_2
Methylmercaptan
Ethylmercaptan
Thiophene
DMS
2-Propanethiol
1-Propanethiol
2-Methyl-2-propanethiol
2-Methyl-1-propanethiol
1-Methyl-1-propanethiol
1-Butanethiol

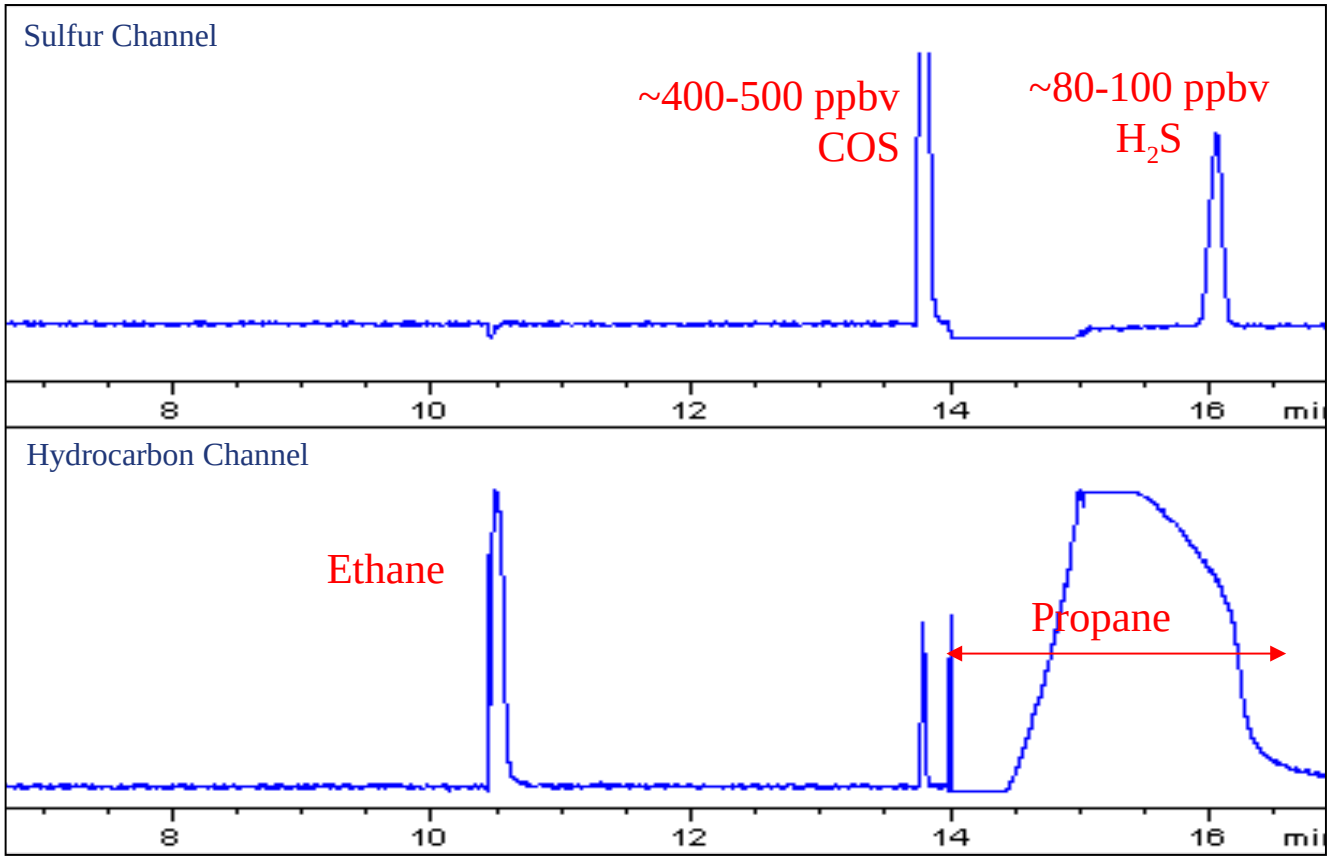
0.2 mL gas sampling loop; split 5:1.
Each compound present in this propylene standard at approximately 1 ppm.

Sulfur in Propane-Propylene Mix

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

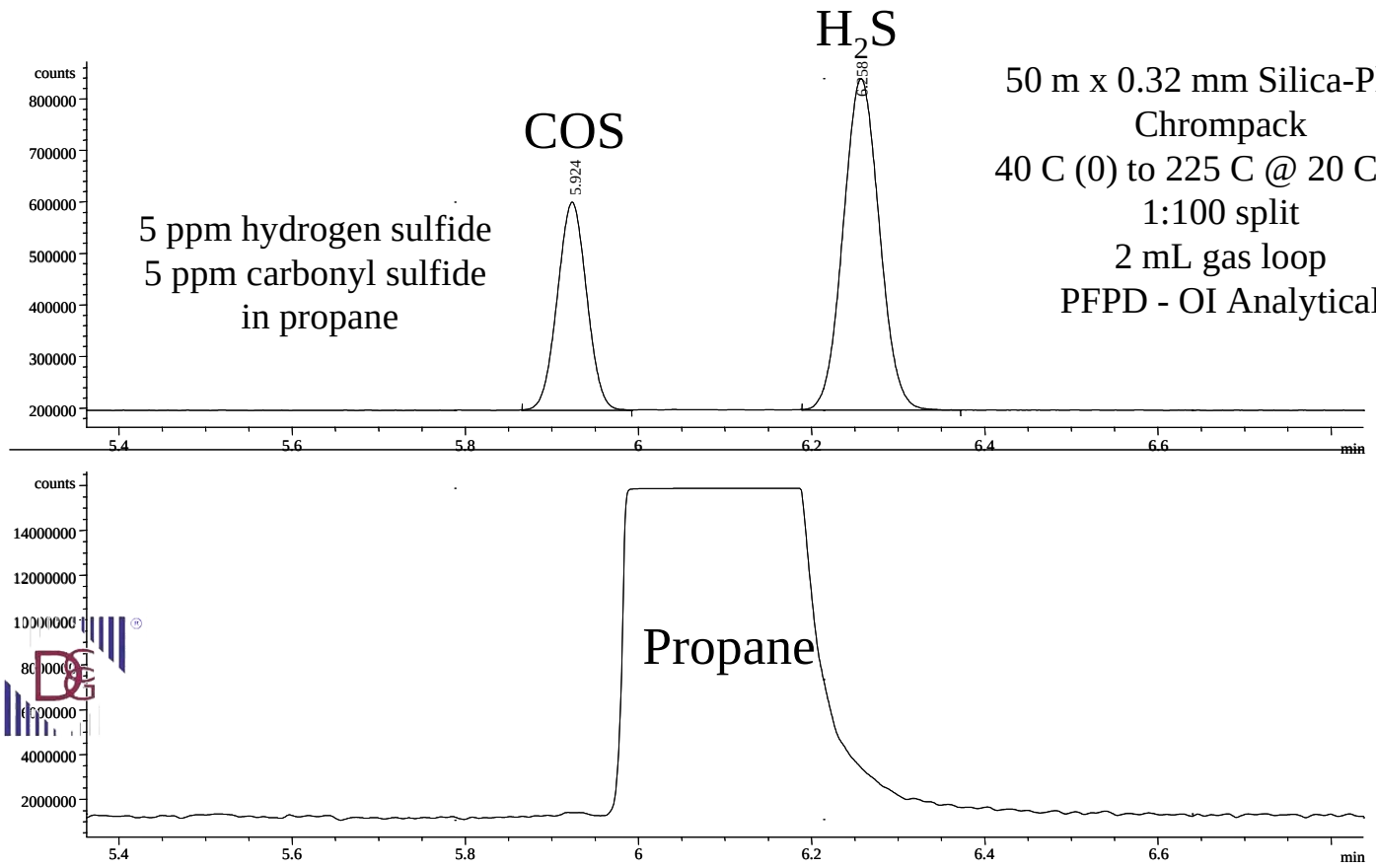


Sulfur in 97% Propane



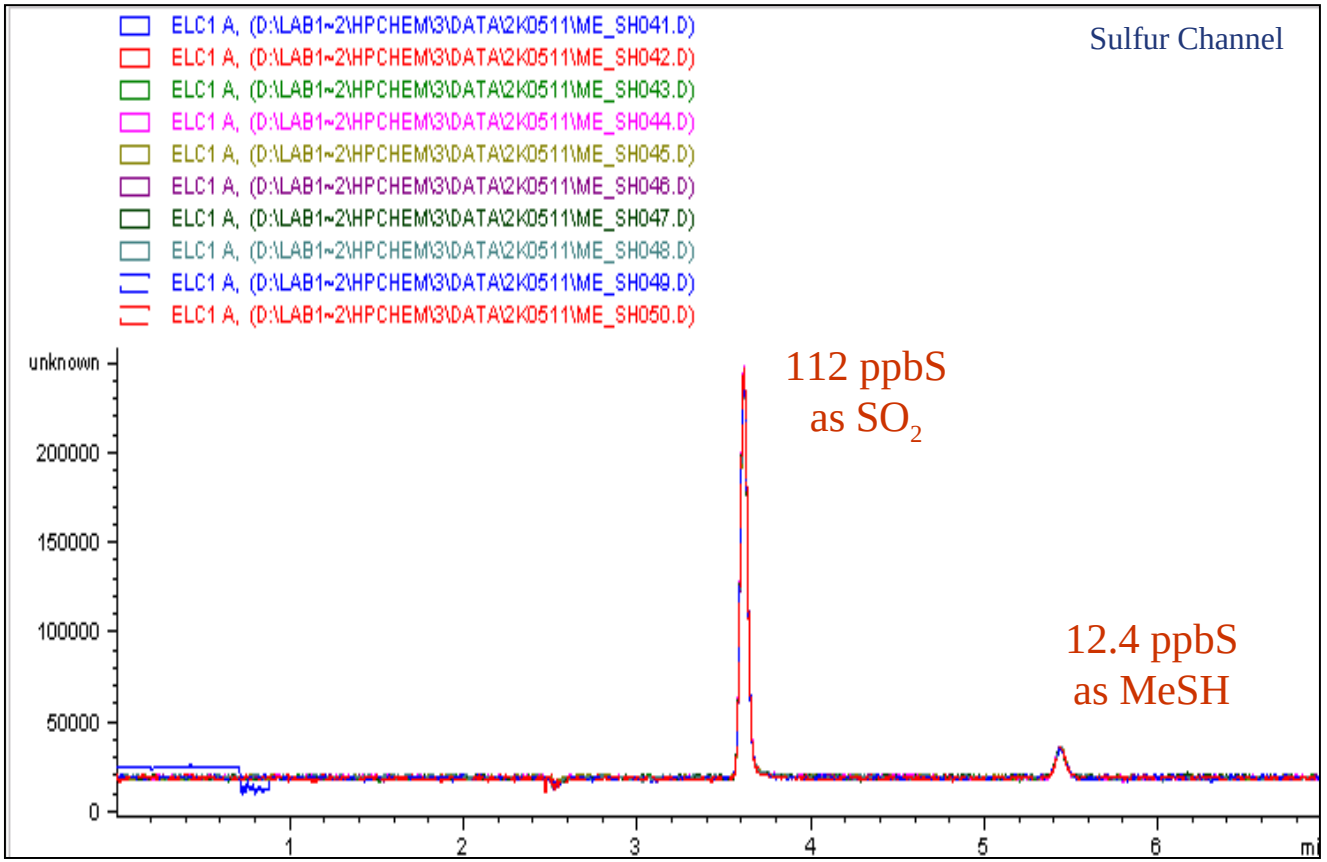
0.5 mL gas sampling loop; split 10:1.
Analyzed on the OI Analytical S-PRO 3200.

COS and H_2S in Propane by PFPD



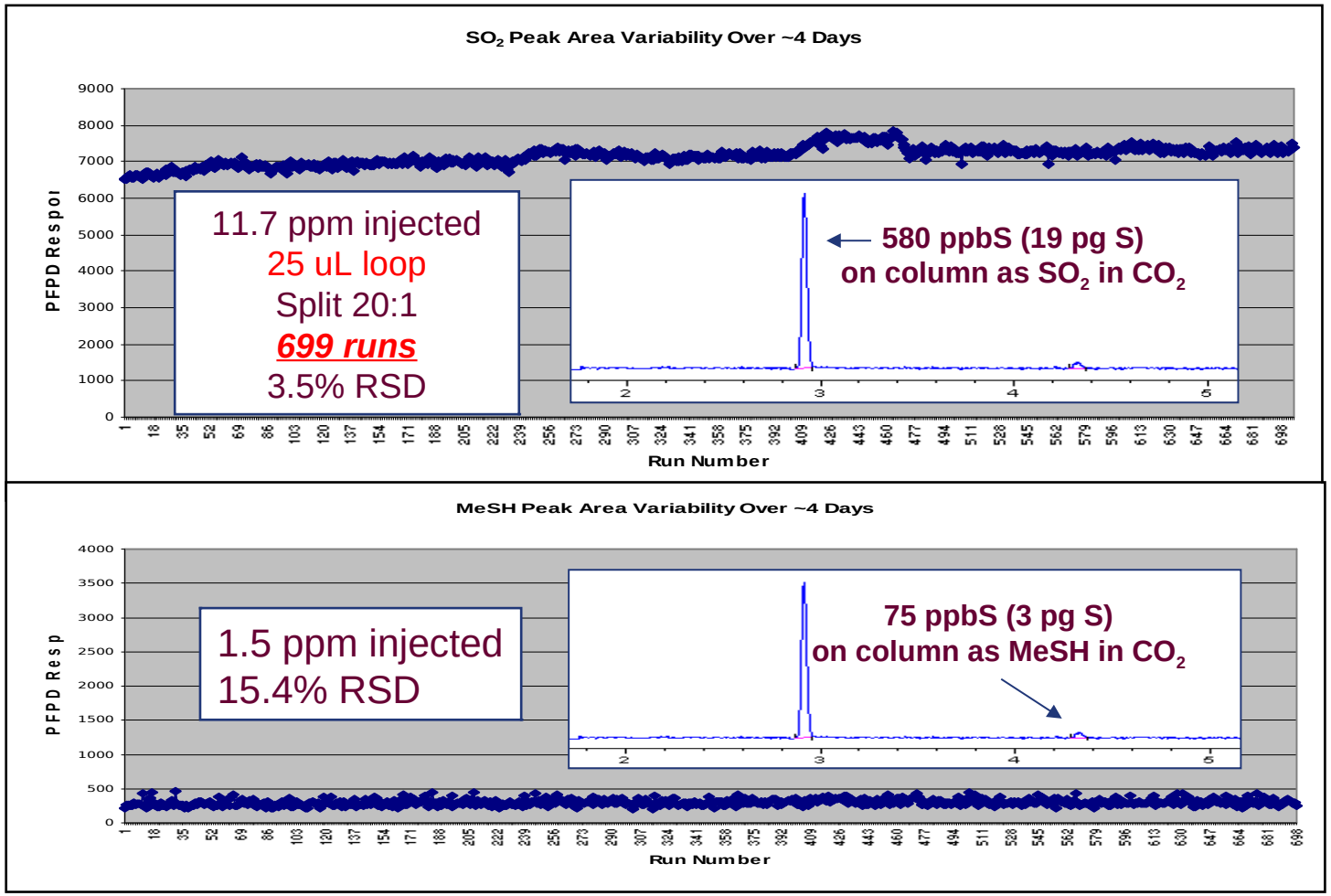
Chromatogram courtesy of DCG Partnership 1, Ltd.

Sulfur Compounds in CO_2



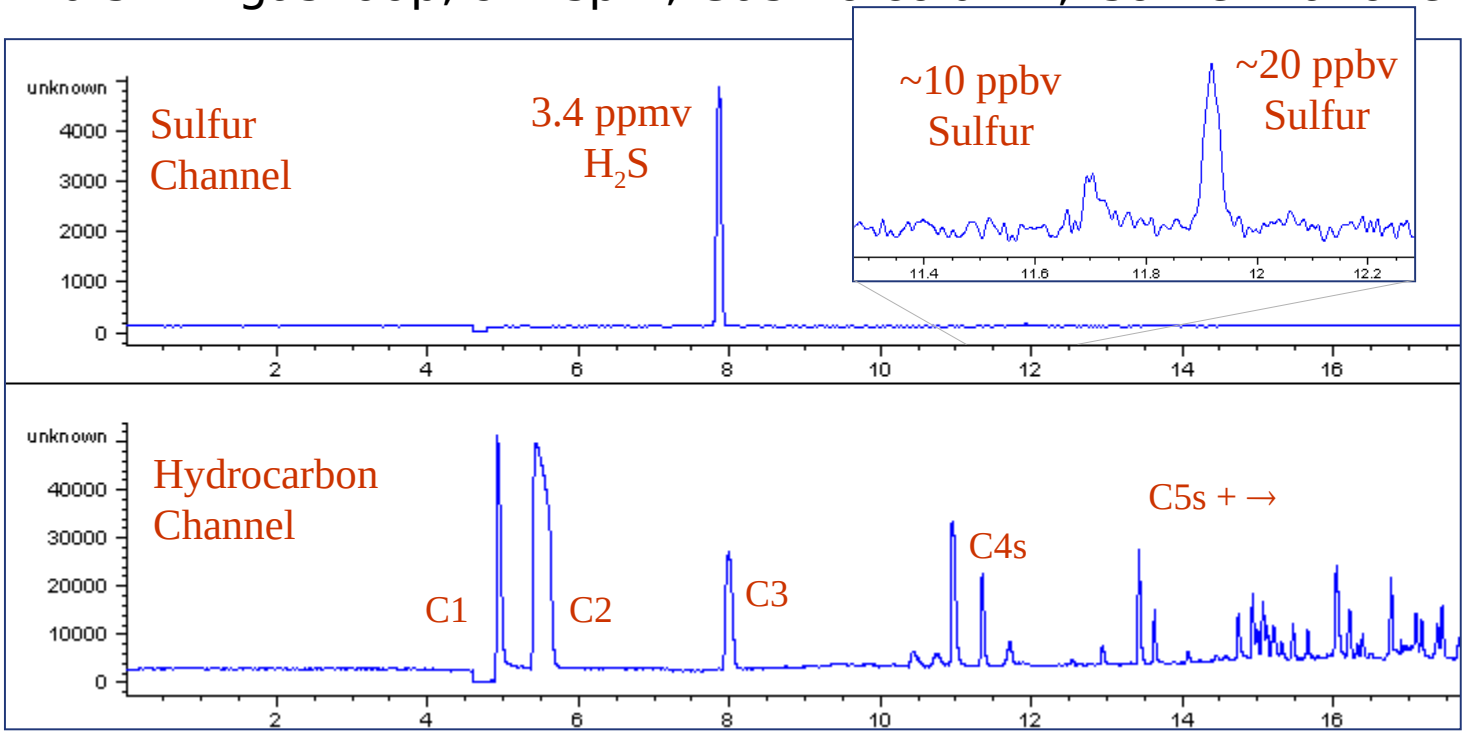
0.5 mL gas sampling loop; slit 20:1.
10 replicate analyses on the S-PRO 3200.

Sulfur in Beverage Grade CO_2

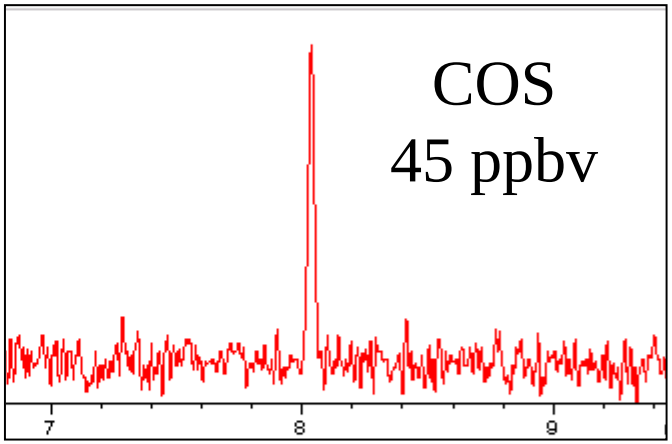


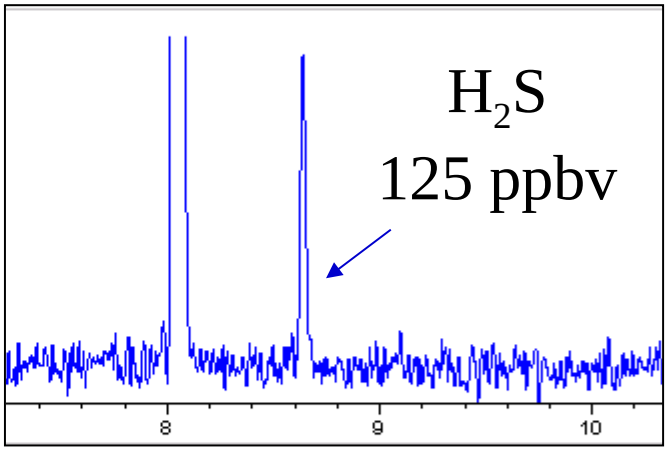
Sulfur in Pipeline Natural Gas

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



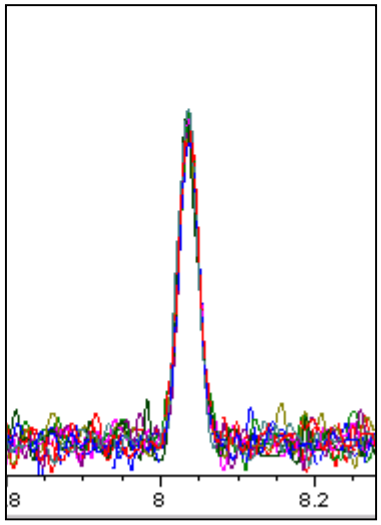
S-PRO Sensitivity





- 1 mL gas sampling loop; 9:1 split ratio
- 60 m GASPRO column (30°C for 1 minute then ramped)
- H_2S is absorptive on the GASPRO column; higher DLs
- H_2S DLs similar to COS on other columns (e.g. DB1 or DB5)

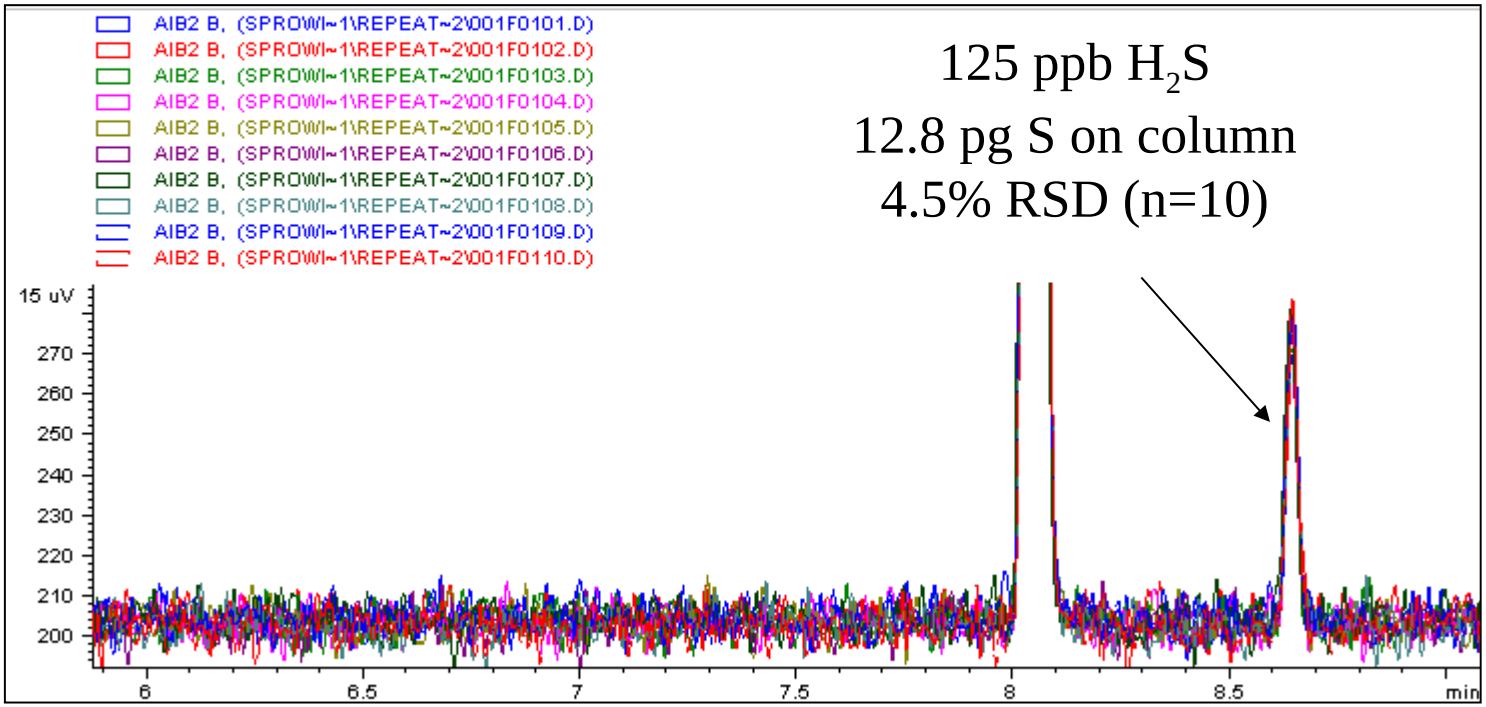
Repeatability of COS at 50 ppbv



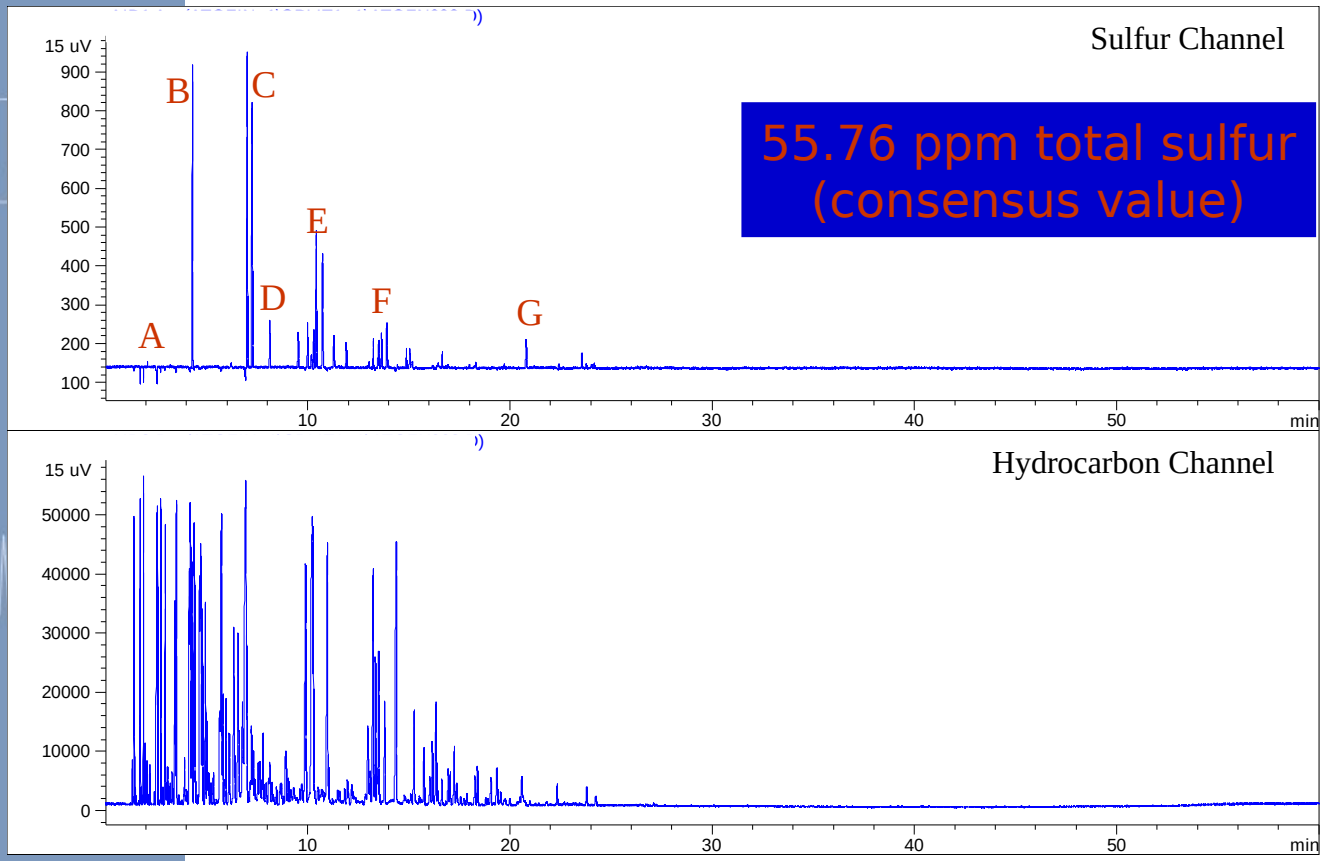
Run Number	Peak Area Counts
1	173.6
2	180.3
3	188.7
4	175.0
5	193.2
6	170.9
7	186.7
8	186.4
9	177.4
10	195.9
Average Count	**182.8**
%RSD	**4.7**

Repeatability of H_2S at 125 ppbv

- 125 ppb H_2S from S-PRO permeation oven
- 1 mL gas sampling loop; split 9:1
- 60 m GASPRO column; 30°C for 1 minute then ramped



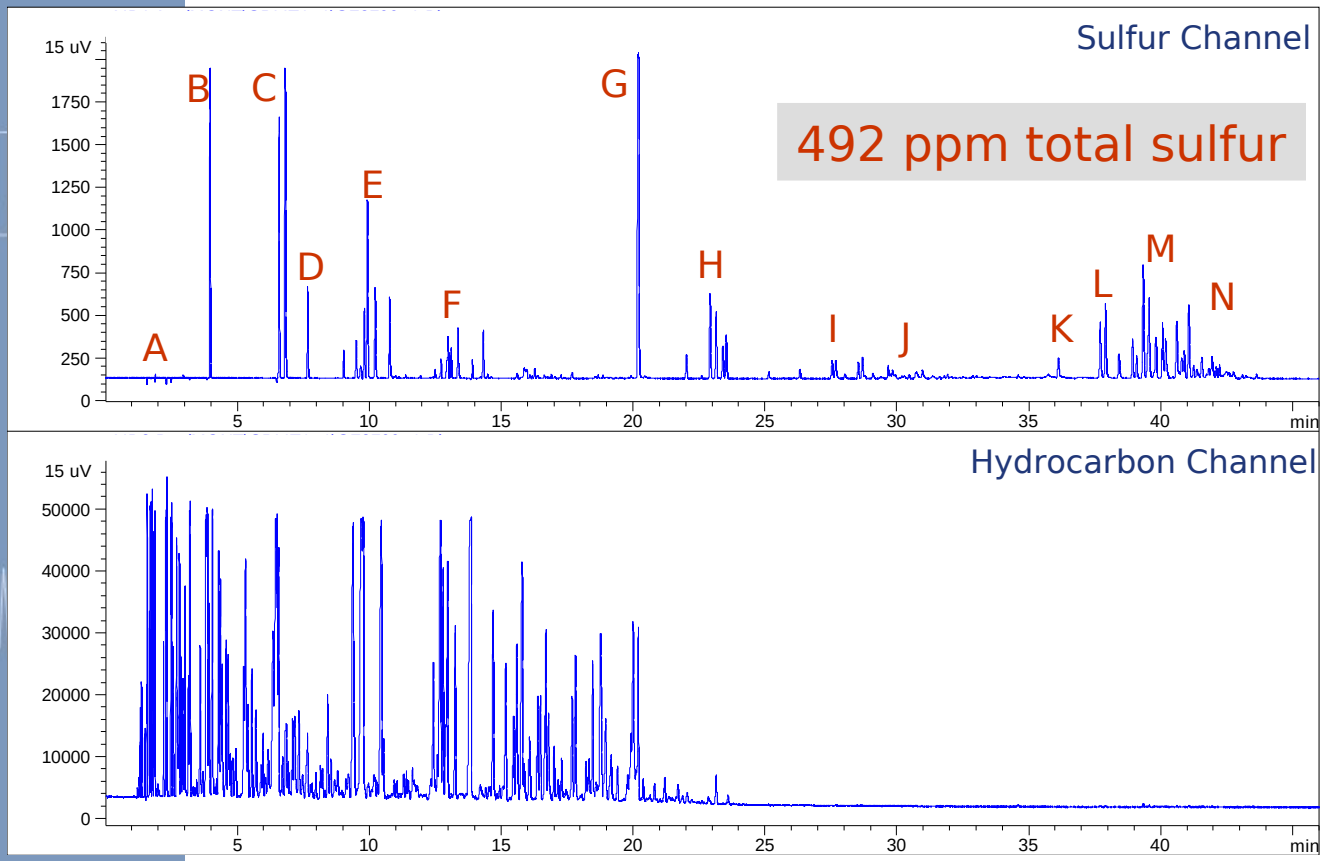
ASTM Round Robin Gasoline #10



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.
Used as an external calibration standard for quantitation of unknowns.

Gasoline Before Sulfur Treatment



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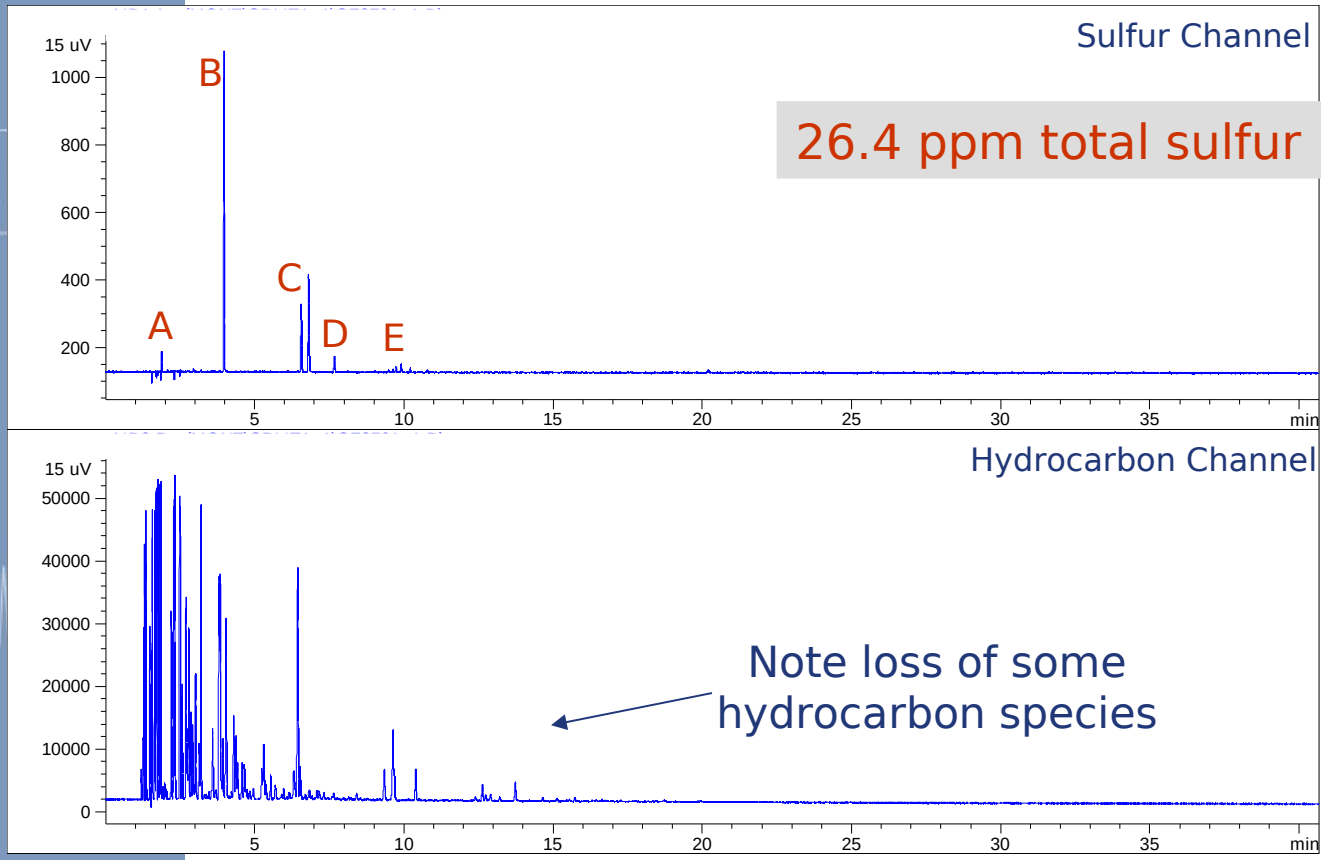
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Gasoline After Sulfur Treatment



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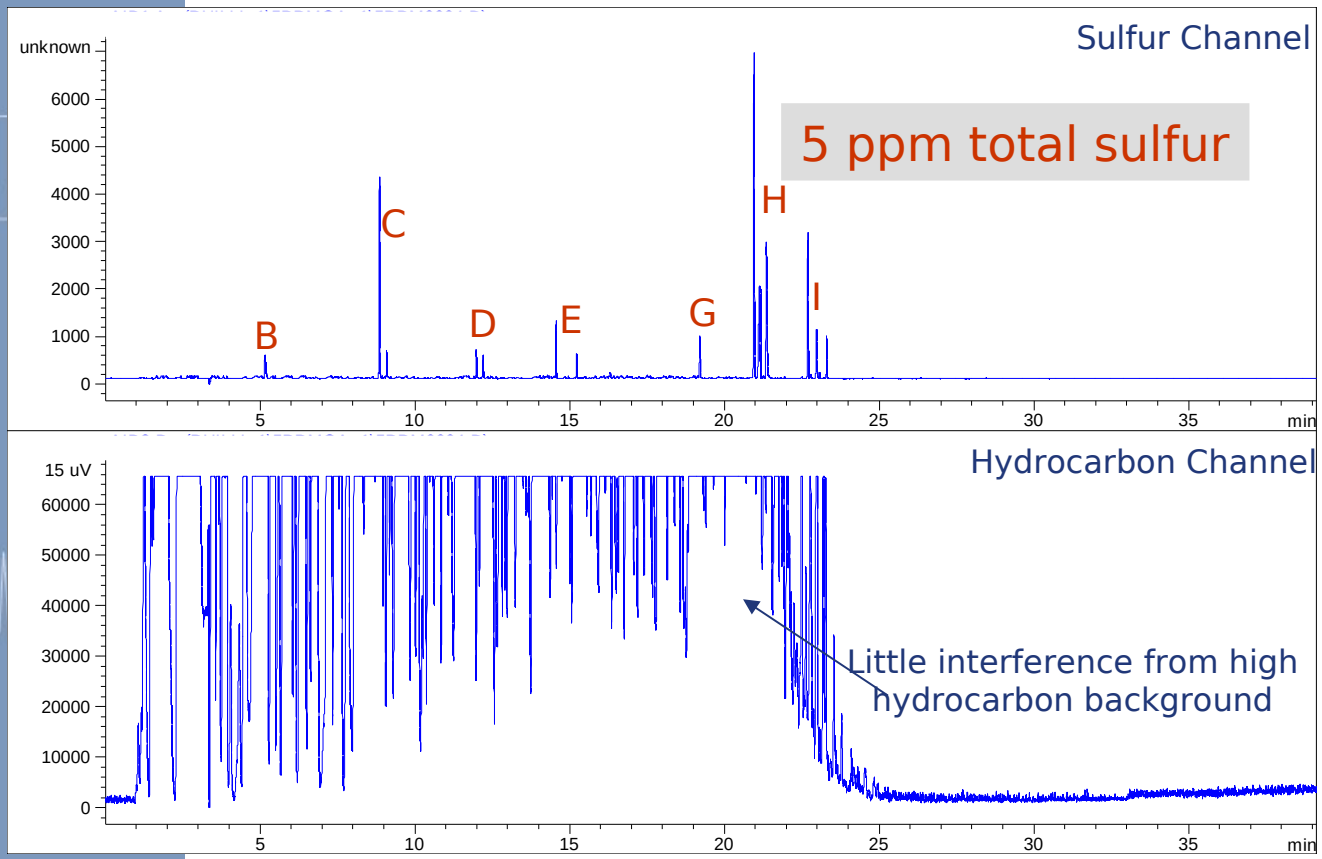
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Low Level Gasoline: 5 ppm Total Sulfur



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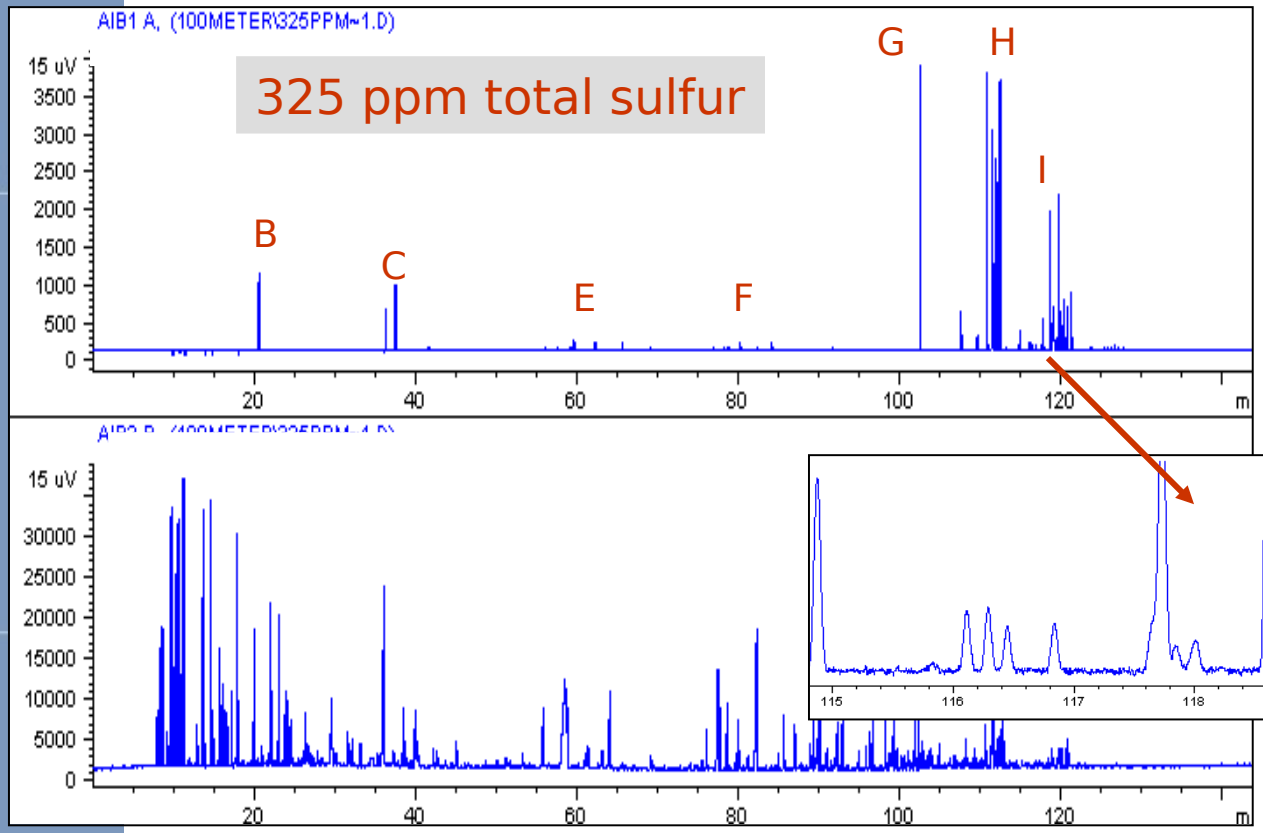
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

“DHA-Type” Analysis of Unknown Gas



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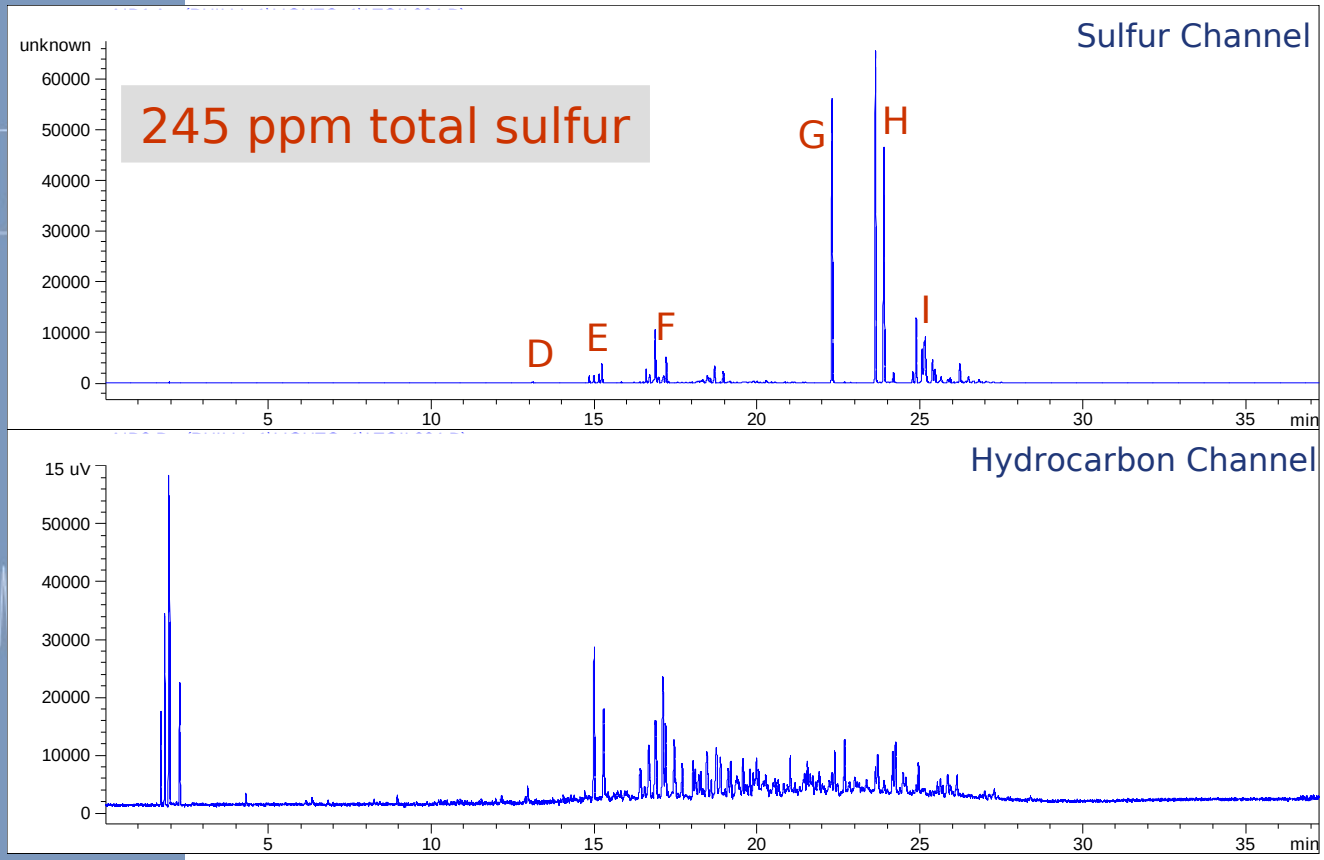
E C2-Thiophenes
F C3-Thiophenes
G Benzothiophene
H C1-Benzothiophenes
I C2-Benzothiophenes

es
nes
es
substituted thiophenes

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

Total Sulfur in LCO



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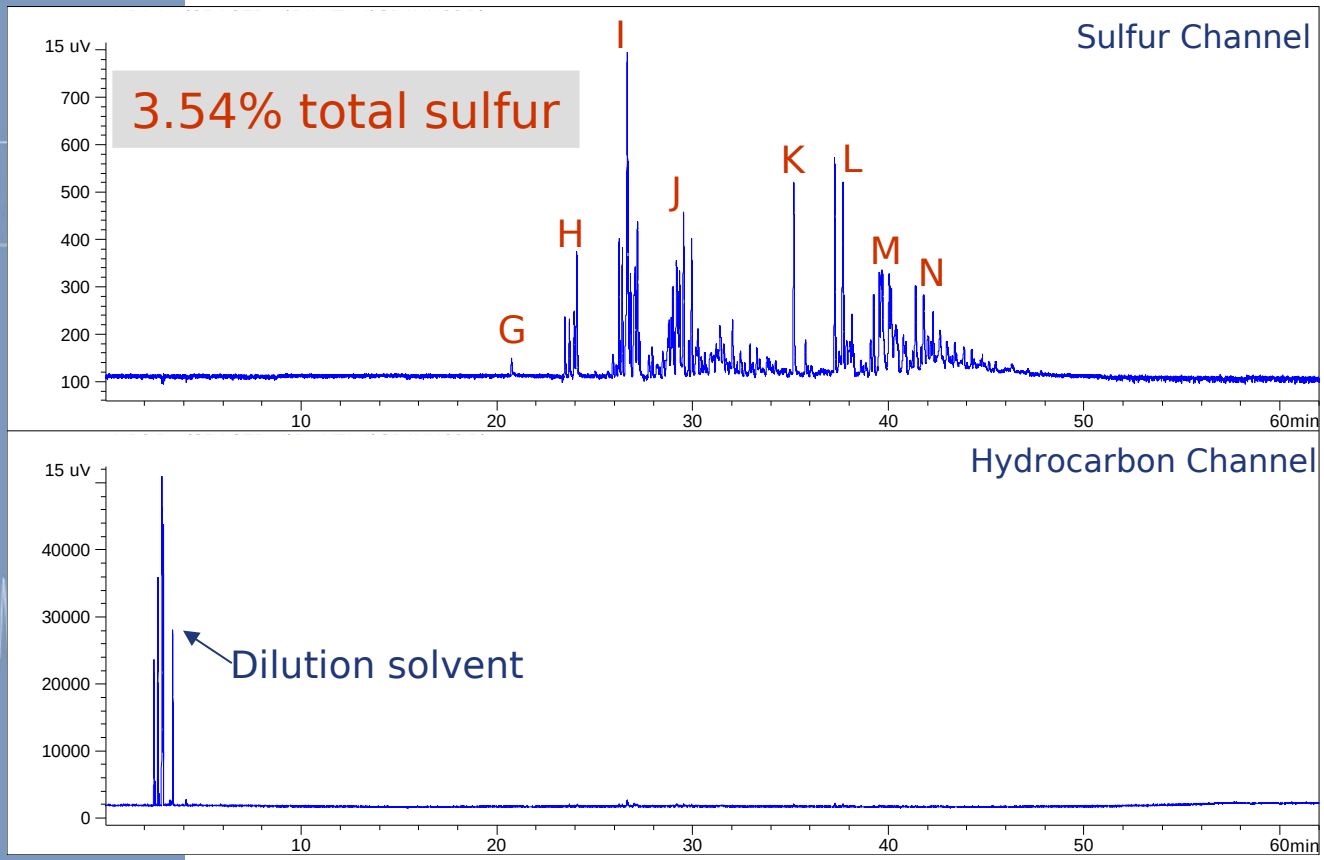
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

o.2 µL injection; split 250:1.
Quantified using ASTM RR gasoline #10
as an external calibration standard.

High Level Total Sulfur in Diesel



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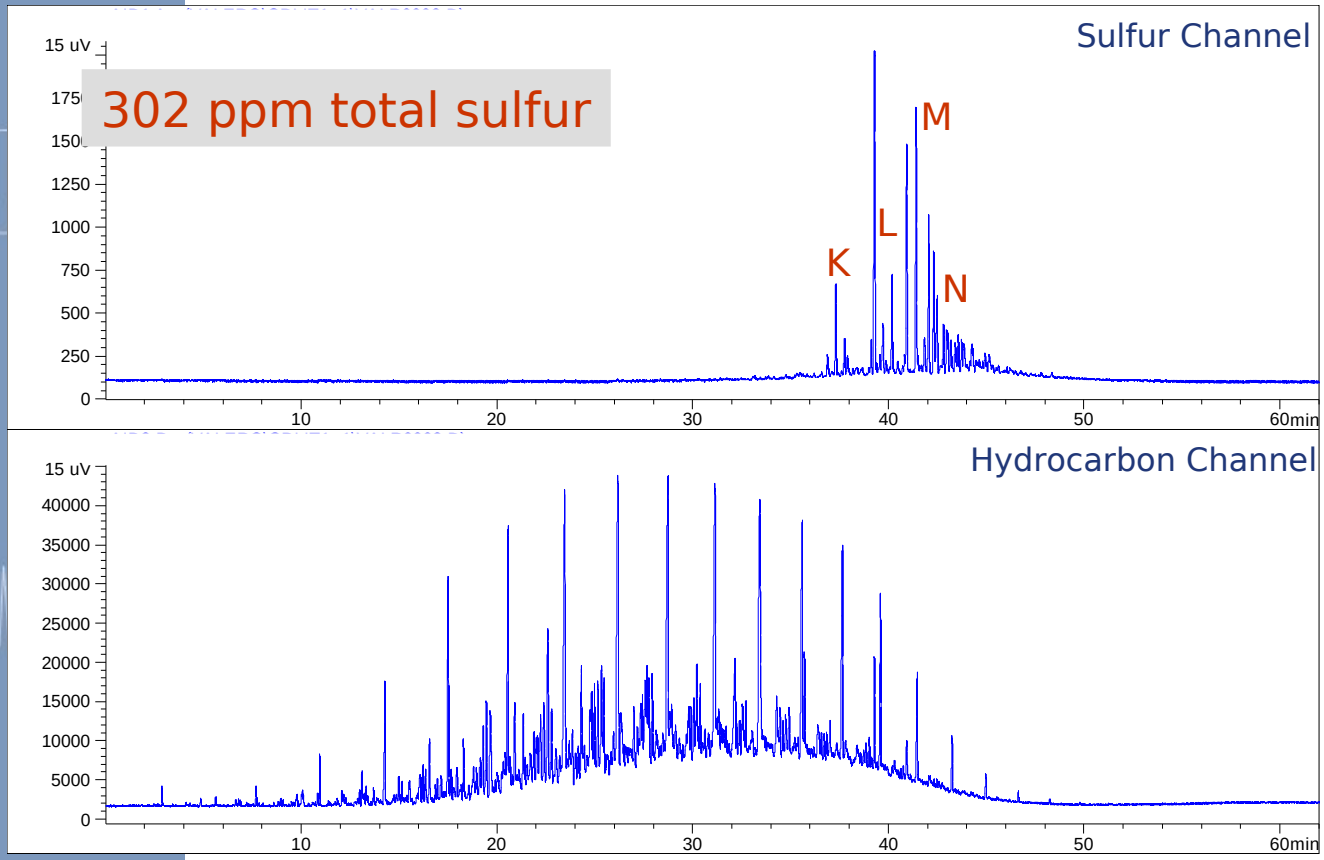
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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



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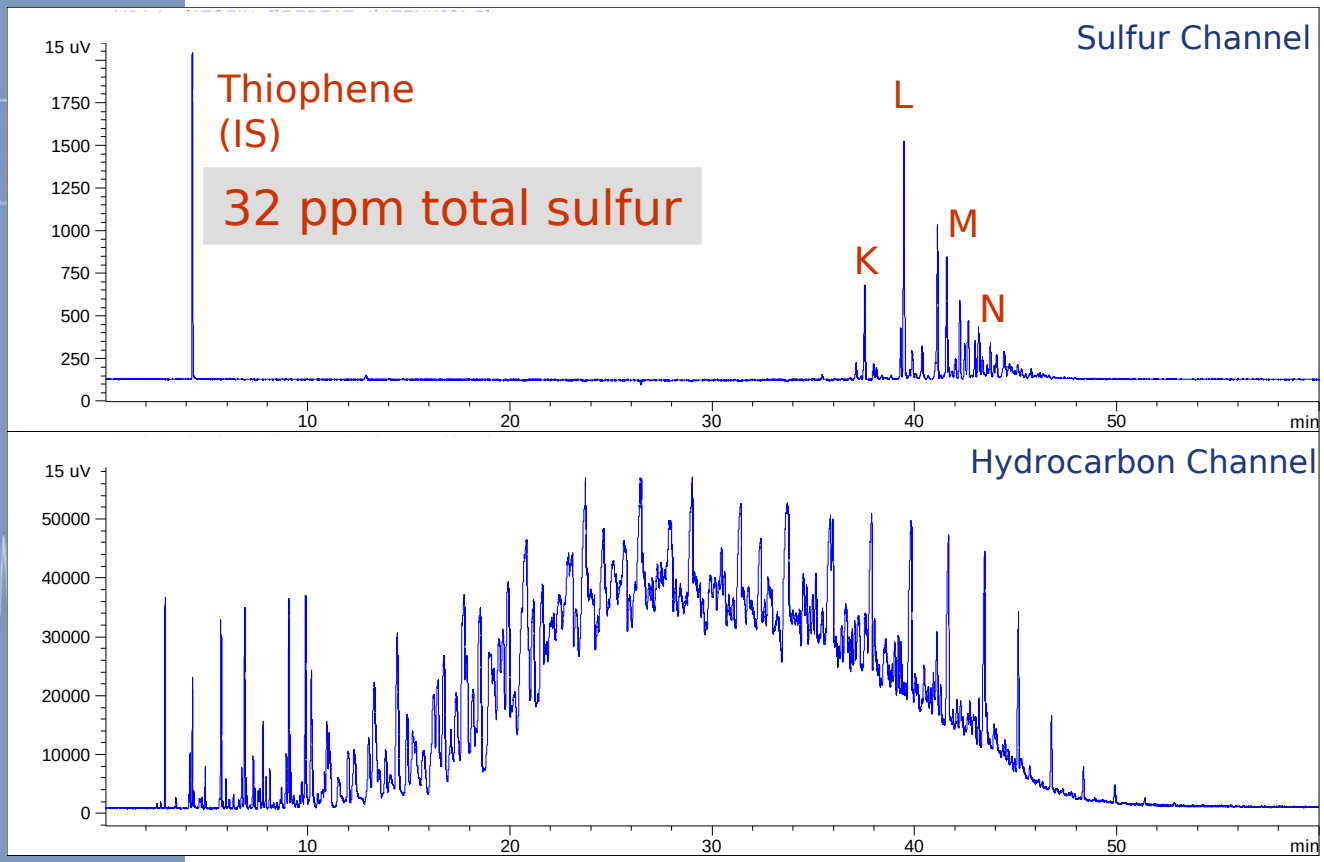
H C1-Benzothiophenes
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Total Sulfur in Diesel Quantified by IS



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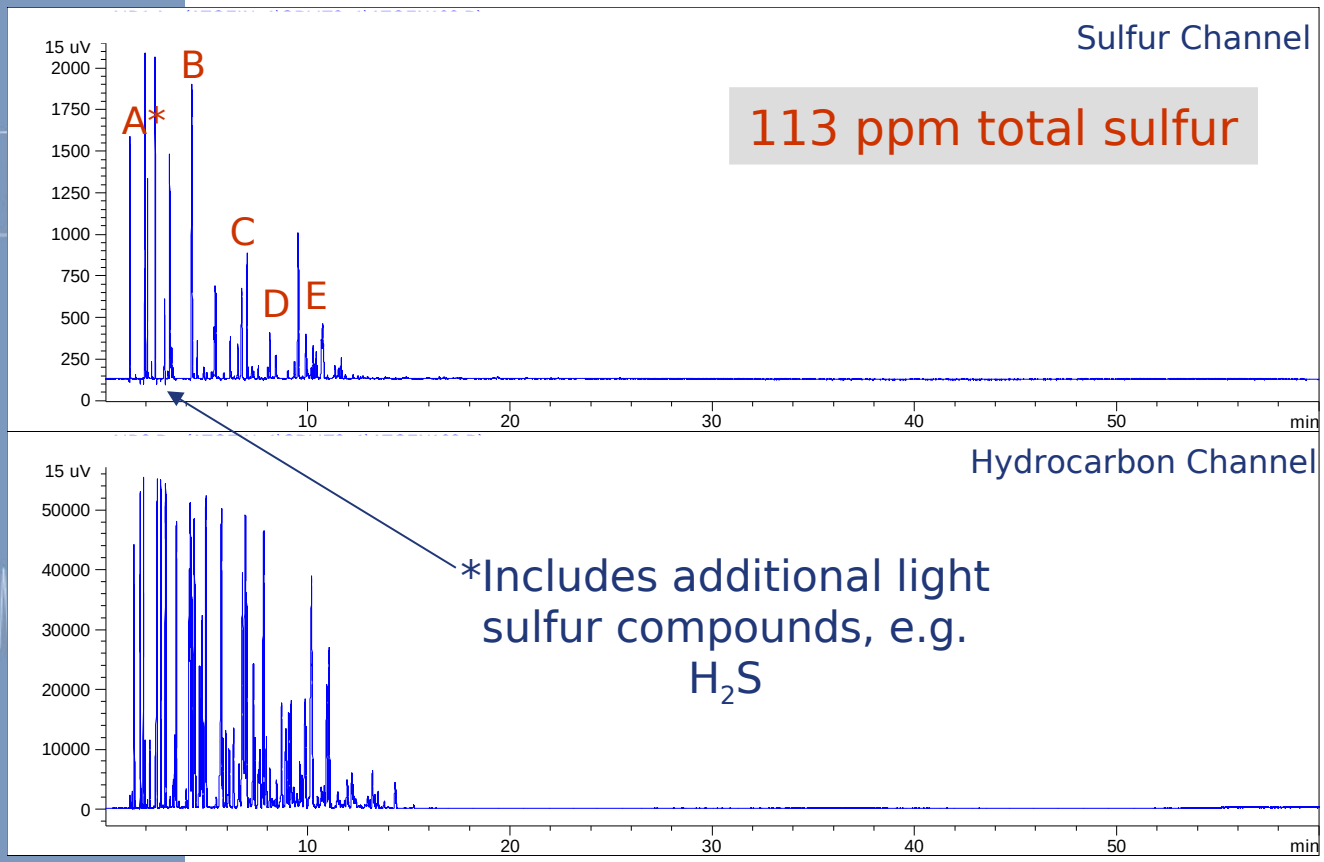
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Naptha Stabilizer Bottoms



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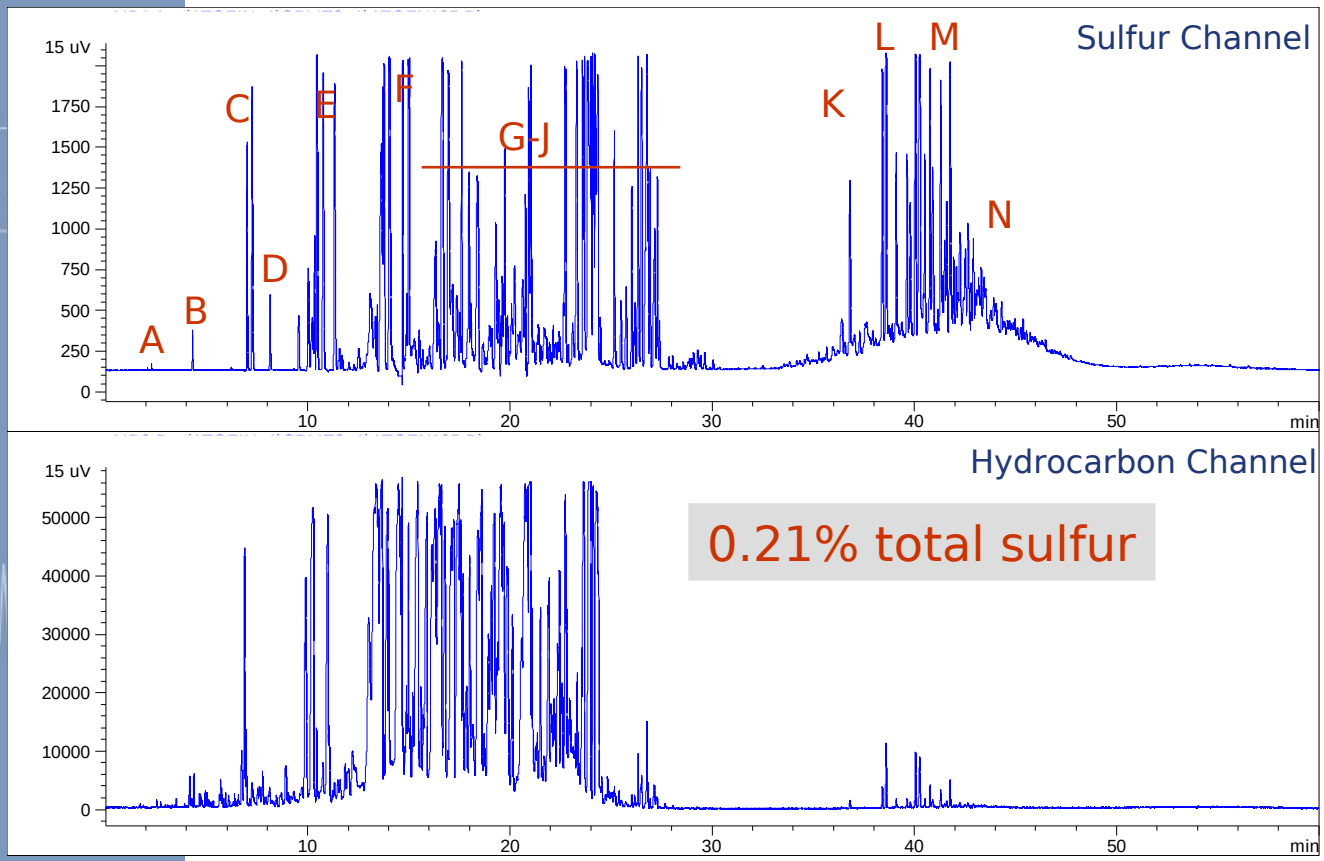
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Heavy Catalytic Naptha Before Merox



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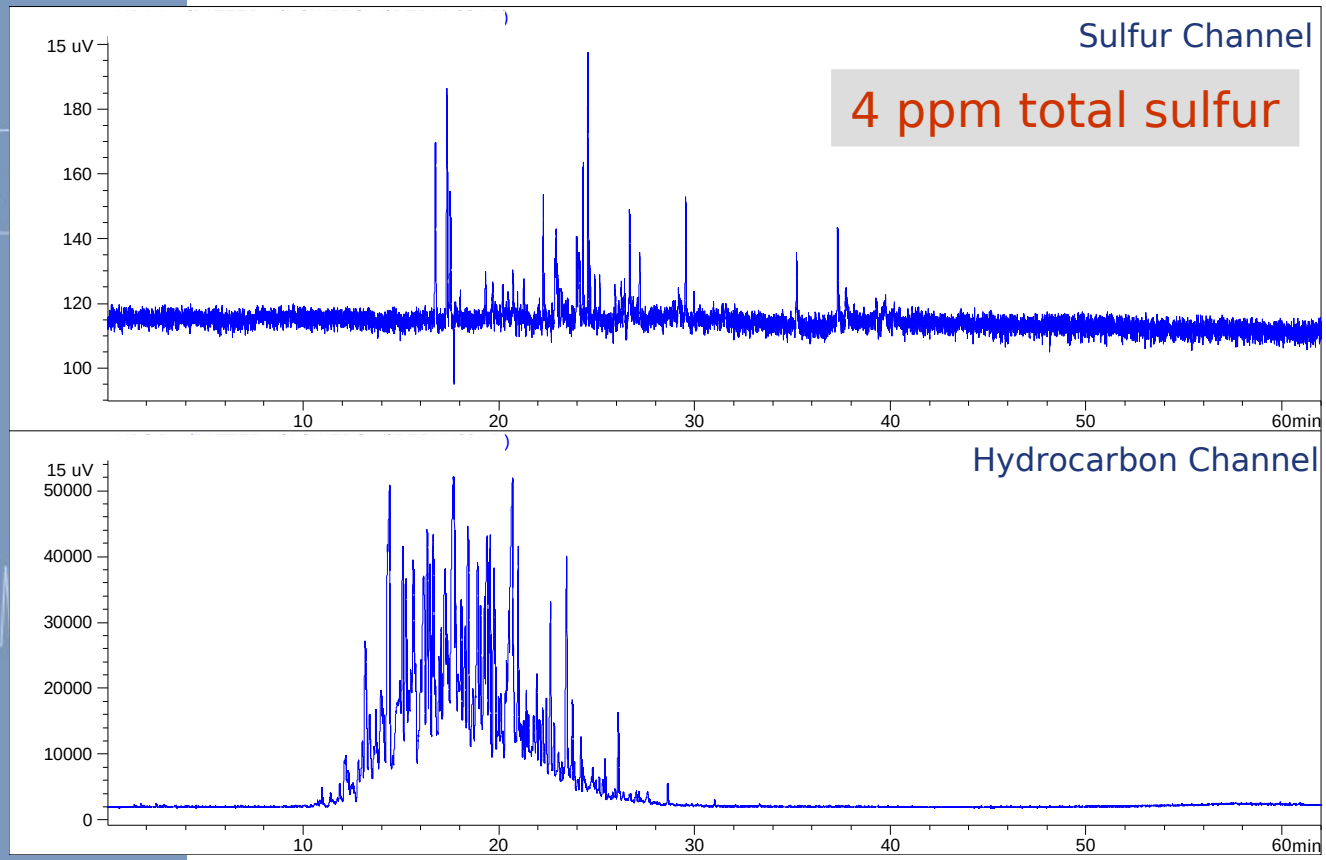
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Low Level Sulfur in Jet Fuel by PFPD



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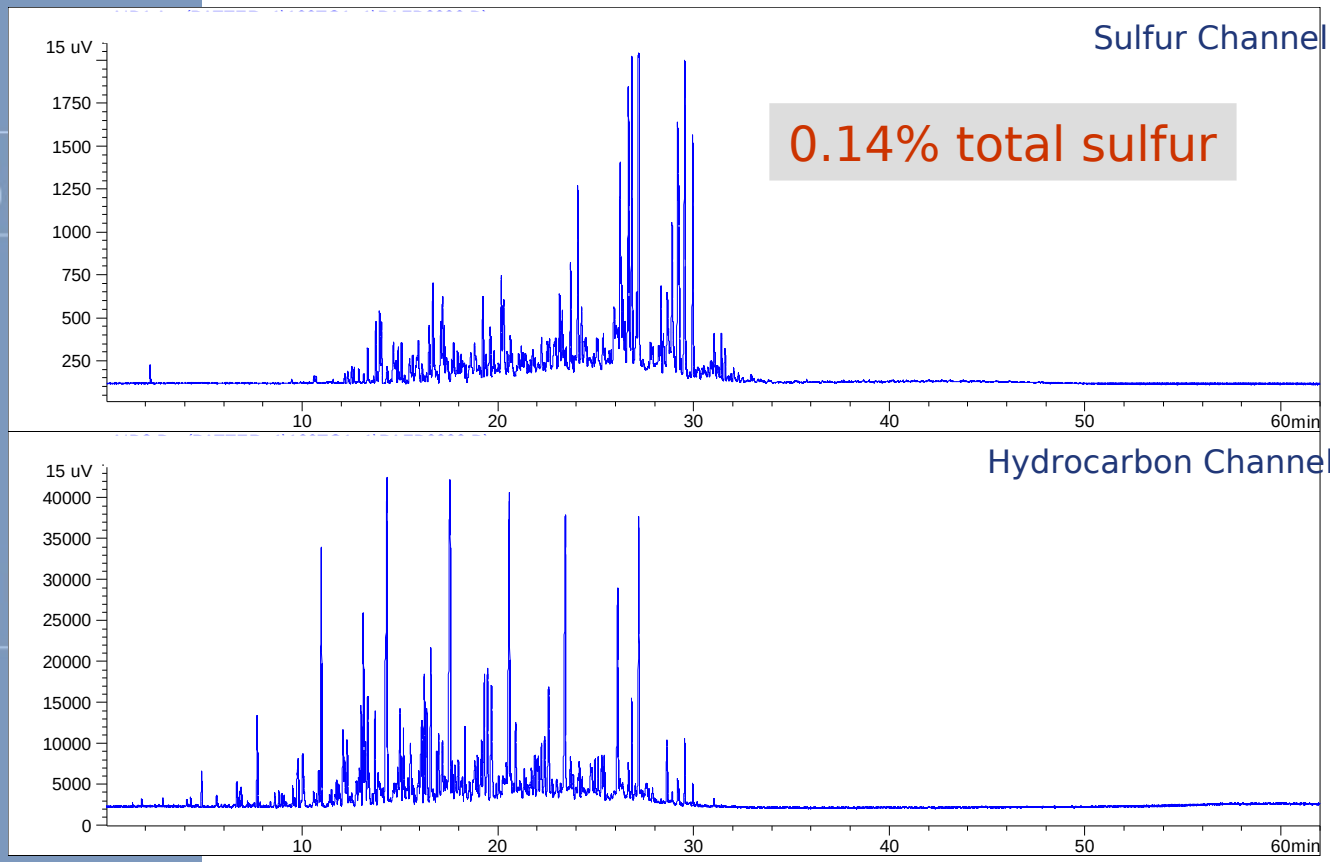
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

High Sulfur Content in Jet Fuel



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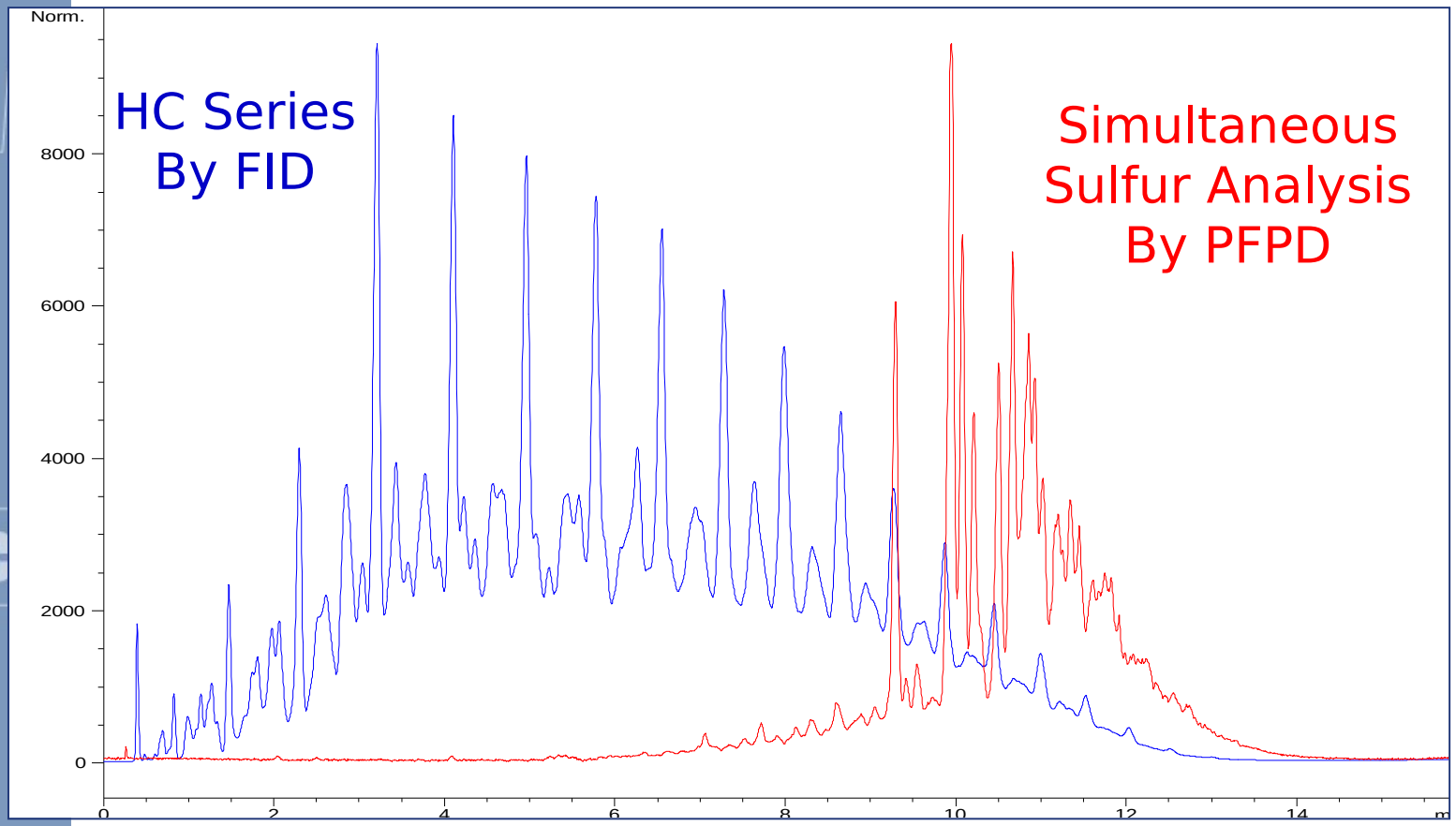
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

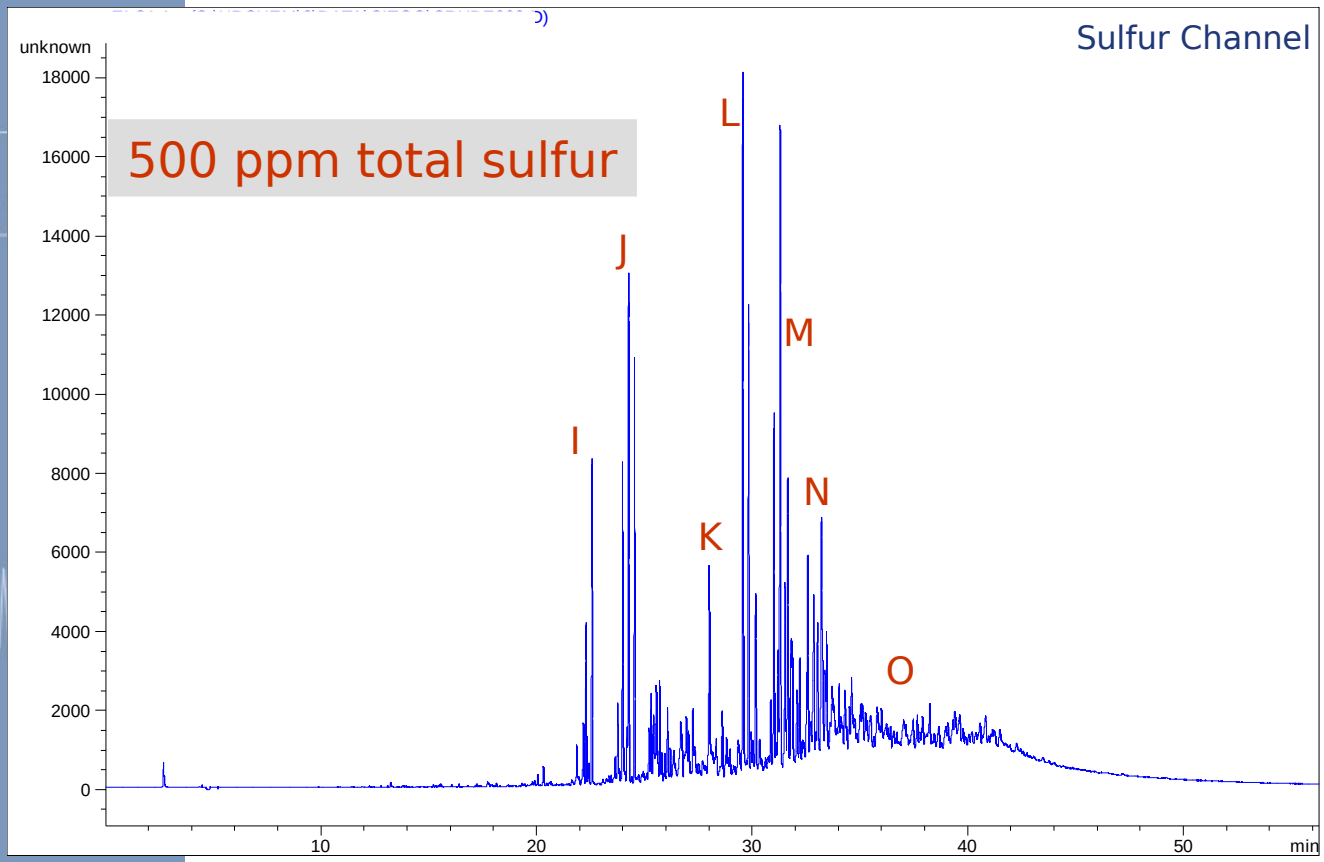
1 μL injection; split 100:1.
No reference was available for identification of sulfur peak groupings in jet fuel.

Sulfur by Simulated Distillation



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

Total Sulfur in Crude Oil by PFPD



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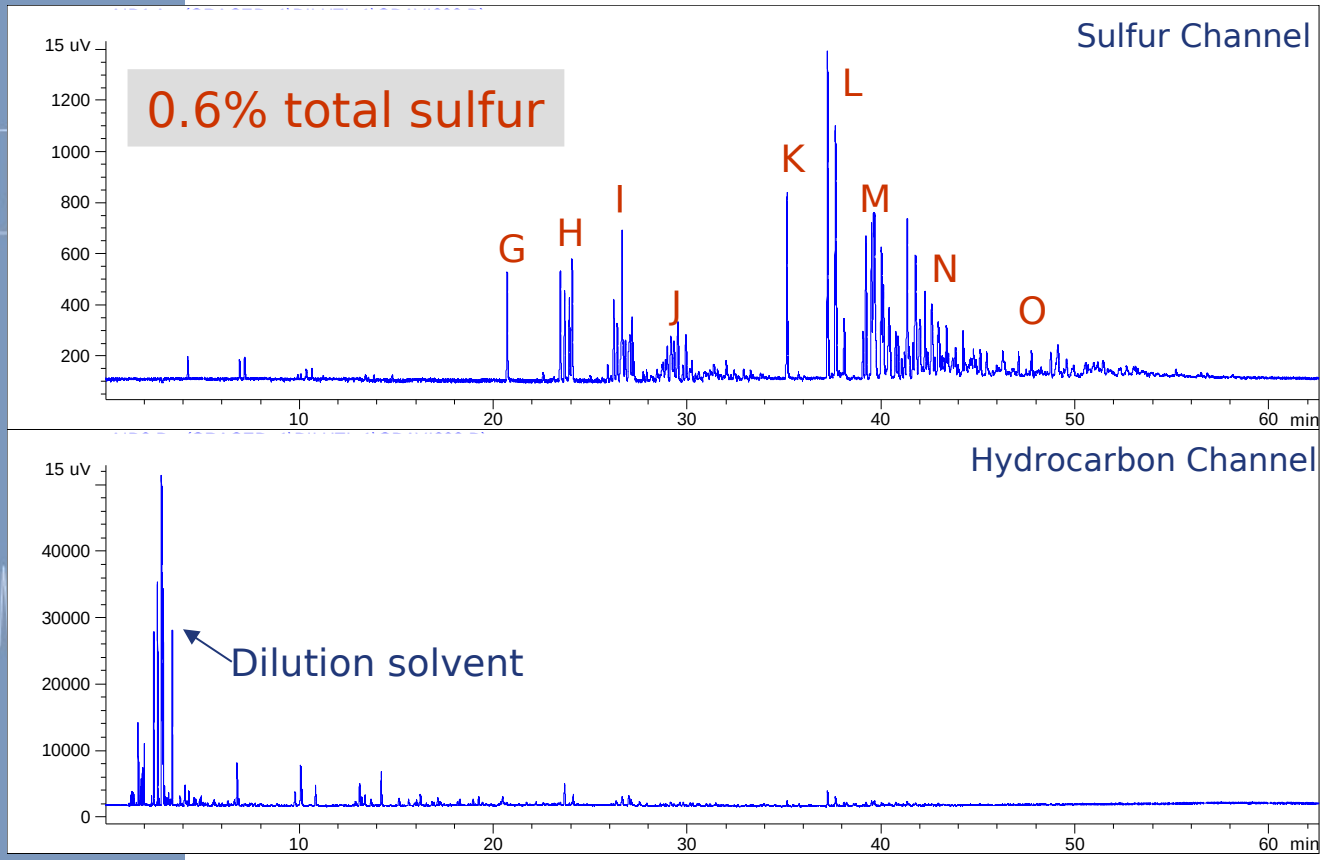
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Synthetic Crude



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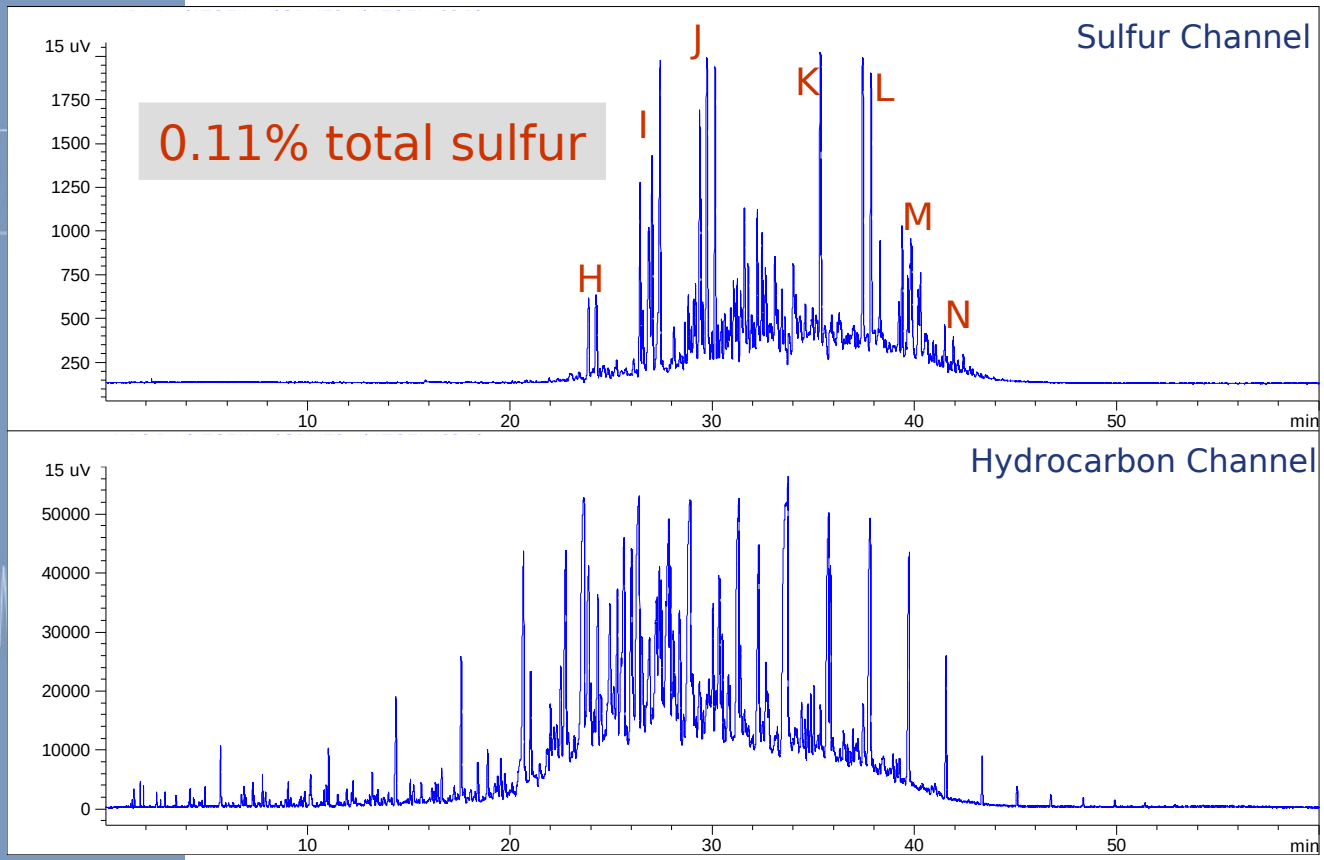
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

High Sulfur Content Furnace Oil



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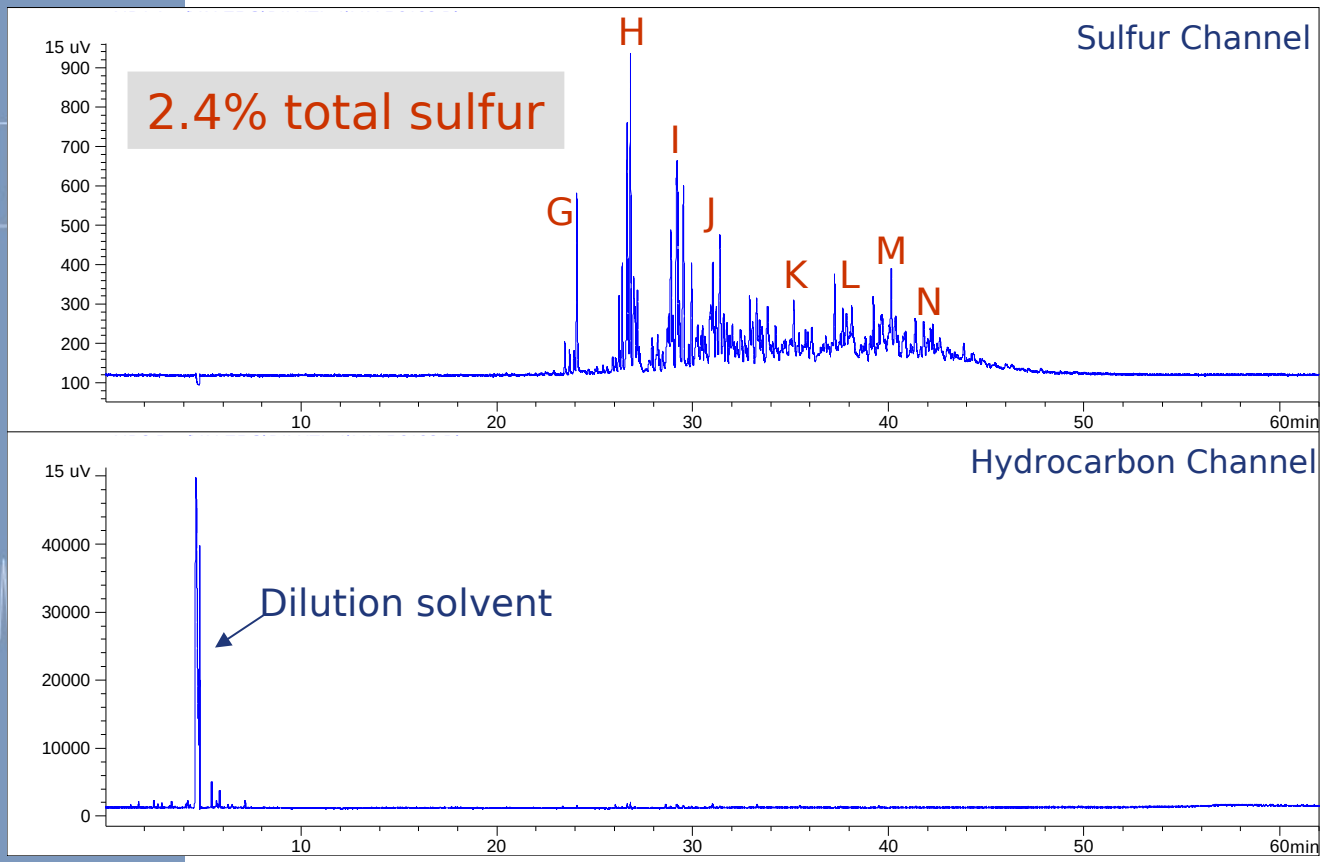
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Coker Light Gas Oil by PFPD



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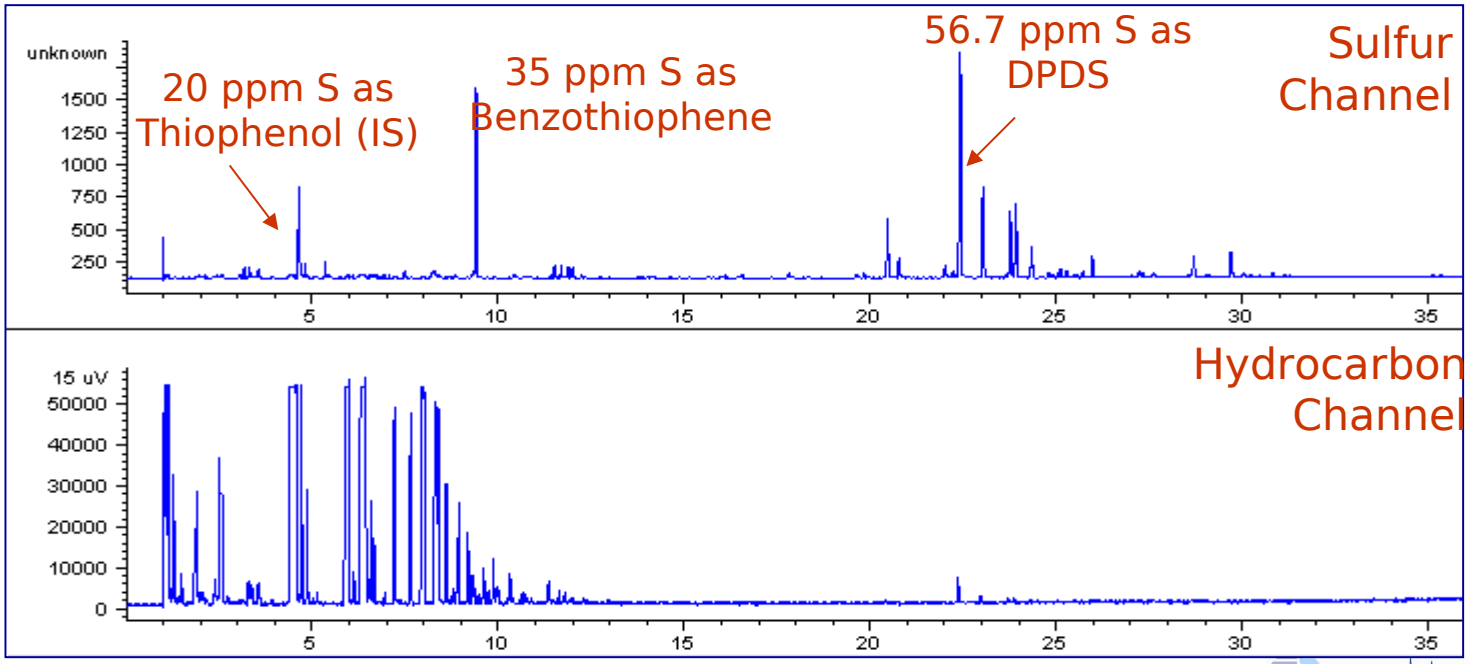
I C2-Benzothiophenes
J C3-Benzothiophenes
K Dibenzothiophene
L C1-Dibenzothiophenes
M C2-Dibenzothiophenes
N C3-Dibenzothiophenes
O Alkyl sulfides & substituted thiophenes

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

Sulfur in an Acidic Product

- 20 ppm S as thiophenol added as Internal Standard
- Two speciated sulfur peaks identified and quantified
- Total sulfur measured at 270 ppm sulfur
- 0.2 μL injection; split 50:1; DB-5MS column; 3 mm combustor; tuned for sulfur



Analysis of Thiophene in Benzene by ASTM Standard Method D4735-09

ASTM Standard D4735 - 96

"Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography"

First re-approved in 2000

Re-approved again in 2002

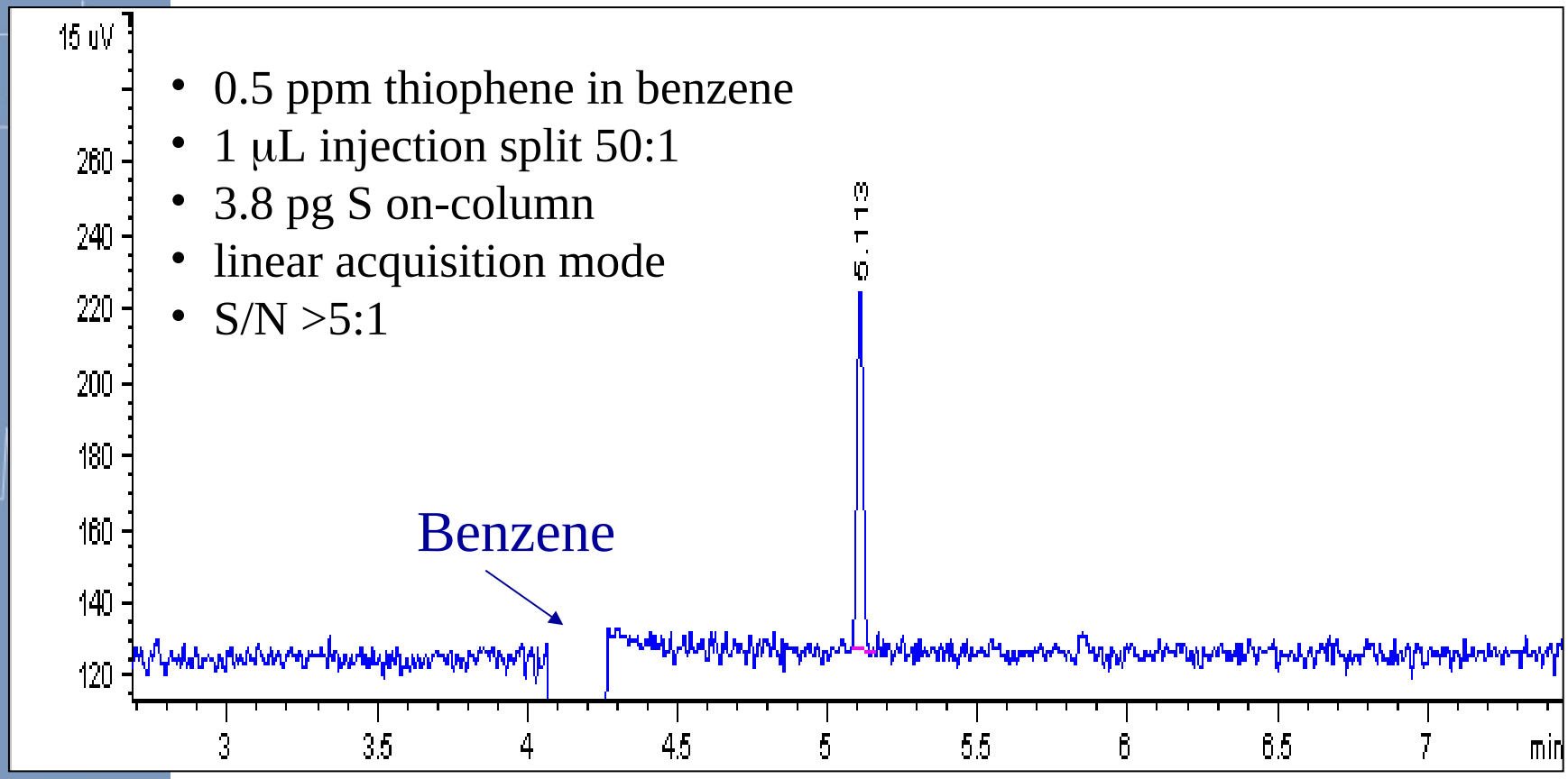
With modifications to include PFPD

Re-approved in 2009 with addition of Interlaboratory Study and new precision statement for PFPD

ASTM Standard D4735 - 96

- Section 5.3 Detector – “Any flame photometric detector (FPD) can be used, provided it has sufficient sensitivity to produce a minimum peak height twice that of the base noise . . .”

0.5 ppm Thiophene by PFPD

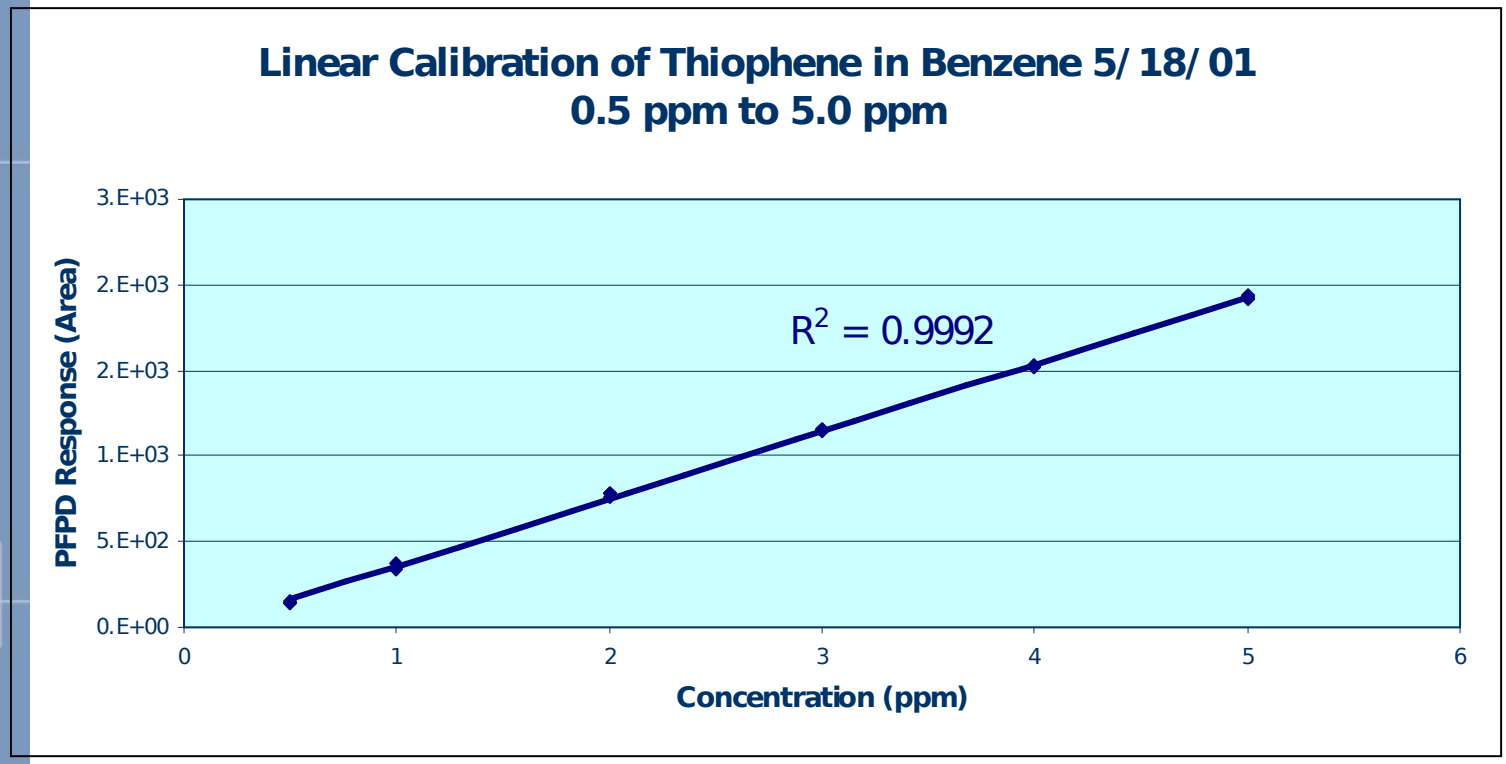


- 0.5 ppm thiophene in benzene
- 1 µL injection split 50:1
- 3.8 pg S on-column
- linear acquisition mode
- S/N >5:1

Thiophene Calibration Repeatability

Calibration Level	% RSD (n = 3)
0.5 ppm	3.7
1.0 ppm	6.1
2.0 ppm	1.9
3.0 ppm	0.6
4.0 ppm	0.2
5.0 ppm	0.6

Thiophene Linear Calibration Plot



Thiophene Calibration Results

- Log/log plot (cited by original method)
  - $R^2 = 0.9995$
- Quadratic plot (PFPD in quadratic mode)
  - $R^2 = 0.9997$
- Linear plot (PFPD in linear mode)
  - $R^2 = 0.9992$

All three plot techniques result in excellent and equivalent calibration curves

Precision Measured as %RSD

Thiophene Calculated Concentrations (ppm)				
Run #1	0.51	0.97	2.98	4.91
Run #2	0.49	0.96	2.92	4.96
Run #3	0.50	0.96	2.97	4.97
Run #4	0.49	0.98	2.98	5.01
Run #5	0.49	0.97	2.97	4.98
Run #6	0.49	0.97	2.96	4.99
Run #7	0.50	0.99	2.99	4.96
Average	0.50	0.97	2.97	4.97
%RSD	**1.4%**	**1.3%**	**0.8%**	**0.6%**

Thiophene Accuracy as % Recy

Expected Concentration (ppm)	Avg. Measured Concentration (n = 7)	% Recovery
0.50	0.50	99.1
1.0	0.97	97.2
3.0	2.97	98.9
5.0	4.97	99.3

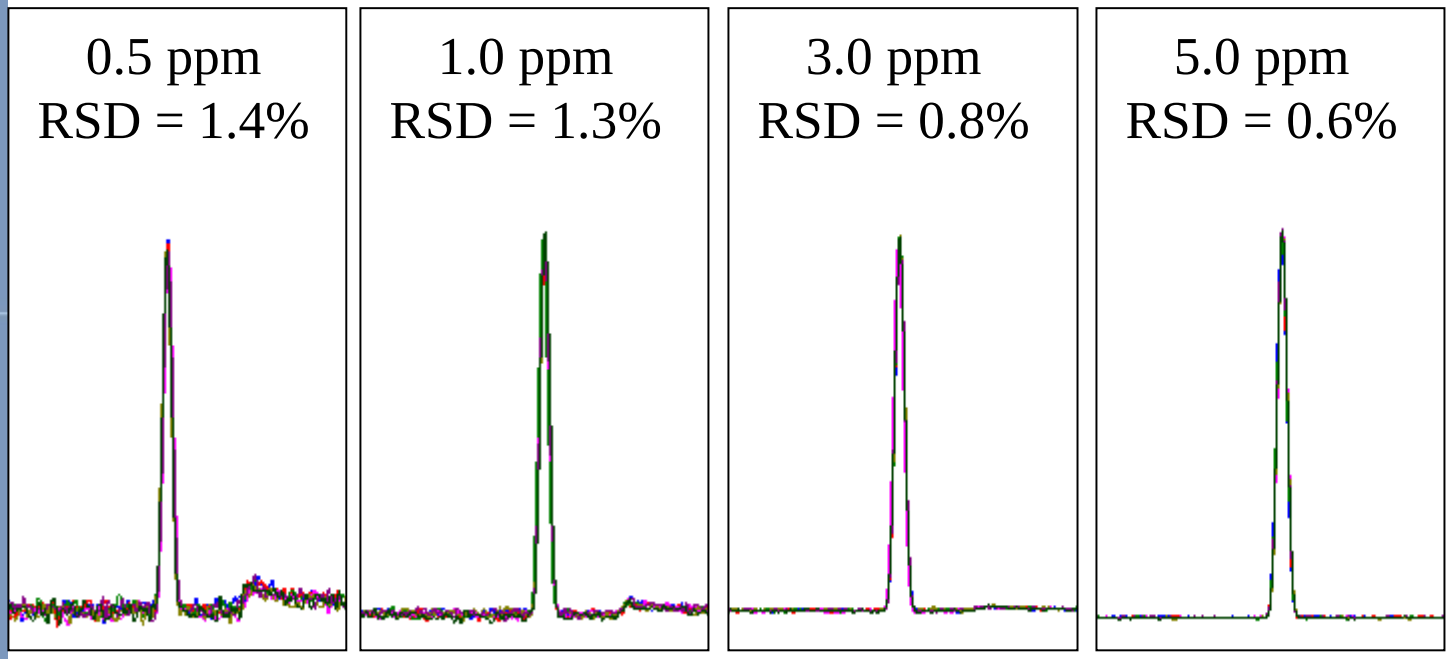
Comparison of Thiophene QC Data

Intermediate Precision Data From D4735 - 96	
Thiophene Conc. (mg/kg)	Intermediate Precision (mg/kg)
0.80	0.040
1.80	0.078
Intermediate Precision Data From D4735 – 02	
Thiophene Conc. (mg/kg)	Intermediate Precision (mg/kg)
0.50	0.010
1.00	0.010
3.00	0.023
5.00	0.031

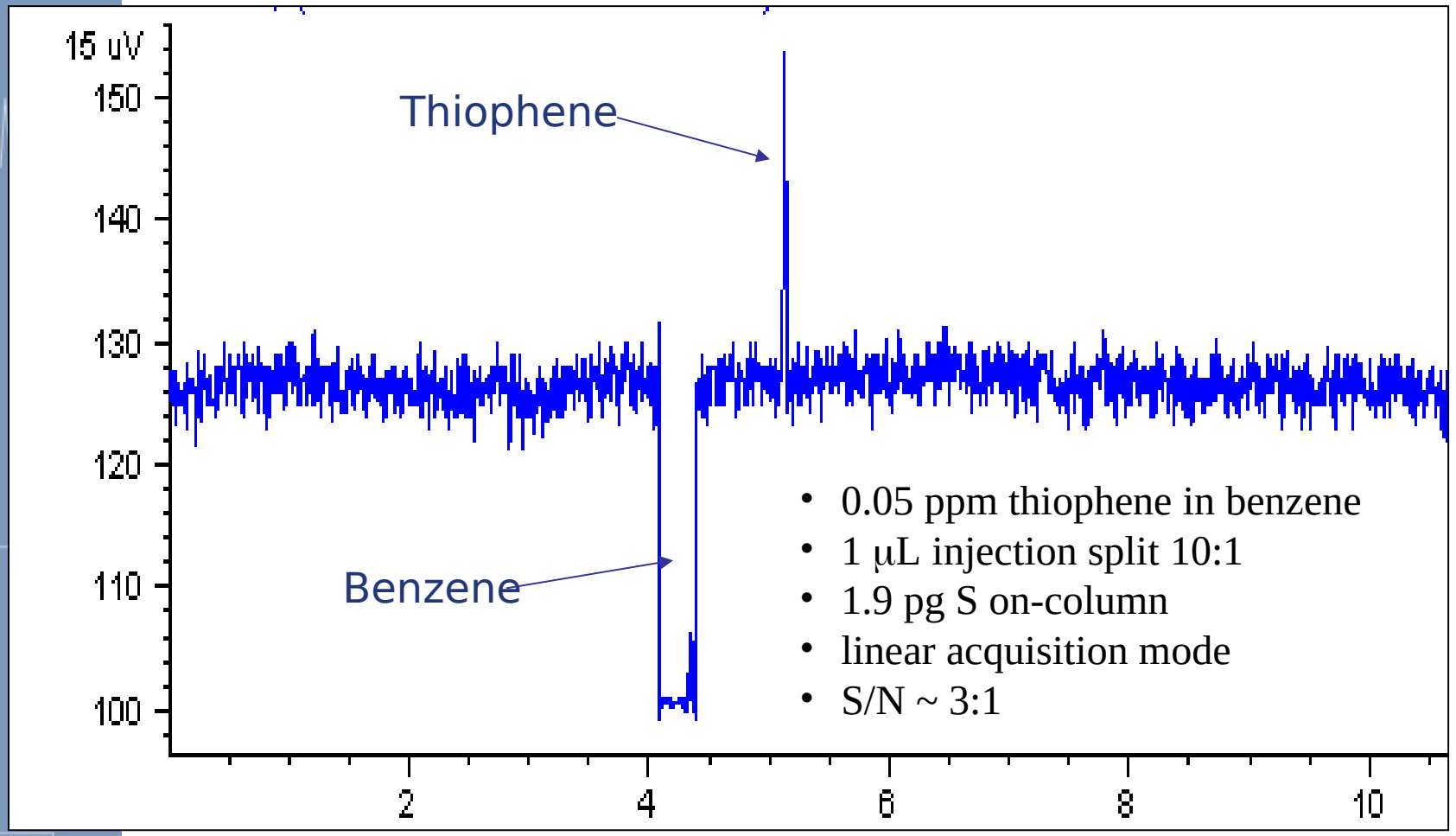
The new PFPD precision is ~3-4 times better than the original FPD precision

Thiophene Precision on the PFPD

- Overlaid chromatograms
- 4 concentrations
- 7 replicate analyses over ~ 1 week

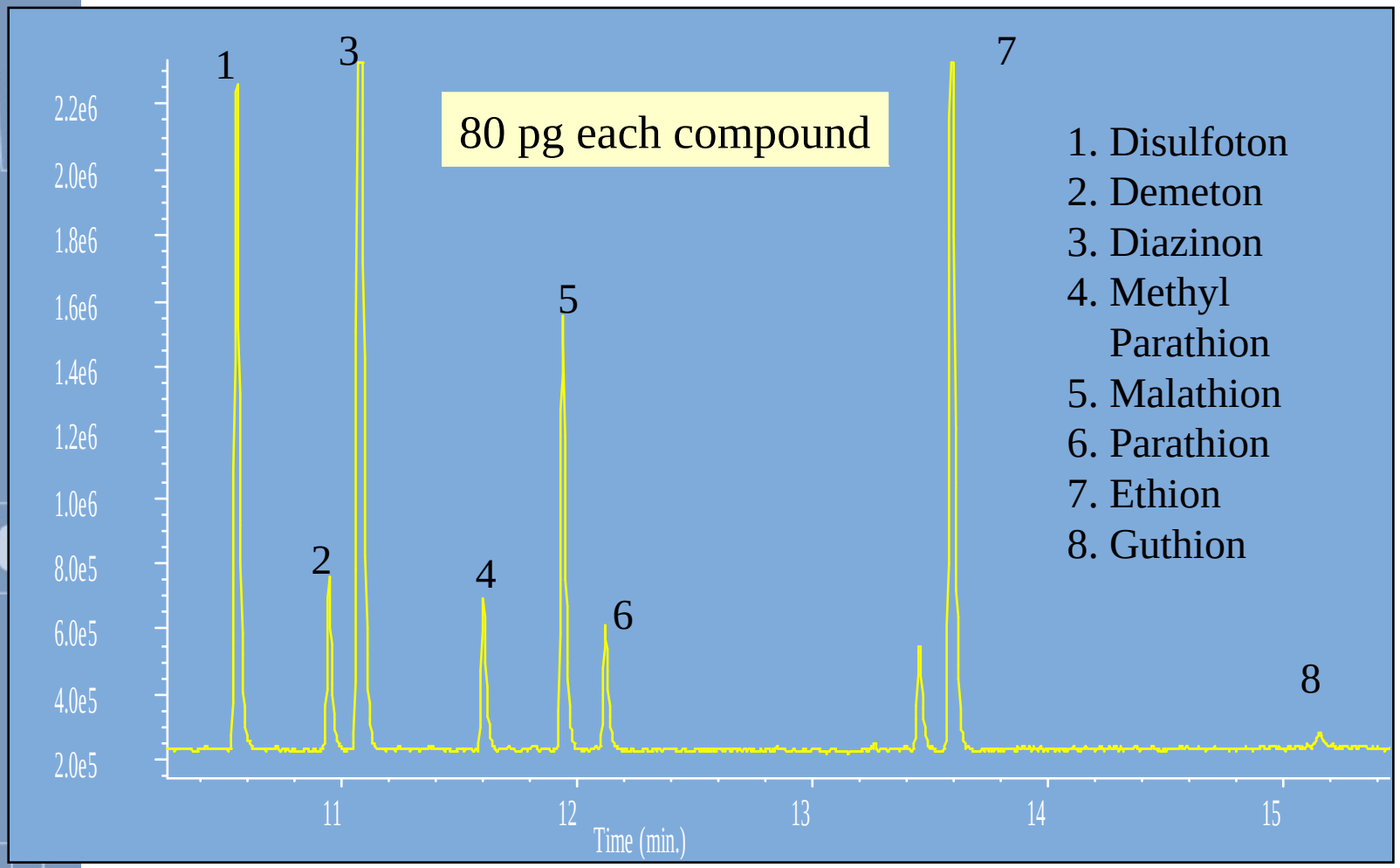


Improved Sensitivity on the PFPD



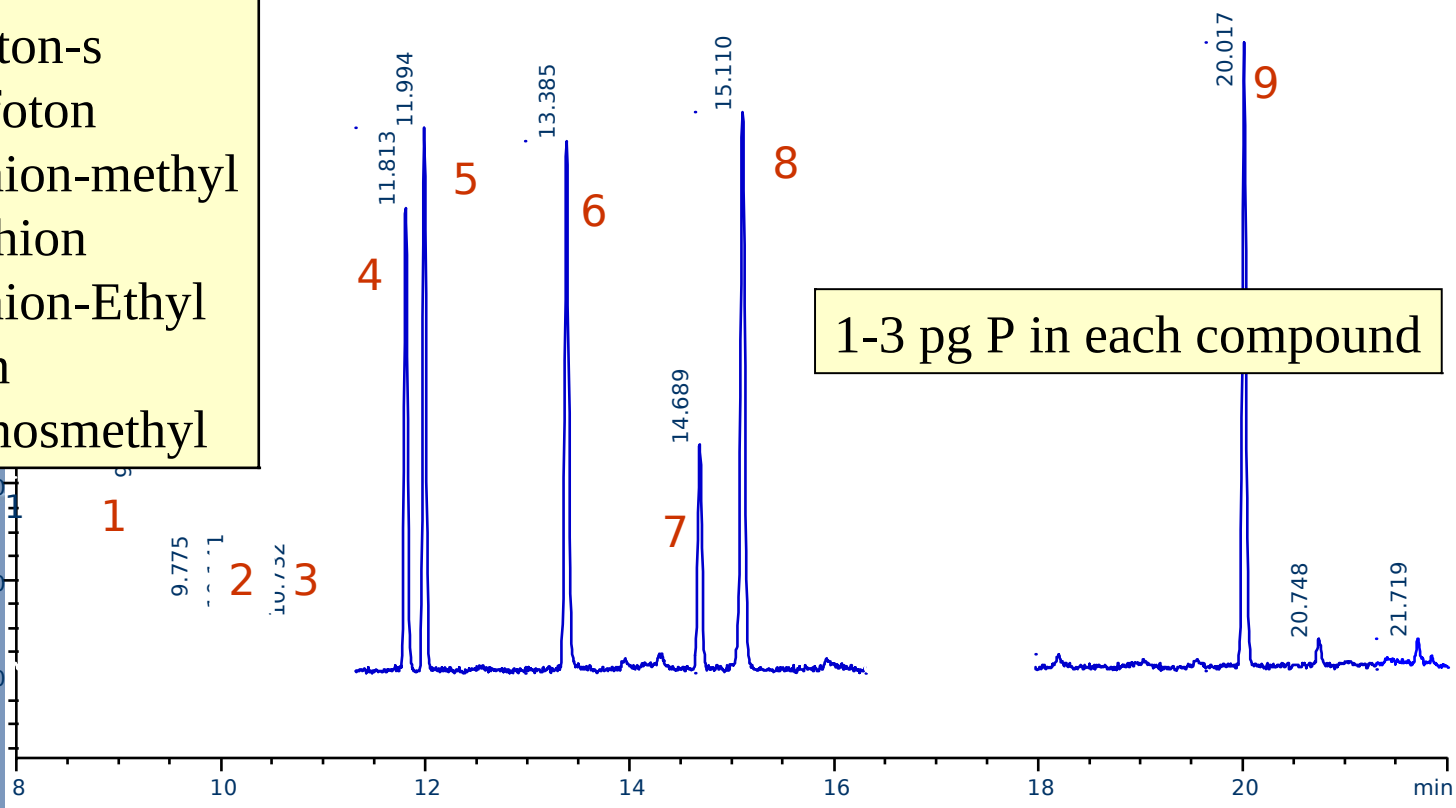
Organophosphorus Pesticides by PFPD

OP Pesticides by PFPD - Sulfur Mode



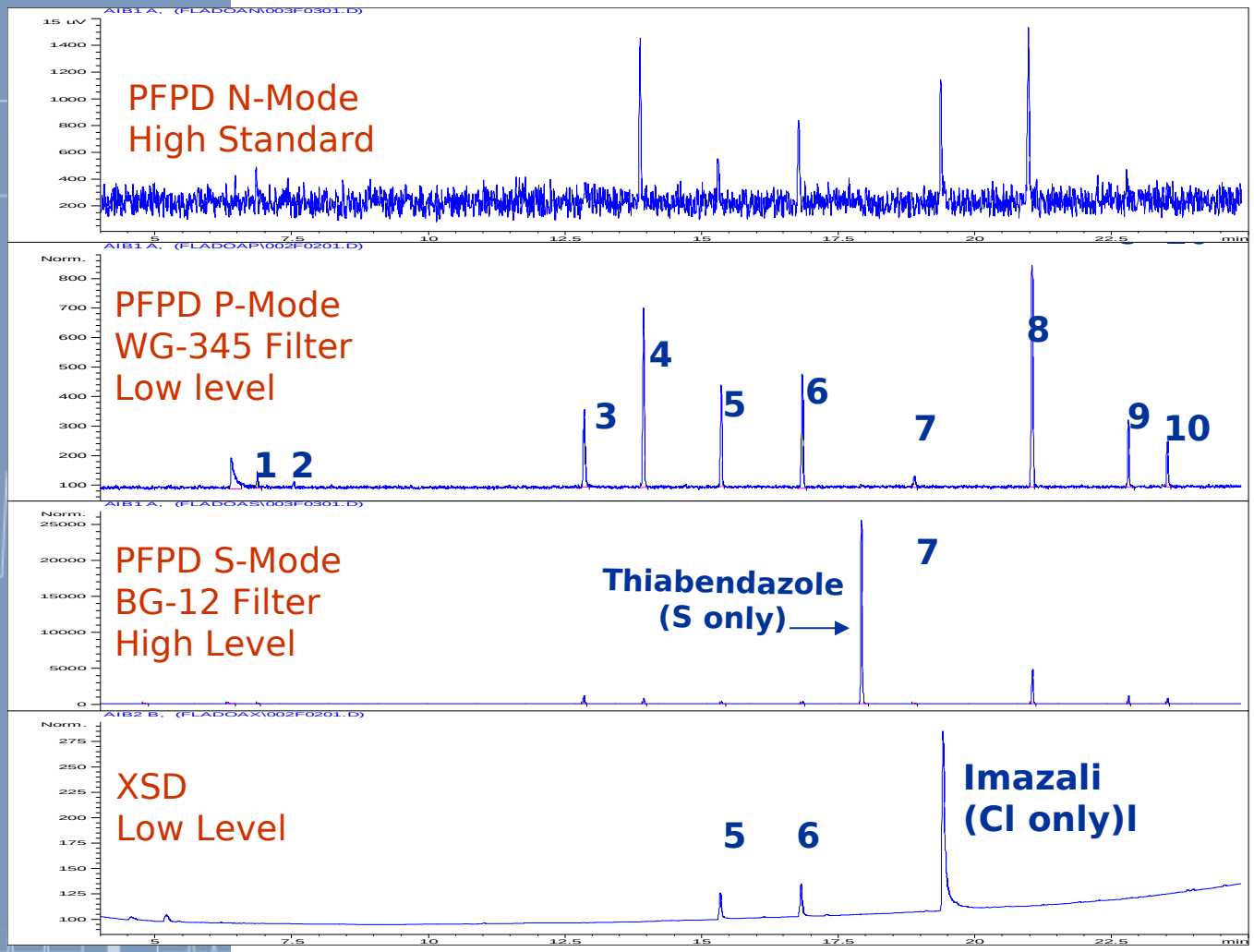
OP Pesticides by PFPD – Phosphorus Mode

1. Dematon-o
2. Diazinon
3. Dematon-s
4. Disulfoton
5. Parathion-methyl
6. Malathion
7. Parathion-Ethyl
8. Ethion
9. Azinphosmethyl



1-3 pg P in each compound

Pesticide Mix on PFPD & XSD

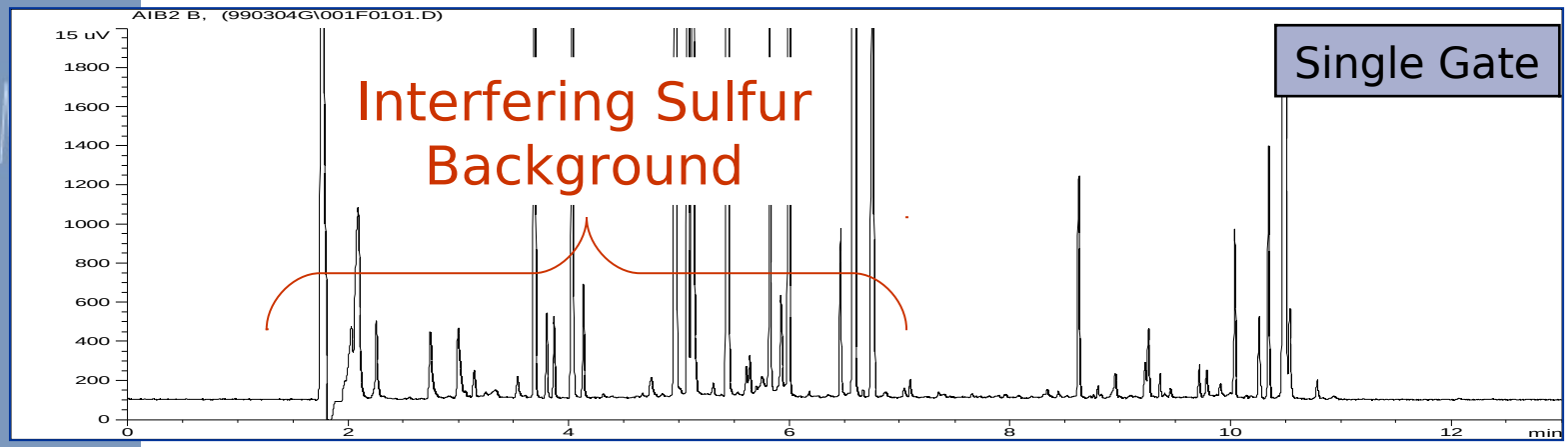


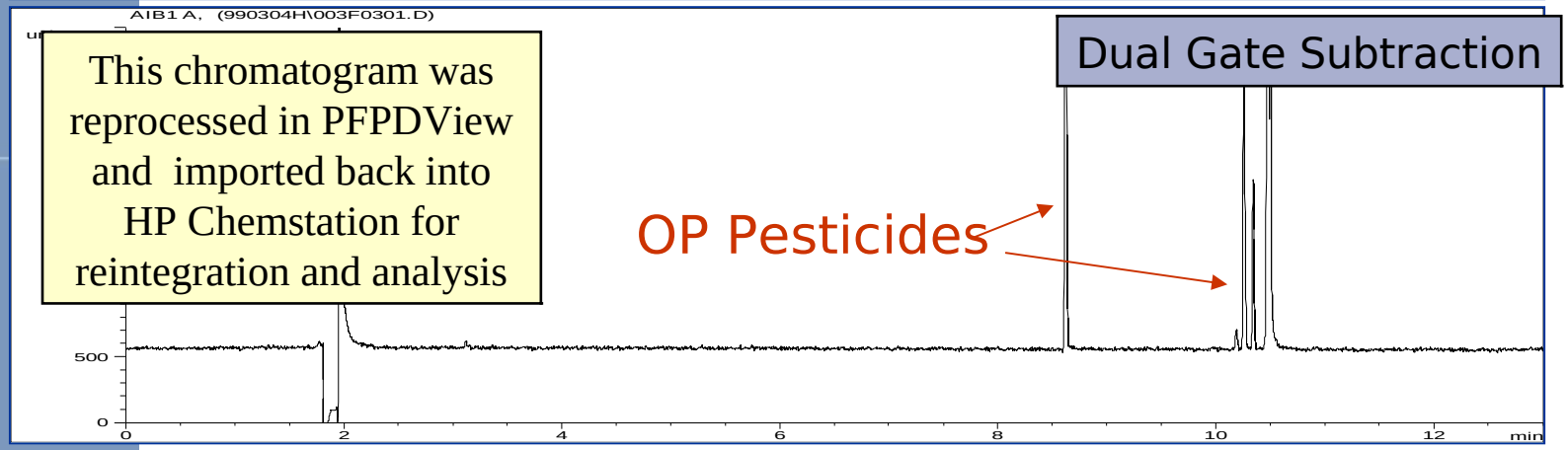
Compound Low Concentration (ppb)

1. Methamidophos – 100
2. Acephate - 60
3. Dimethoate - 60

4. Diazinon – 60
5. me. Chlorpyrifos – 50
6. Chlorpyrifos – 50
7. Disulfoton sulfone – 50
8. Ethion – 60
9. Phosmet – 100
10. Azinphos-me – 150

Garlic Extract on PFPD

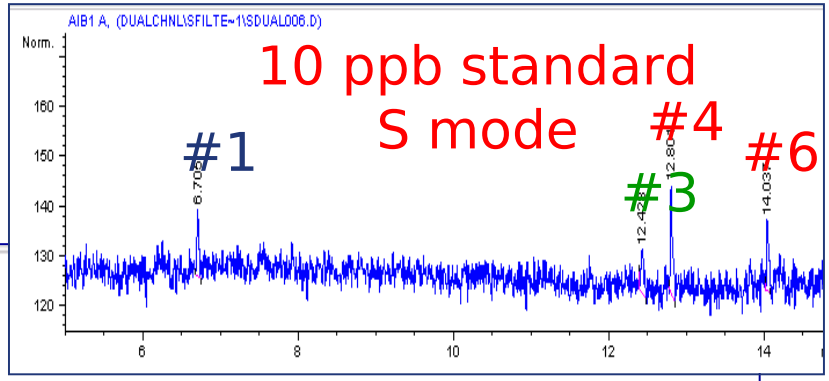


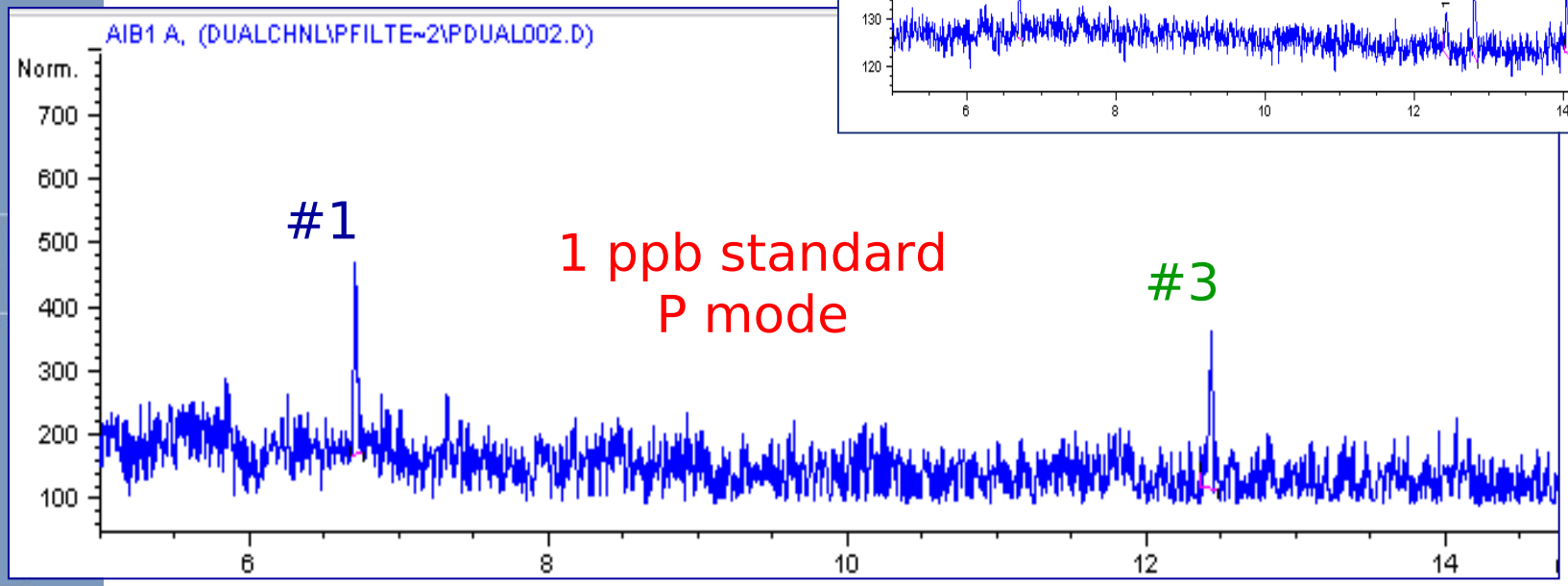


This chromatogram was reprocessed in PFPDView and imported back into HP Chemstation for reintegration and analysis

Lowest Concentration Phosphorus

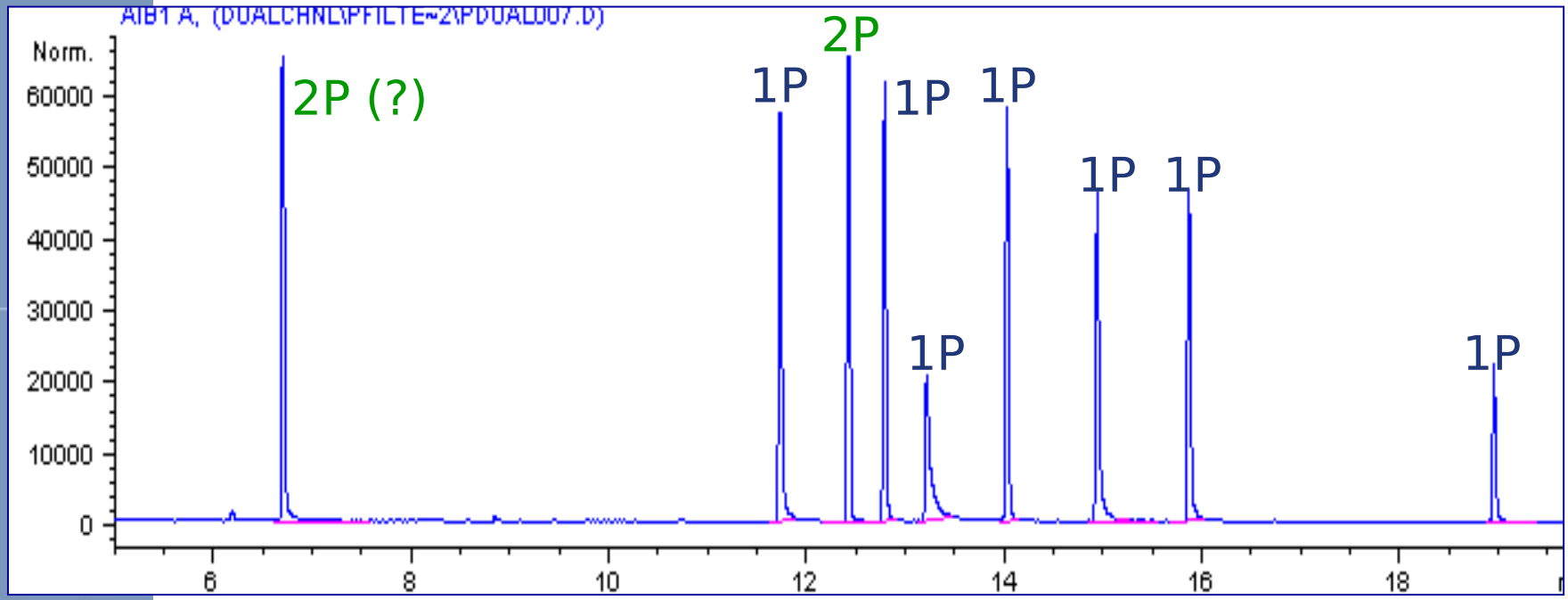
- Two compounds detected at 1 ppb
- #1 with unknown number of P atoms
- #3 with 2 P atoms
- Compare to 10 ppb in S mode



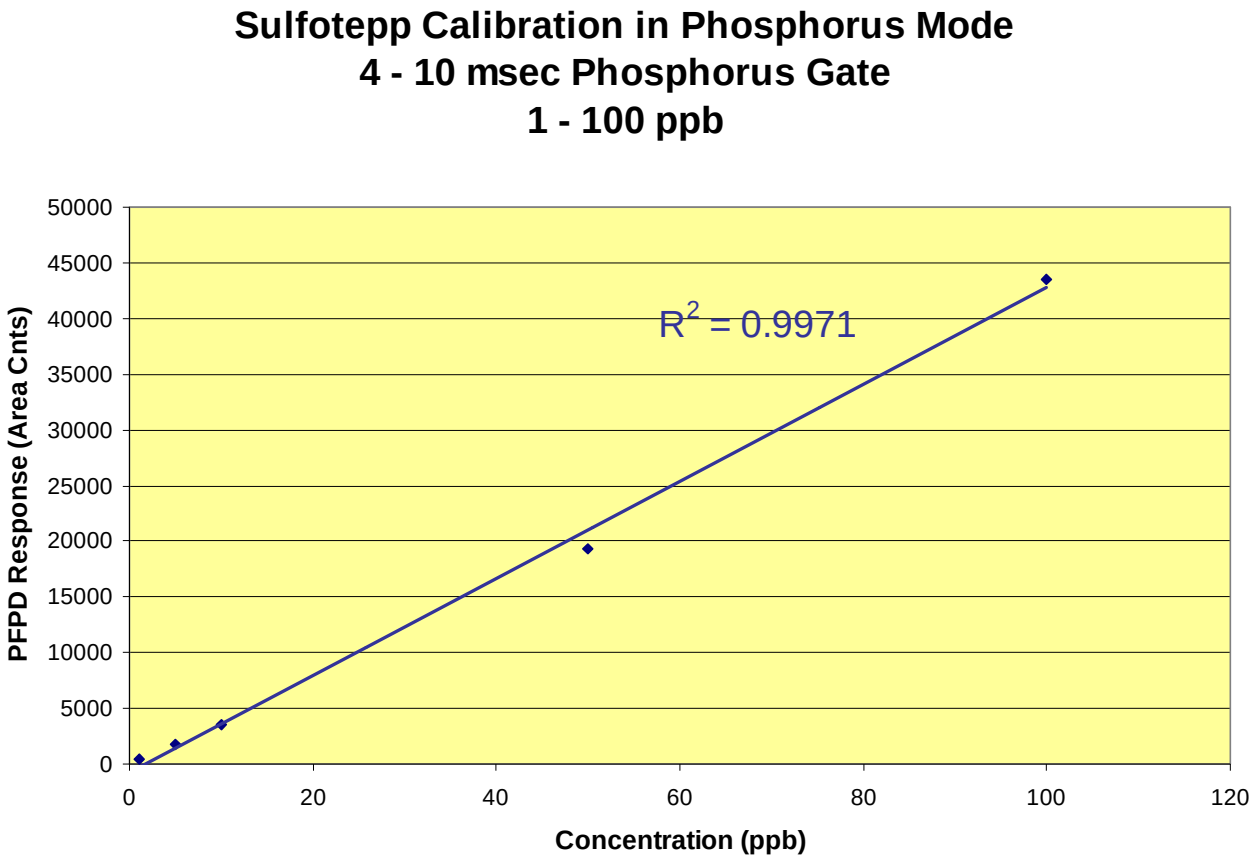


Elemental Confirmation

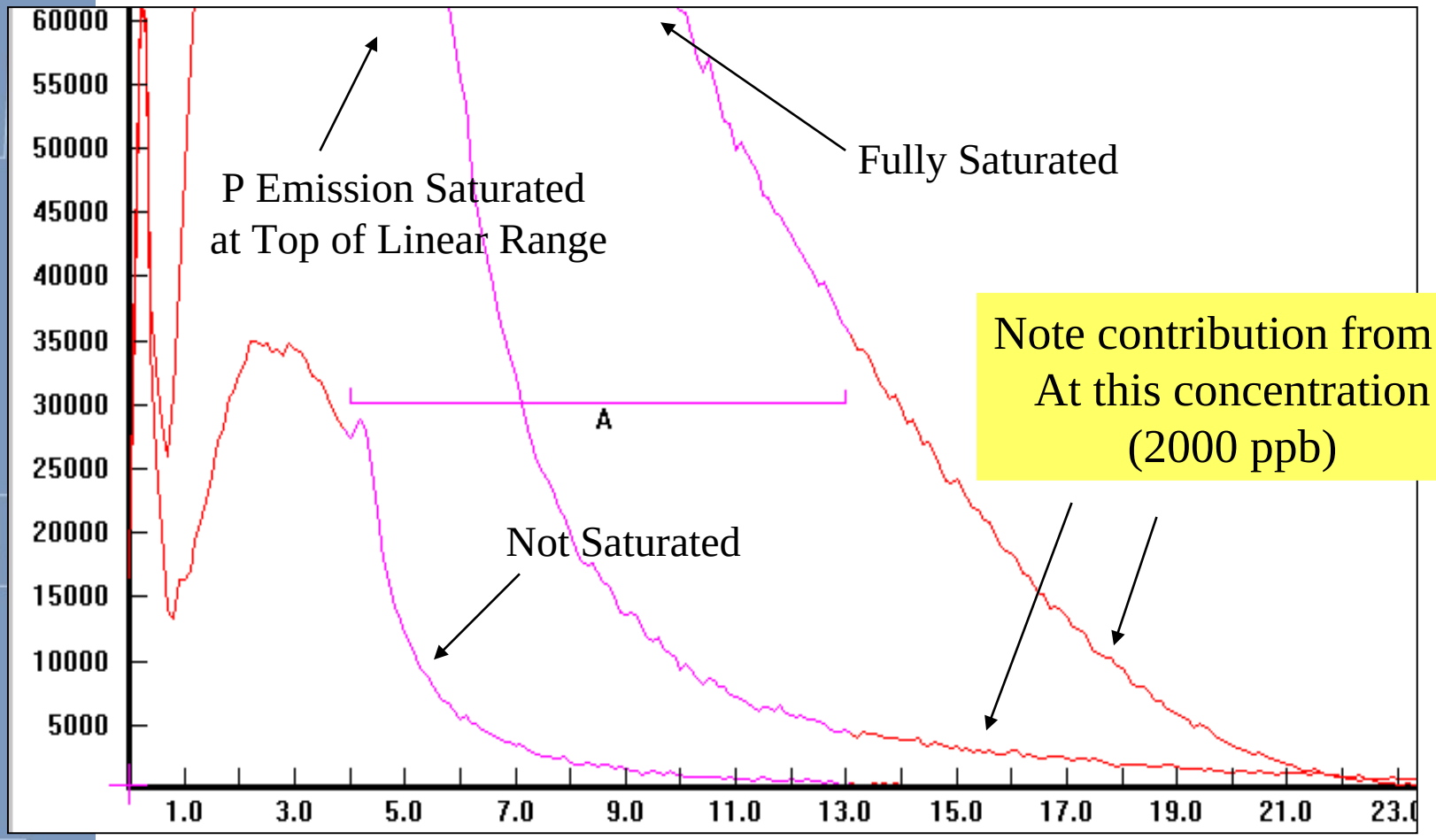
- Chromatogram of 100 ppb mix has all 9 stds
- Labeled with # of P atoms on each compound
- Areas closely match wt % of P in each



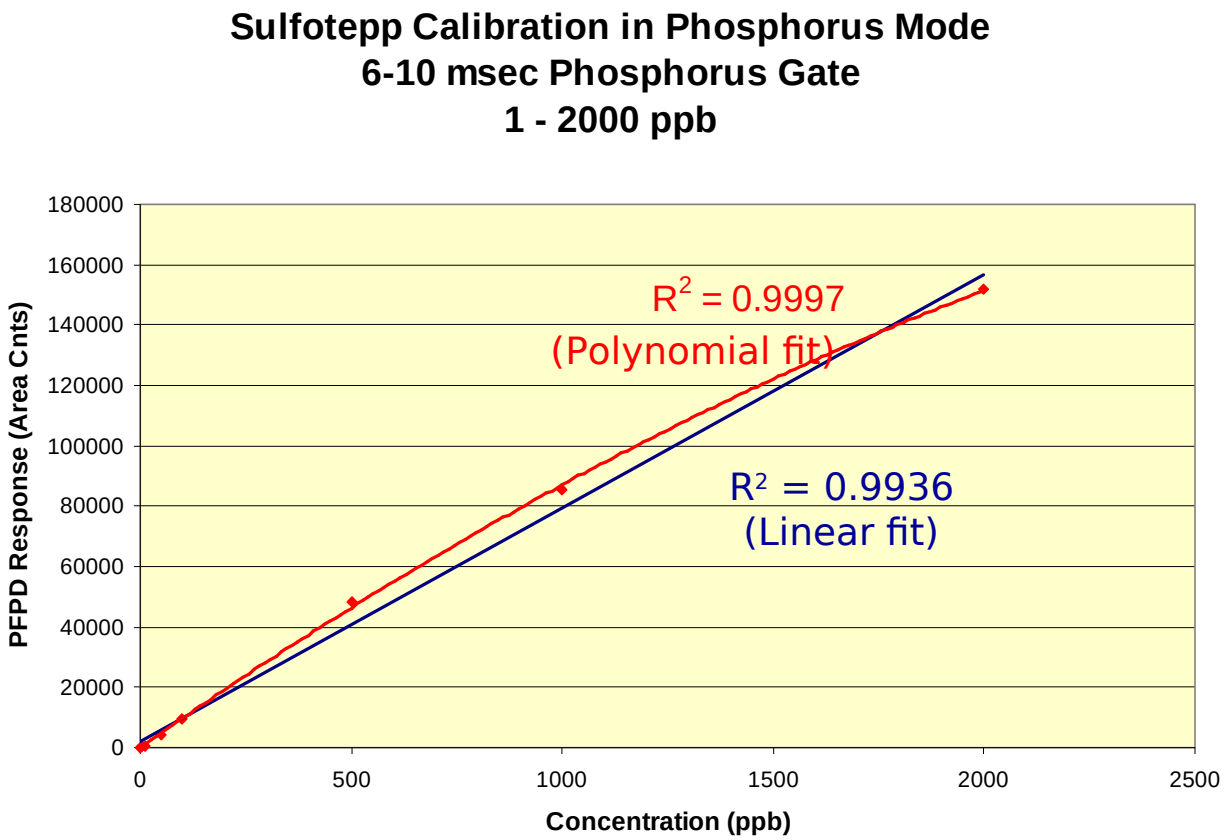
Calibration Over Linear Range



Identify The Linear Range For P



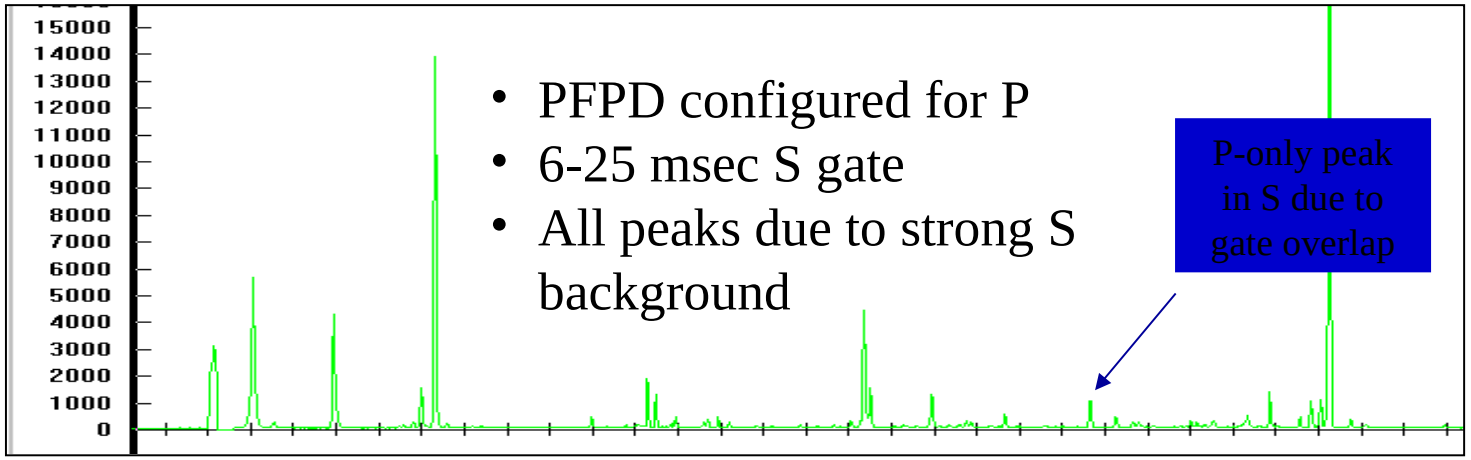
Calibration Over Linear Range



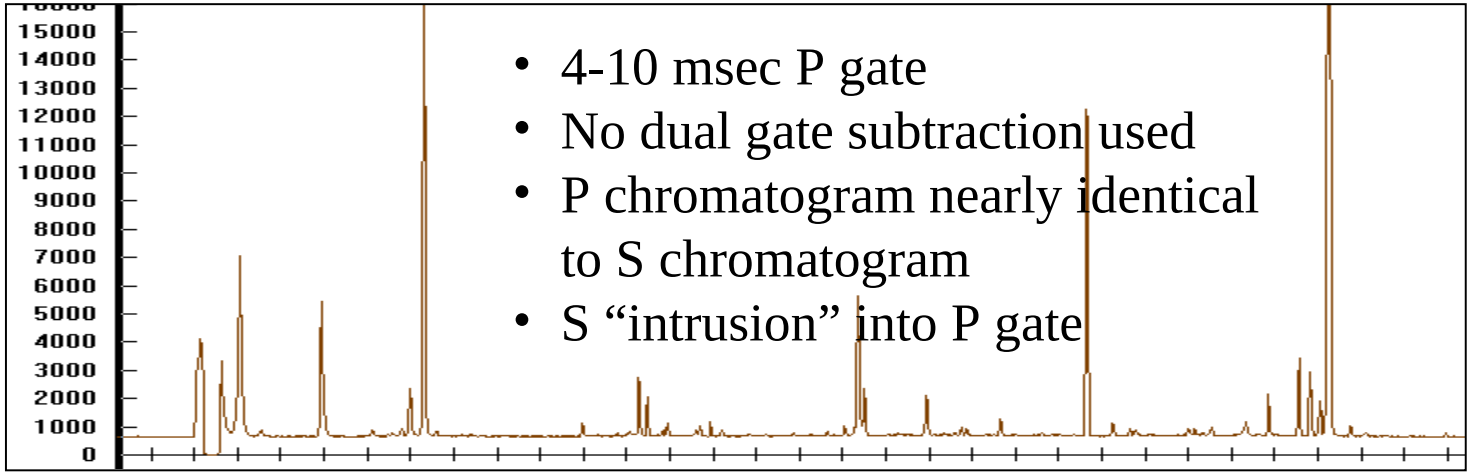
Summary of P-Mode Results

- 10x lower detection levels in P mode
  - 1 ppb in P mode
  - 10 ppb in S mode
- Choice of proper gate can extend calibration range
  - 4-10 msec gate: 1-100 ppb
  - 6-10 msec gate: 1-2000 ppb
- Watch for contributions from sulfur at high concentrations, even in “P only” mode
  - Especially important for matrices with lots of sulfur background, such as onion or garlic

Garlic Matrix in P Mode

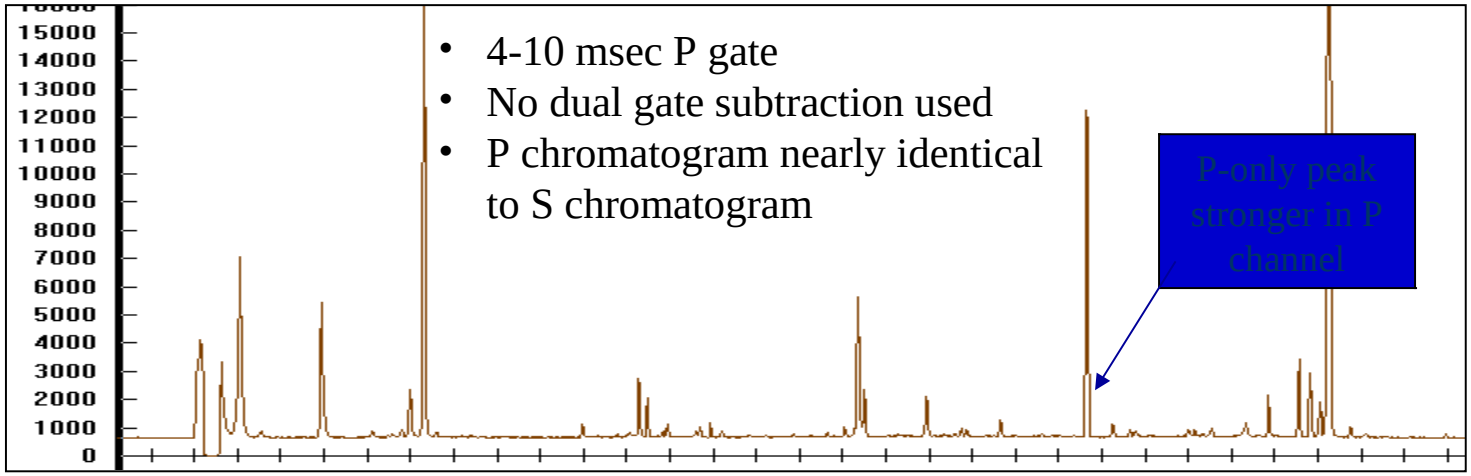


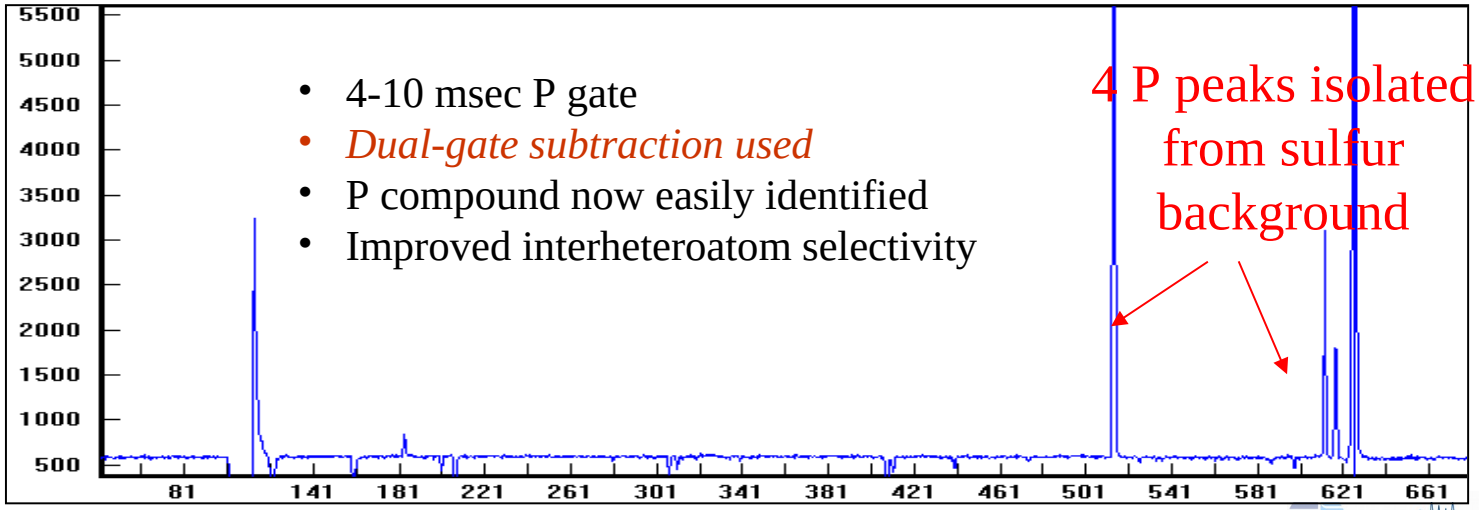
- PFPD configured for P
- 6-25 msec S gate
- All peaks due to strong S background



- 4-10 msec P gate
- No dual gate subtraction used
- P chromatogram nearly identical to S chromatogram
- S “intrusion” into P gate

Garlic Matrix in P Mode

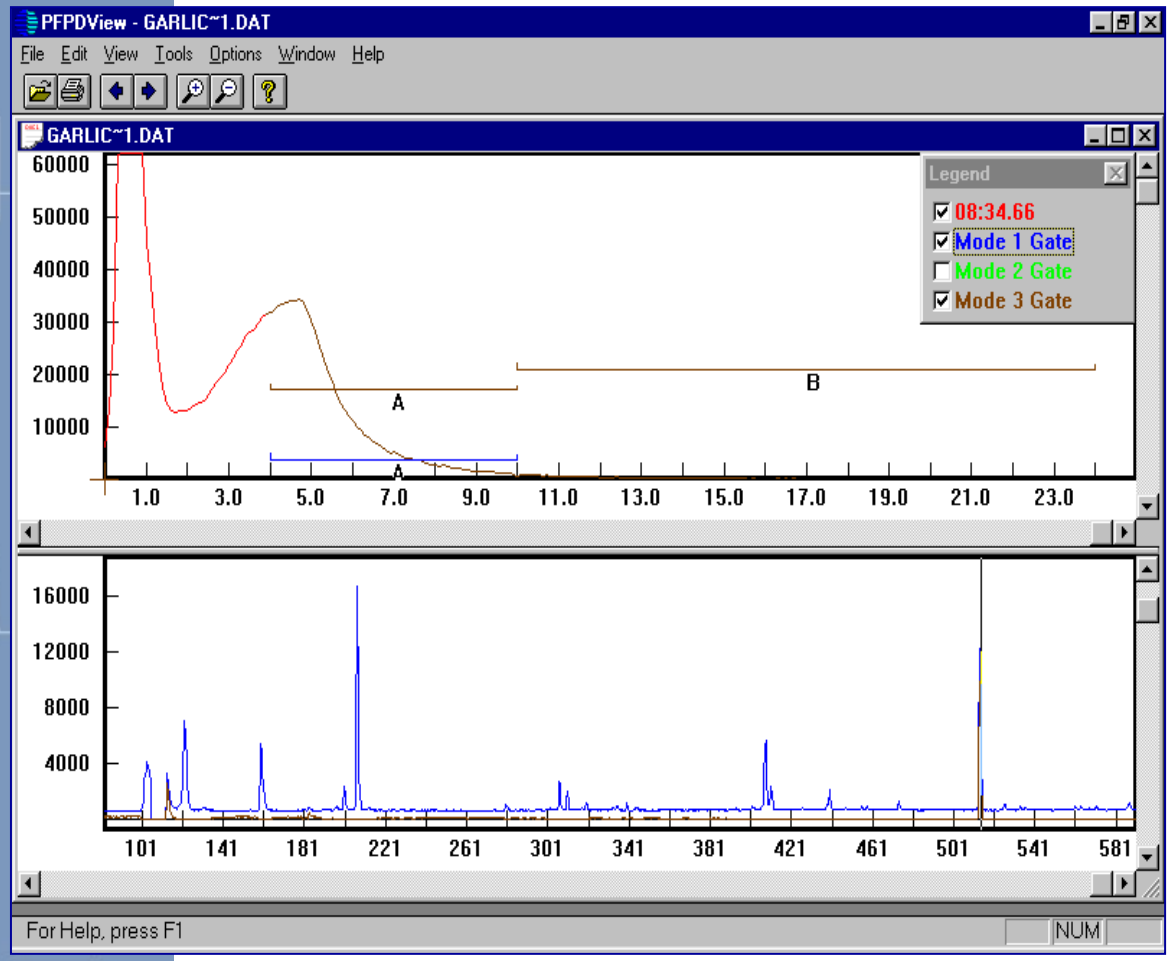




Dual-gate Subtraction

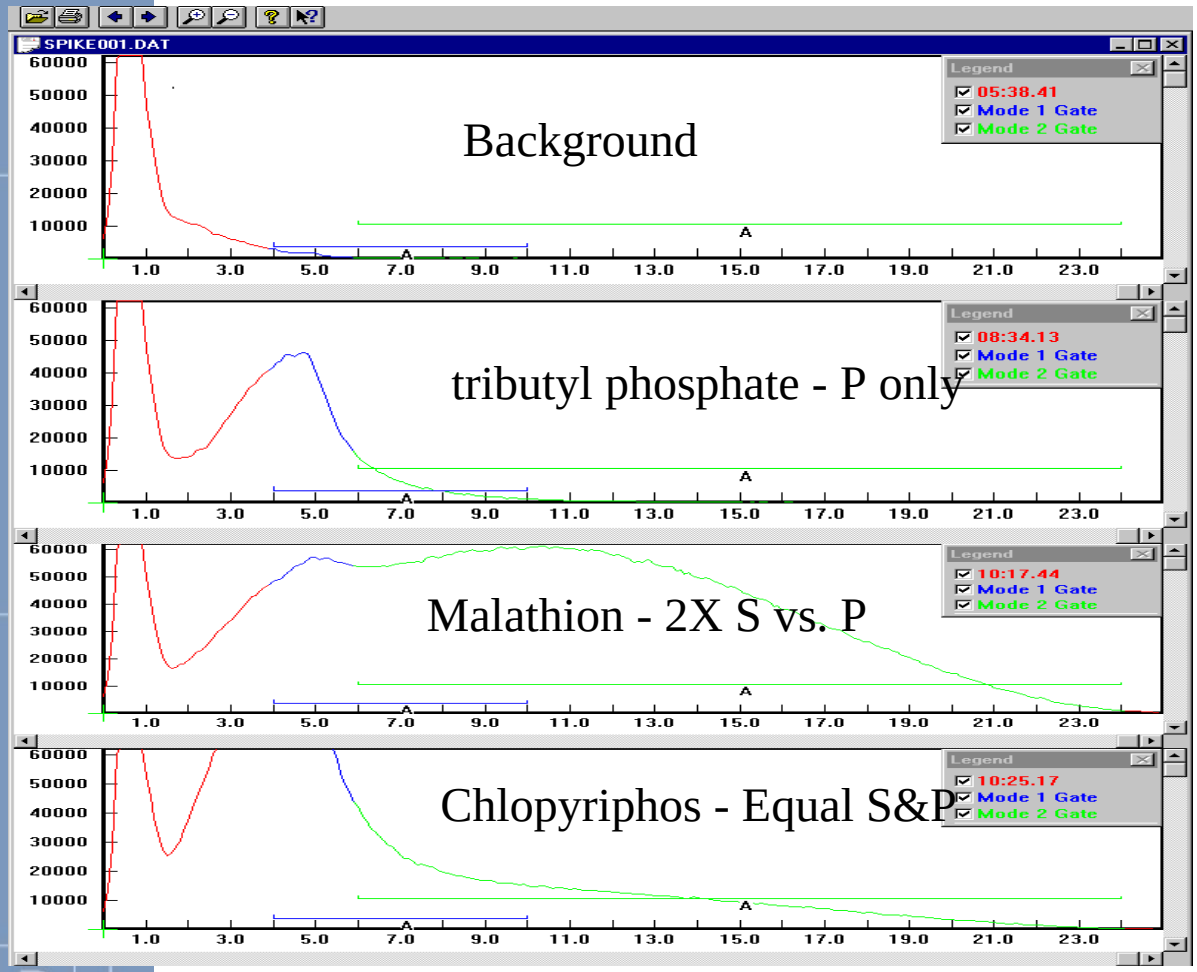
- Advanced selectivity technique that can be used to remove sulfur background (matrix) for phosphorus identification
- Semi-quantitative, depends on relative concentrations of S and P
- Can improve calibration curves
- Conditions are optimized using PFPDView software
  - Optional software package with PFPD

PFPDView Software



- Allows post-run optimization of dual gate parameters
- View emission profiles of individual peaks to confirm S or P
- Also used for troubleshooting

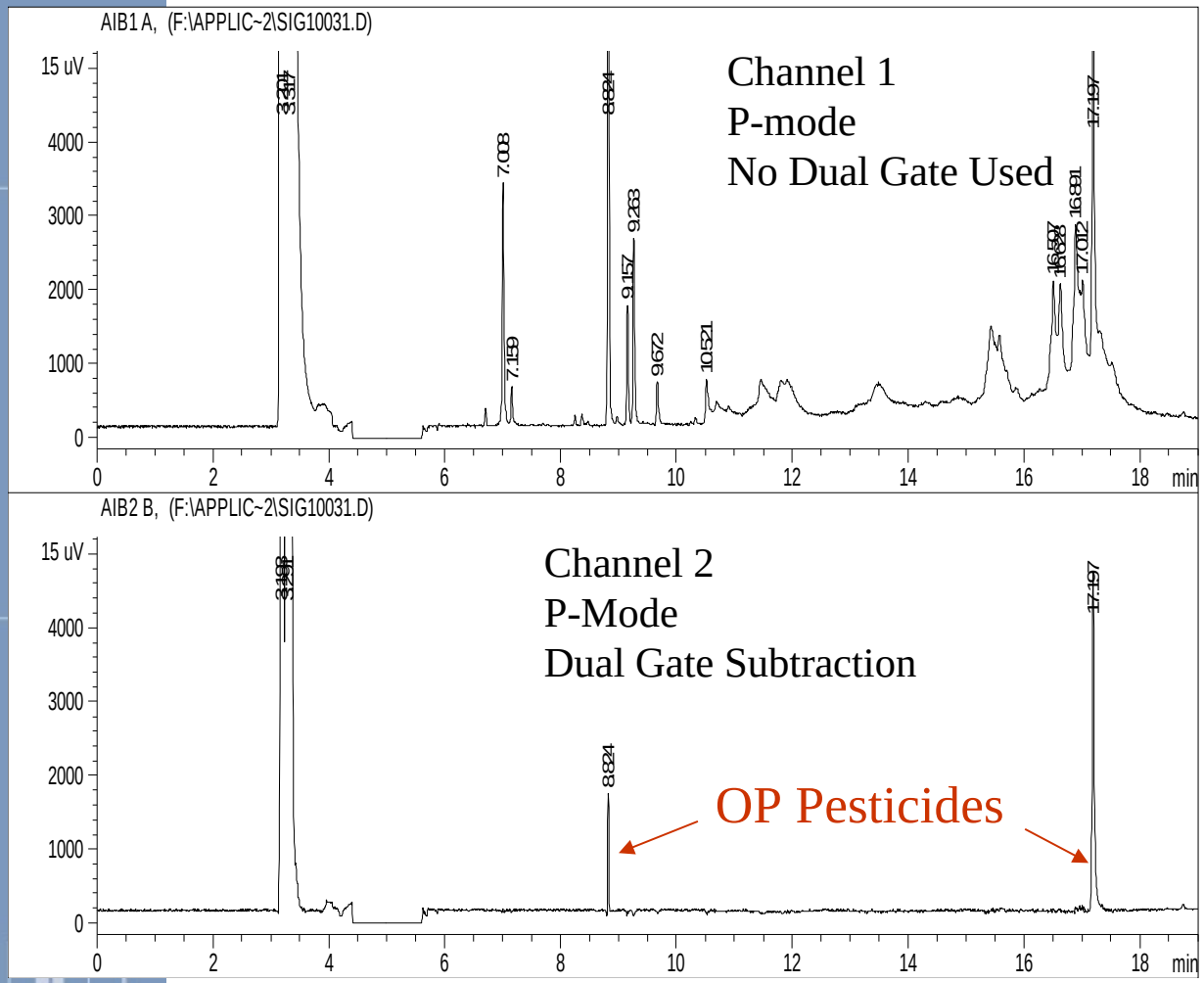
PFPDView For Unknowns



- Get heteroatom composition information using PFPDView
- Elemental composition of the unknowns

- Blue = P
- Green = S

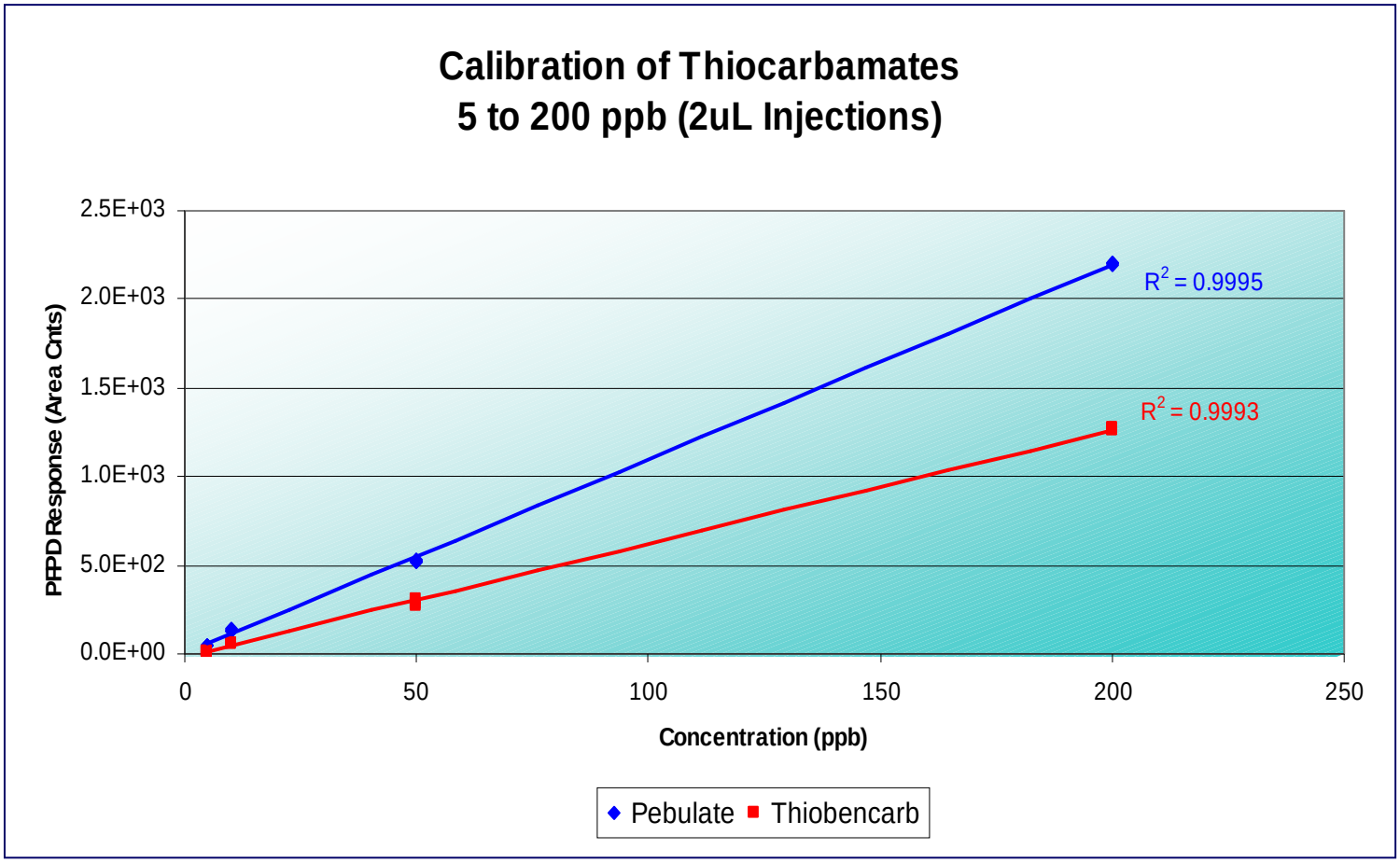
Dual Gate Subtraction



- Onion extract; no clean-up
- Large interfering sulfur background
- Ch1 – No subtraction
- Ch2 – sulfur background subtracted using PFPDView & dual gating

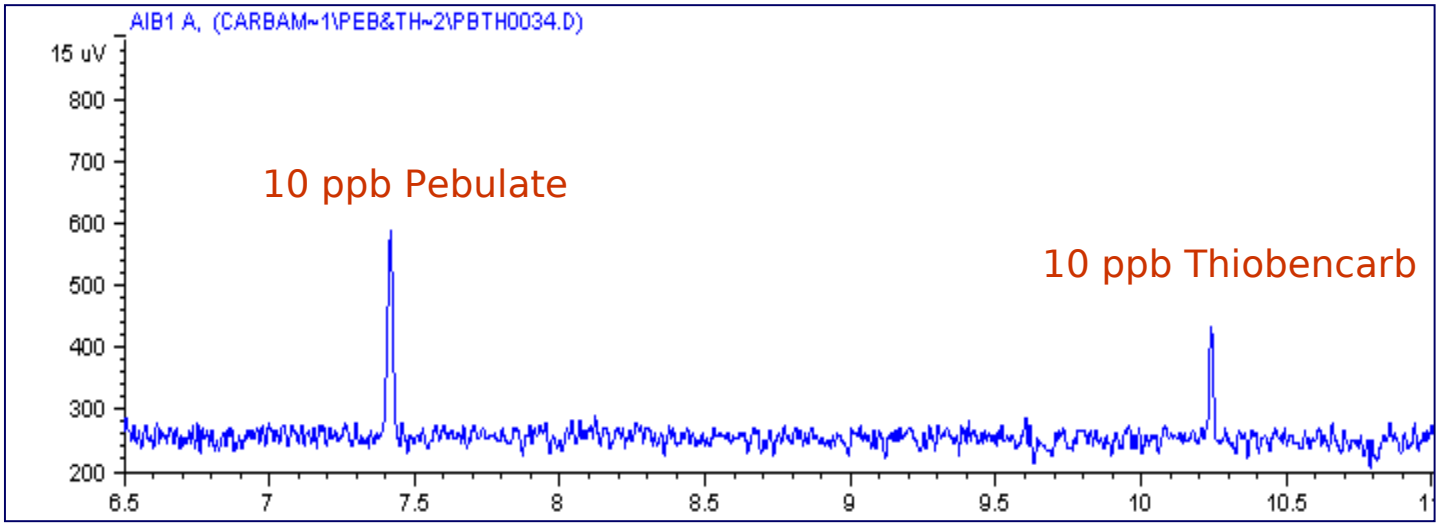
Carbamate Pesticides by PFPD

Calibration Curves 5 - 200 ppb



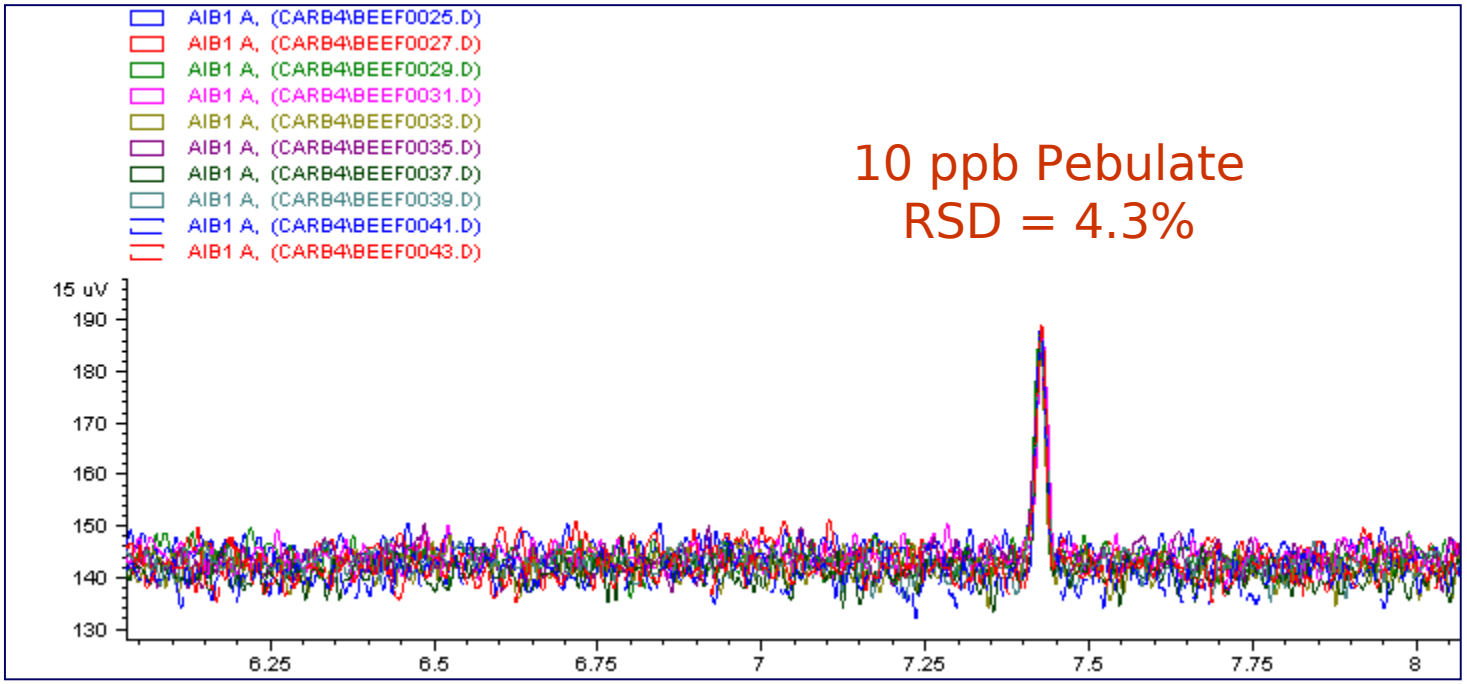
10 ppb Pebulate & Thiobencarb

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

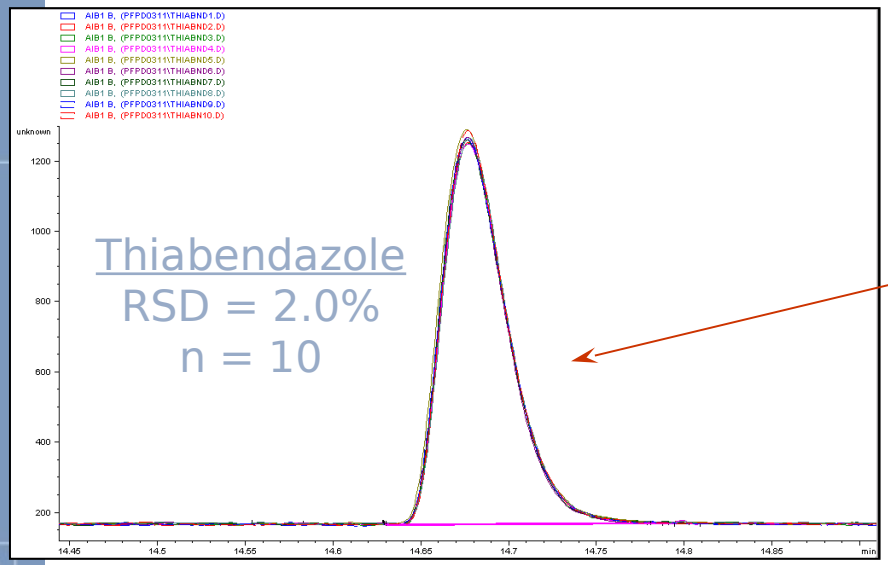


Repeatability at 10 ppb

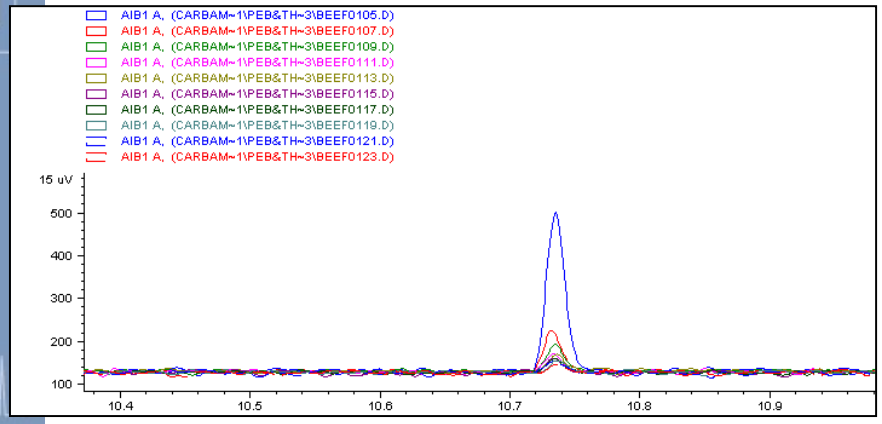
- 10 ppb Pebulate RSD = 4.3% (n=10)
- 10 ppb Thiobencarb RSD = 6.9% (n=10)



Thiabendazole



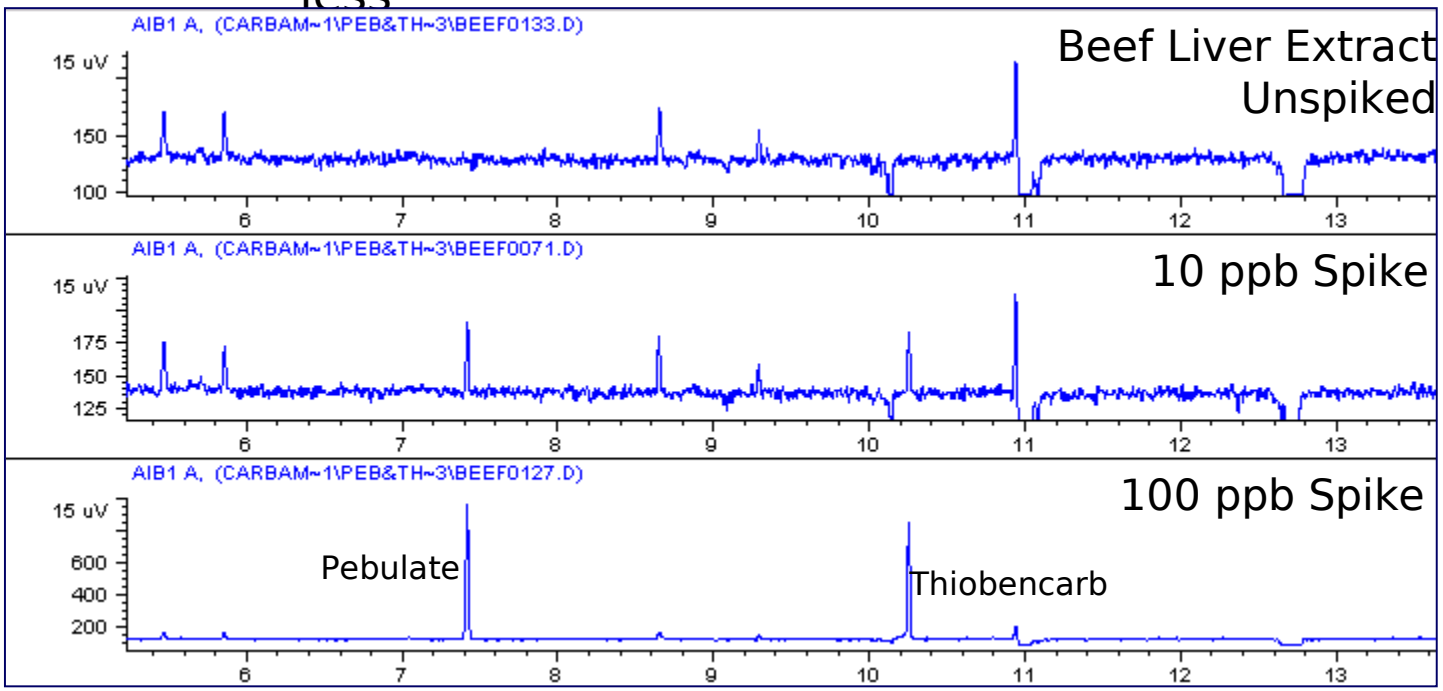
Repeatability at 100 ppb
Restek Siltek™ Uniliner®
in the injection port
RSD = 2.0%
(n = 10)



Without the special liner
significant breakdown
prevented reliable
analyses of thiabendazole

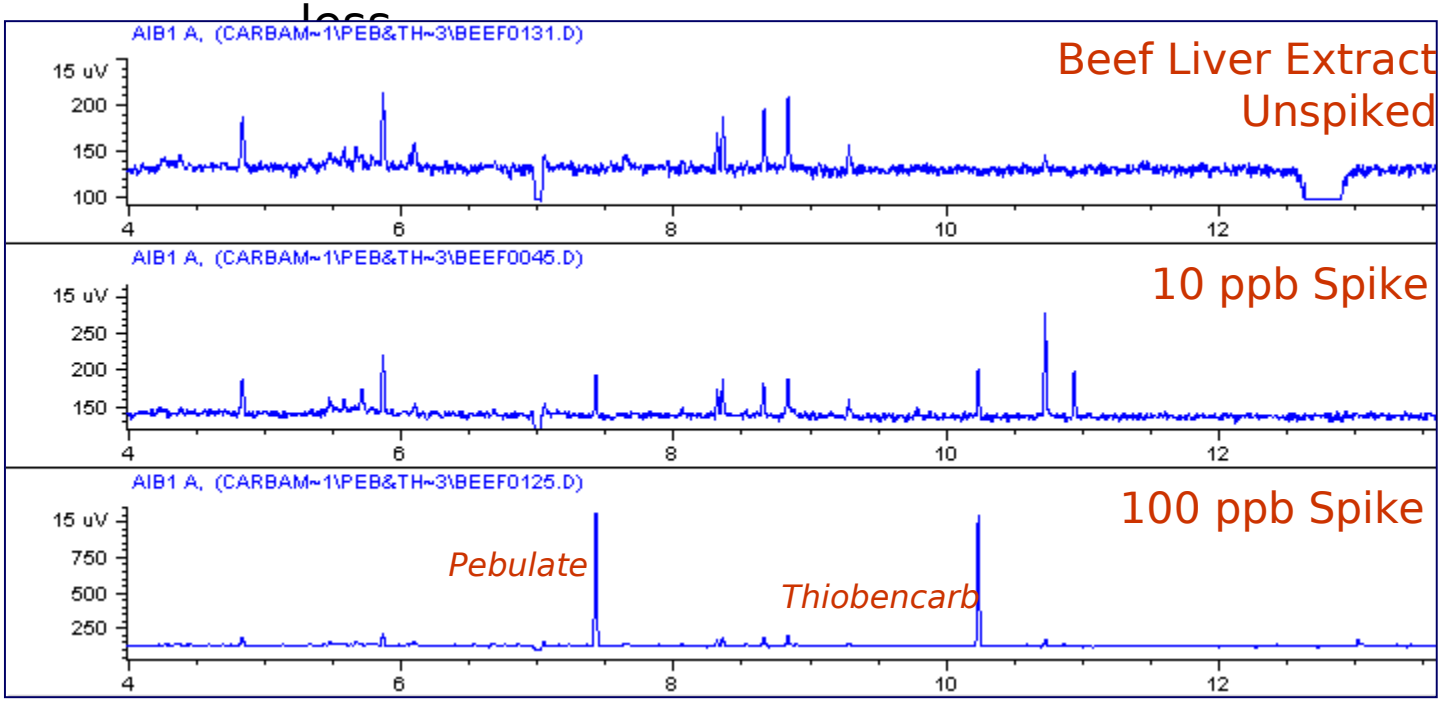
PFPD: Carbamates in Beef Fat

- Direct injection – GC – PFPD
  - Pulsed Flame Photometric Detector
  - Sulfur selective & Equimolar
  - 2 μL injection; splitless
- Pebulate & Thiobencarb at 10 ppb or less



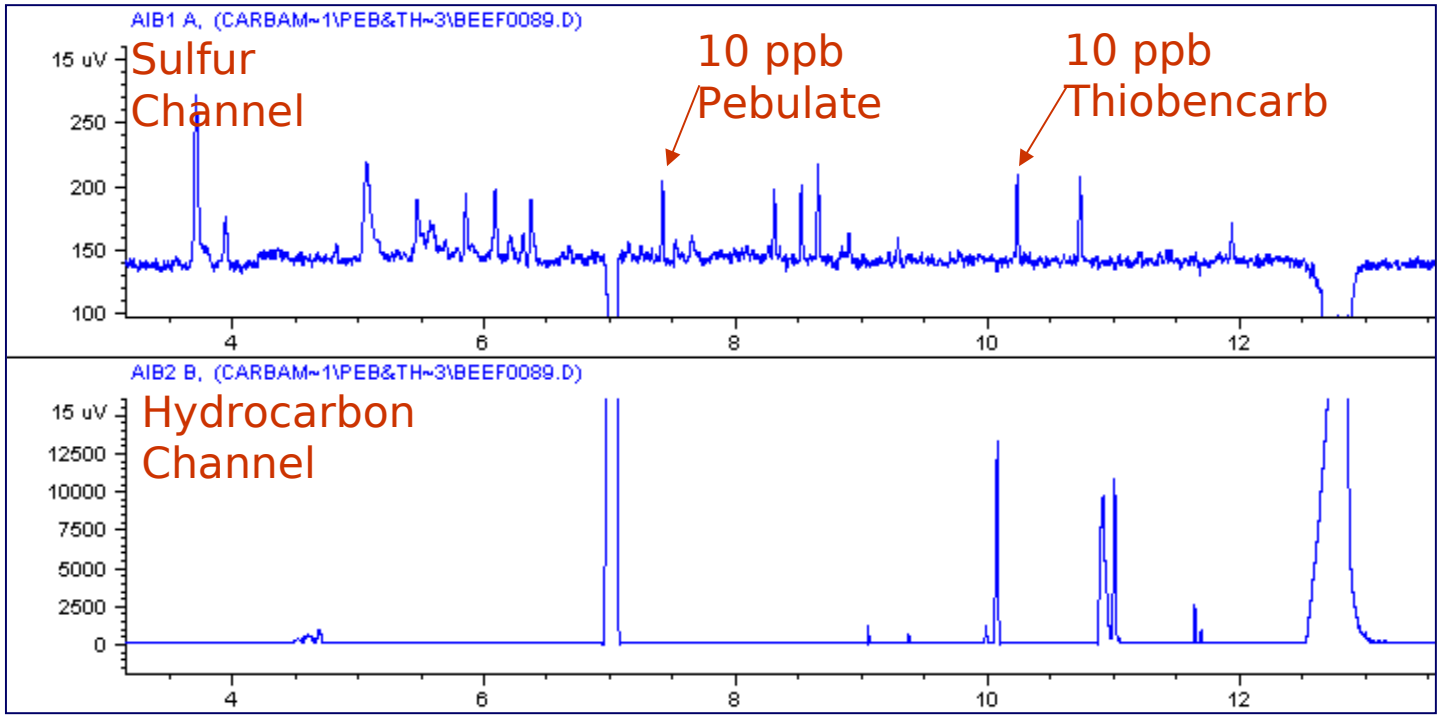
PFPD: Carbamates in Beef Muscle

- Direct injection – GC – PFPD
  - Pulsed Flame Photometric Detector
  - Sulfur selective & Equimolar
  - 2 μL injection; splitless
- Pebulate & Thiobencarb at 10 ppb or



Two Simultaneous Signals

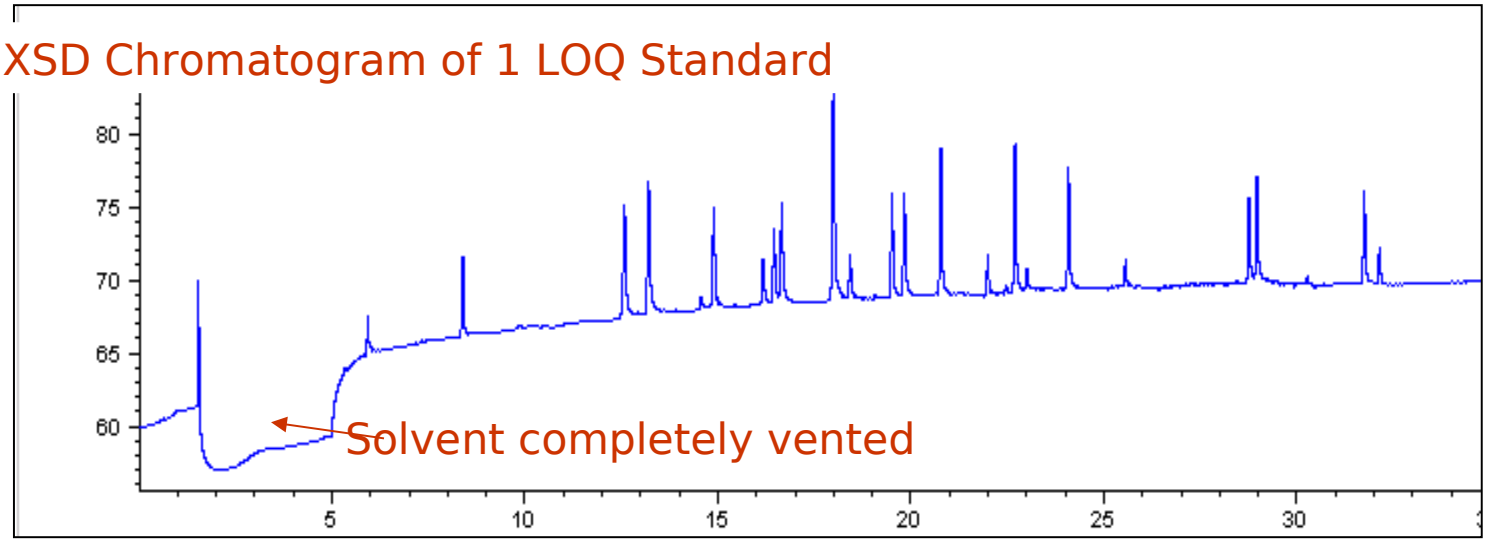
- 10 ppb spike in beef liver extract
- S channel to quantify S compounds
- HC channel to monitor potential interferences



Chlorinated Pesticides by XSD™

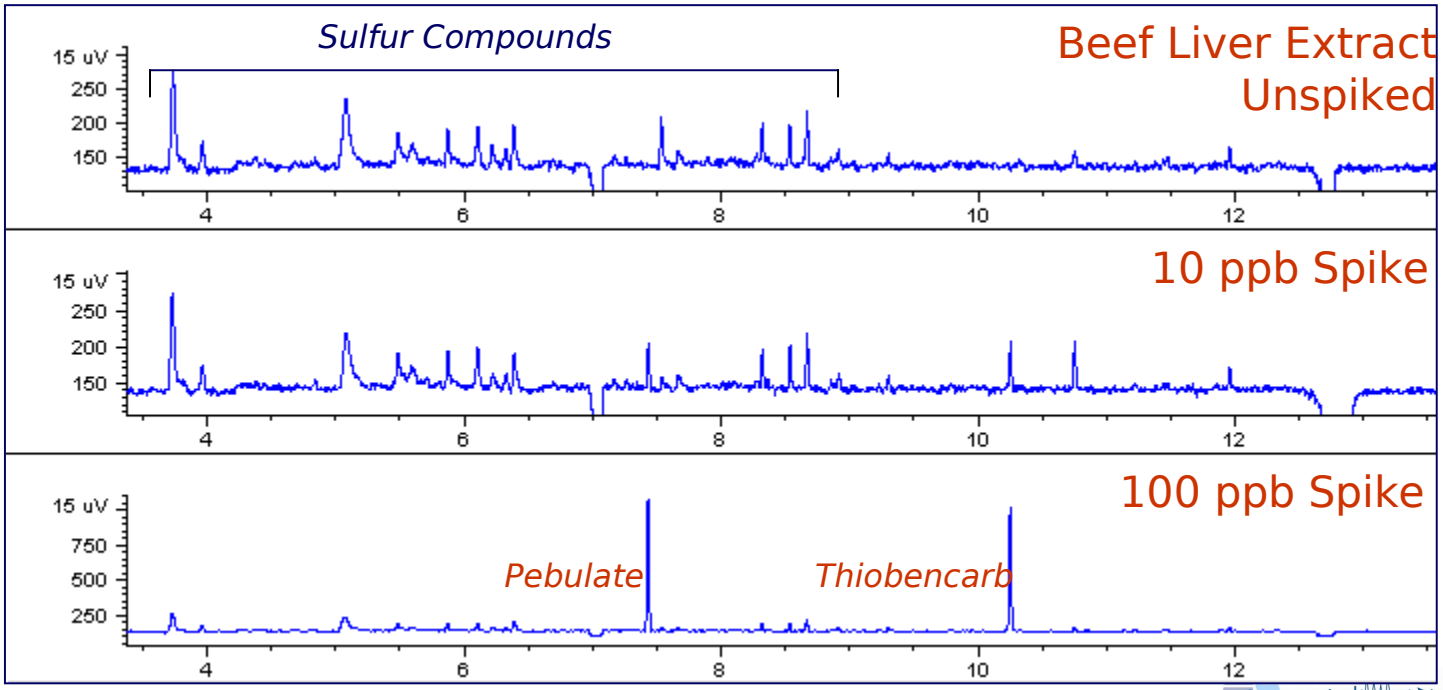
- Direct injection – GC – XSD™
  - Halogen Specific Detector
  - 1 μL injection; split 9;1
- 1 LOQ Standard
- Solvent venting option for chlorinated solvents

XSD Chromatogram of 1 LOQ Standard



PFPD: Carbamates in Beef Liver

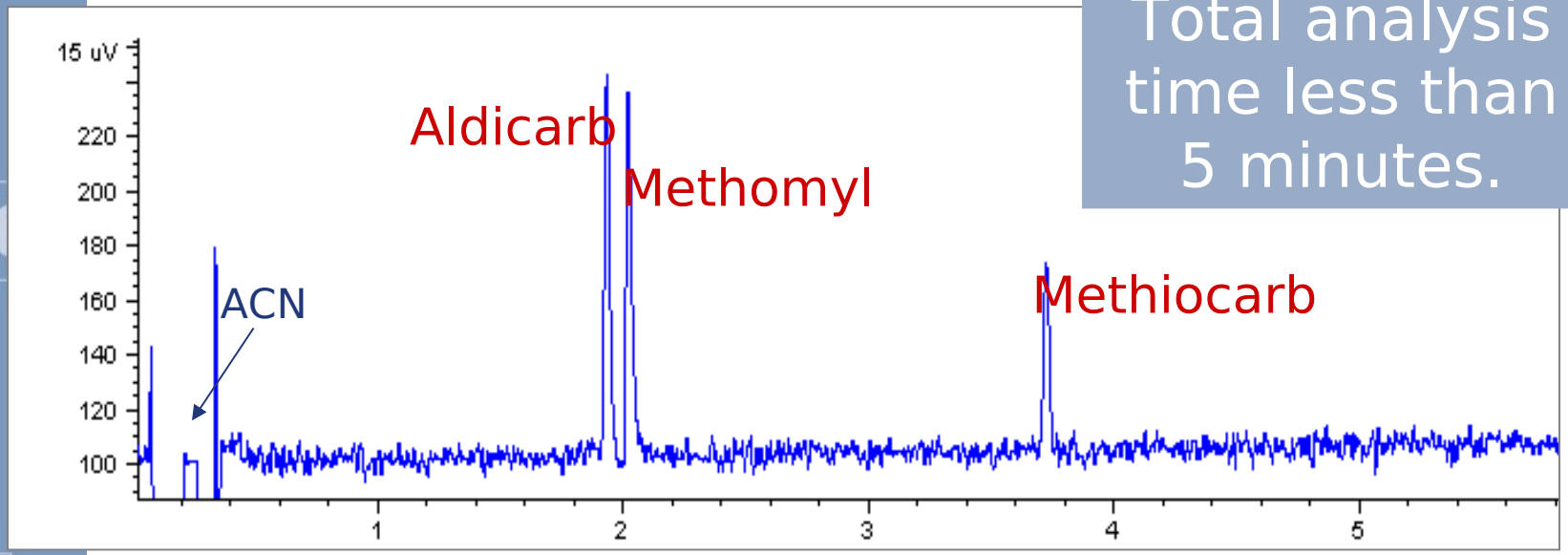
- Direct injection – GC – PFPD
  - Pulsed Flame Photometric Detector
  - Sulfur selective & Equimolar
  - 2 μL injection; splitless
- Pebulate & Thiobencarb at 10 ppb or less



Analysis of Aldicarb, Methomyl, and Methiocarb by GC/PFPD in Under 5 Minutes!

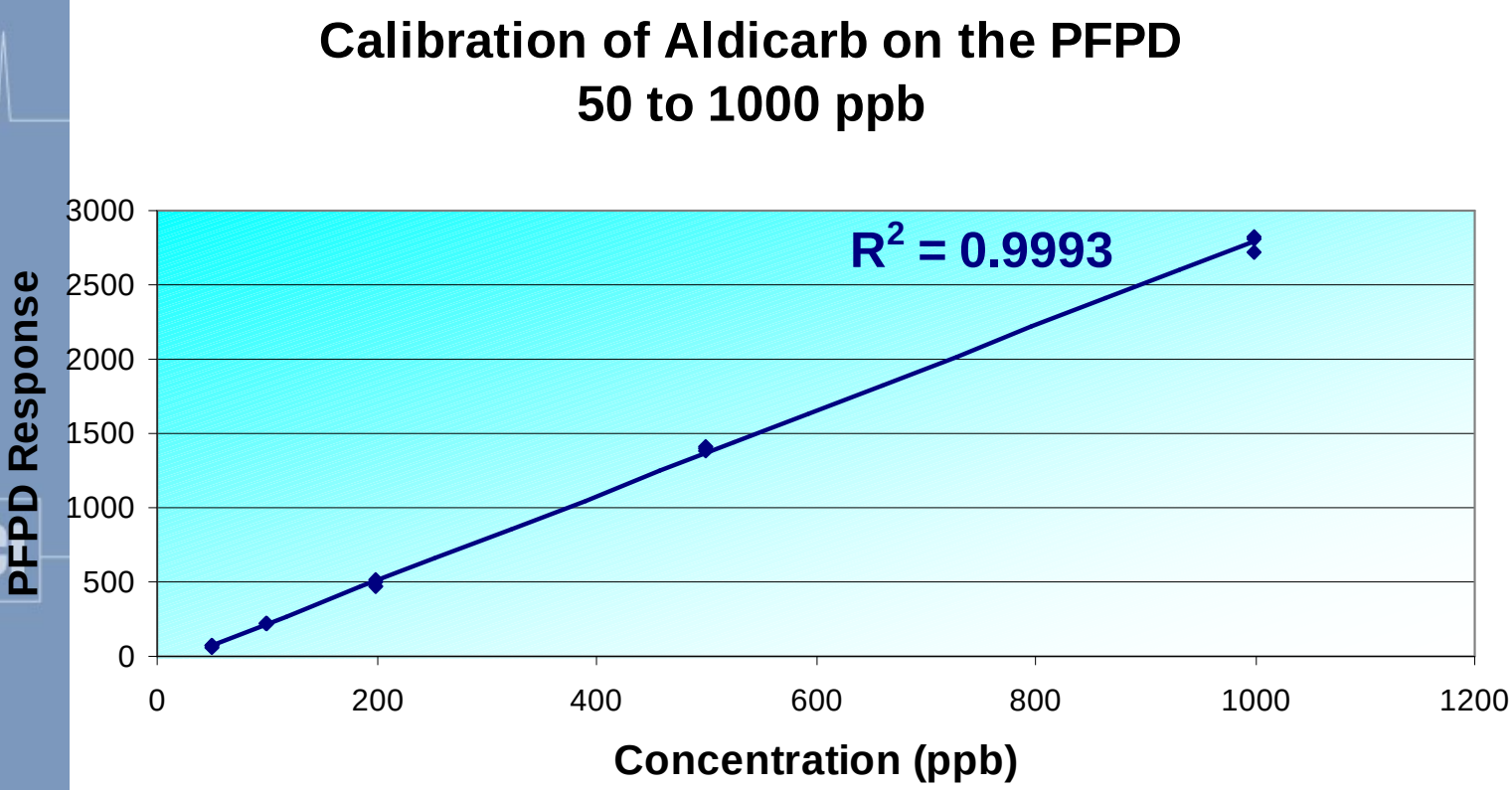
Chromatogram at 100 ppb

- 100 ppb each aldicarb, methomyl, and methiocarb
- Linear acquisition mode
- S/N of 10 or better



Total analysis time less than 5 minutes.

Aldicarb Calibration Curve

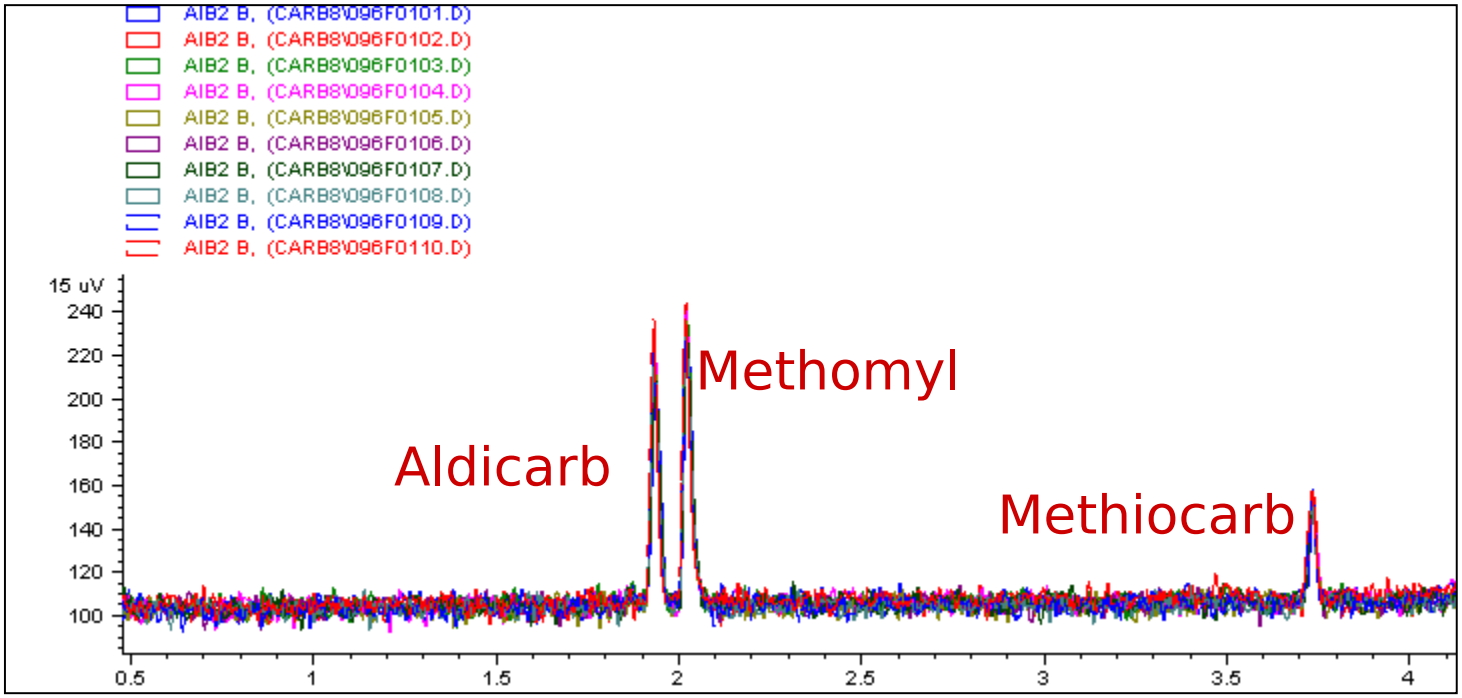


Calibration Summary

Compound	Calibration Range	R^2
Aldicarb	50 – 1000 ppb	0.9993
Methomyl	50 – 1000 ppb	0.9990
Methiocarb	50 – 2000 ppb	0.9987

Repeatability at 100 ppb

- Overlaid chromatograms; n = 10
- 100 ppb
- 1 μL splitless injections; 4 m column



Repeatability Summary

%RSD for 10 Replicate Analyses
At Different Concentrations

Compound	100 ppb	500 ppb	1 ppm
Aldicarb	5.5	4.0	2.5
Methomyl	6.1	6.8	3.9
Methiocarb	9.4	6.2	3.2

Carbamate Conclusions

- Thiocarbamates thermally labile
- Usually analyzed by LC methods
- GC with PFPD works well for selected thiocarbamate pesticides
- Faster, simpler, more sensitive
- Monitor for hydrocarbon interferences
- Use with XSD for simultaneous measurement of Cl pesticides

Food & Flavor Analysis by PFPD

Introduction

- Sulfur compounds are an important component of flavor analysis
- Responsible for specific and distinctive flavors in many foods & beverages
- Difficult to analyze and identify because present at minimal concentrations
- MS or FID commonly used, but not sensitive enough to detect sulfur compounds at trace levels

GC Configuration MS/FID/PFPD

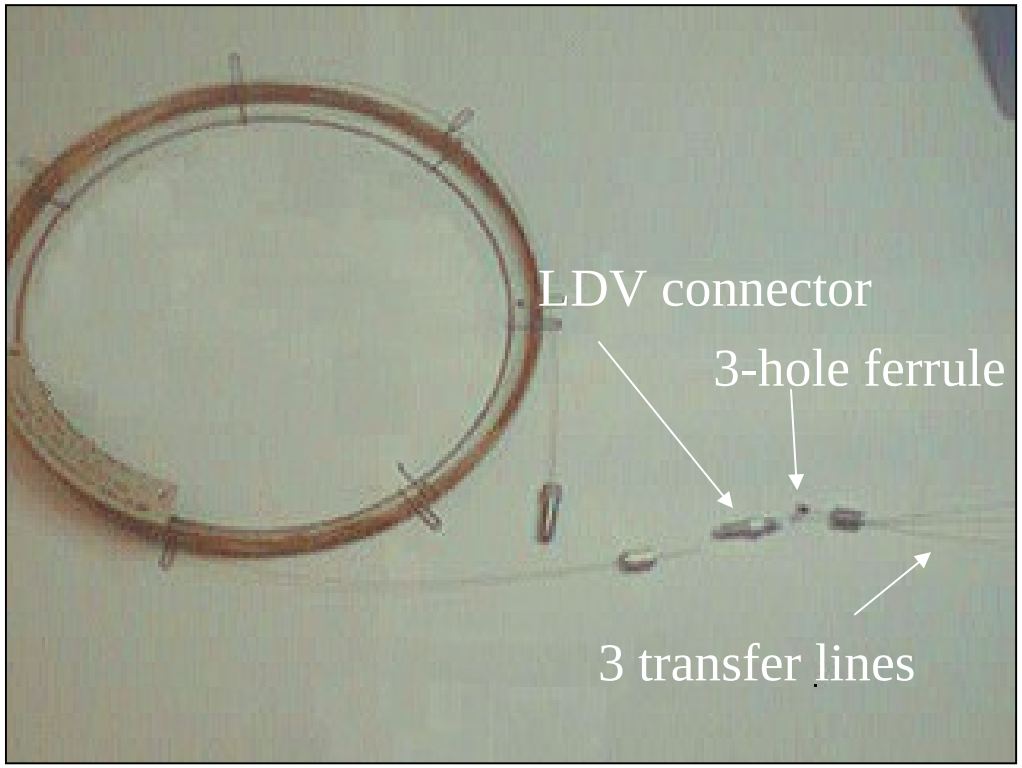
6890N GC with
5973N MS

Agilent FID in Front
for Sulfur Marking

OI Analytical PFPD in Back
For Quantitation

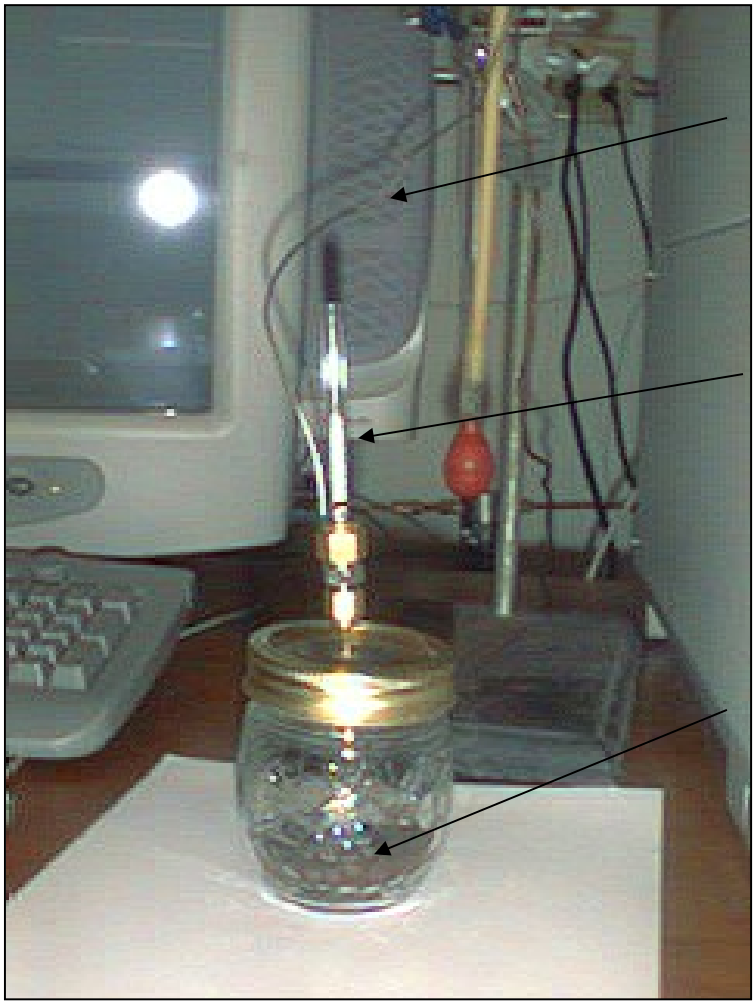
Column Configuration for 3 Detectors

Standard installation at injection port



Detector end split using low dead volume connector and a 3-hole ferrule

Headspace Apparatus



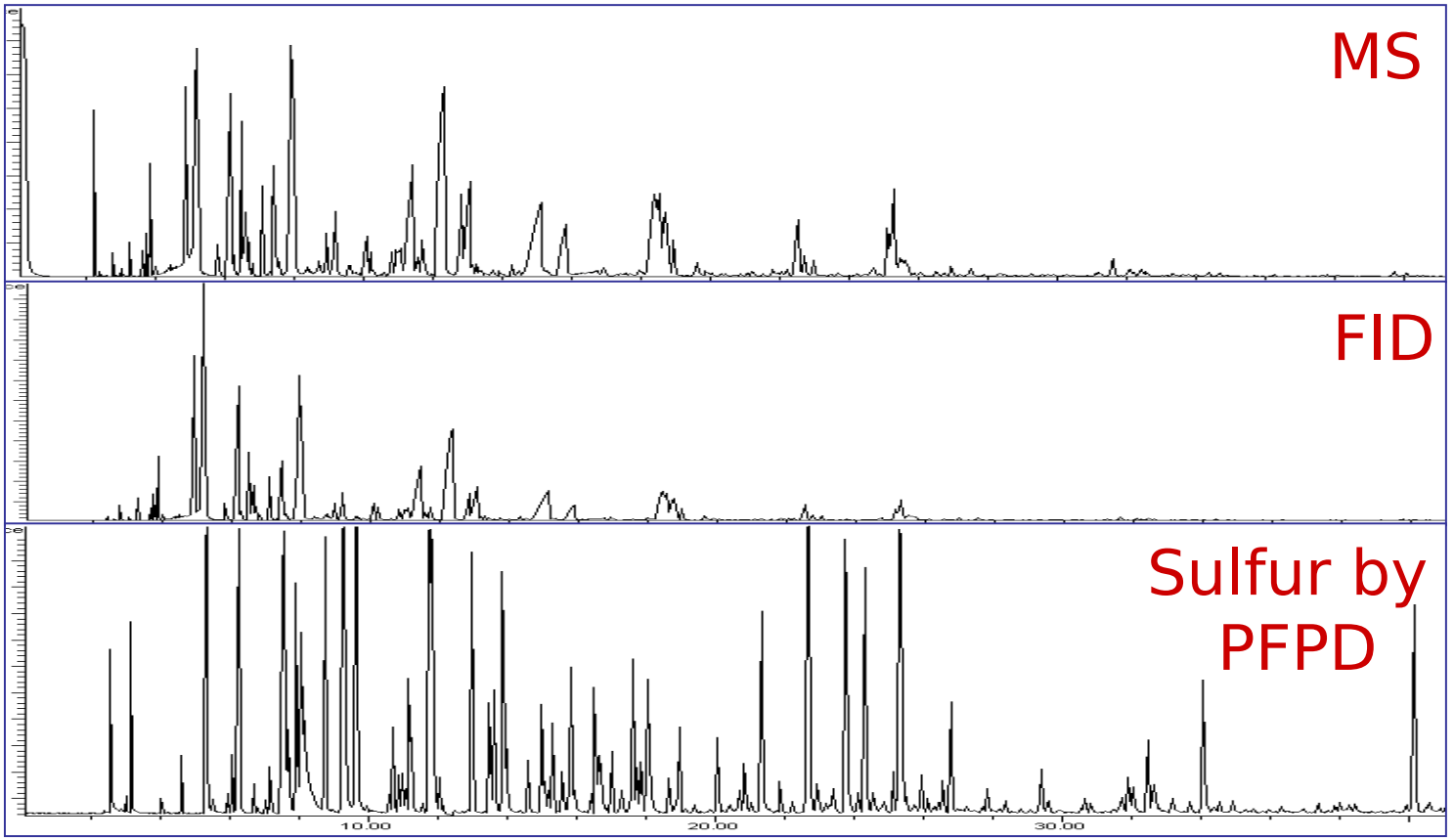
Line carrying He purge gas

GC inlet liner packed With 100 mg Tenax

~20 grams coffee

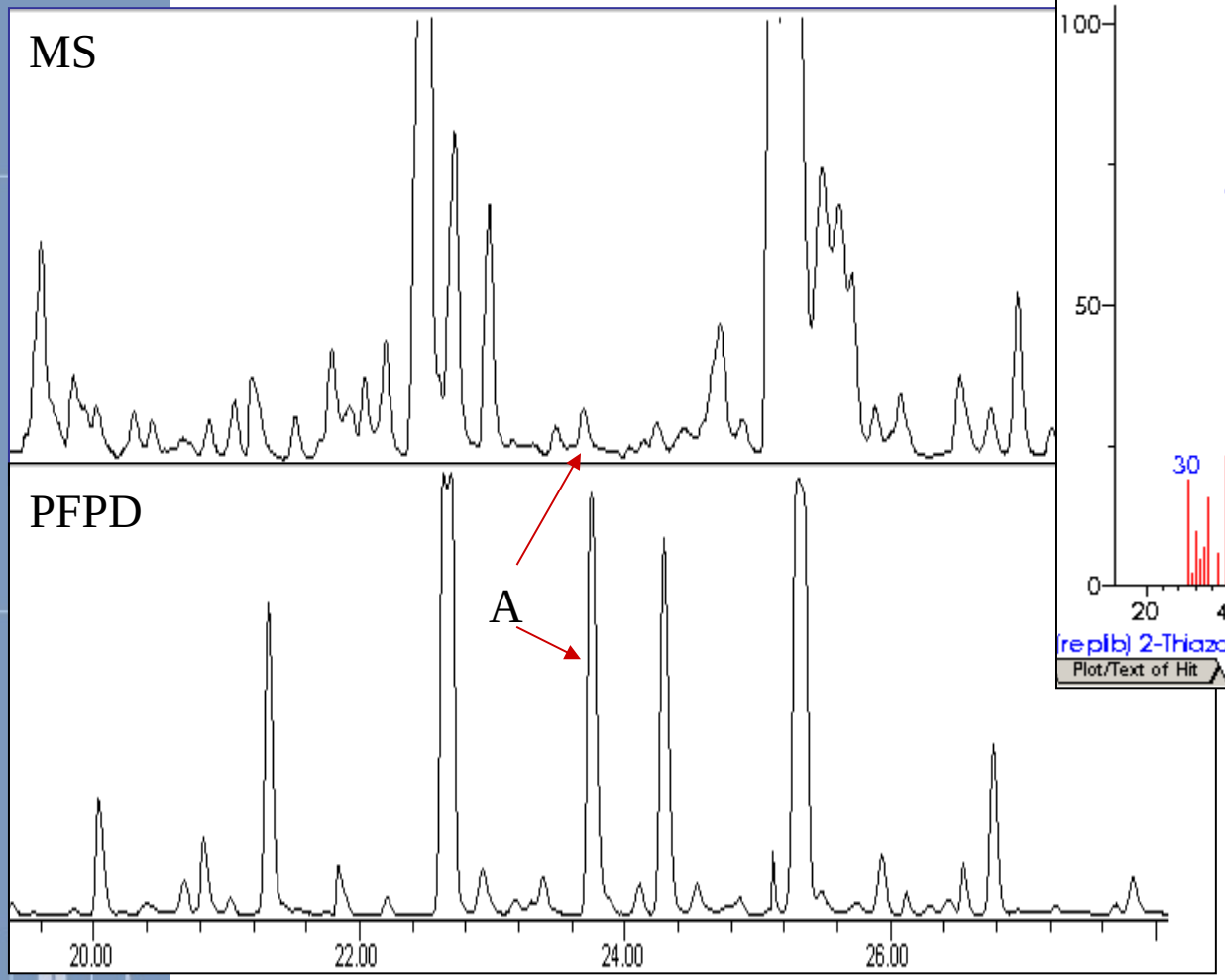
Coffee Headspace by MS/FID/PFPD

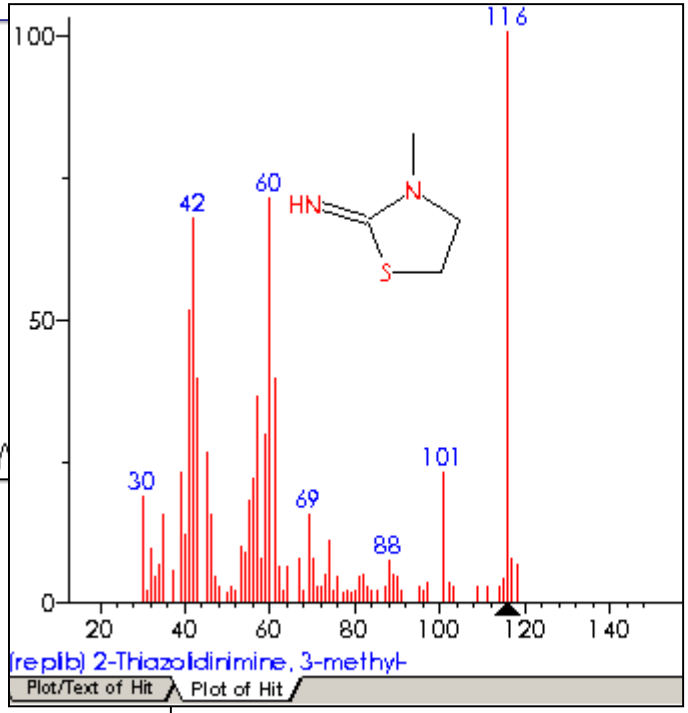
3 Simultaneous Chromatograms From Coffee “A”



Over 200 sulfur peaks detected

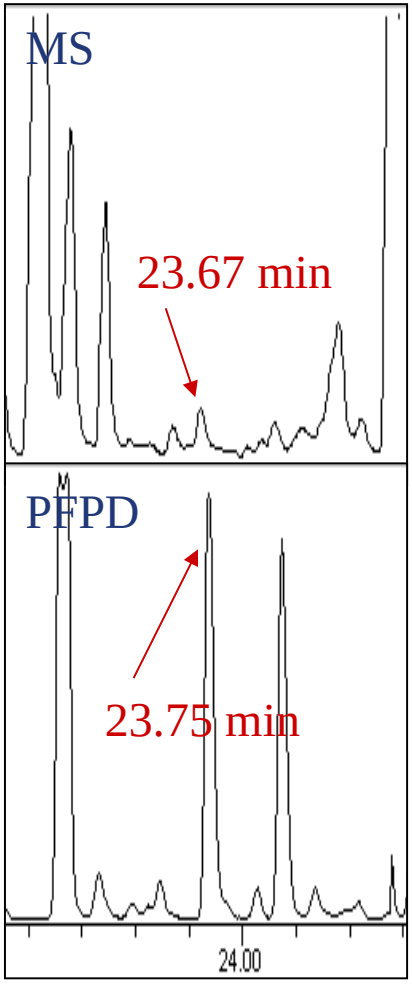
PFPD Used To Identify Sulfur RTs





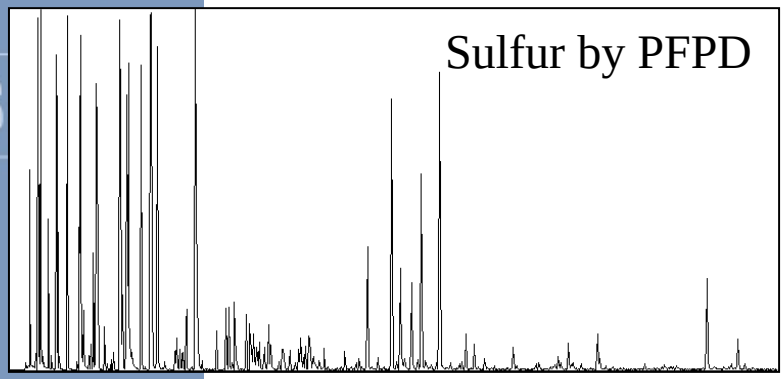
NIST search results for peak “A”

Compound Retention Times



- MS and PFPD (and FID) chromatograms very slightly offset by 4-5 seconds
  - Reproducible
- Due to fact that MS is under vacuum and PFPD and FID are under slightly positive pressure
- Offset easily determined with a standard prior to analysis of unknowns

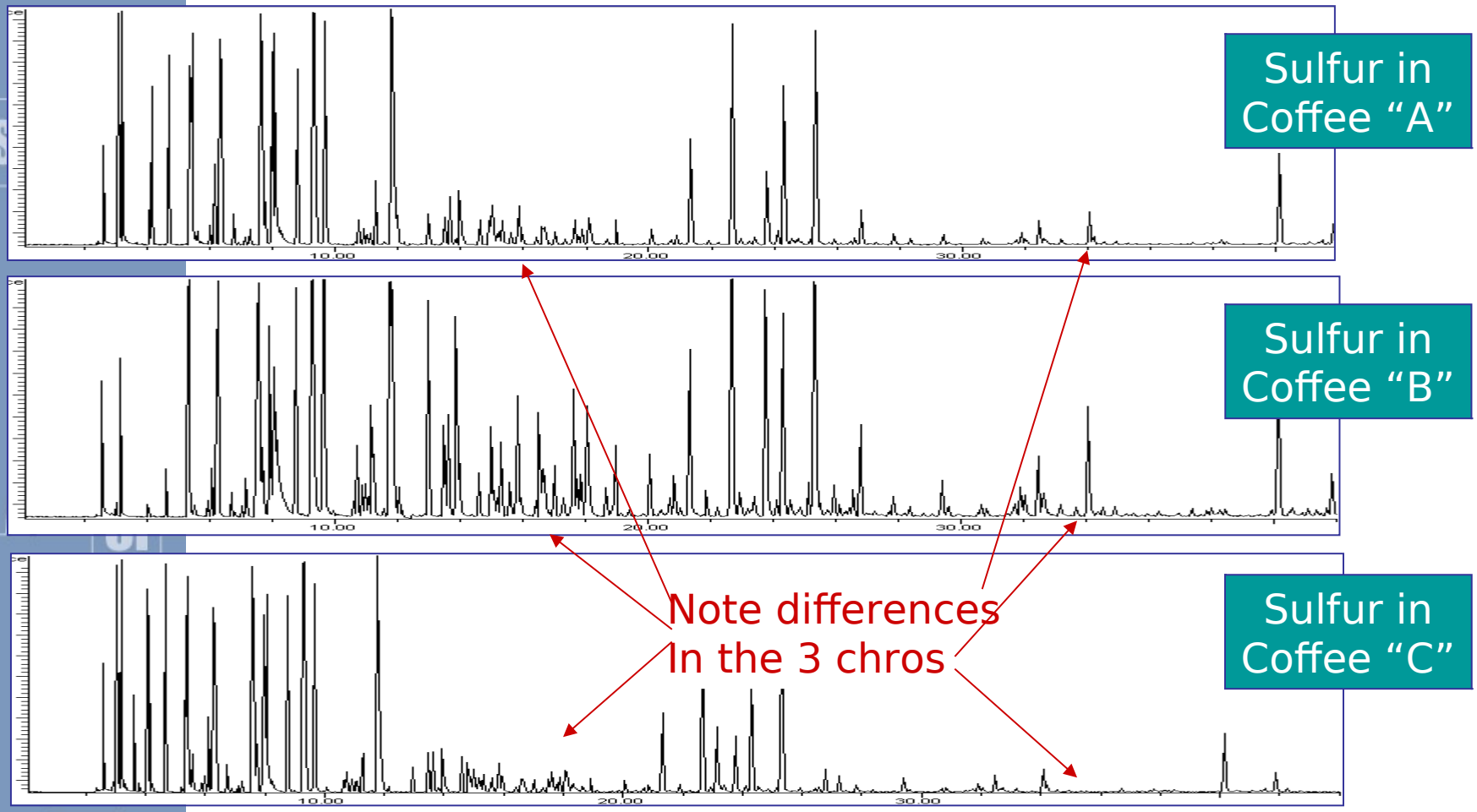
Competitive Analysis



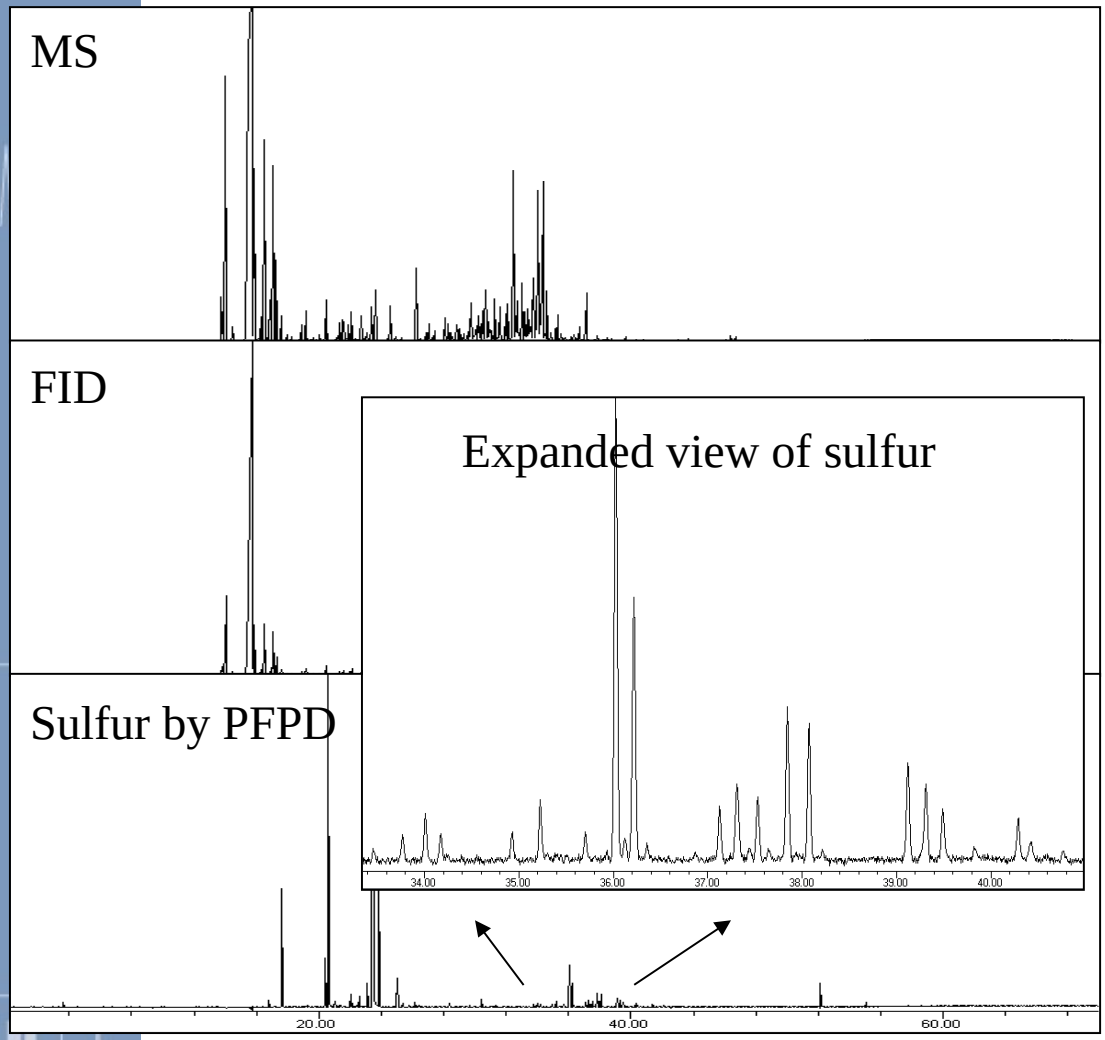
•The sulfur chromatogram, or “fingerprint” is unique for each coffee blend

- Can be used to identify differences between specific blends
- Determine which sulfur compounds contribute distinctive flavor and aroma

Competitive Analysis of 3 Coffees

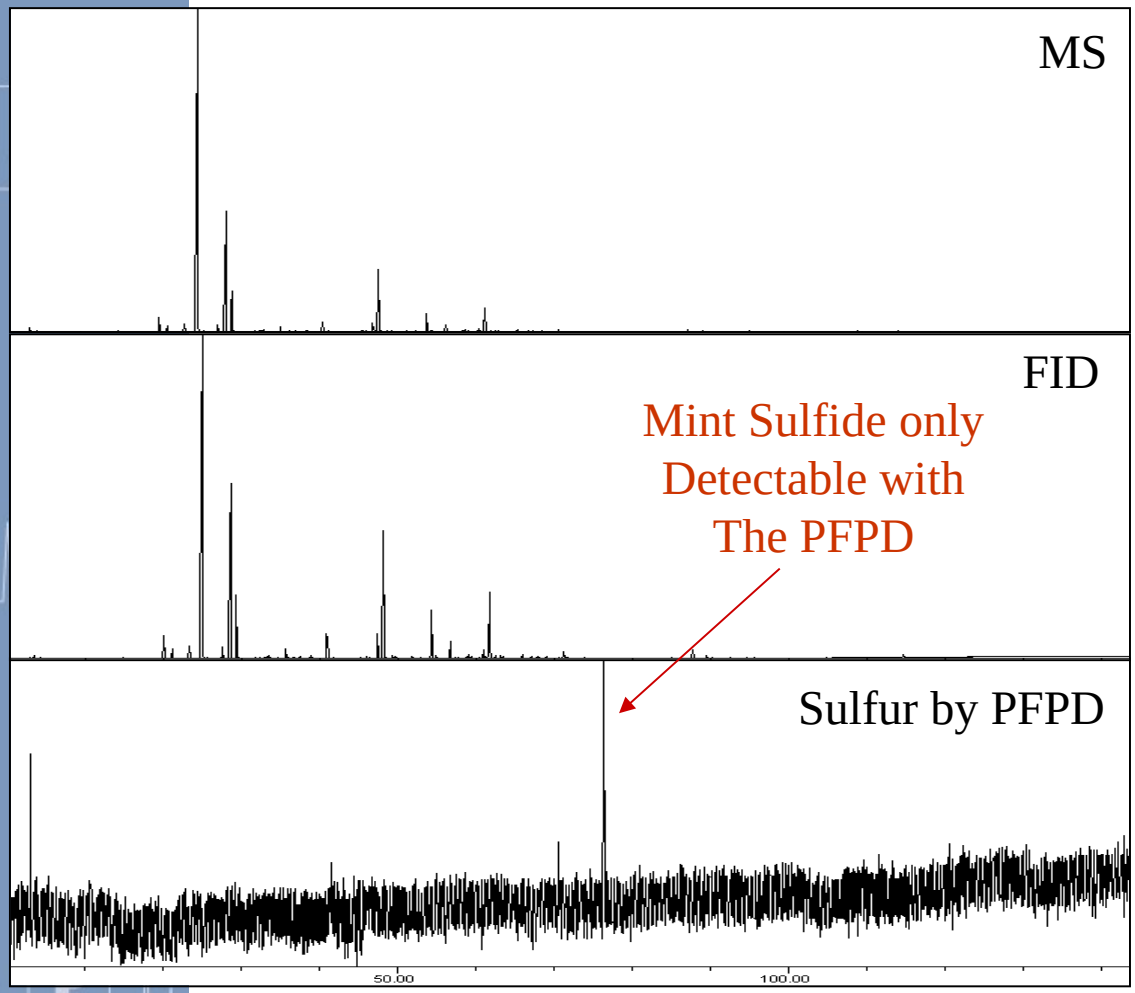


Sulfur in Galbanum Oil by PFPD



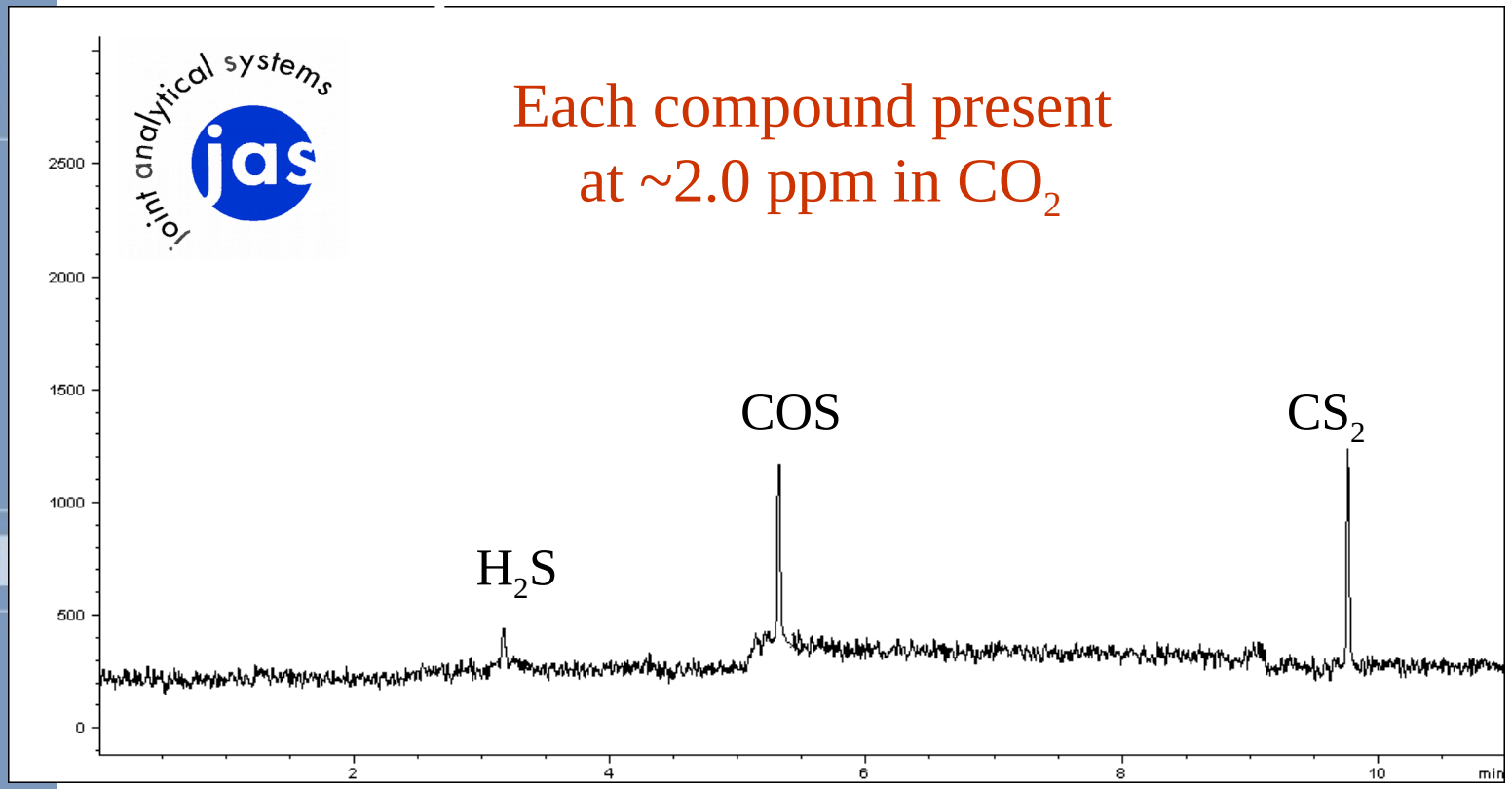
- Essential oil distilled from the galbanum plant
- Green, fresh leafy odor, dry woody undertones, pine highlights
- Used in production of fragrances
- Using an FPD only 4 sulfur peaks were detected

Sulfur in Fishwort Oil



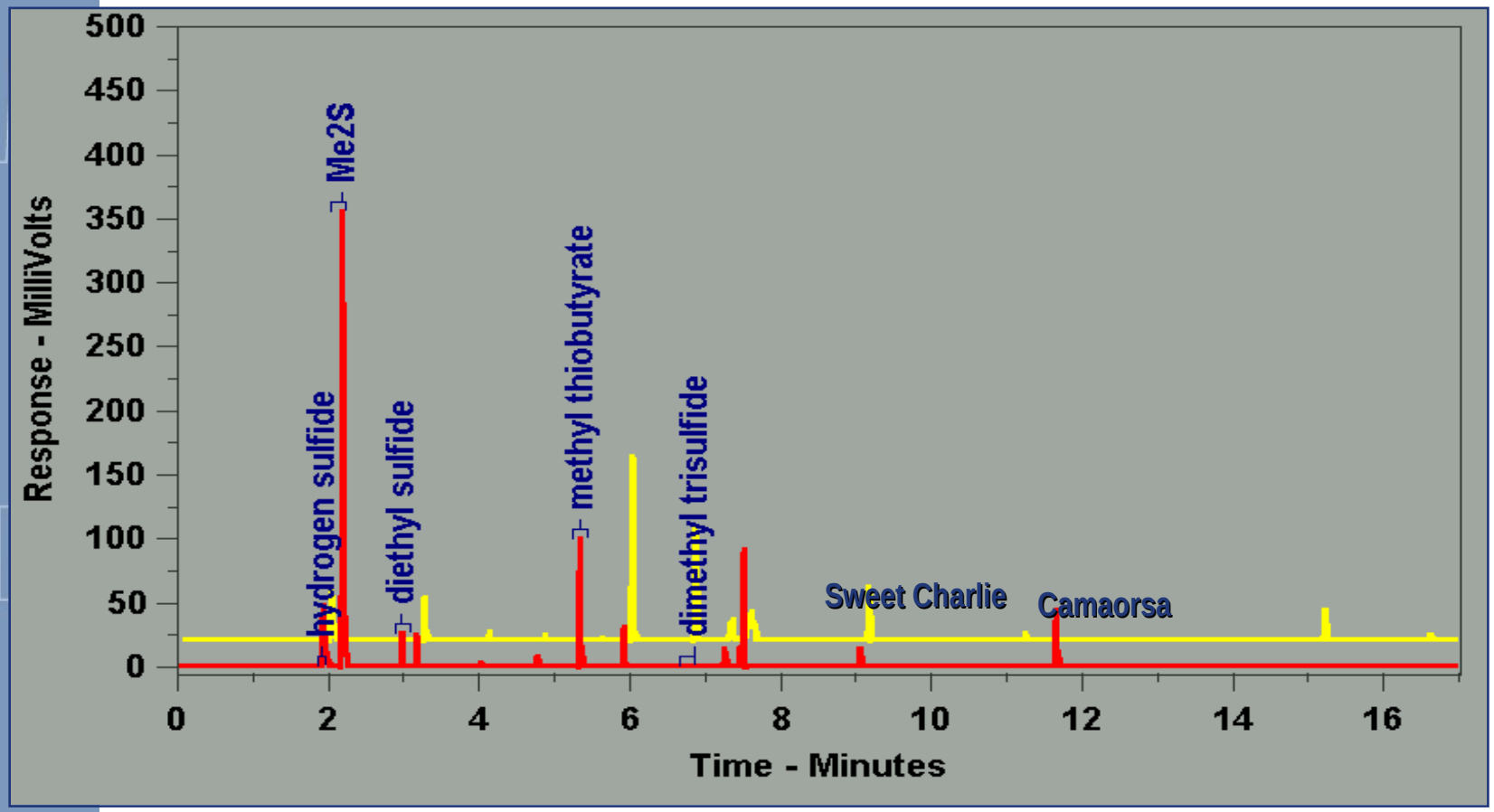
- 0.1 μL injection
- Essential oil distilled from the fishwort, or "Chinese Lizard Tail", plant (2 varieties)
- Corriander aroma or lemon/orange odor
- Used in production of flavors
- Using an FPD no sulfur peaks were detected

Sulfur in Beverage Grade CO_2



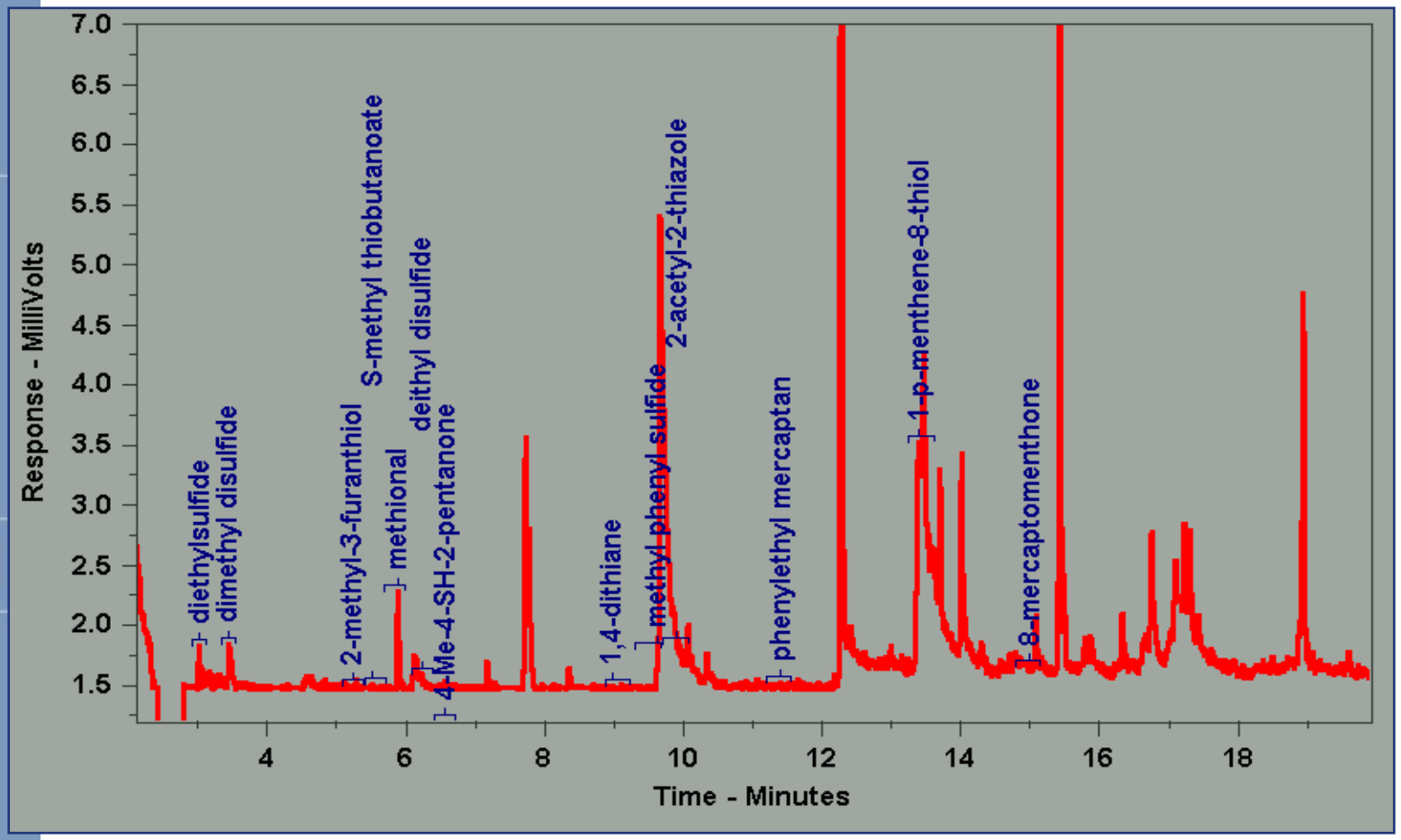
Chromatogram courtesy of JAS

Sulfur in Strawberry by PFPD



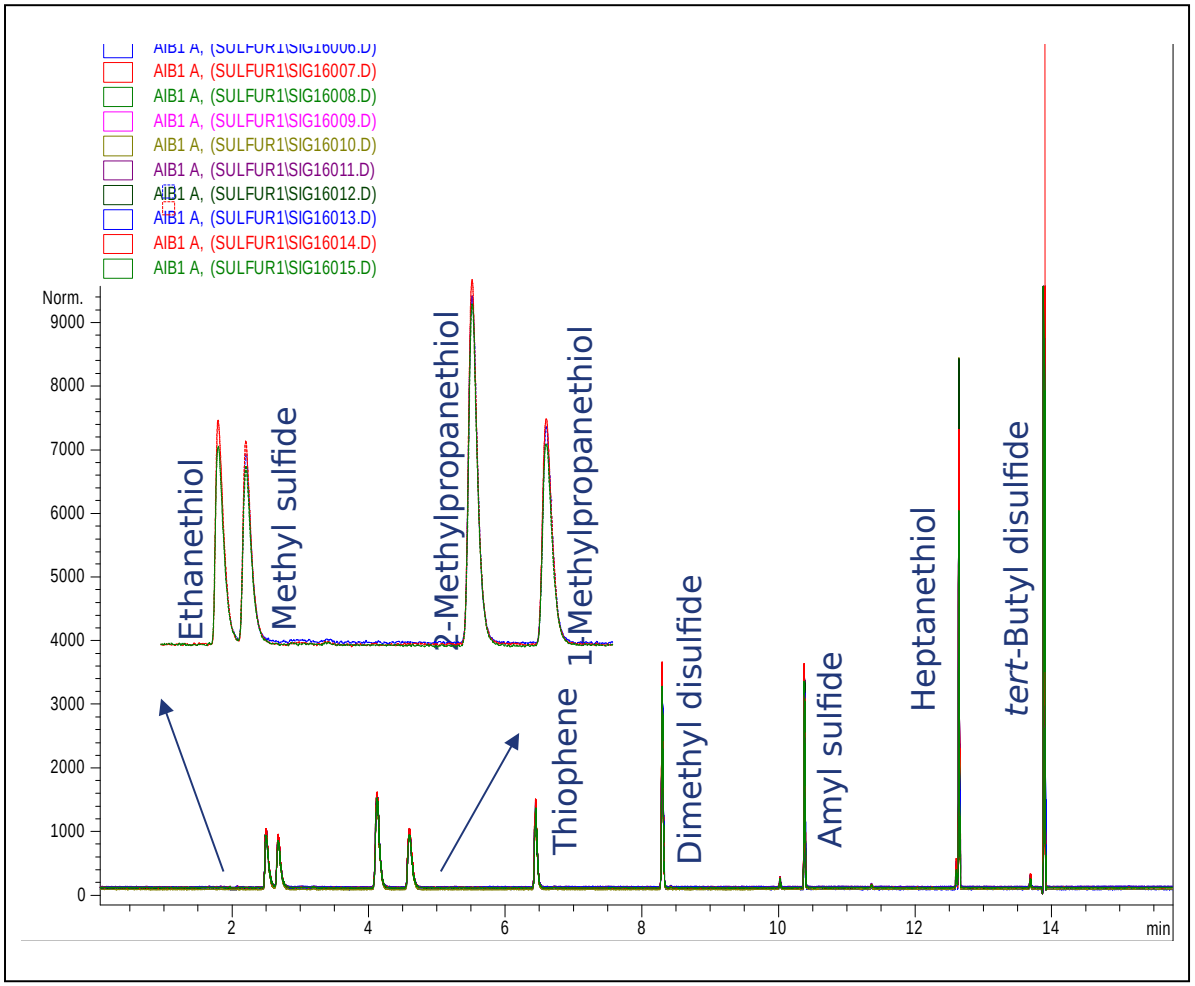
Chromatogram courtesy of Russell Rouseff, PhD, at University of Florida

Sulfur in Grapefruit by PFPD



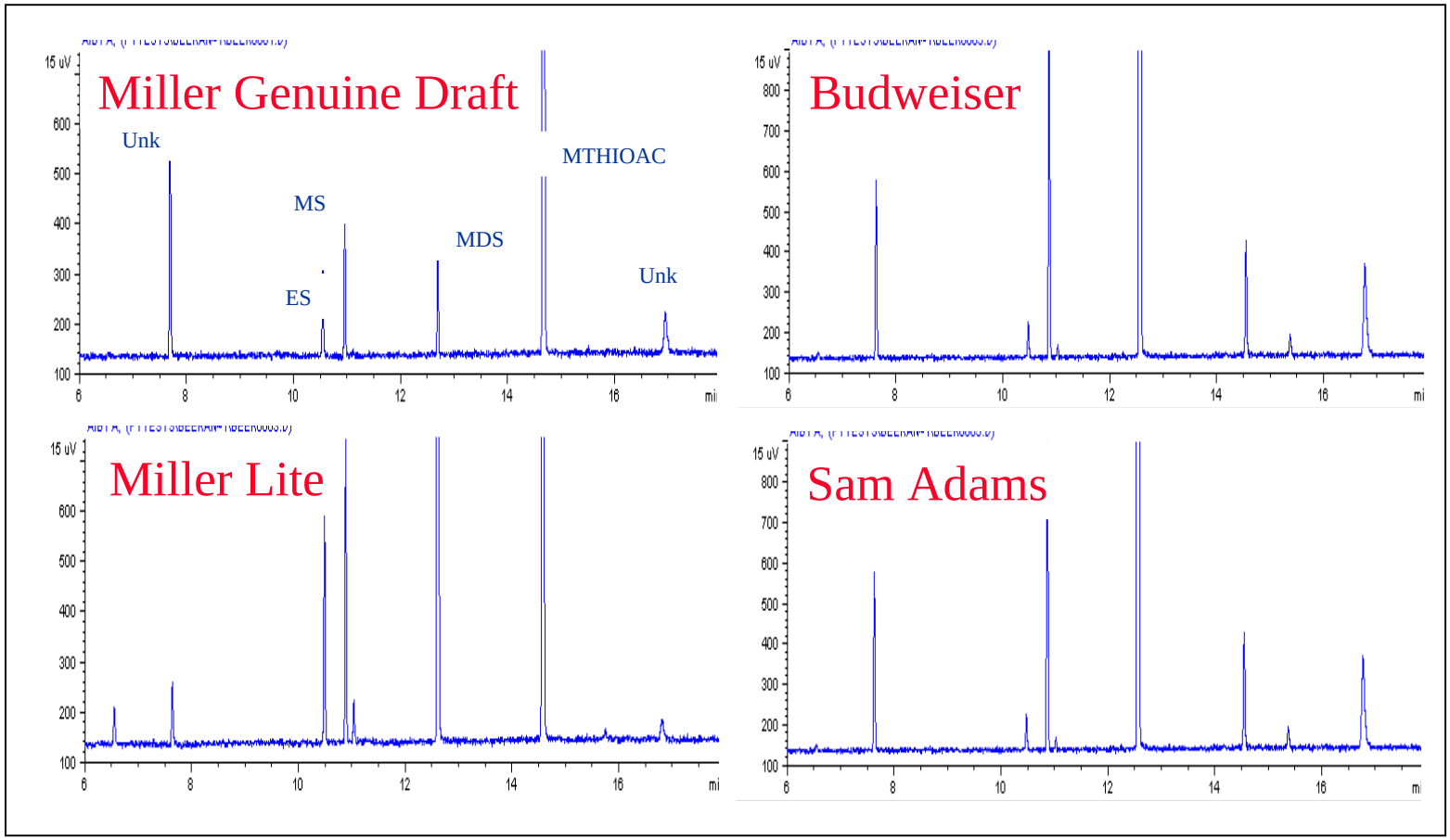
Chromatogram courtesy of Russell Rouseff, PhD, at University of Florida

Sulfur in Beer by Headspace



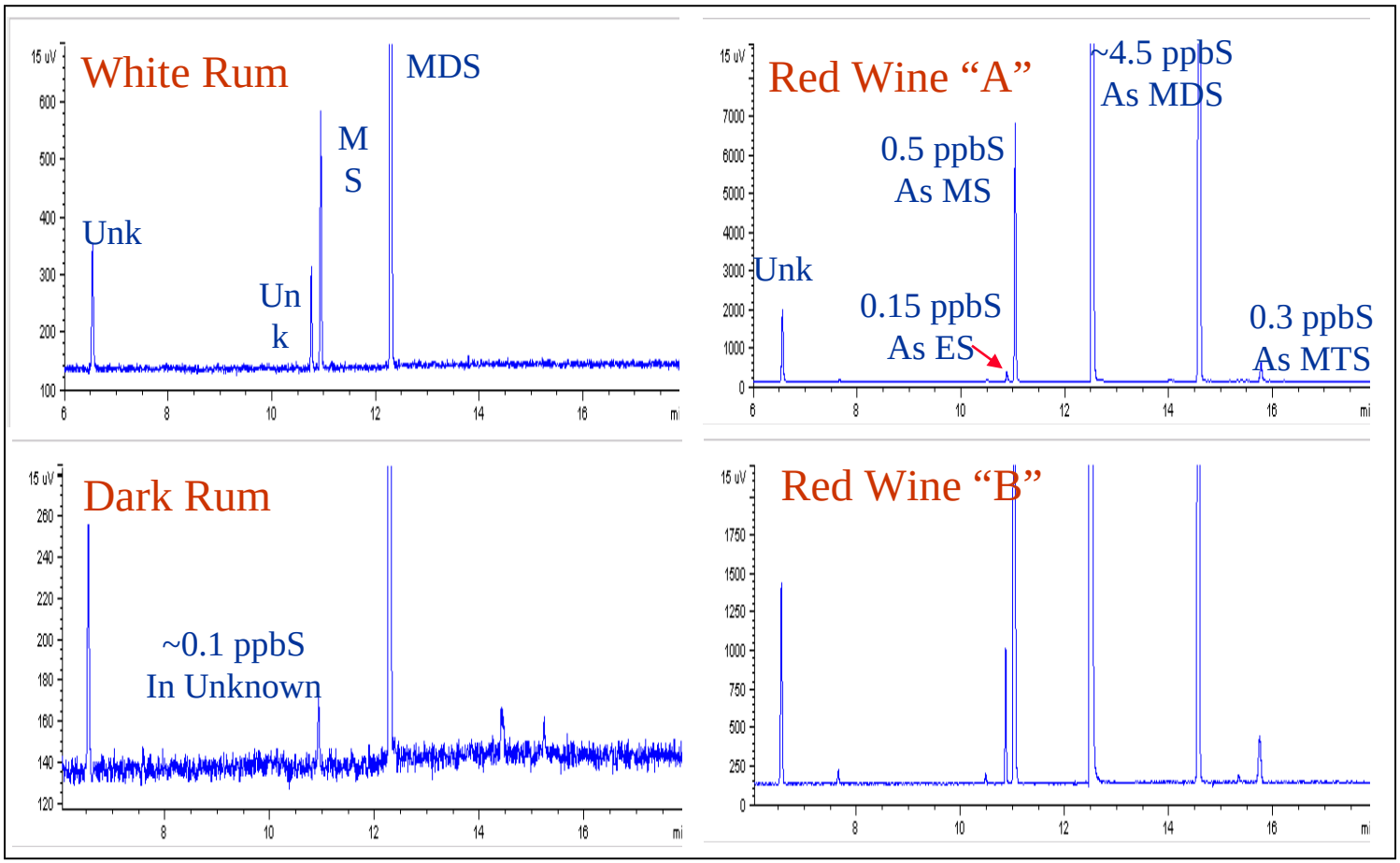
PFPD repeatability at 10 ppb better than 10%

Sulfur in Beer by PFPD

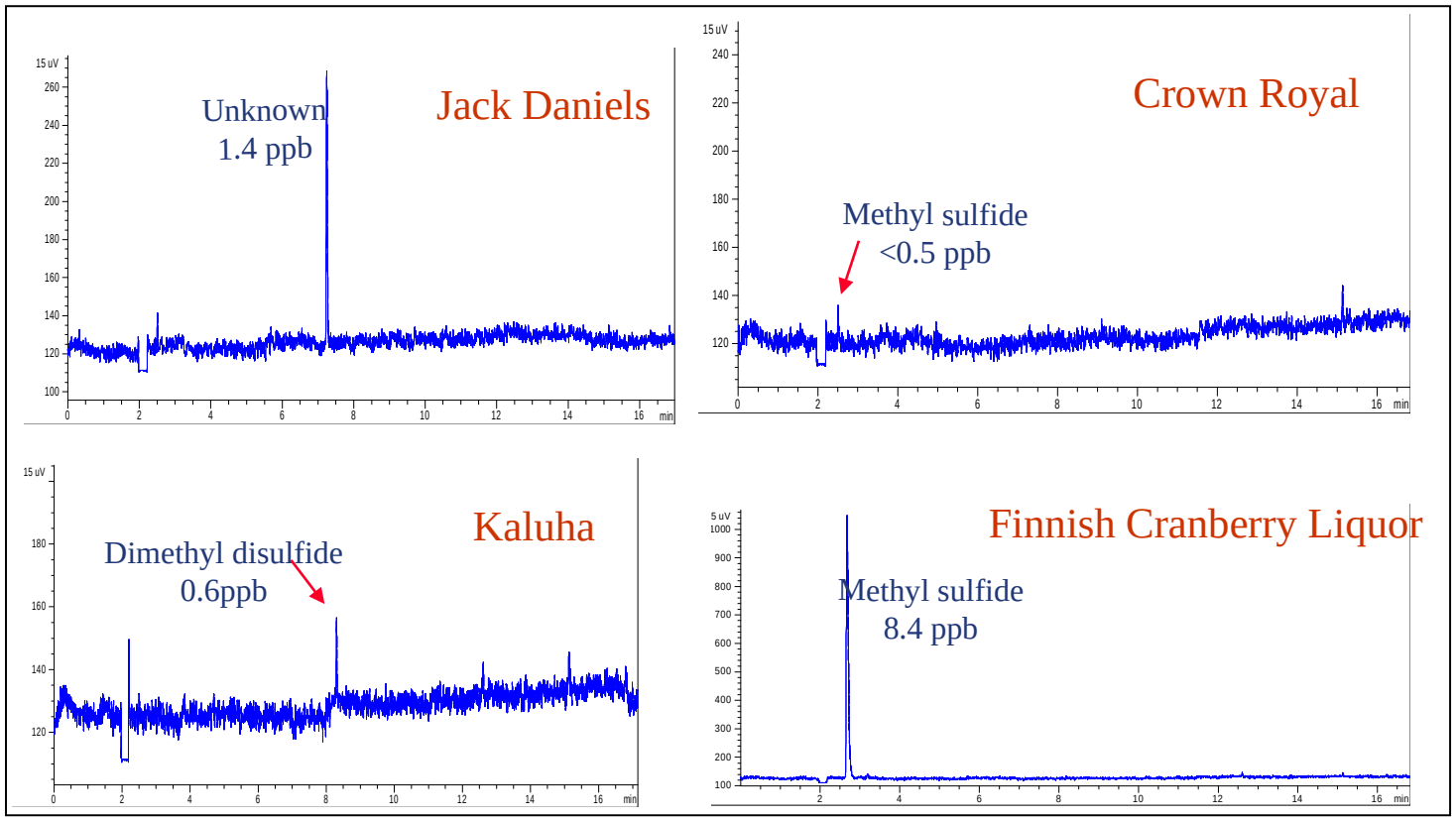


Sulfur concentrations in beers tested ranged from 0.1 ppbS to ~4 ppbS

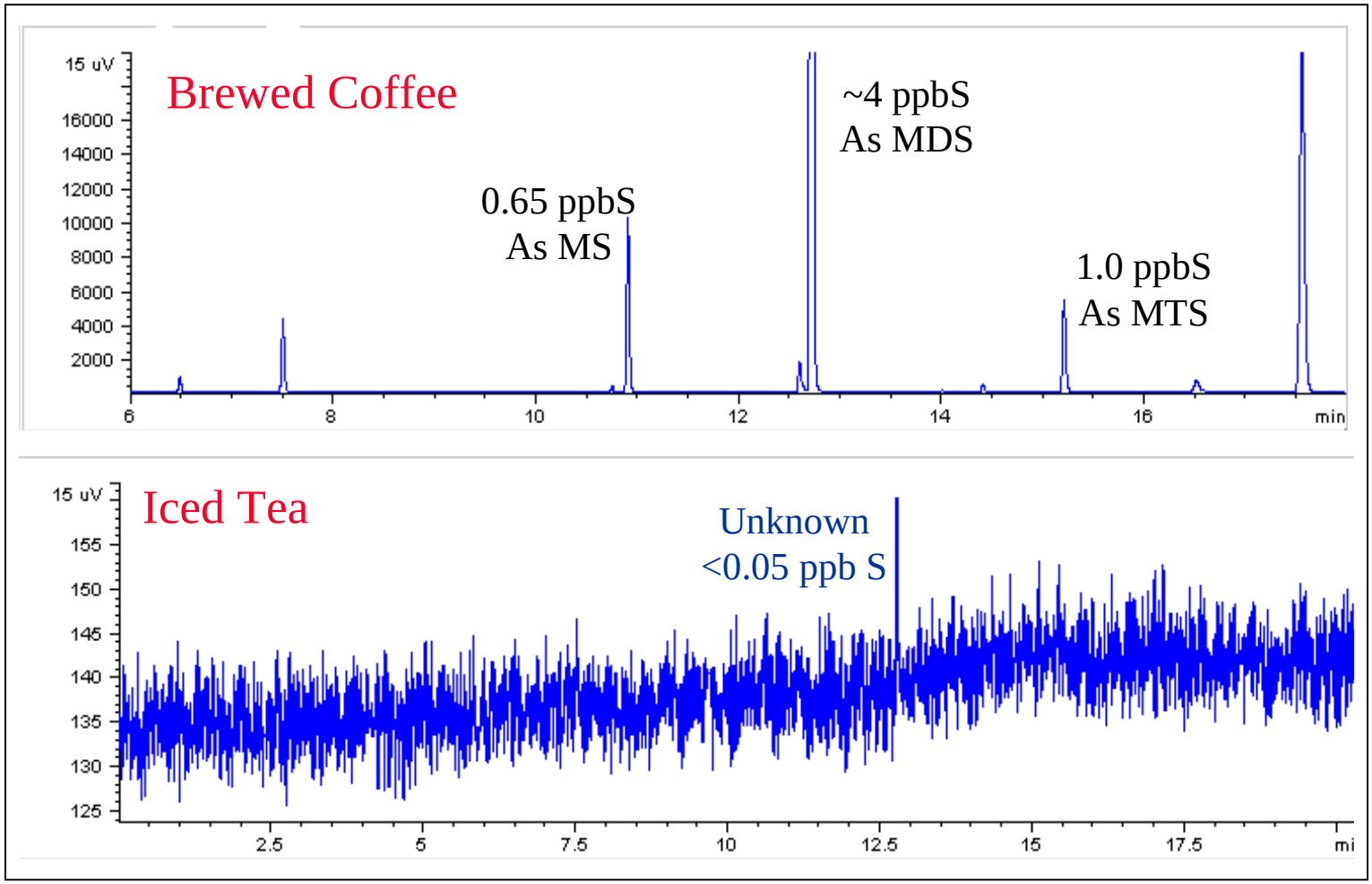
Sulfur in Wine and Rum by PFPD



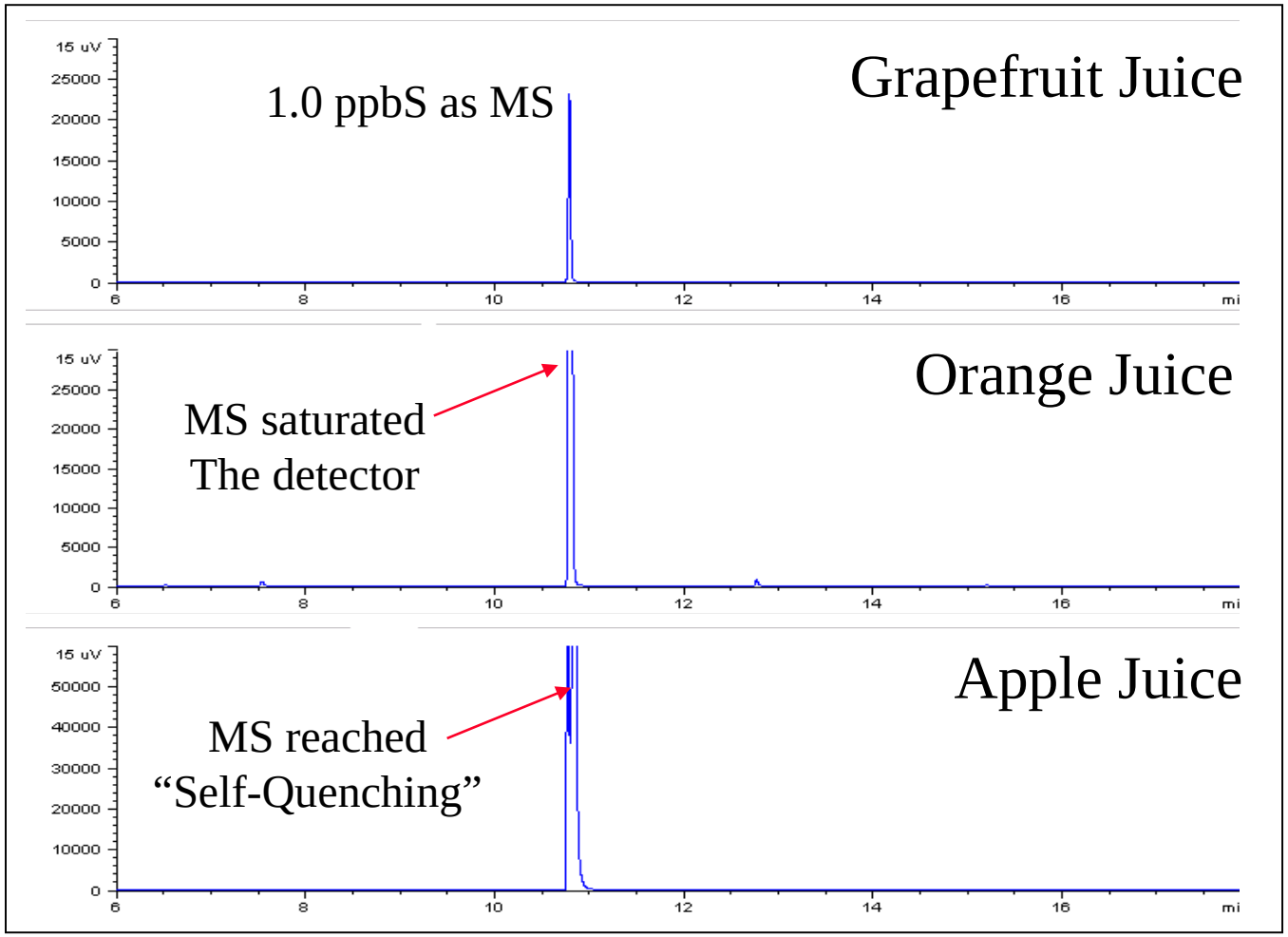
Sulfur in Liquor by PFPD



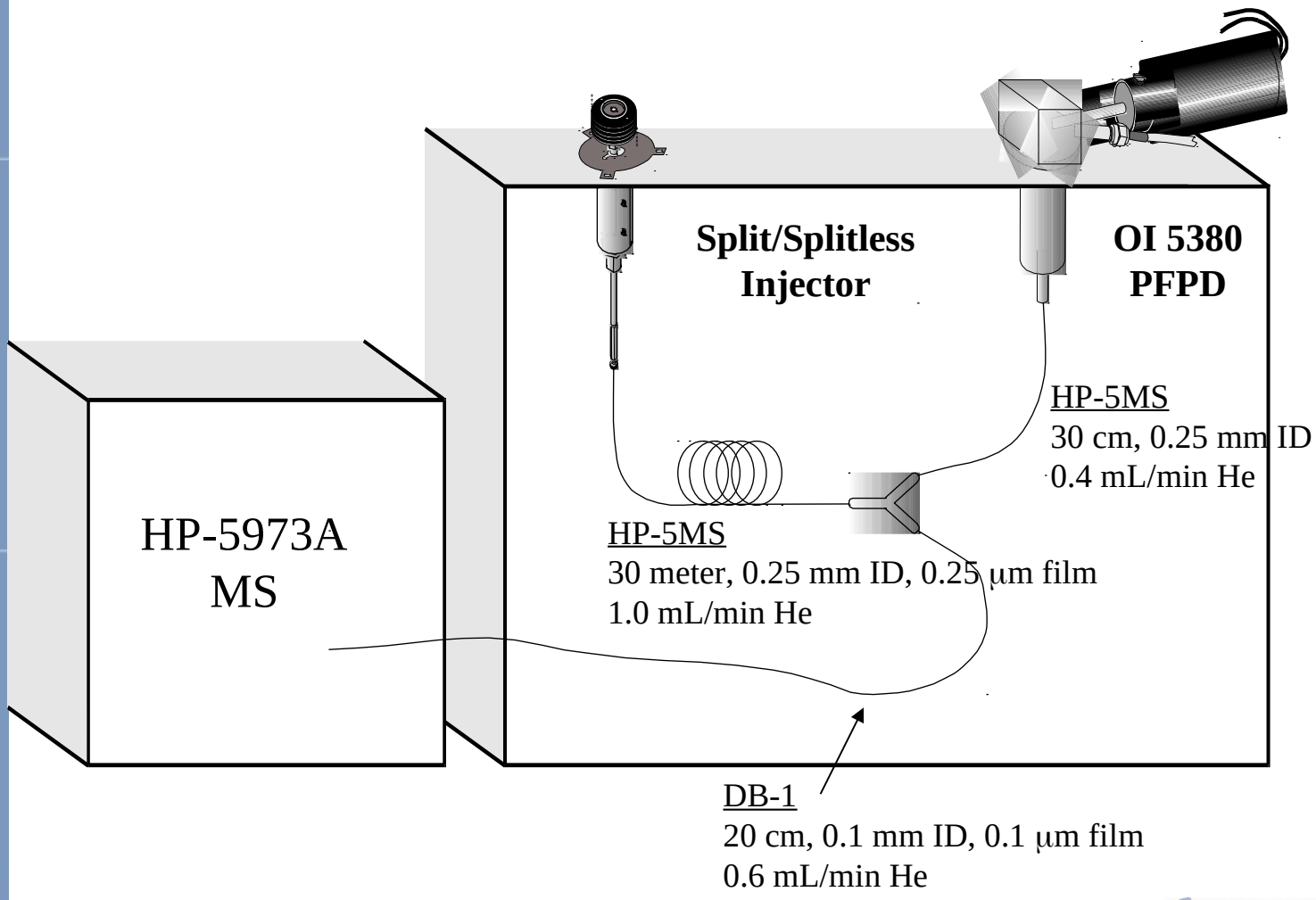
Sulfur in Coffee & Tea by P&T/PFPD



Sulfur in Juice by P&T/PFPD

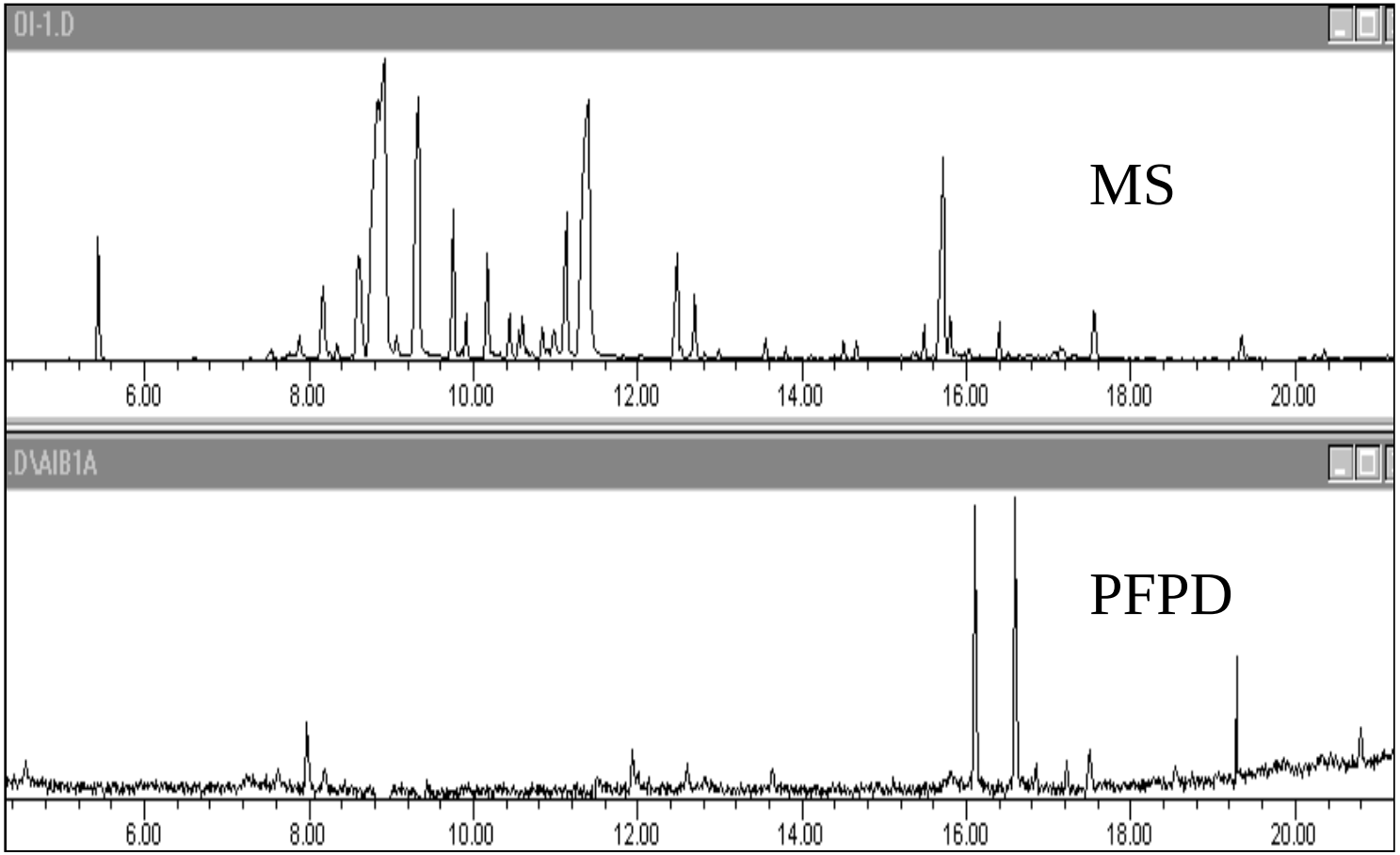


PFPD-MS Configuration

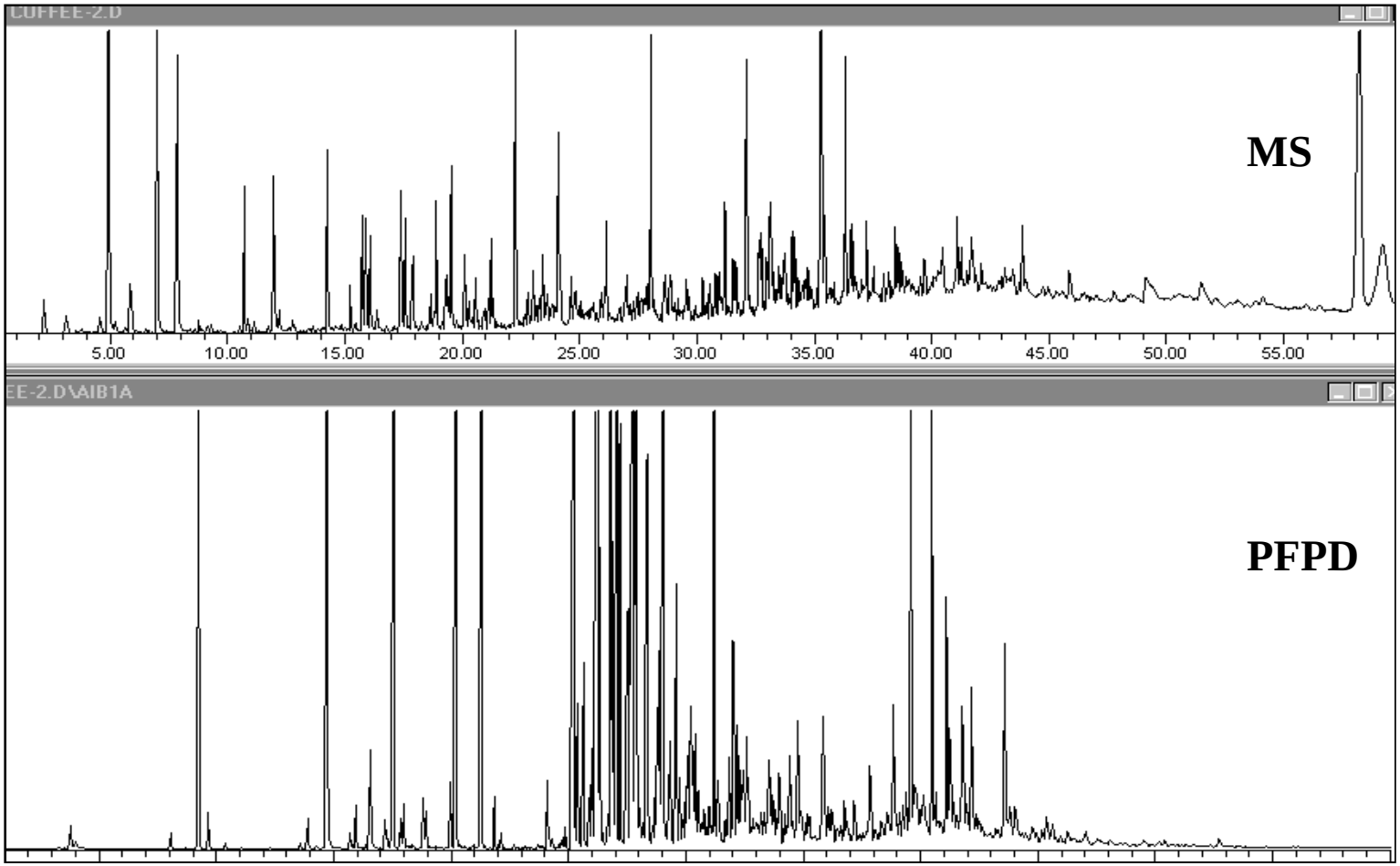


Twister™ by Gerstal, Inc.

Sulfur in Cola by PFPD/MS with Twister™

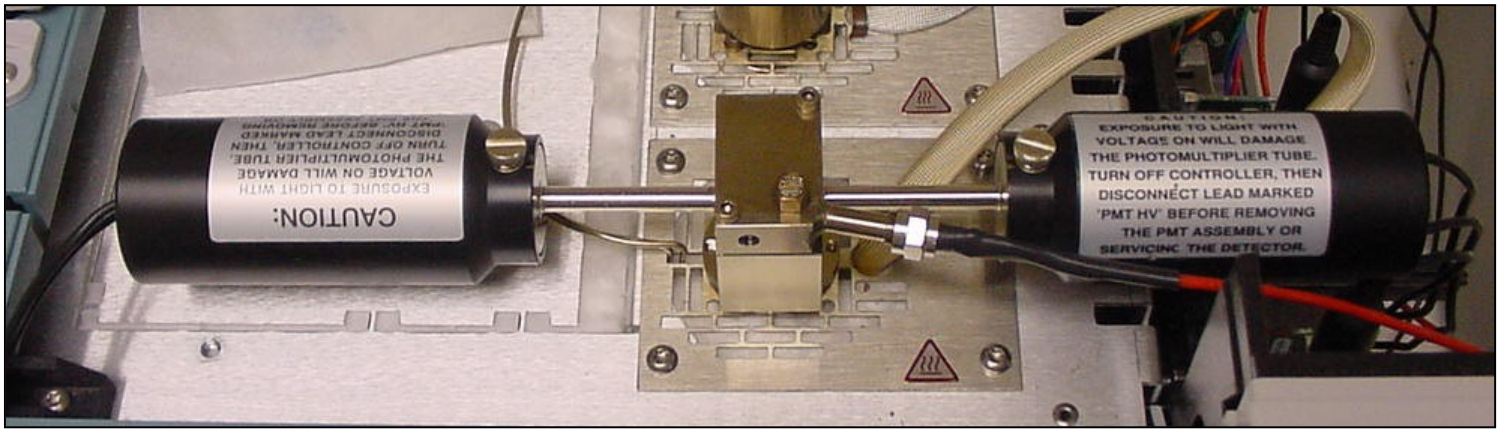


Sulfur in Coffee by PFPD/MS with Twister™



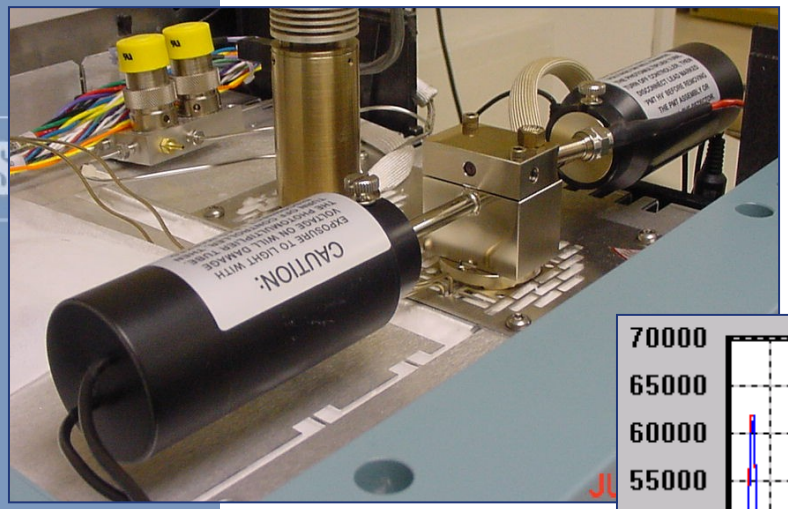
Other Applications by PFPD

Chemical Warfare Analyses



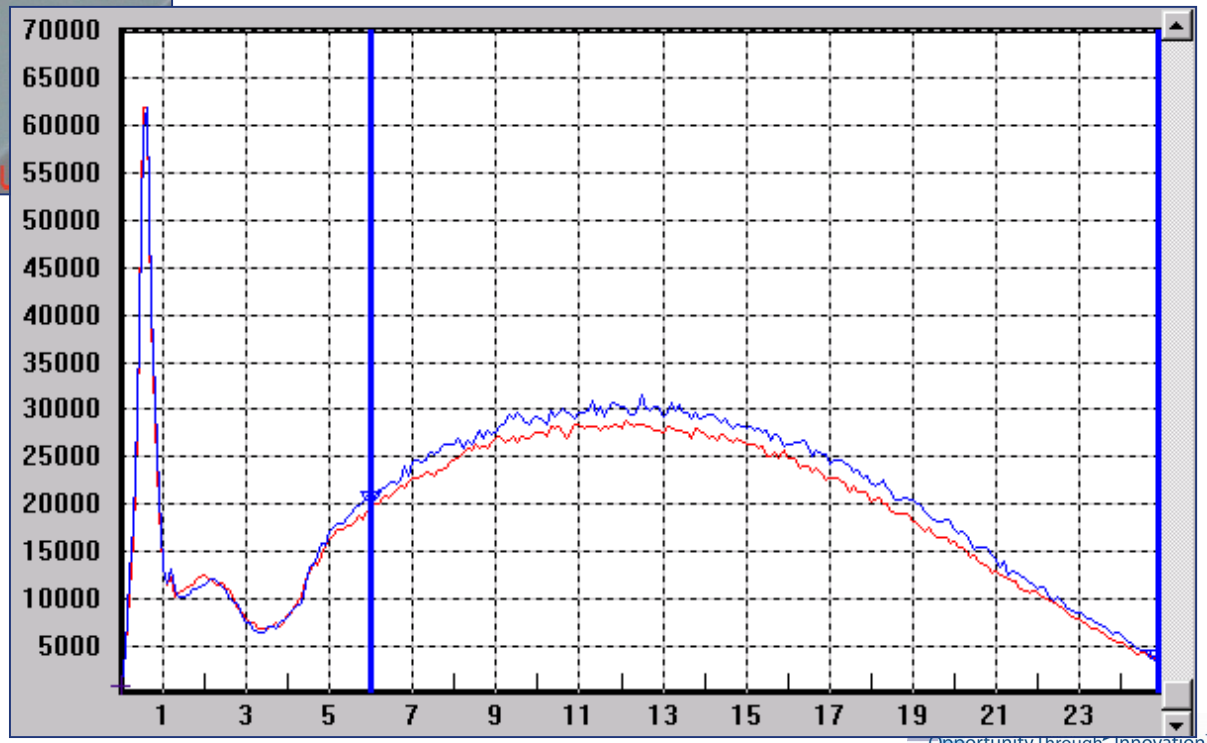
- A 2-headed PFPD for simultaneous, selective P and S detection
- One body/combustor, two filter/PMTs
- One side filter and gates optimized for S
- One side filter and gates optimized for P

Dual-Headed PFPD

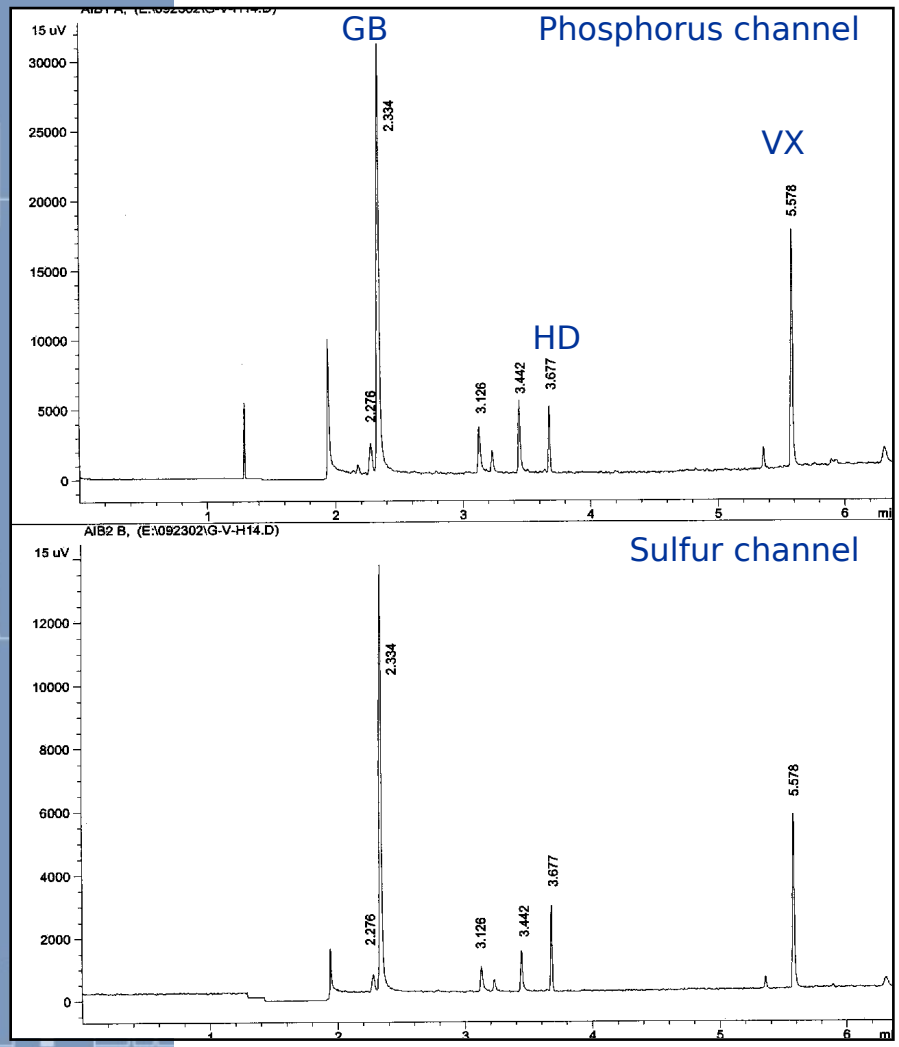


This one configured for S on both “sides”

Identical, matching S emissions



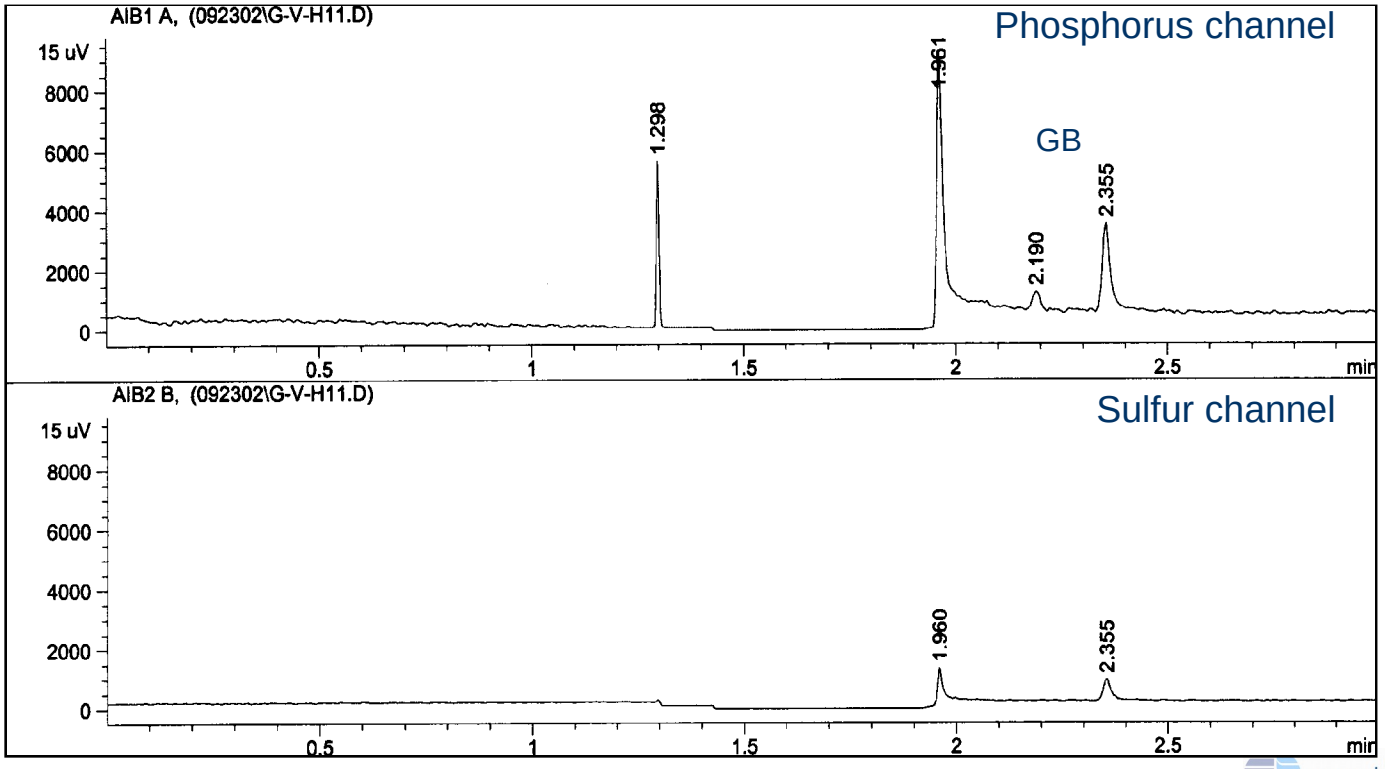
CW Agent Detection with PFPD



- Typical GB, VX and HD chromatogram
  - HP 6890 with PFPD configured to favor phosphorus response
  - HP-5 30-m x 0.32-mm-od x 25µm film with He flow of 2.5 mL/min; ramped from 40° to 230°C
  - P gate: 4-15 msec; S Gate: 6-24.9 msec
  - 39 pg GB; 39 pg VX; 50 pg HD
- Excellent peak shapes and responses illustrate detector potential for multi-element-based multi-agent analysis
- Background peaks lower in S channel than P channel, although S gate opens only two msec after P gate
  - Proper gate settings allow enhanced discrimination against background constituents.

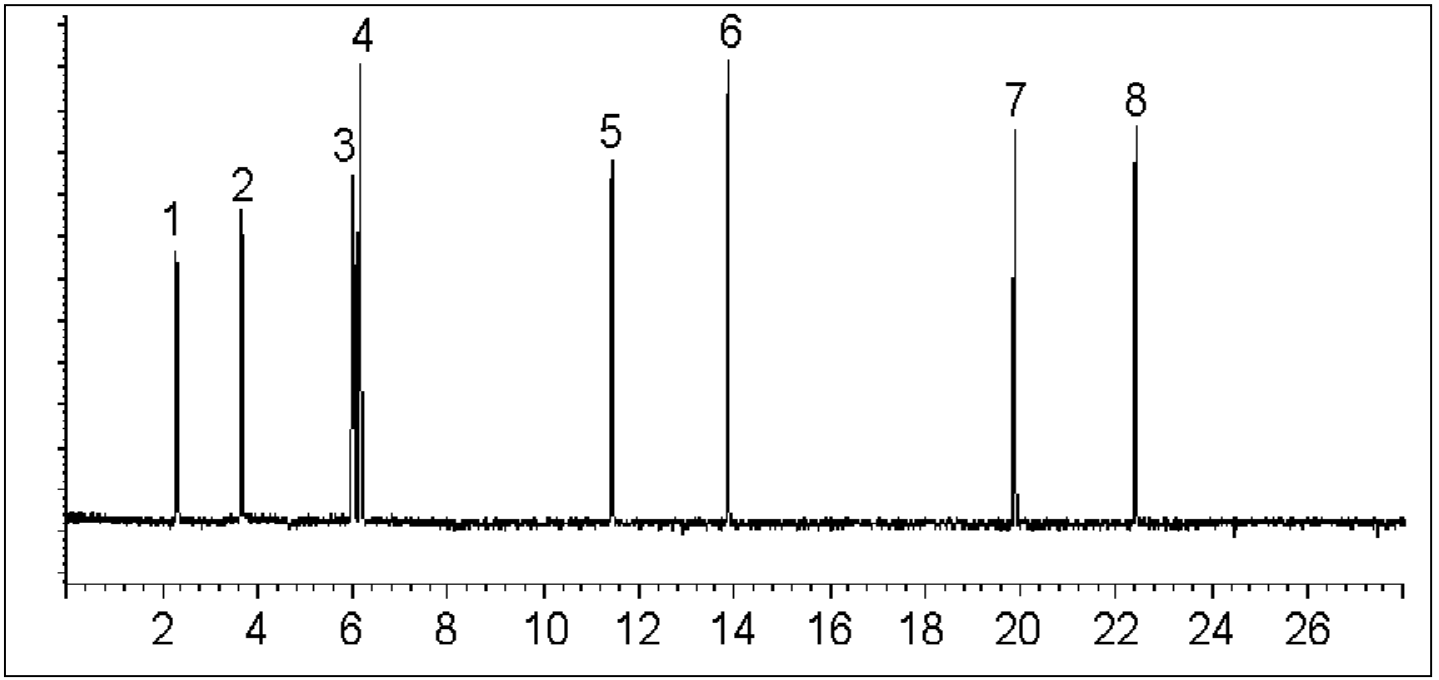
P Detectivity and GB Limit of Detection

- Response from a 1.9 pg injection of GB, assuming S/N of three as the LOD
  - GB LOD ≅ 400 fg
  - Phosphorus detectivity ≅ 43 fg P/sec
- PFPD was configured for general use; LOD and detectivity can be improved by optimizing for P response



Reduced Sulfur in Pulp Mill Effluent

200 μg S/L aqueous standard



Chromatogram courtesy of NCASI

End of Part 5