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Analysis of Speciated Sulfur in Gasoline Using the PFPD Without Hydrocarbon Quenching

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Analysis of Sulfur in Gasoline

- Total sulfur by XRF or other technique
- Speciated sulfur by GC with a sulfur-selective detector, e.g., Pulsed Flame Photometric Detector (PFPD)
- PFPD advantages
  - *Low maintenance, long-term stability*
  - *Ease of use*
  - *Wide range of matrices, gas phase to high MW*
  - *Wide range of sulfur concentrations, single-digit ppb sulfur for single components to % total sulfur*

Analytical Challenge

- Historically, co-eluting hydrocarbons in gasoline have the potential to quench or reduce the sulfur signal
- This presentation shows how to analyze for sulfur in gasoline on the PFPD with little or no quenching from the hydrocarbon background

Project Objectives

1. Define sulfur saturation and hydrocarbon quenching, and illustrate how to identify and distinguish between them
2. GC techniques to reduce hydrocarbon quenching
3. PFPD techniques to reduce or eliminate hydrocarbon quenching

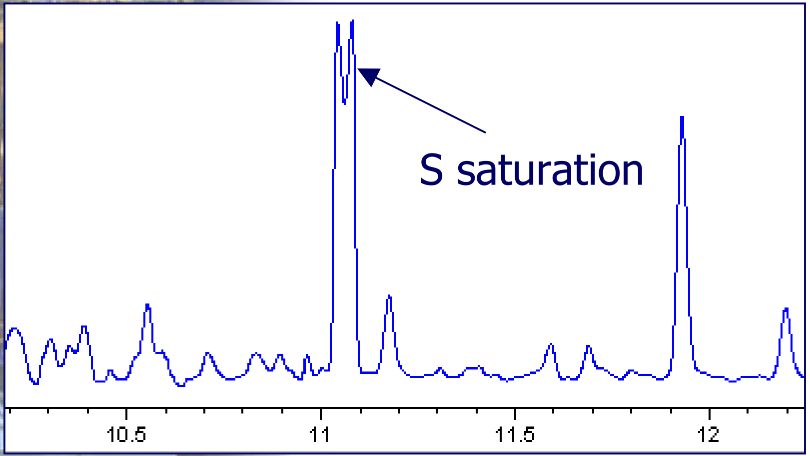
Quenching or Saturation?

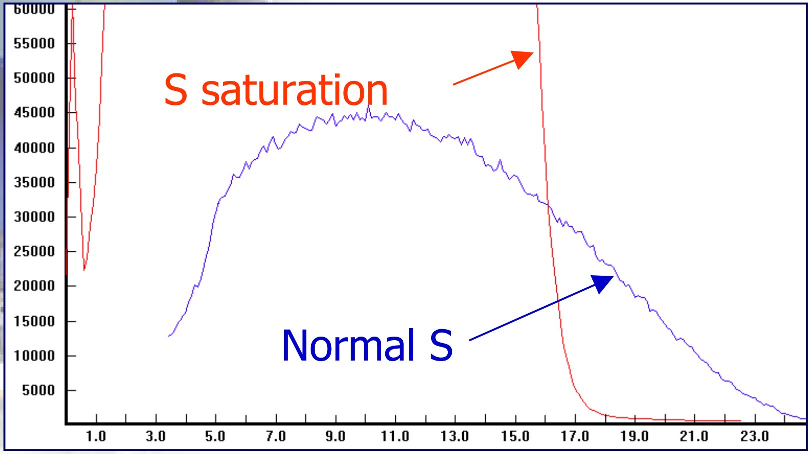
- Two different phenomenon on the PFPD
  - *Sulfur saturation*
  - *Hydrocarbon quenching*
- Caused by different conditions within the detector
- Sometimes occur simultaneously
- Each can be easily identified by “reading” the emission profile
  - *Real time, or*
  - *Post-acquisition with PFPDView software (preferred)*

Sulfur Saturation

- Sulfur saturation occurs when there is an excess of the emitting species (S_2*) within the detector and the emissions are self-absorbed before reaching the PMT
- Sometimes misidentified as quenching
- Easily identified in the chromatogram
  - *Symmetric, split peak top*
- Confirmed by viewing the emission profile
  - *PFPDView*

Sulfur Saturation





Identification

- Peaks in the sulfur chromatogram with split tops
- Usually very symmetrical
- Only occurs on peaks that are offscale

Confirmation

- Less delayed emission profile, sharply folded back on itself
- Use PFPDView
- ≥1,000 pg S to the detector

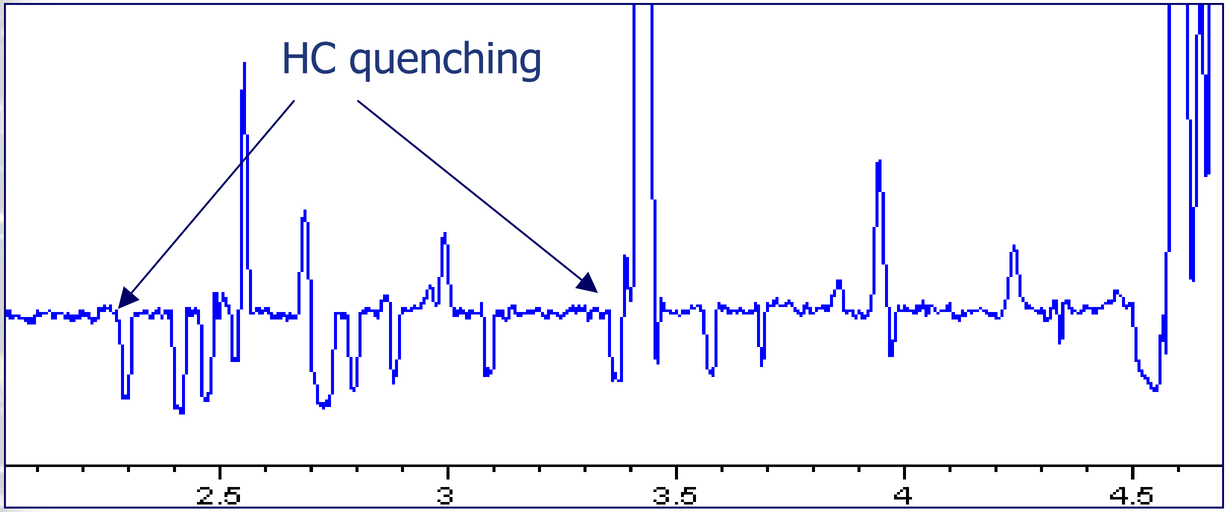
Hydrocarbon Quenching

- The more common term “hydrocarbon quenching”, or just “quenching”, refers to a reduction of the sulfur signal by a co-eluting hydrocarbon
  - *High concentration of HC co-eluting with the sulfur peak*
- Occurs when a high concentration of HC consumes the oxygen and produces an excess of CO instead of CO_2
  - *Results in incomplete combustion of HC*
  - *Does not go completely to* CO_2*, forms more CO*

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 available sulfur
- Loss of S_2 and sulfur atoms to form COS causes sulfur signal reduction

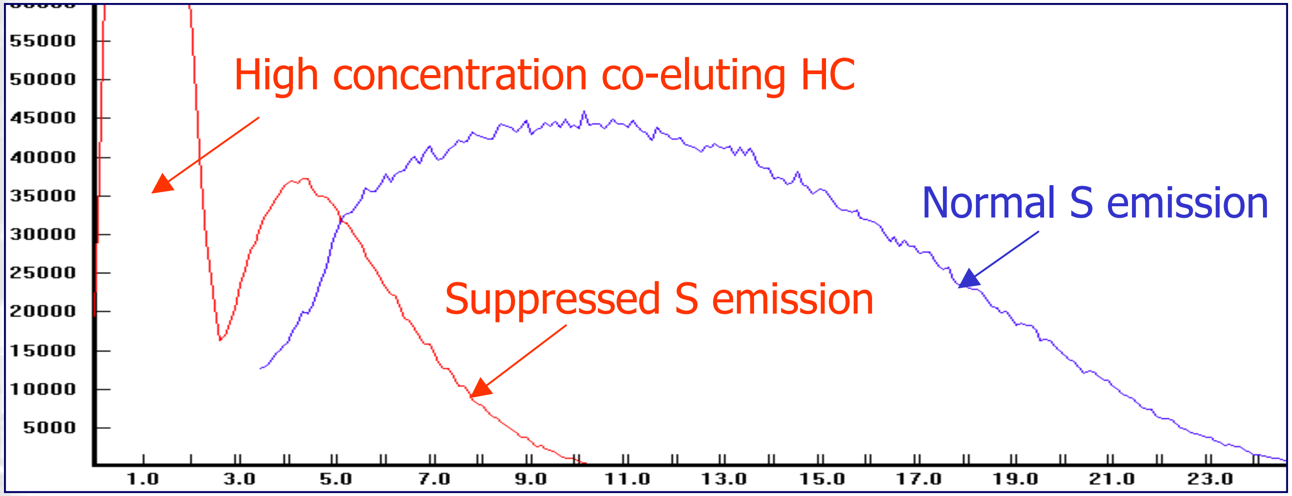
Hydrocarbon Quenching



Identification

- Dips in the sulfur chromatogram baseline caused by HC quenching of background emissions
- Background emissions come from trace amounts of sulfur in gases, ferrules, stainless steel, etc., or imperfections in the fused silica
- Indicates conditions exist that may quench the targeted sulfur signal as well

Quenching the Sulfur Signal



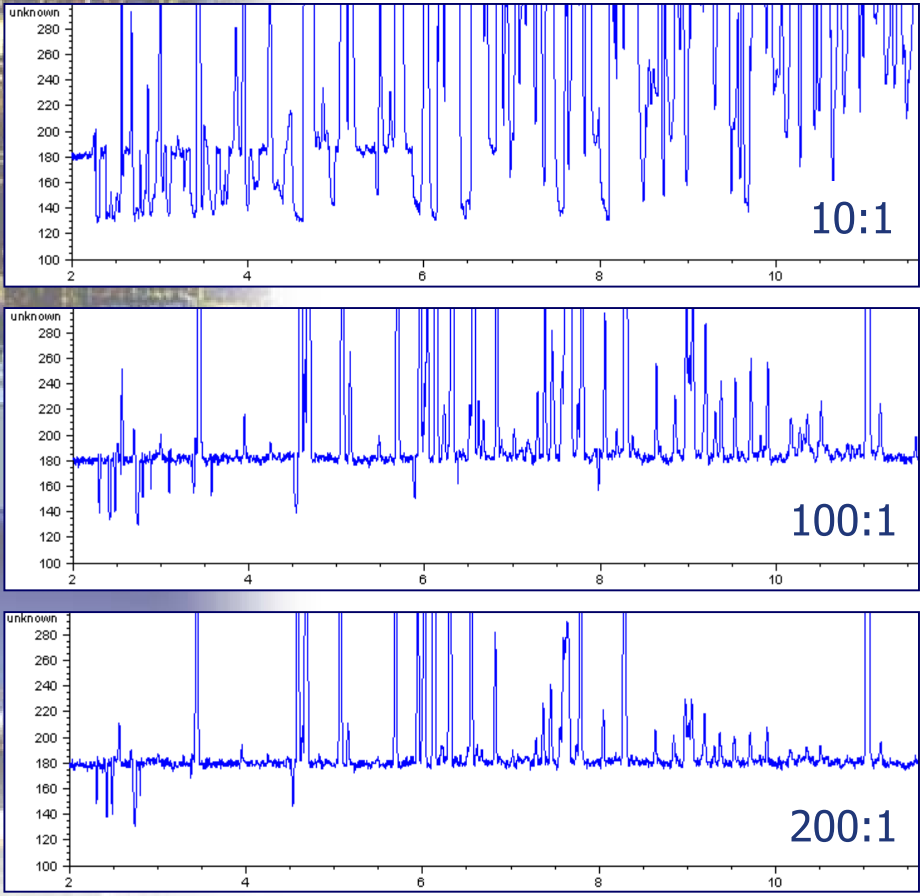
<u>Confirmation</u>

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

GC Techniques

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

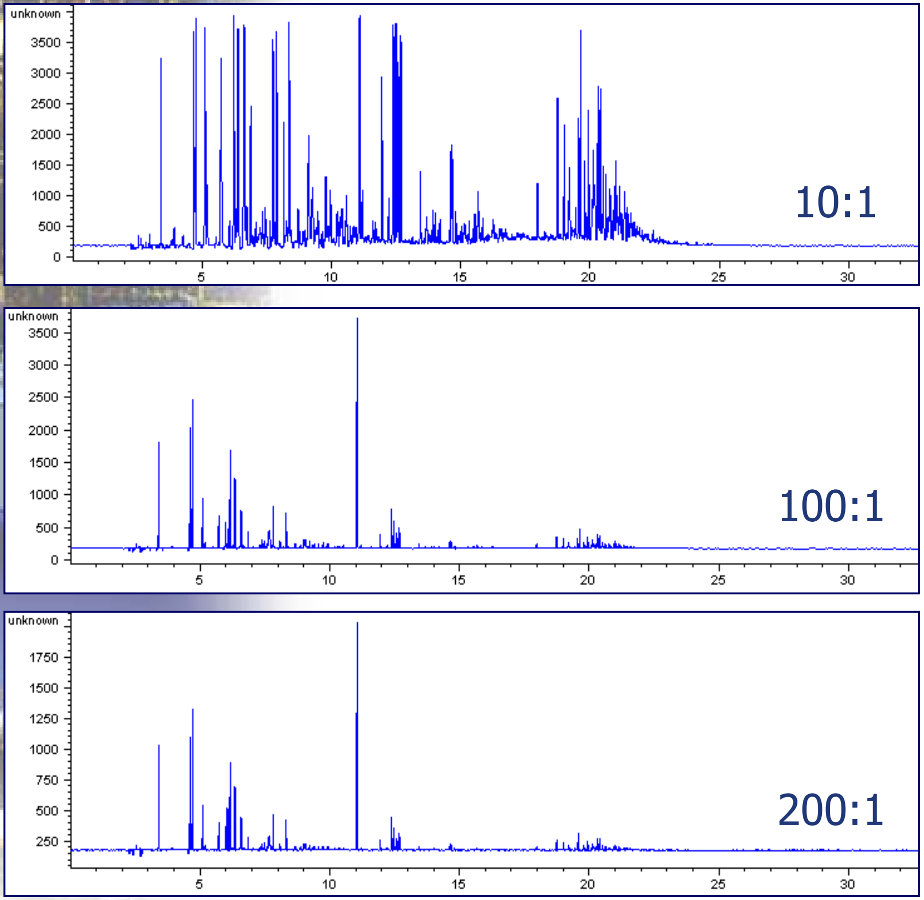
Increased Split Ratio



S baseline at varied split ratios

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

Increased Split Ratio



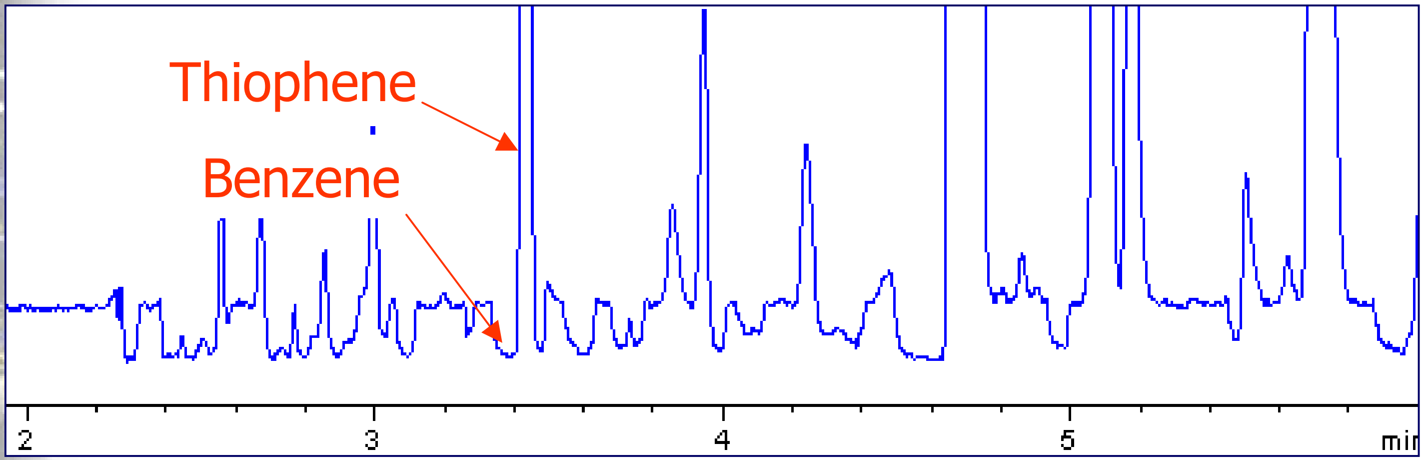
S signal at varied split ratios

- 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 200:1
- A good choice for high sulfur gasoline like this one
  - *High ppm to %*
- Not good for low sulfur samples

Column Selection

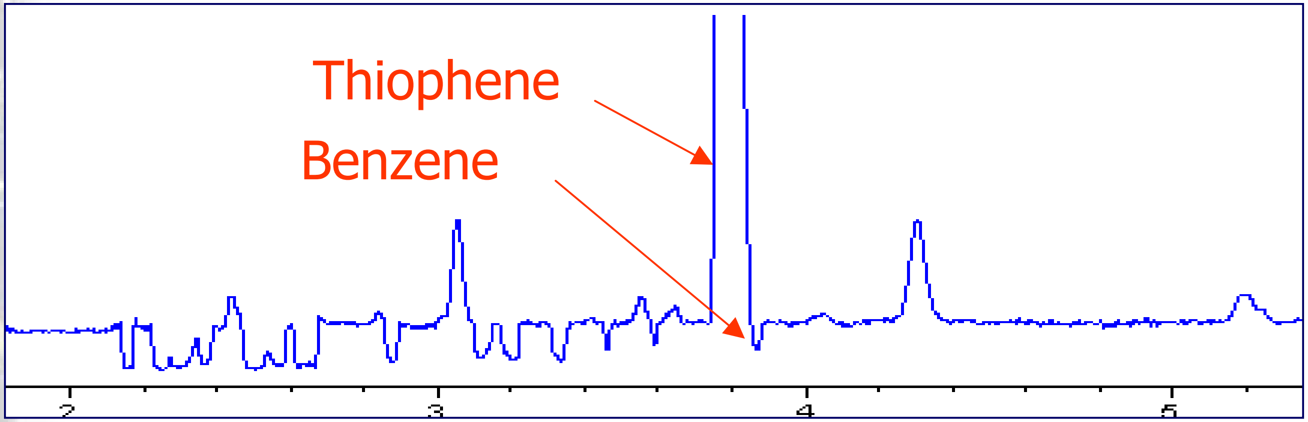
- In gasoline, only a few “critical pairs” of HC/sulfur are subject to quenching
    - *Benzene and thiophene*
    - *Toluene and methylthiophene*
- They occur early in the chromatogram, where the highest concentration of HC exists
    - *Less quenching potential later in the chromatogram*
- Use a more polar GC column with thick film to chromatographically separate the “critical pairs”
- No co-elution → 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 the dip in the sulfur baseline
- Co-eluting thiophene signal was suppressed (reduced) but still visible

“Critical Pair” Example



- 1-µL injection, split 10:1 onto a thick film, mid- to high-polarity column
- 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)

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PFPD Techniques

- Three PFPD techniques to reduce or minimize the quenching effect:
  - *3-mm combustor*
  - *Adjust* H_2*/air ratio of combustor gas to increase the amount of air*
  - *Proper gate selection*

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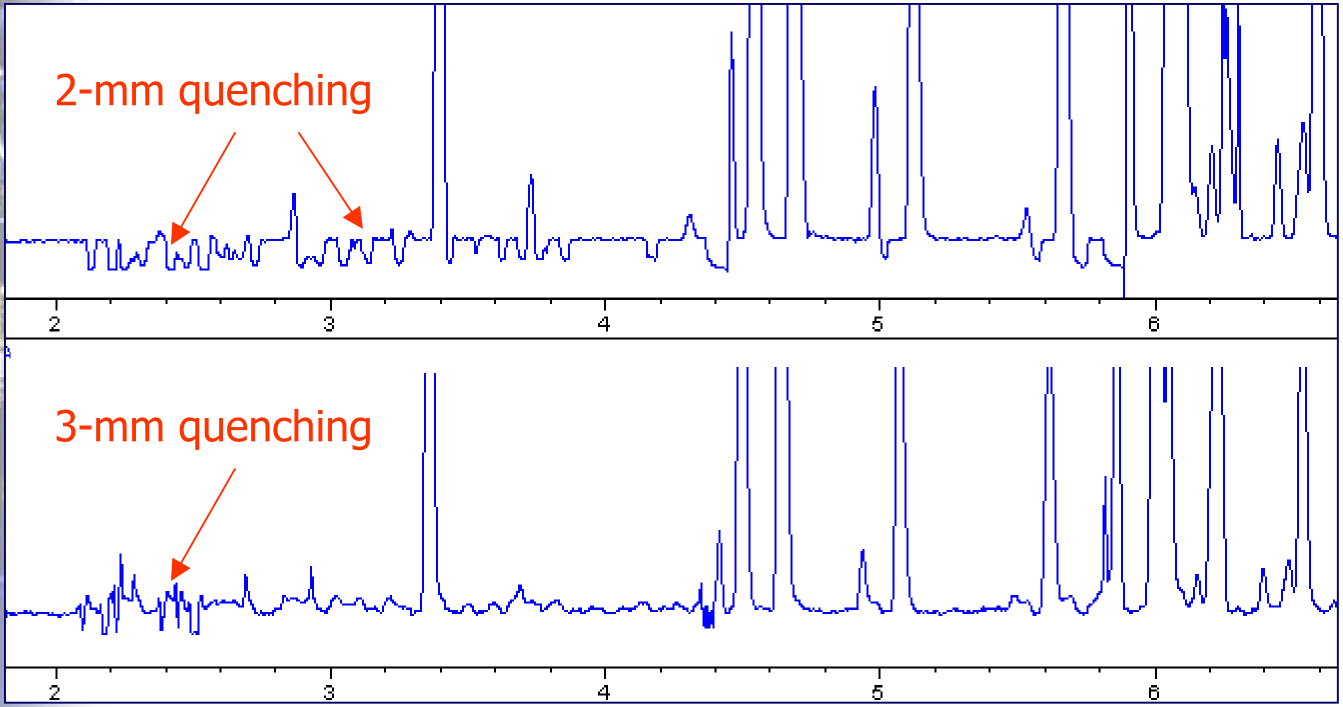
3-mm Combustor

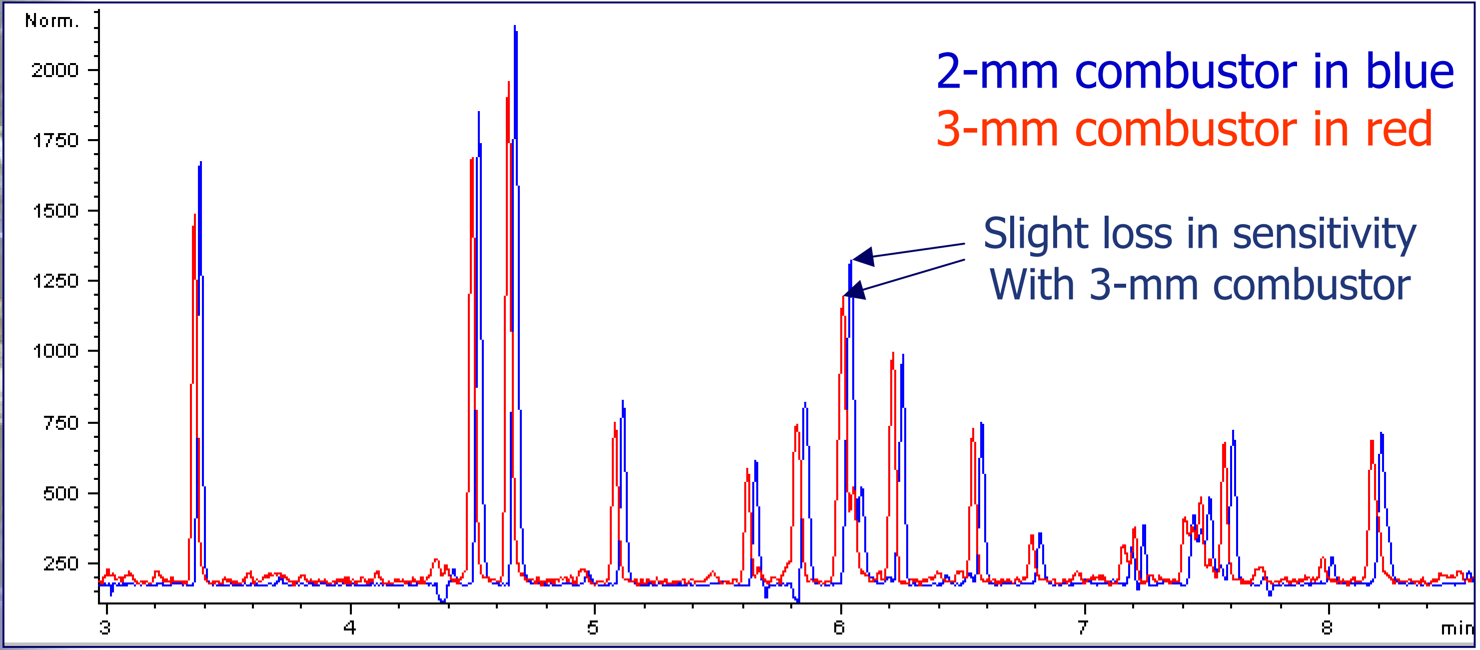
- Larger combustor size creates flame conditions that favor hotter post-pulsed flame temperature through less effective heat transfer to walls
  - *2-mm combustor normally used for sulfur*
- Thermodynamic conditions unfavorable for scavenging of sulfur atoms and formation of COS (quenching)

3-mm Combustor



- 1-µL injection, split 25:1
- Identical GC conditions
- Quenching significantly reduced using the 3-mm combustor

3-mm Combustor



2-mm combustor in blue
3-mm combustor in red

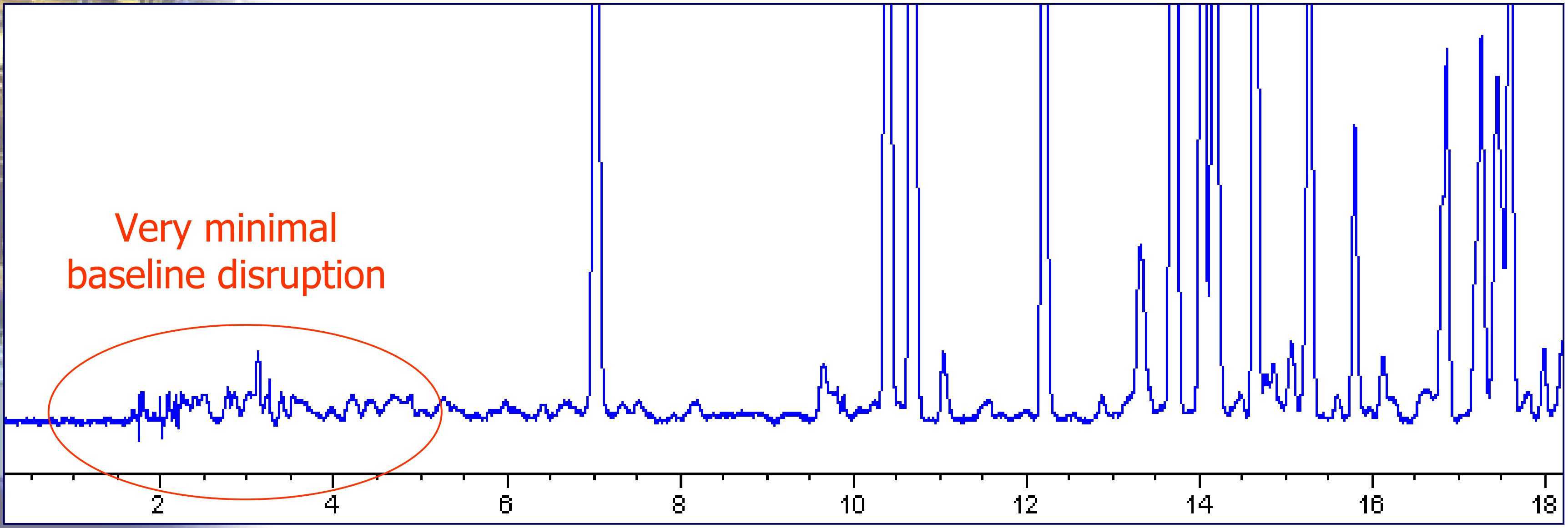
Slight loss in sensitivity
With 3-mm combustor

- 2-mm combustor vs. 3-mm combustor
- Identical GC conditions
- Slight drop in sensitivity using the 3-mm combustor made up for ability to use lower split ratio

H_2/Air Ratio

- Slightly more air-rich combustor gas also favors more complete combustion of hydrocarbons and further heats the post-pulsed flame gases to suppress COS formation
  - *Increase "Air 1" by 1.0 to 1.5 mL/minute*
- Added air converts CO to CO_2, thus suppressing formation of competing COS
- Less quenching

H_2/Air Ratio

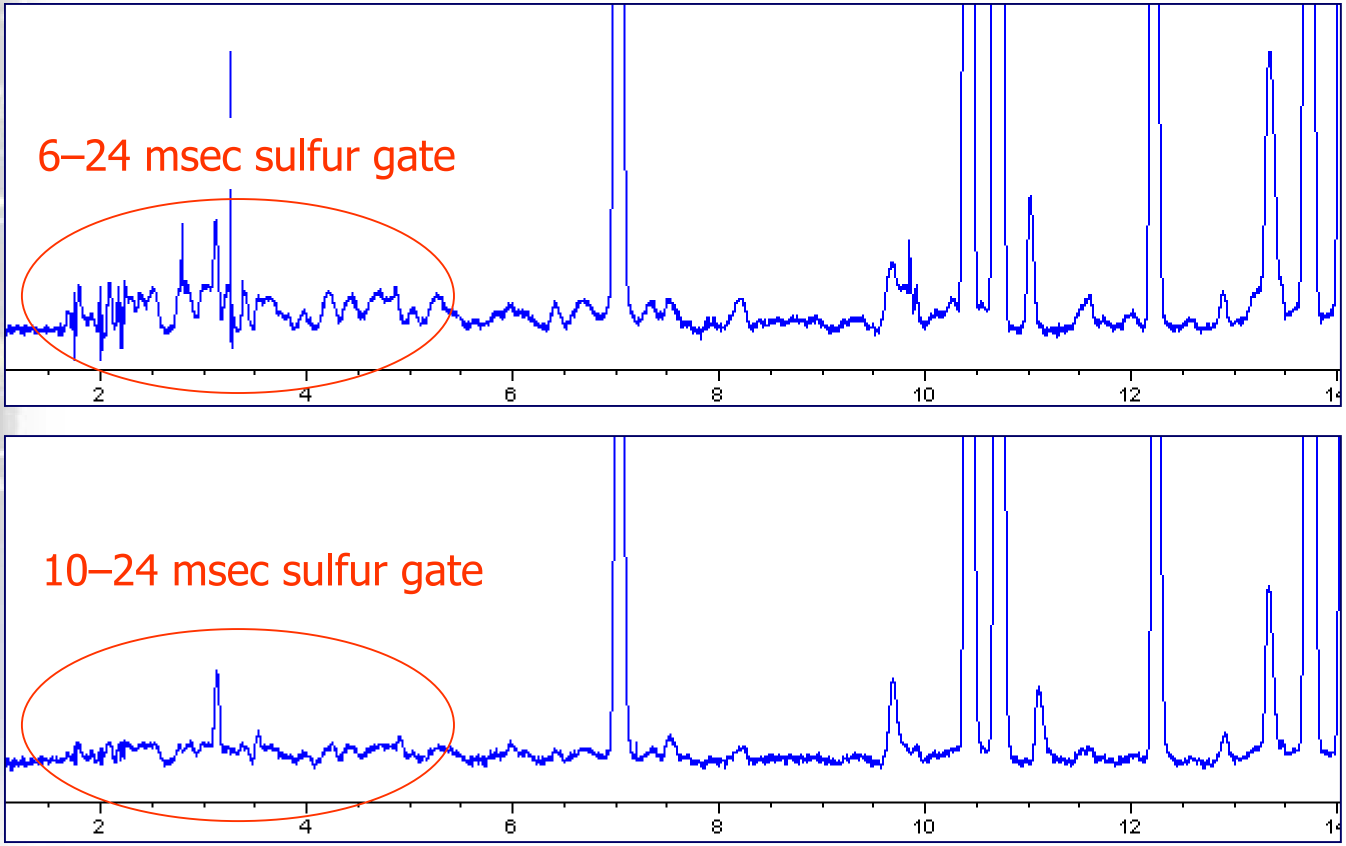


- 1-µL gasoline injected, split 10:1, Rtx-35MS column
- 3-mm combustor, 1.0 mL/minute additional “Air 1”
- Quenching all but eliminated using this combination of techniques
- Very few sulfur peaks in early part of chromatogram

Proper Gate Selection

- Some disruption in the early part of chromatogram is due to “gate invasion”
- Slowing of the flame propagation with high concentrations of HC can cause emission to “creep” into the sulfur gate
  - *Appears as a 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*

Proper Gate Selection



- 1-µL gasoline injected, split 10:1, Rtx-35MS column
- 3-mm combustor, air-rich combustor gas

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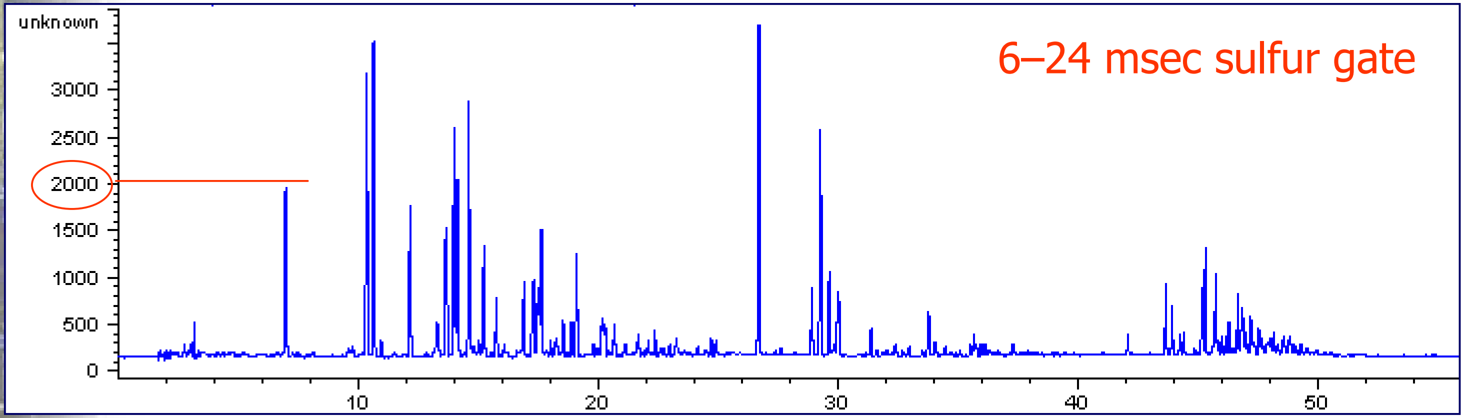
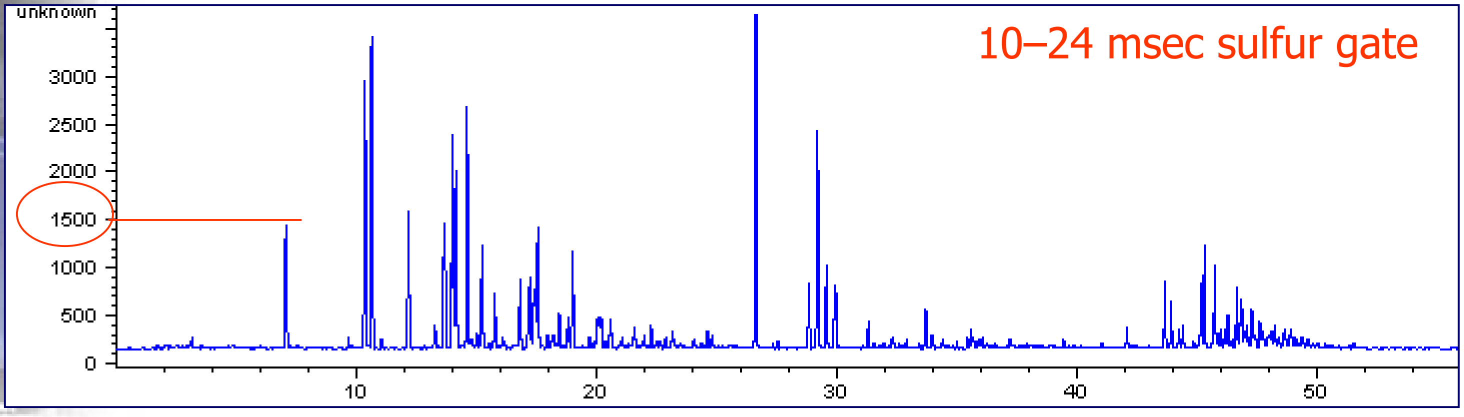
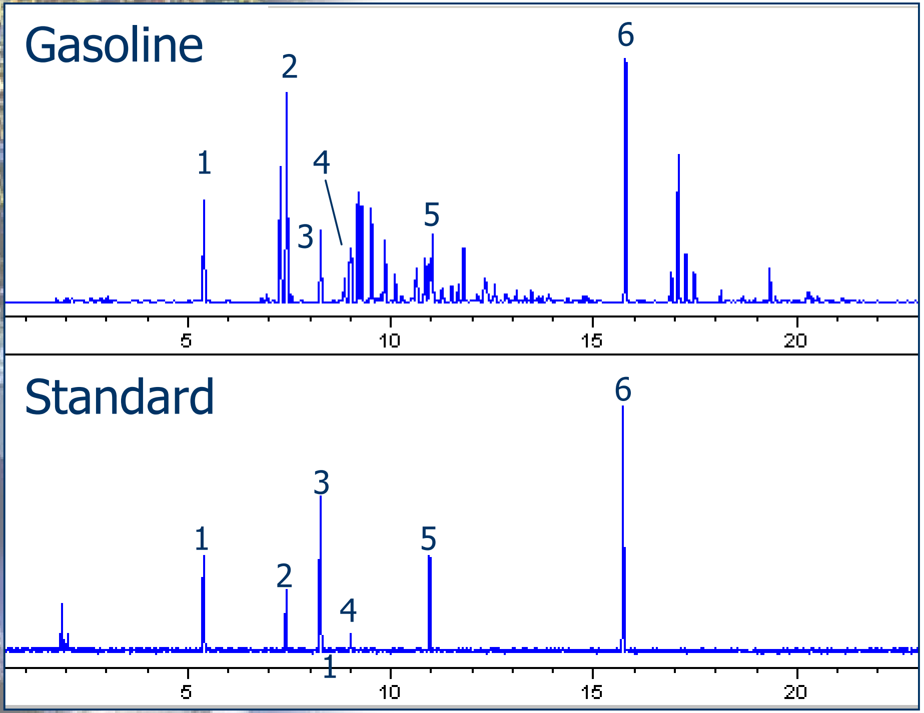
Proper Gate Selection





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

Analysis of Gasoline


Gasoline

Standard

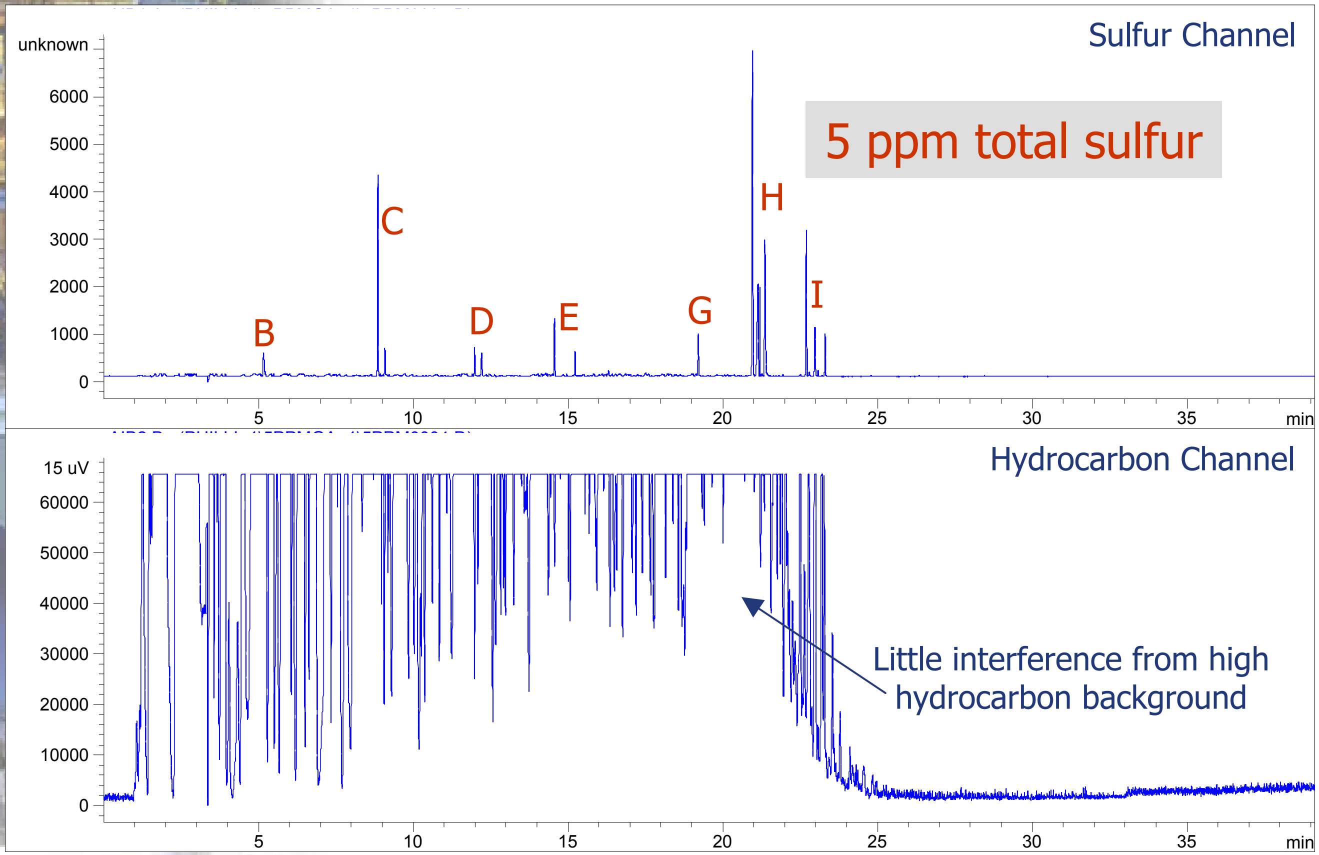
Specific compounds can be quantified using individual RFs:

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

Analysis of Gasoline, 5 ppm



5 ppm total sulfur

Little interference from high hydrocarbon background

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
3-mm PFPD combustor, increased air

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Conclusions

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

Acknowledgements

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