Pittcon 2005 Abstract 700-1

Improved Analysis of Sulfur Compounds in Gasoline and Diesel Matrices Using the Pulsed Flame Photometric Detector (PFPD)

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Pulsed Flame Photometric Detector

- The PFPD, the next generation of Flame Photometric Detectors (FPD), has gained acceptance for analysis of sulfur in petrochemical matrices
- PFPD advantages over standard FPD
  - *10-fold increase in sensitivity*
  - *10-fold increase in selectivity*
  - *Linear, equimolar response not possible with the FPD*
  - *Self-cleaning, low maintenance*
    - Long-term stability
  - *Wide range of sulfur concentrations, single-digit ppb sulfur for single components to % total sulfur*
  - *Wide range of matrices, gas phase to high MW*

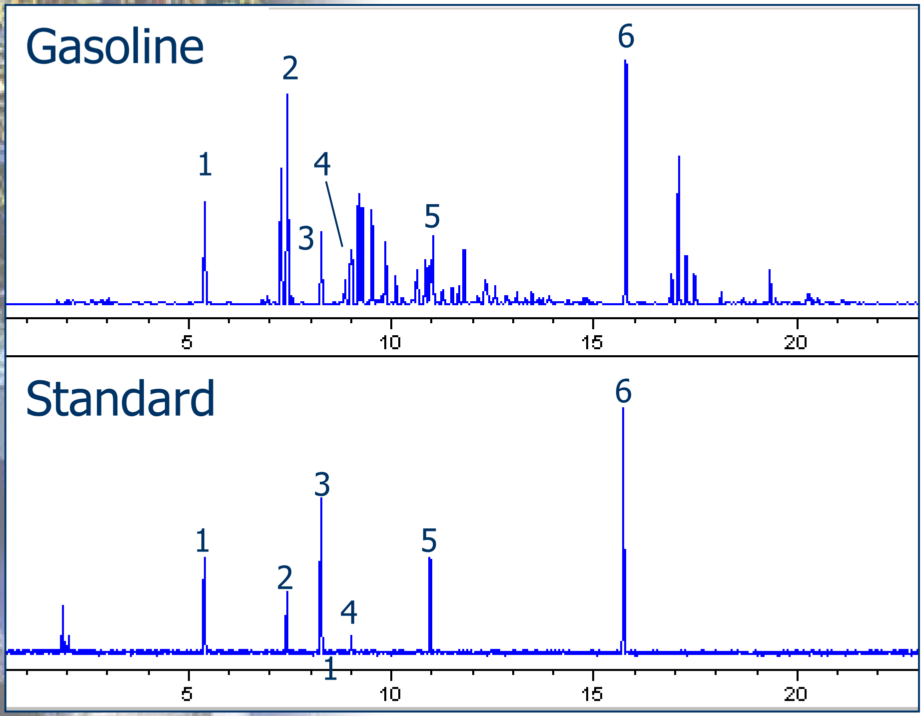
Analytical Challenge

- Until recently, analyzing for low level sulfur in gasoline was difficult
  - *High-level sulfur in gasoline has always been possible*
- High concentrations of low-molecular-weight hydrocarbons in gasoline can co-elute with sulfur compounds and have the potential to quench, or reduce, the sulfur signal

Analytical Challenge

- Simple modifications to the PFPD configuration allow analysis of low-level sulfur in gasoline with little or no quenching
- Single-digit ppm total sulfur in gasoline
  - *10-ppb sulfur for individual compounds*
- At least a 20-fold increase in sensitivity

Analysis of Gasoline



Linear, equimolar sulfur response simplifies the calibration and quantitation process

Specific compounds can be quantified using individual RFs:

Thiophene	7.2 ppm S
3-Methylthiophene	12.2 ppm S
THT	4.1 ppm S
2-Ethylthiophene	5.3 ppm S
2,3,5-Trimethylthiophene	4.9 ppm S
Benzothiophene	18.5 ppm S

Or, total sulfur can be quantified using an average RF:

Total sulfur = 175 ppm sulfur

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Hydrocarbon Quenching

- The common terms “hydrocarbon quenching” and “quenching” refer to reduction of the sulfur signal by a co-eluting hydrocarbon
- Two conditions must occur for quenching to take place
  - *Co-elution with sulfur peak*
  - *High concentration of hydrocarbon*

Hydrocarbon Quenching

- Occurs because HC consumes all available oxygen during the combustion process
- Hydrocarbon not completely oxidized to CO_2
- Incomplete combustion leads to formation of excess CO

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Hydrocarbon Quenching

- Presence of incompletely combusted CO allows competing side reactions
  - $CO + S + M \rightarrow COS + M$
  - $CO + S_2 \rightarrow COS$
- These sulfur scavenging reactions reduce sulfur available to form S_2*, the emitting species
- Loss of S_2* causes reduction of the sulfur signal

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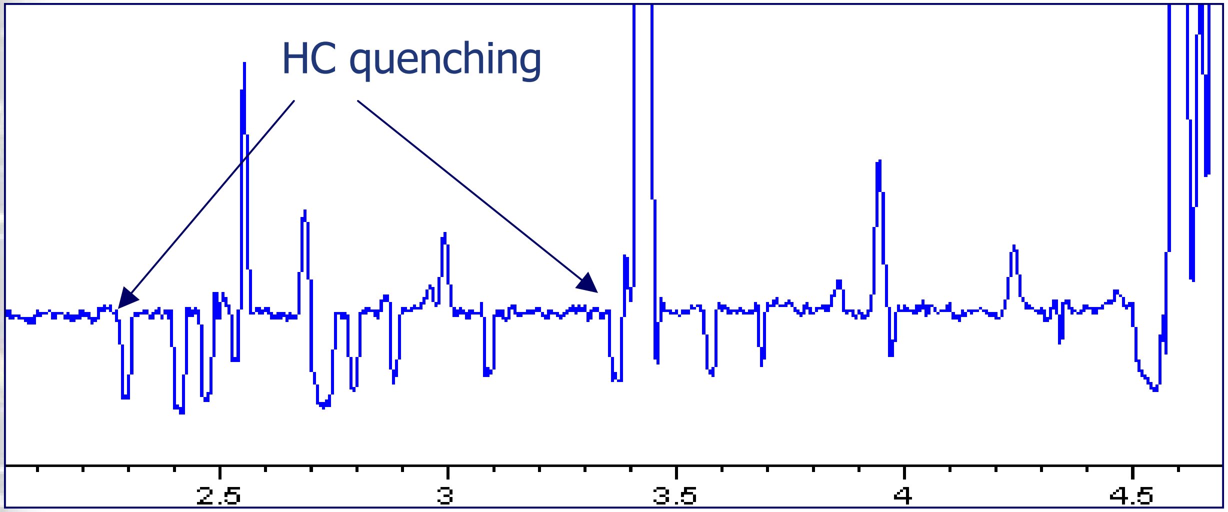
Identification of Quenching



<u>Identification</u>

- Dips in baseline of sulfur chromatogram caused by HC quenching of background emissions
- Background emissions come from trace amounts of sulfur in gases, ferrules, stainless steel, sample pathway, column, etc.
- Indicates conditions exist that <u>may</u> quench the targeted sulfur signal as well

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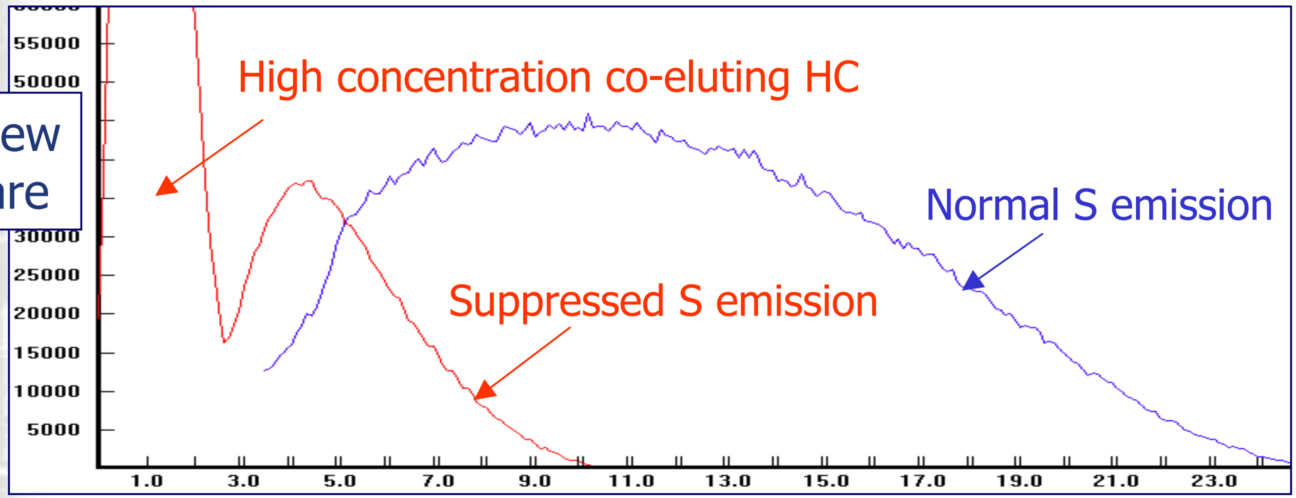
Confirmation of Quenching

PFPDView Software



Confirmation

- Use PFPDView software to confirm quenching
- Sulfur emission suppressed by the presence of large amounts of co-eluting hydrocarbon
- Shortened emission delay, <25 msec
- Degree of quenching varies with amount of HC
- Use dual-gate ratio technique

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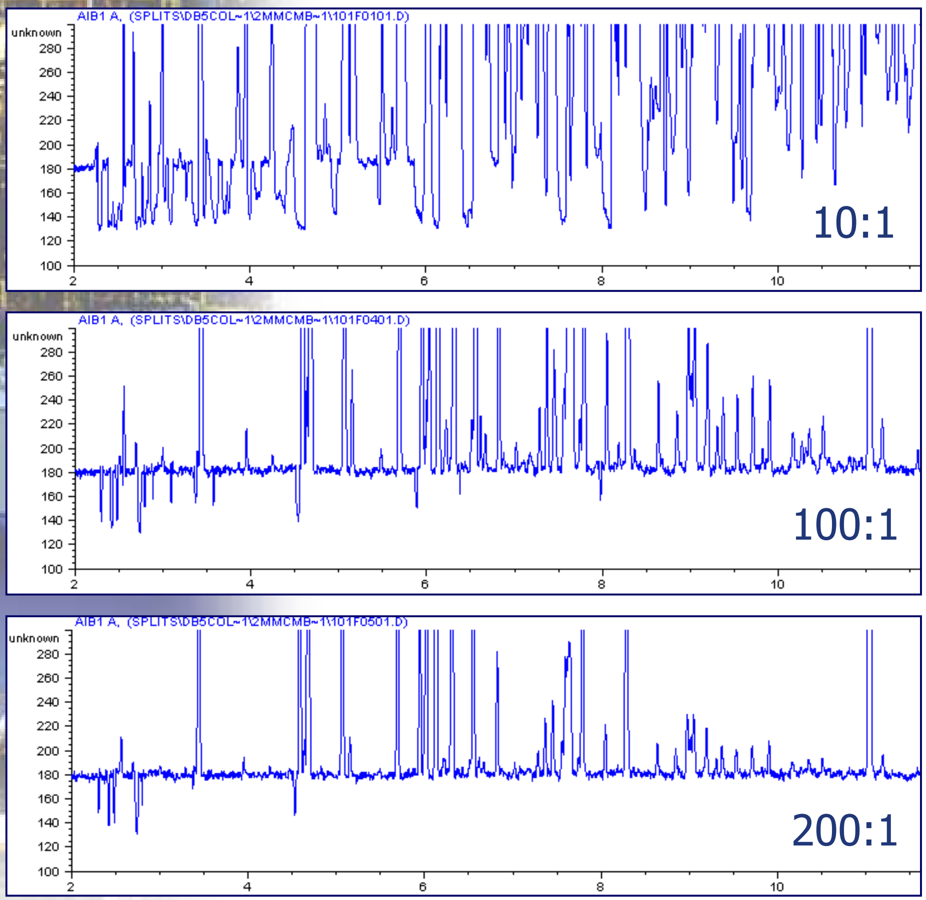
GC Techniques to Minimize Quenching

- Two GC techniques reduce or minimize the quenching effect
- Increase split ratios
  - *Pro: Decreases HC to the detector, fewer competing reactions, less or no quenching*
  - *Works well for high-sulfur gasoline*
  - *Con: Also decreases amount of sulfur to the detector, raising detection limits*
- Column selection
  - *Pro: Chromatographically resolve sulfur from the main HC peaks to eliminate quenching*
  - *Con: Method development to find the right column*

Increased Split Ratio



<u>S baseline at varied split ratios</u>

- Shown here: 1-µL gasoline injection, variable split ratios, zoom in on sulfur baseline
- Increasing the split ratio decreases the amount of HC to the detector
- HC quenching identified by dips in the chromatogram
- Only minimal potential for quenching observed with a 200:1 split

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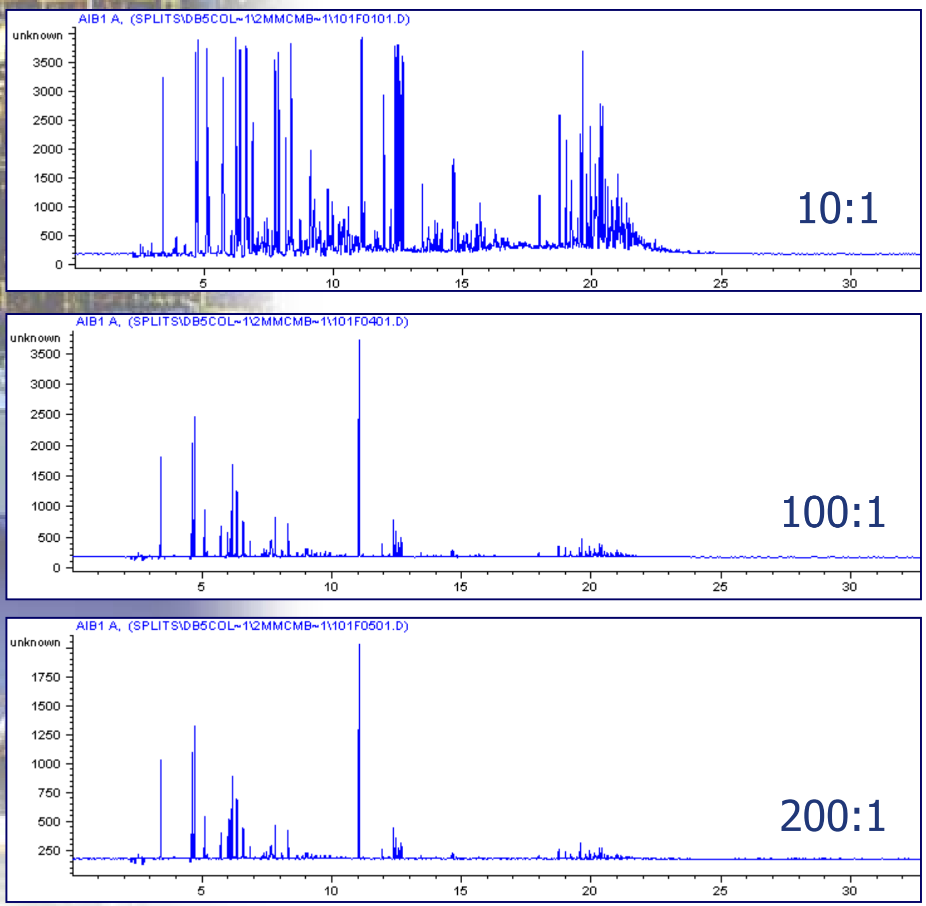
Increased Split Ratio



S signal at varied split ratios

- Full sulfur signal with sulfur saturation in the first half of the chromatogram
- Higher split decreases the amount of sulfur on the column
- All sulfur peaks are on scale at a 200:1 split ratio
- A good choice for high-sulfur gasoline like this one
  - *High ppm to %*
- Not good for low-sulfur samples

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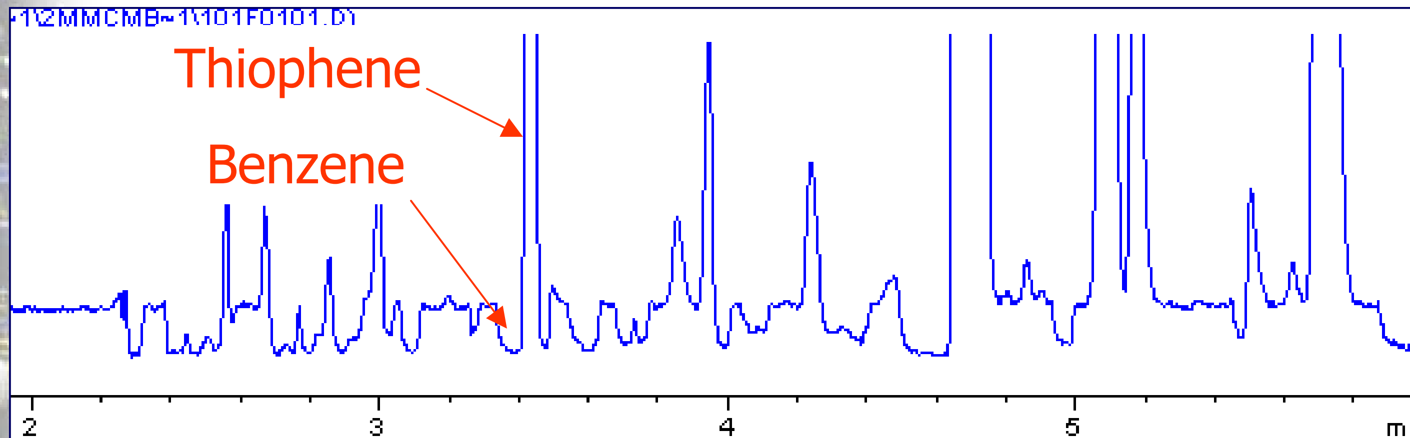
Column Selection

- In gasoline, only a few “critical pairs” of HC/sulfur are subject to quenching
  - *Benzene and thiophene*
  - *Toluene and methylthiophene*
- They occur early in the chromatogram, where the highest concentration of HC exists
  - *Less quenching potential later in the chromatogram*
- Use a slightly more polar GC column with thick film to chromatographically separate the “critical pairs”
- No co-elution $\rightarrow$ no quenching

"Critical Pair" Example



- 1-µL injection, split 10:1 onto a nonpolar, 5% phenyl methylpolysiloxane column (e.g., Rtx-5 or DB-5)
- Benzene and thiophene co-elute
- High concentration of benzene identified by a dip in the sulfur baseline
- Signal of the co-eluting thiophene was suppressed (reduced), but still visible

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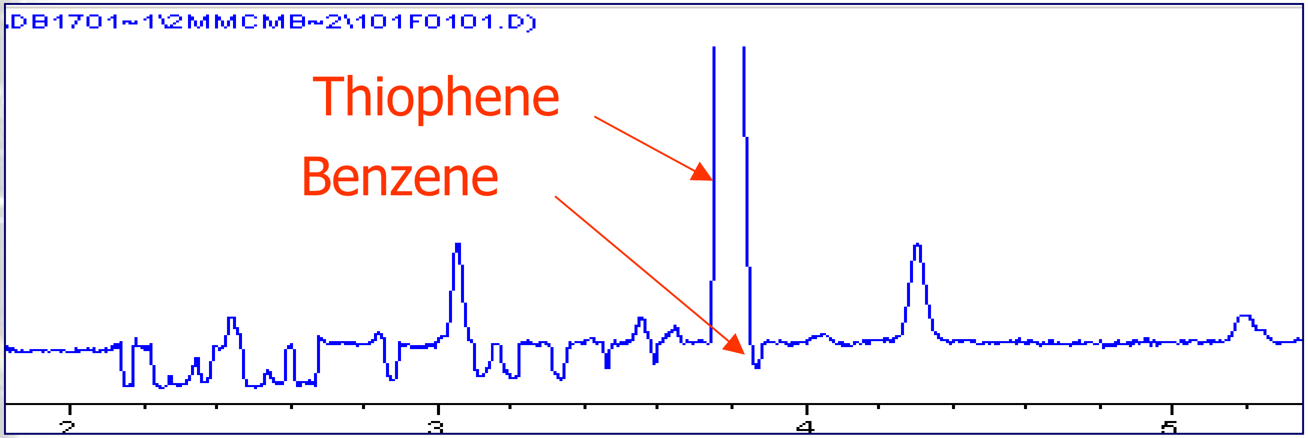
"Critical Pair" Example



- 1-µL injection, split 10:1 onto a thick film column, slightly more polar
- Longer GC run
- Better separation between benzene and thiophene
- Minimizes or eliminates potential for quenching
- E.g., Rtx-35, DB-35, Rtx-17, DB-17

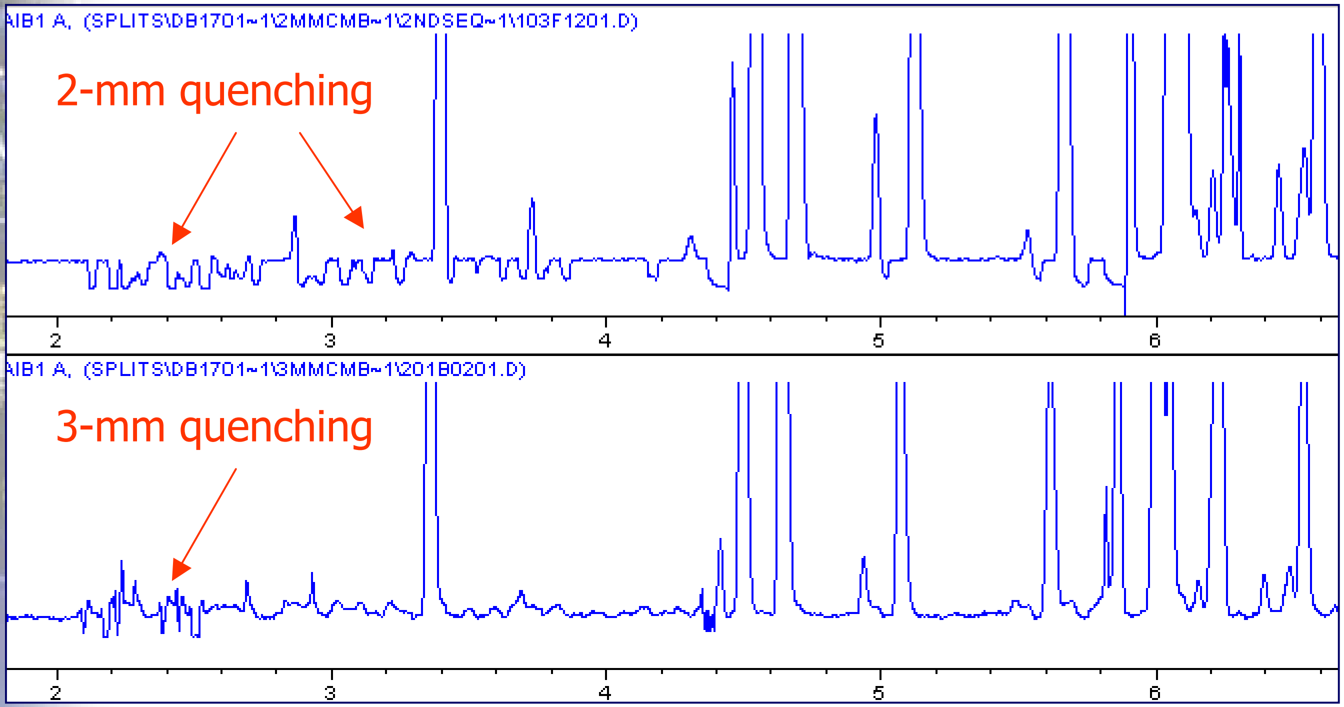
PFPD Techniques to Minimize Quenching

- Chromatographic separation of sulfur and HC minimizes the potential for quenching, but does not address the root cause
- Three PFPD techniques to reduce or completely eliminate the quenching effect
  - *3-mm combustor*
  - *Adjust H_2/air ratio of combustor gas to increase the amount of air*
  - *Modified gate selection*

3-mm Combustor

- 2-mm combustor used for most S applications
  - *Relatively cool flame conditions favor extended lifetime of* S_2*
- The larger 3-mm combustor creates flame conditions that favor hotter post-pulsed flame temperature
  - *Less effective heat transfer to walls*
- Thermodynamic conditions unfavorable for scavenging of sulfur atoms and formation of COS (quenching)

3-mm Combustor



- High-sulfur gasoline, 1-µL injection, split 25:1
- 2-mm and 3-mm combustors, identical GC conditions
- Quenching significantly reduced using a 3-mm combustor

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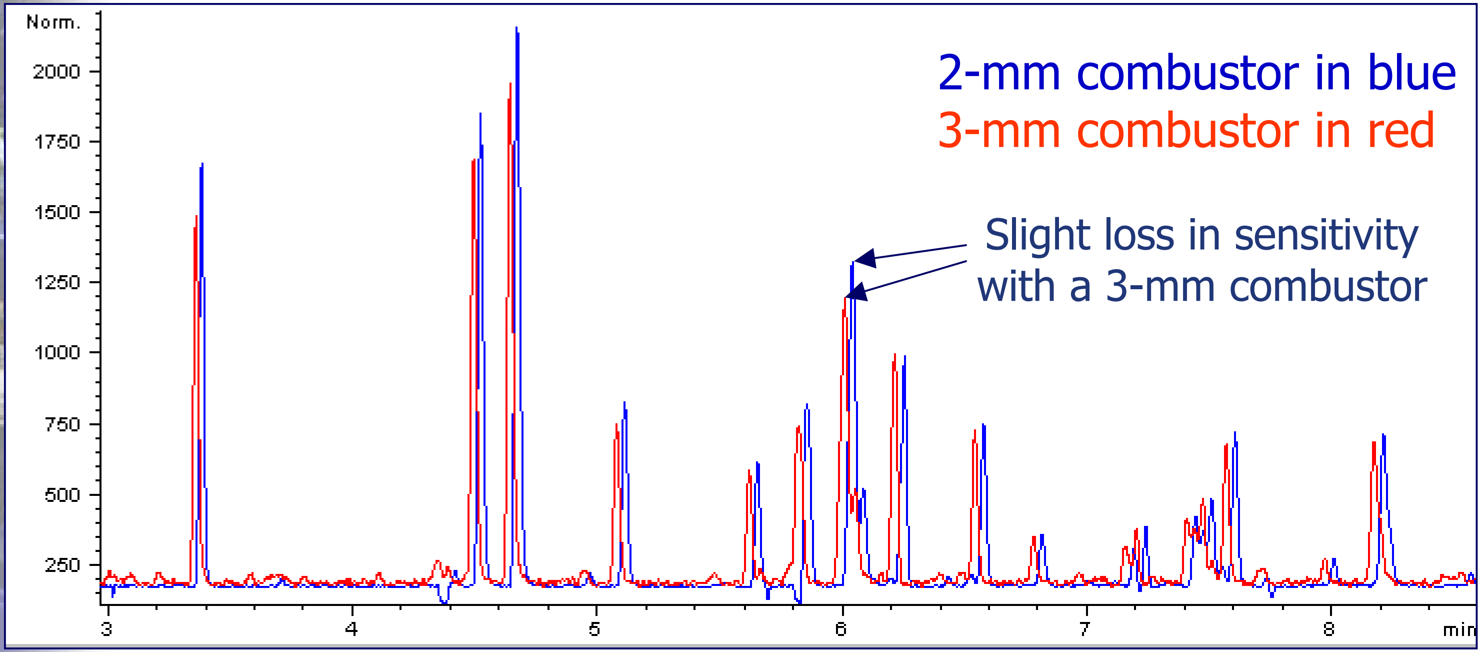
3-mm Combustor



- 1-µL injection of high-sulfur gasoline, split 100:1
- 2-mm combustor vs. 3-mm combustor
- Identical GC conditions
- Slight reduction in sensitivity using a 3-mm combustor

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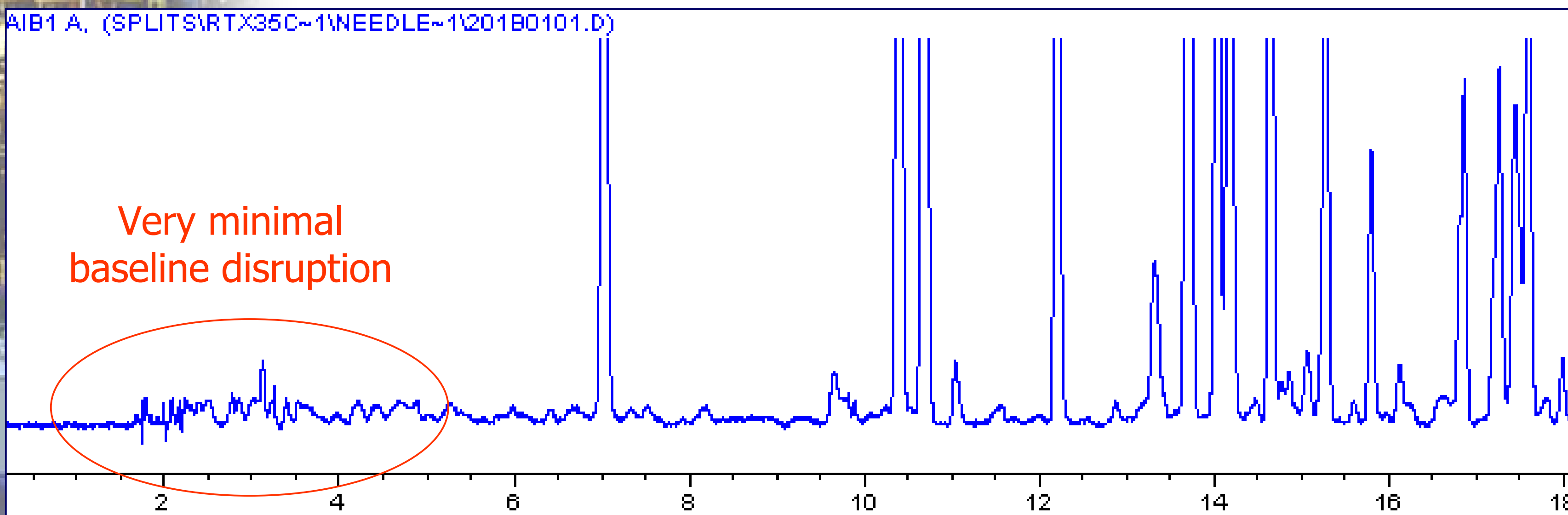
H_2/Air Ratio

- Slightly more air-rich combustor gas also favors more complete combustion of HC
  - *Increase "Air1" by 1.0 to 1.5 mL/minute*
- Heats the post-pulsed flame gases to suppress COS formation
- Added air converts CO to CO_2 thus suppressing formation of competing COS
- Significantly reduces quenching when used with the 3-mm combustor

H_2/Air Ratio

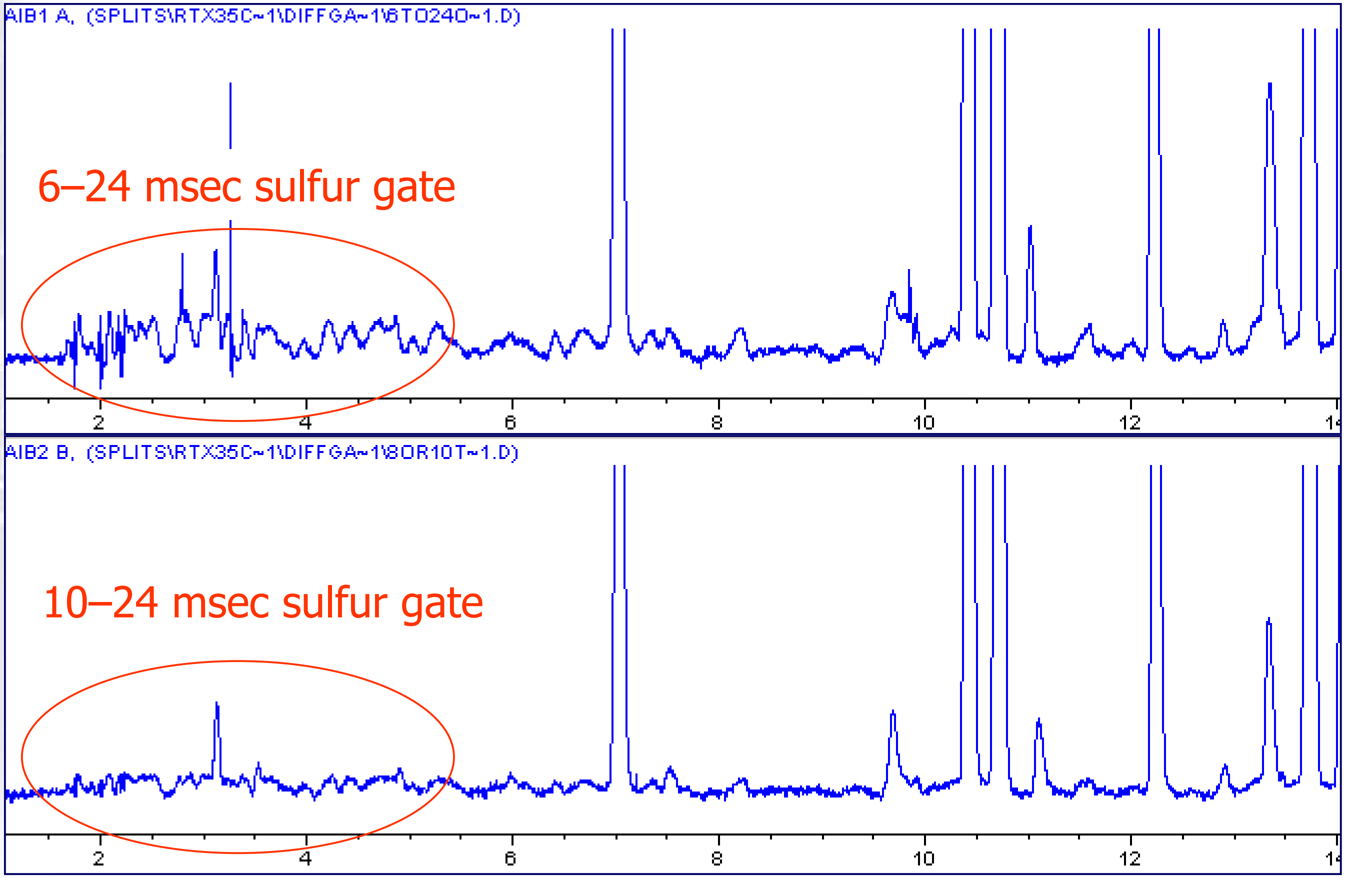


- 1-µL gasoline injected, <u>split 10:1</u>, Rtx-35MS column
- 3-mm combustor, 1.0 mL/minute additional “Air1”
- Quenching all but eliminated using this combination of techniques

Modified Gate Selection

- Slight disruption in the early part of chromatogram is due to "gate invasion"
- Flame propagation through the combustor may be slowed if any residual incompletely combusted HC remains
  - *Appears as slightly disrupted baseline*
- Move the sulfur gate back to avoid "gate invasion"
- Reduce the gate end, where the quenching effect is highest
  - *Stop at 18 msec instead of 24 msec*

Modified Gate Selection



- 1-µL gasoline injected, split 10:1, Rtx-35MS column
- 3-mm combustor, air-rich combustor gas
- S/N remains the same, no loss of sensitivity

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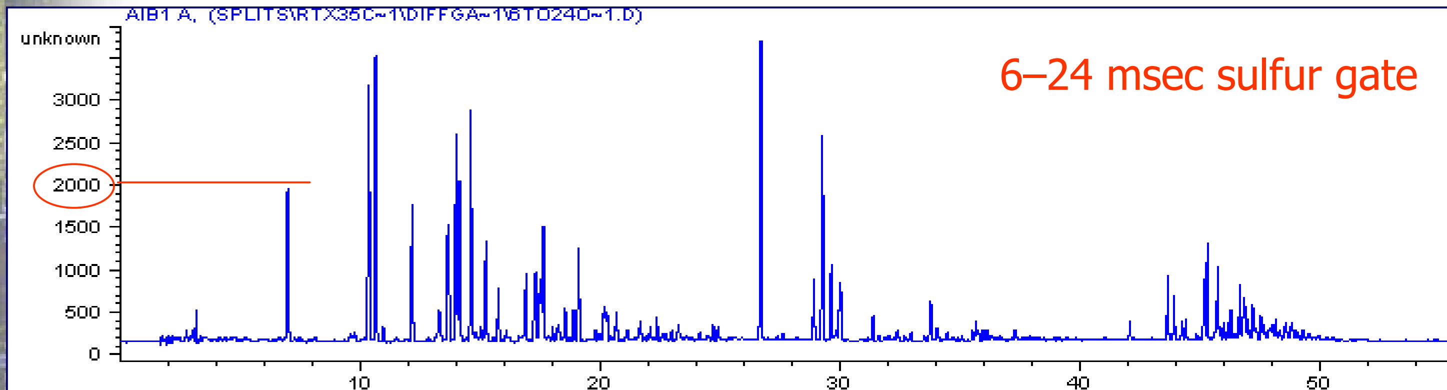
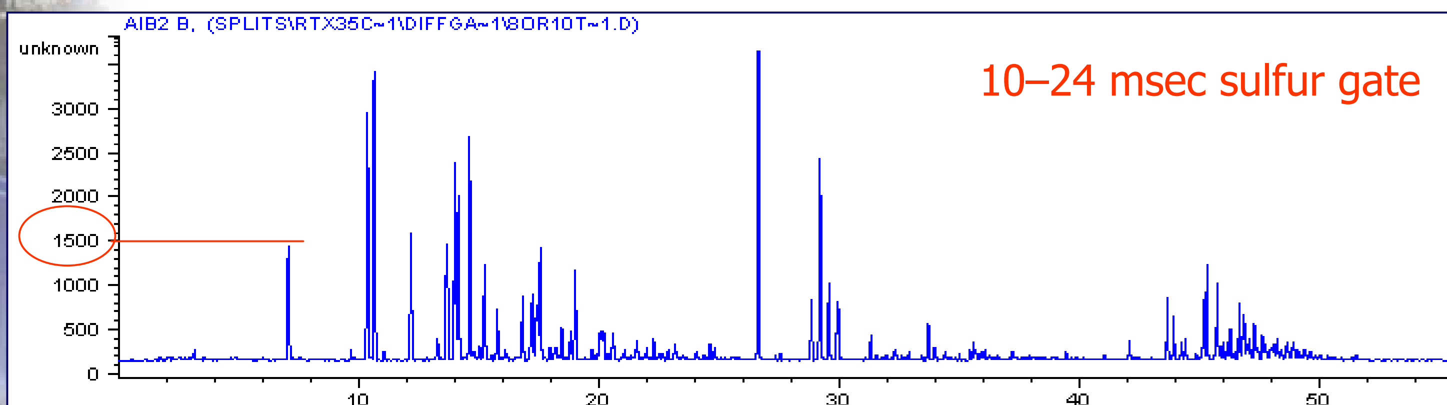
Proper Gate Selection





- Slight reduction in peak height with a shorter gate
- Simultaneous reduction in noise
- S/N remains the same; no loss in sensitivity

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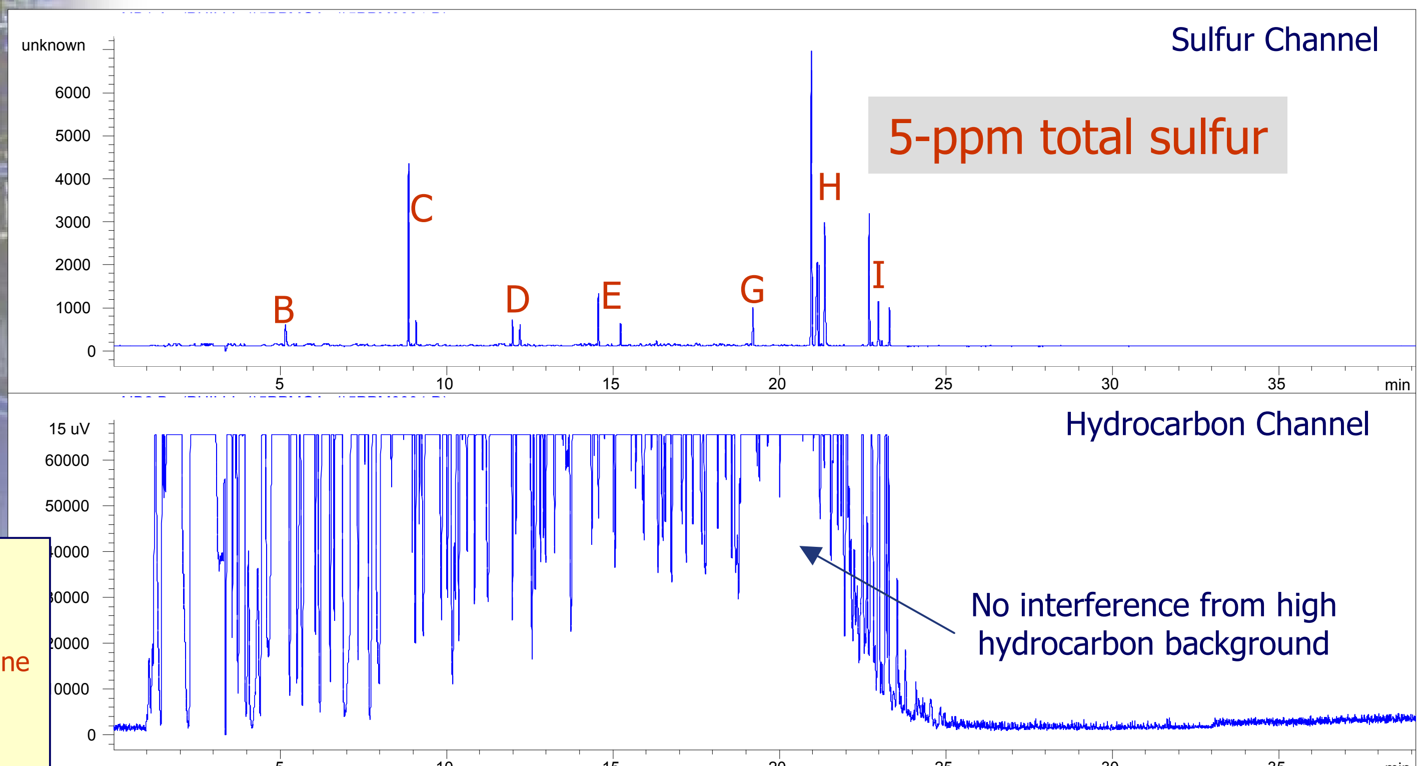
Analysis of Gasoline, 5-ppm Total Sulfur

Single-digit ppm total sulfur now possible on the PFPD using the 3-mm combustor, increased "Air 1", and modified S gate



- 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-μL injection, split 10:1, Rtx-35MS column

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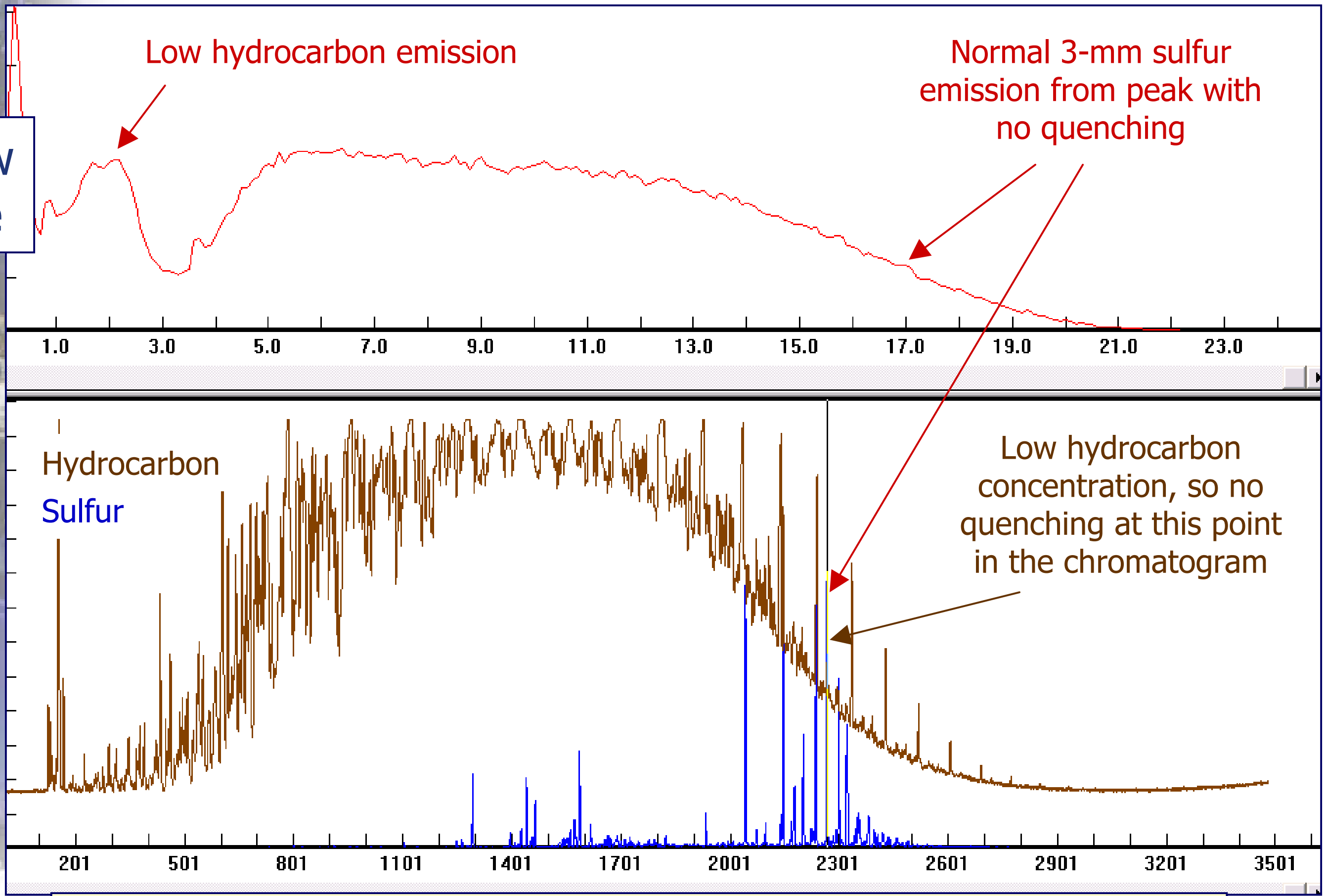
Sulfur in Diesel Fuel, Modified Conditions

PFPDView Software



<u>Diesel fuel analyzed using modified PFPD sulfur conditions</u>
3-mm combustor, 1 mL/min additional air, 6–24 msec S gate
1-µL injection; split 10:1

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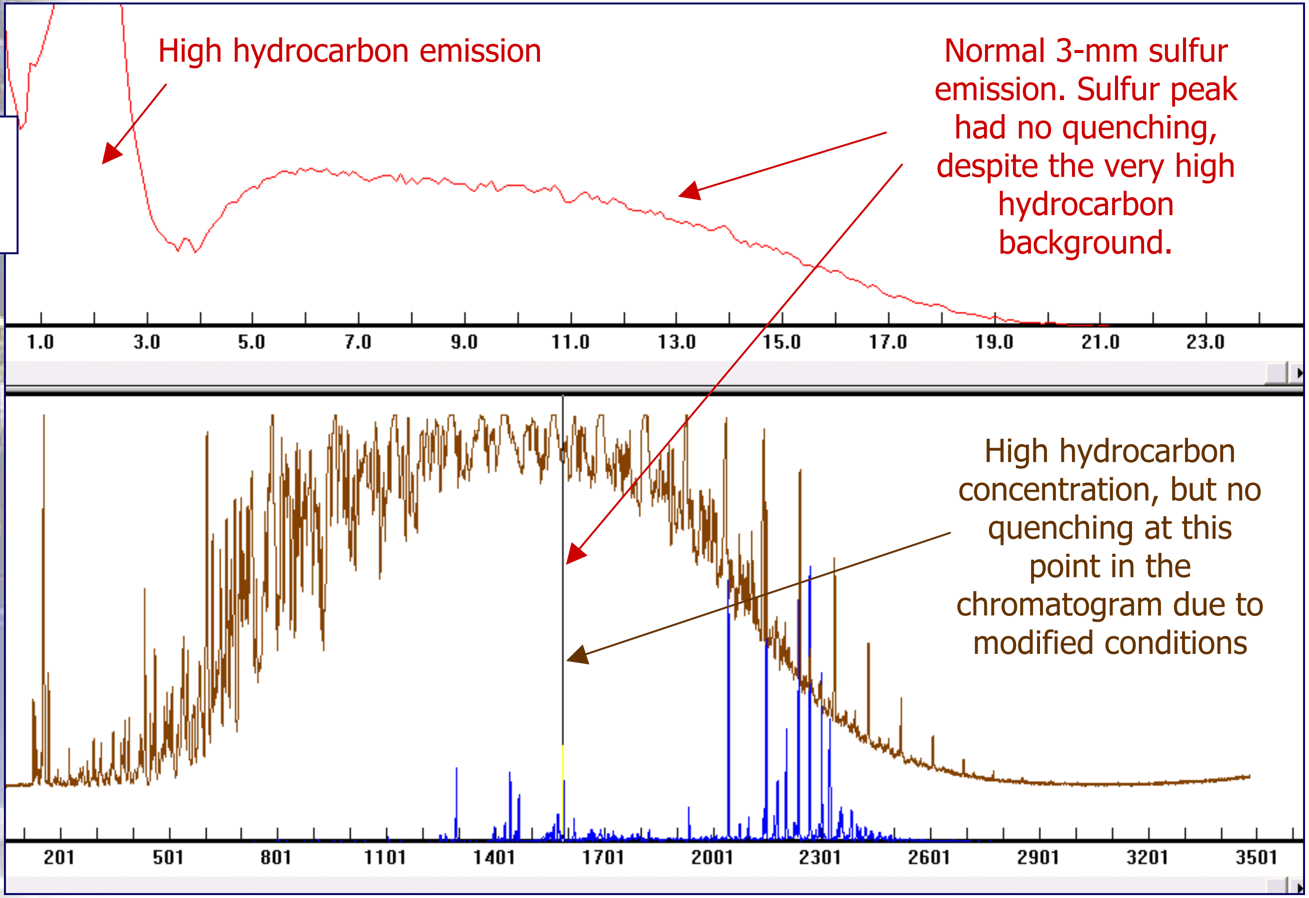
Sulfur in Diesel Fuel, Modified Conditions

PFPDView Software



Diesel fuel analyzed using modified PFPD sulfur conditions
3-mm combustor, 1 mL/min additional air, 6–24 msec S gate
1-μL injection; split 10:1

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Conclusions

- Using the conditions described here, analyzing for low-level sulfur in gasoline and diesel on the PFPD is possible with no quenching
  1. *3-mm combustor to minimize side reactions*
  2. *Increase air in H_2/air mix to further minimize any side reactions*
  3. *Gate selection to minimize "gate invasion"*
  4. *Slightly more polar, thick film column to separate "critical pairs"*
  5. *10:1 split ratio to maximize sensitivity*
     - Overall 10–20 fold increase in sensitivity

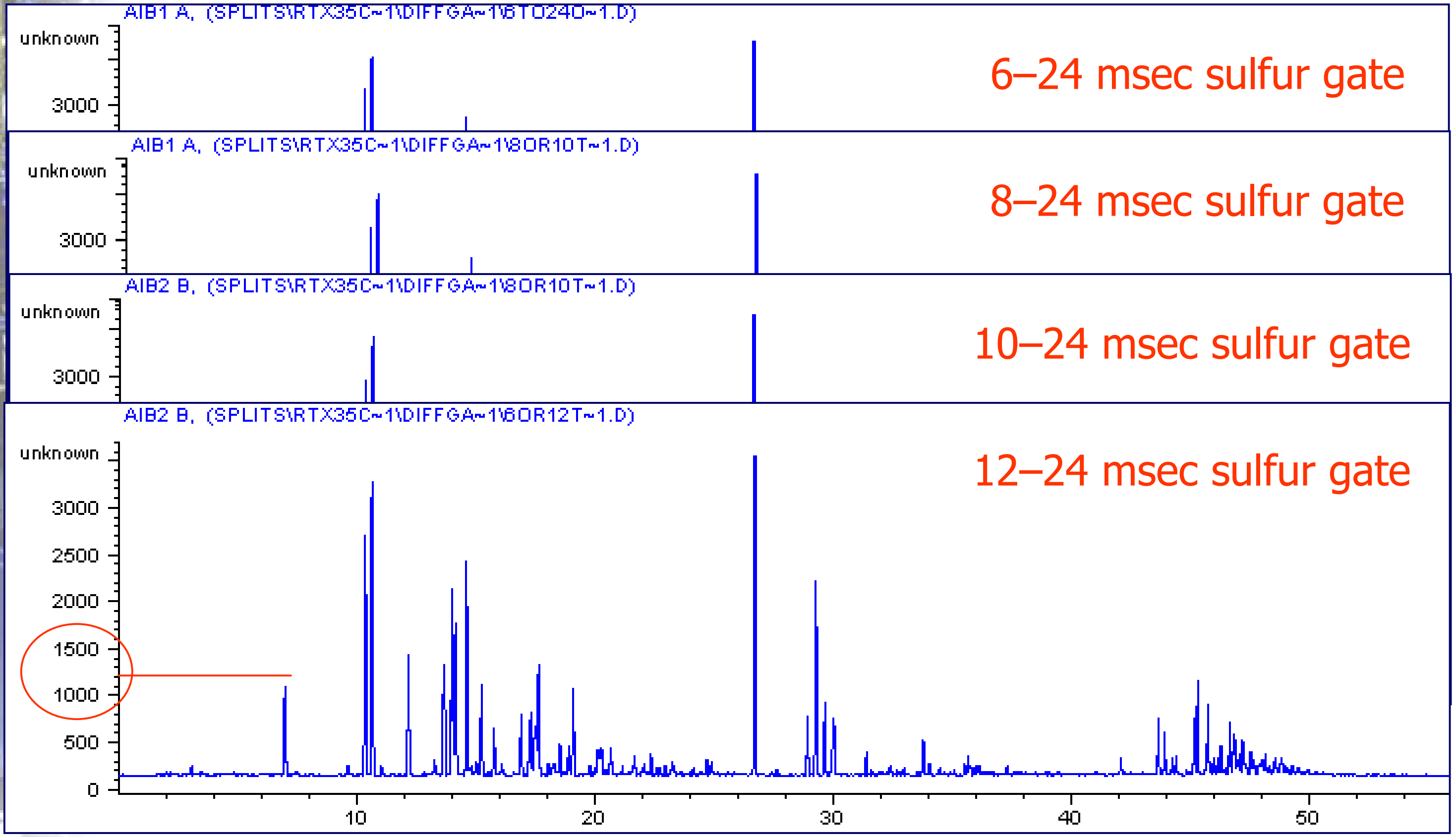
Acknowledgements

- Aviv Amirav, Tel Aviv University
- Dr. Richard Simon, OI Analytical

Thank you for your attention!
Questions?

This presentation can also be viewed at booth 2219, or on our website at www.oico.com

Proper Gate Selection



- Reduction in peak height with shorter gate
- Simultaneous reduction in noise mitigates loss in sensitivity

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