PFPD Training Course – Part 4
Applications Development

www.oico.com

O·I·Analytical

Most Common Questions

1. What is the sensitivity of the PFPD?
2. Is the PFPD linear?
3. What is the dynamic range?
4. How do I calibrate the PFPD?
5. Is the response equimolar
6. What is quenching?

Question #1

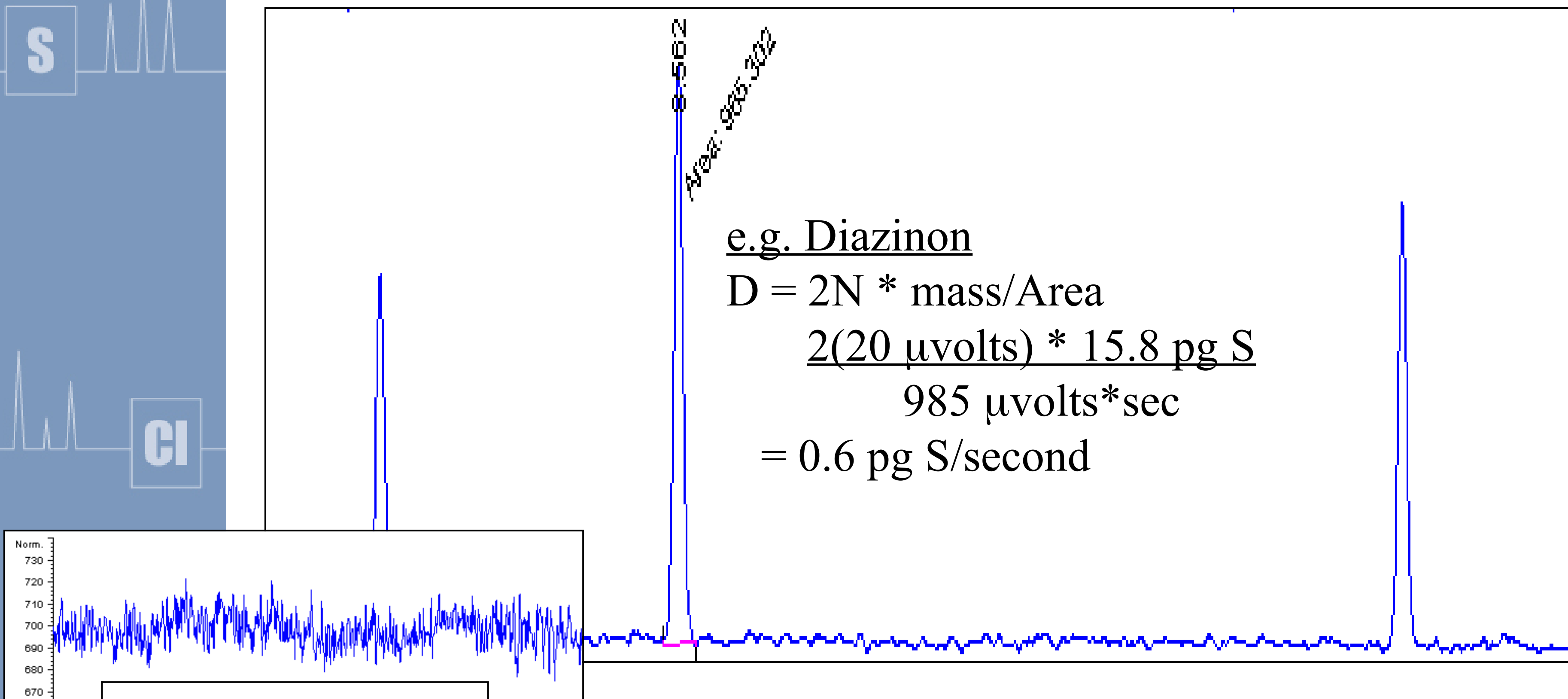
What is the sensitivity of the PFPD?

PFPD Sensitivity

- Minimum detectability is the mass flow rate of atoms (S or P) in the carrier gas that gives a detectable signal equal to twice the peak-to-peak noise level (ASTM definition)
- Calculated from the measured sensitivity and noise level
- D = 2N/S, where S = Area/mass
- D = 2N * mass/Area *(linear response only)*

Detectivity Calculation

PFPD specification: Detectivity < 1 pg S/second



e.g. Diazinon

D = 2N * mass/Area

$$= \frac{2(20\ \mu\text{volts}) * 15.8\ \text{pg S}}{985\ \mu\text{volts*sec}}$$

= 0.6 pg S/second

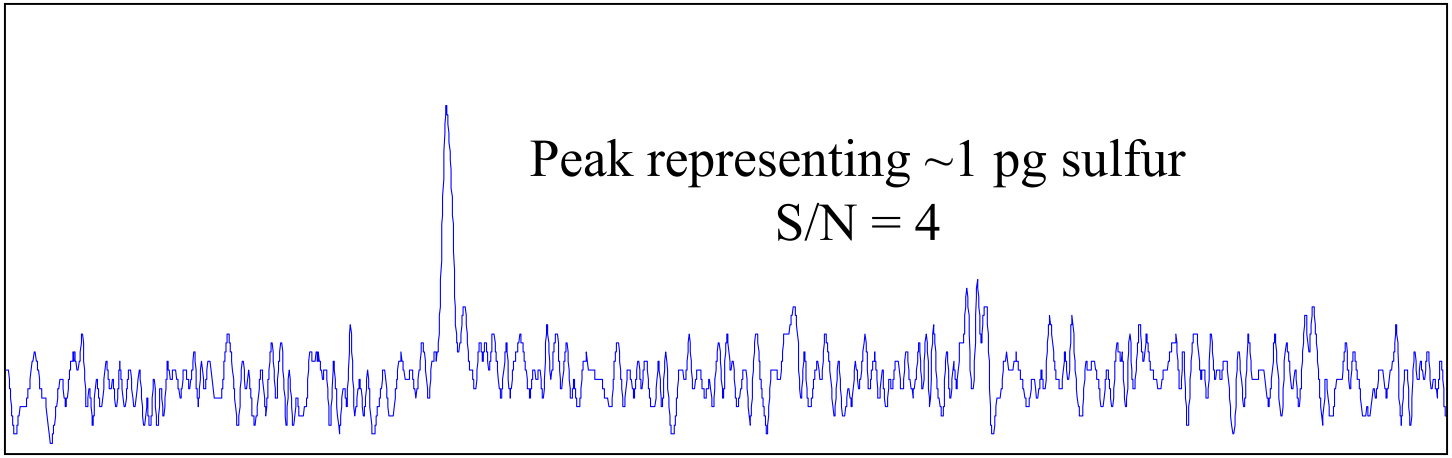
N = 710 – 690 μvolts
= 20 μvolts

Method Development

- Adjust method parameters for 1-2 pg S on column:
  - Introduction technique
  - Sample volume
  - Split ratio
  - % Sulfur in compound
- Use this as your lowest instrument calibration point

PFPD Sensitivity

Eg. 1 μL of 19 ppb (pg/μL) methyl sulfide standard injected with 9:1 split ratio
= 1.9 pg methyl sulfide to the detector
= 1 pg S to the detector



PFPD Sensitivity

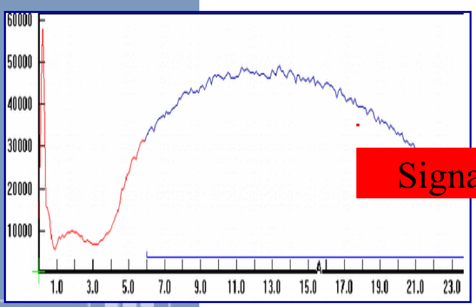
- Minimum amount of sulfur that can be detected by the PFPD is approx. 1–5 pg
  - Configured specifically for sulfur
  - Well behaved compound
  - Dependent on chromatography, interferences, etc.
- Phosphorus detectivity is about 10x lower
  - DP specification < 100 fg P/second
  - Minimum 0.1 pg P on-column
- Nitrogen detectivity is about 25-50x higher
  - DN specification < 25-50 pg N/second
  - Minimum ~50 pg N on-column

Question #1
Is the PFPD linear?

Sulfur Linearity

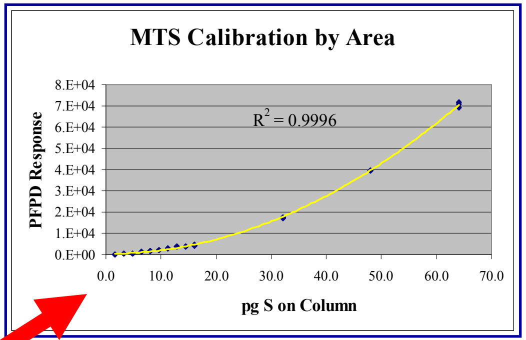
- Chemistry of the S_2* within the pulsing flame produces a naturally occurring quadratic response
- Same for PFPD and for FPD
- In OI PFPD the signal is digitally processed
- Allows application of a linearizing algorithm
- Outputs a linearized signal

Sulfur Signal



Signal

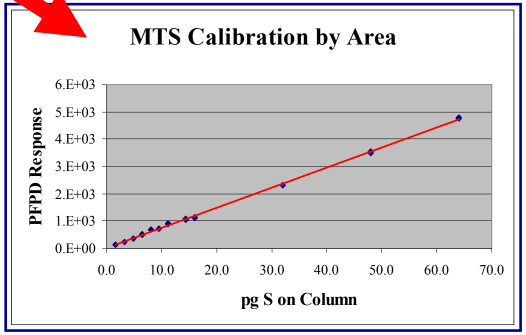
Model 5380
PFPD
Controller



Quadratic Output

or

Linear Output



Demonstration of Calibration

Mix of 4 sulfur compounds:
Methyl sulfide (MS)
Ethyl methyl sulfide (EMS)
Methyl disulfide (MDS)
Methyl trisulfide (MTS)

25 Calibration concentrations
1.0 pgS - 1000 pgS

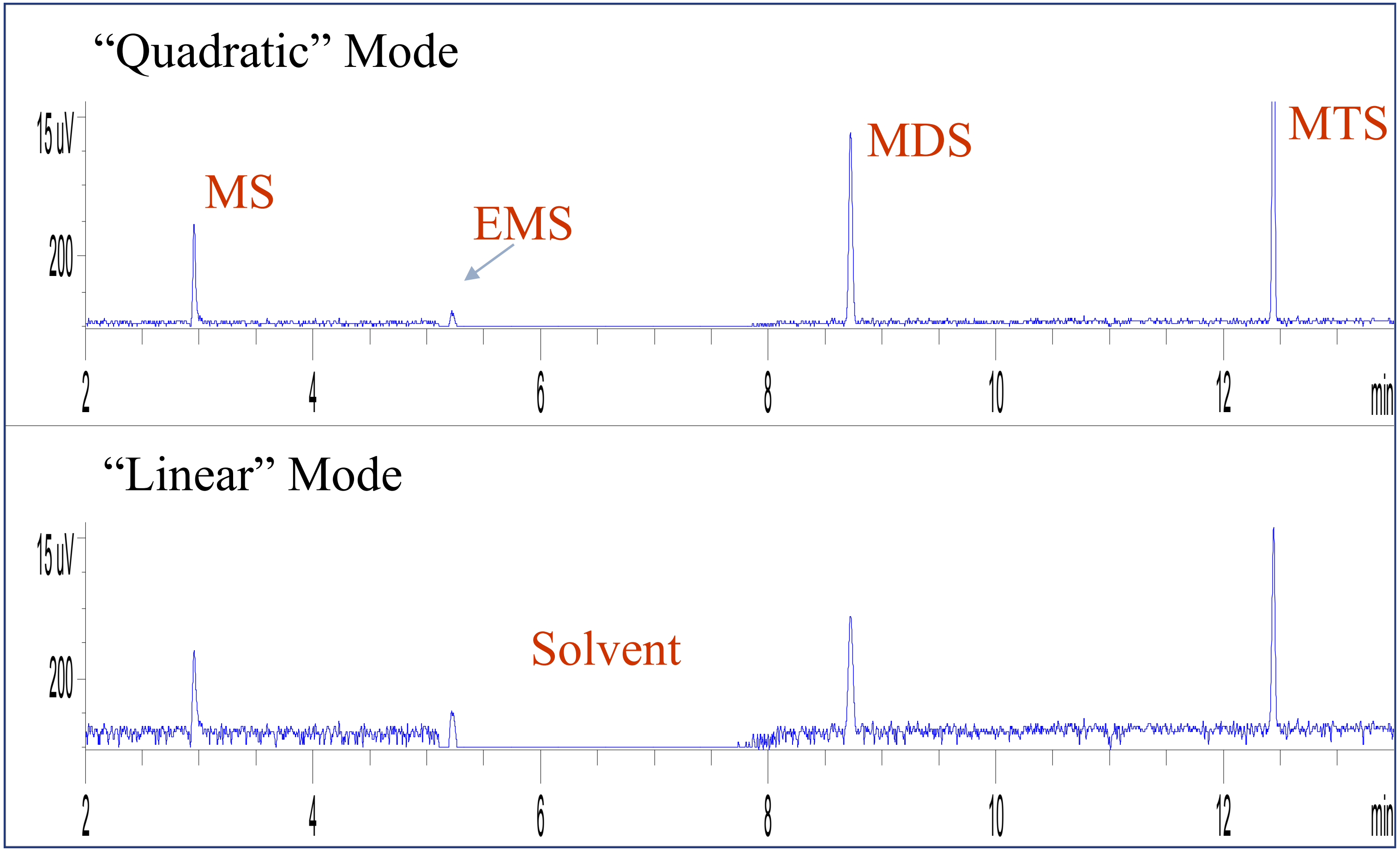
Triplicate injections
1 μL injection

Instrument Conditions

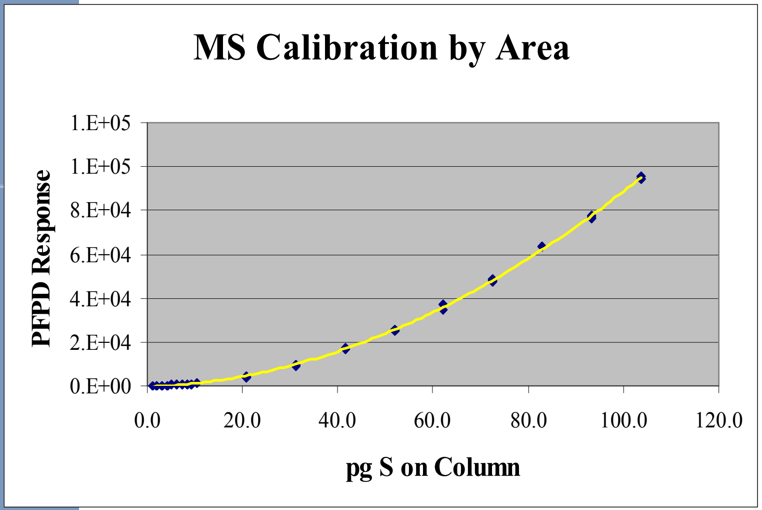
Agilent 6890 GC with EPC
Agilent autosampler
1 μL split injection, 10:1, 200°C
DB-5MS column (30m x 0.25mm x 1.0 μm film)
35°C for 5 min, 15°C/min to 220, hold 2 min

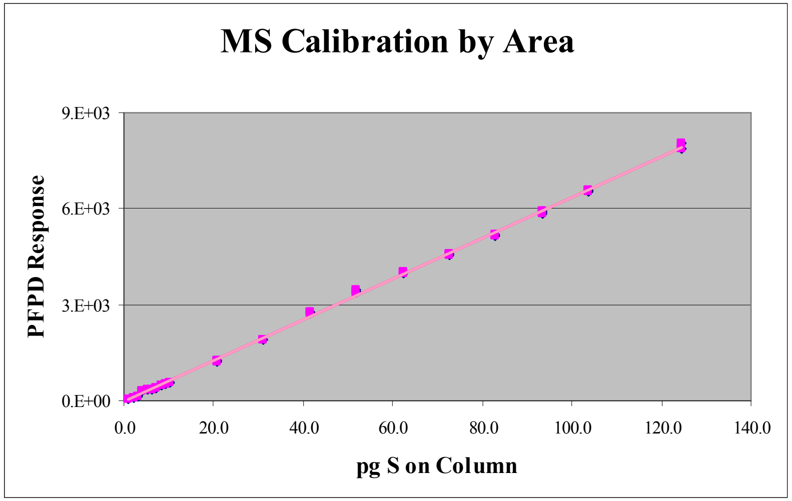
OI Analytical Model 5380 PFPD
2 mm combustor
H_2 rich (H_2/Air ~ 1.1)
BG-12 filter, R1924 PMT
Collected both linear and quadratic modes

Calibration Standard at ~5 pg Sulfur



Methyl Sulfide Calibration



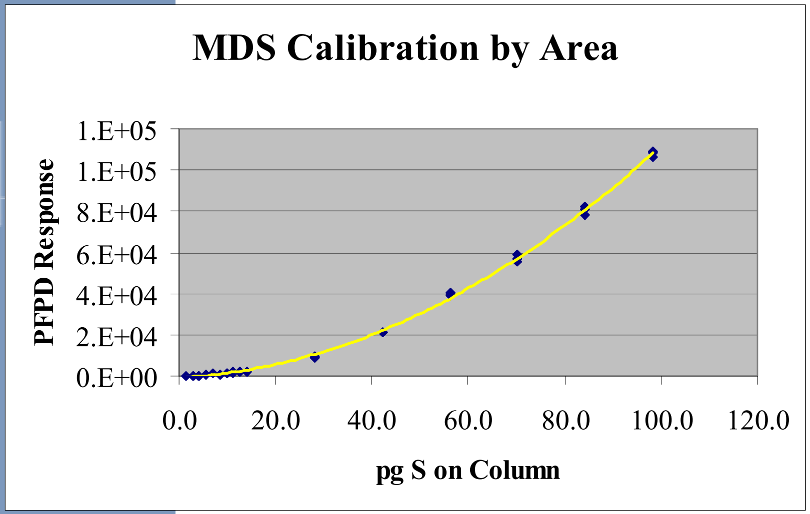


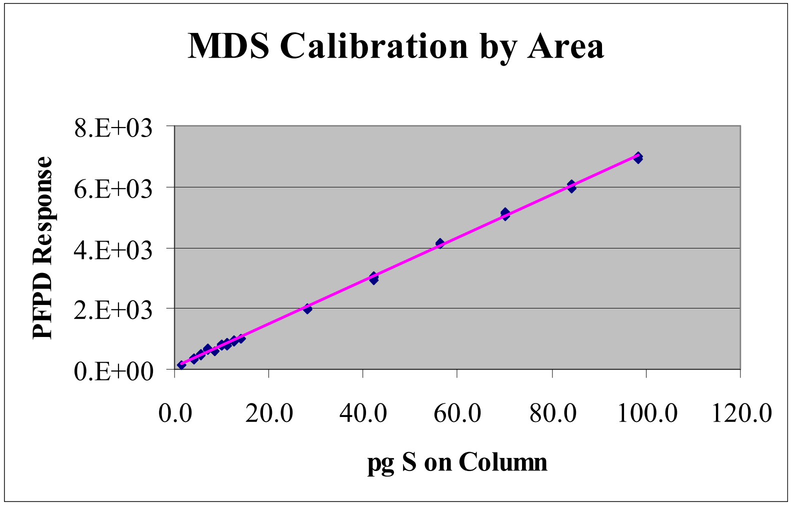
Quadratic
$R^2 = 0.9995$

Linear
$R^2 = 0.9992$

19 Calibration Levels x 3 injections each
Range from 1.0 to 103.7 pg sulfur

Methyl Disulfide Calibration



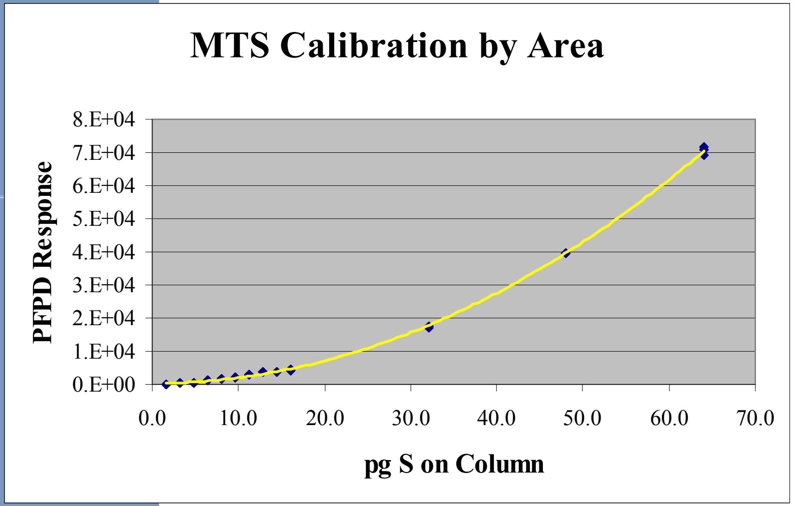


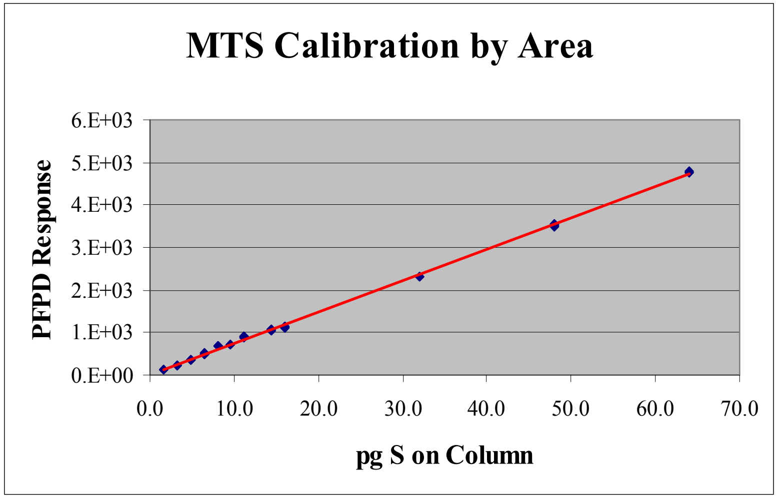
Quadratic
$R^2 = 0.999$

Linear
$R^2 = 0.9992$

16 Calibration Levels x 3 injections each
Range from 1.4 to 98.4 pg sulfur

Methyl Triulfide Calibration



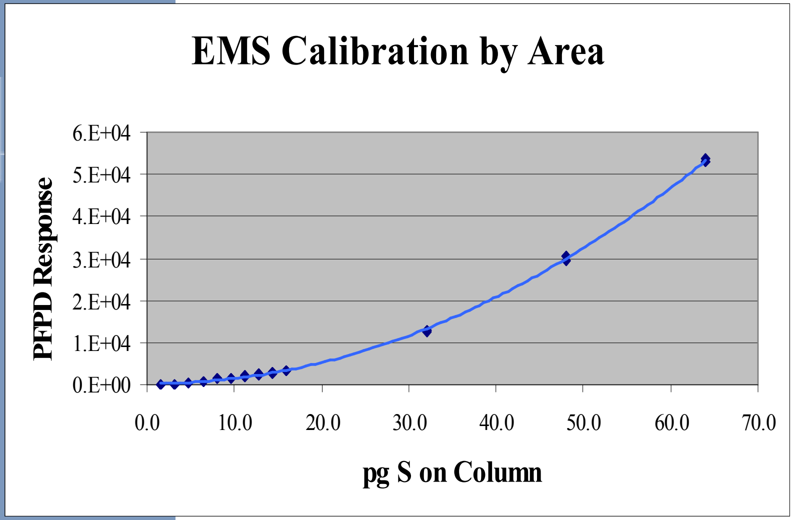


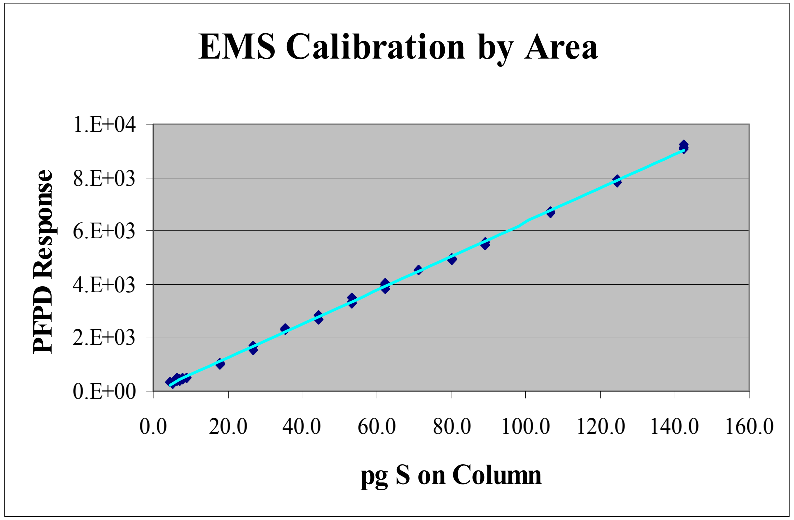
Quadratic
$R^2 = 0.9996$

Linear
$R^2 = 0.9992$

13 Calibration Levels x 3 injections each
Range from 1.6 to 64.1 pg sulfur

Ethyl Methyl Sulfide Calibration





Quadratic
$R^2 = 0.9995$

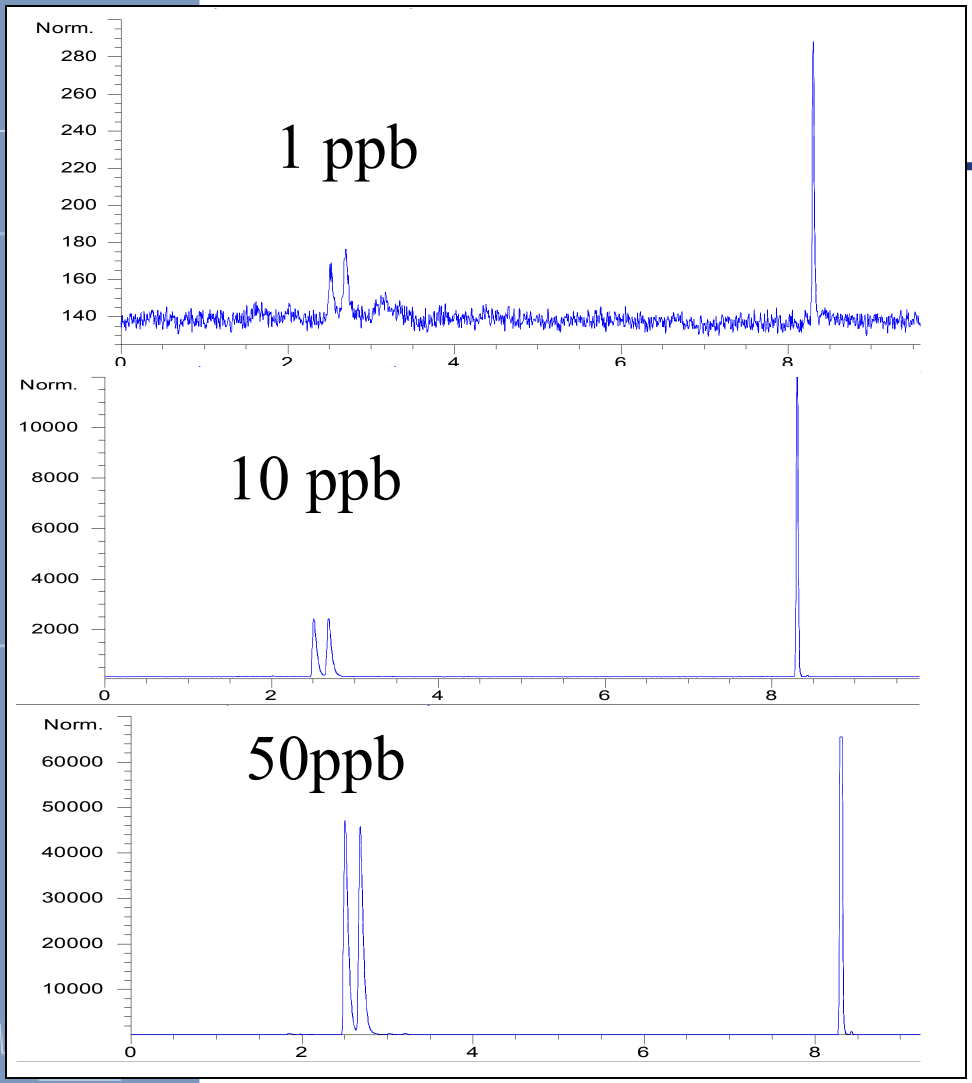
Linear
$R^2 = 0.9991$

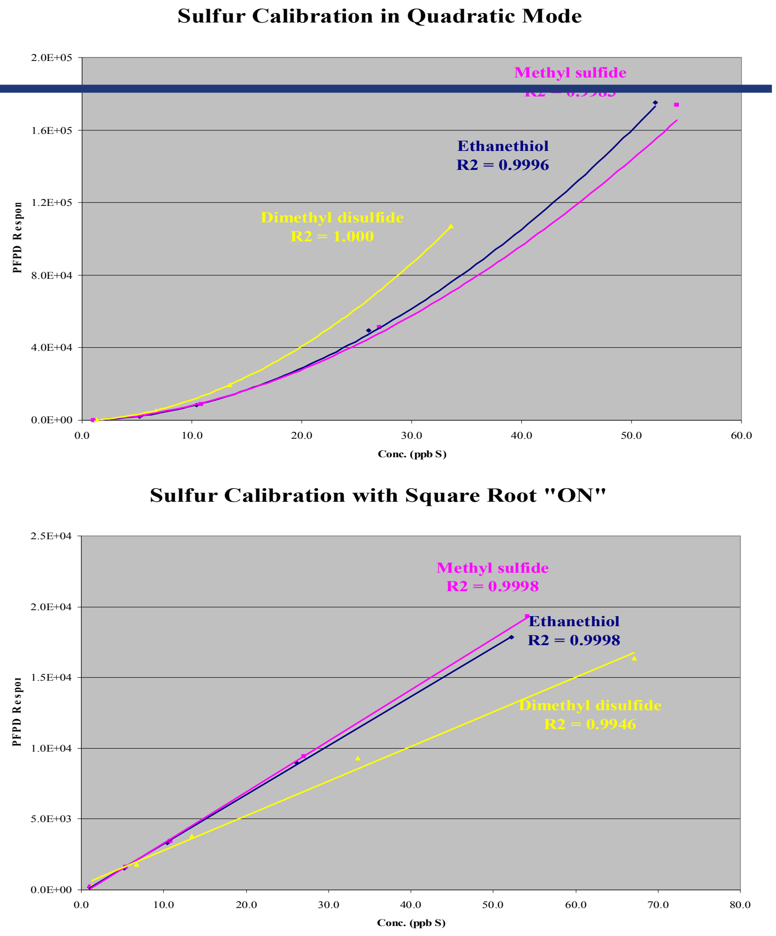
18 Calibration Levels x 3 injections each
Range from 4.5 to 147.4 pg sulfur

Average Reproducibility

	Quadratic	Linear
MS	2.2%	1.0%
MDS	1.6%	1.4%
MTS	2.0%	1.1%

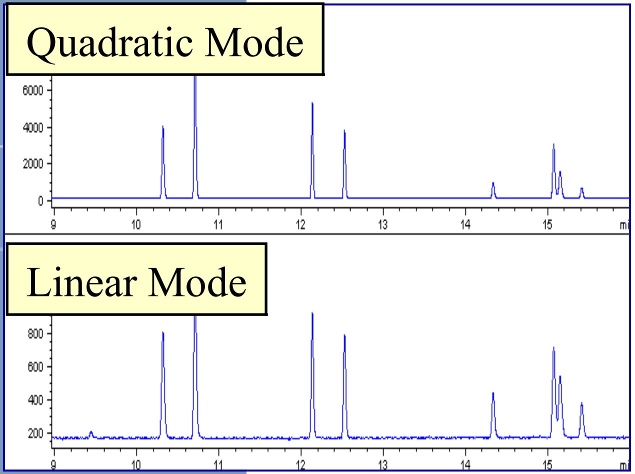
Calibration By Headspace

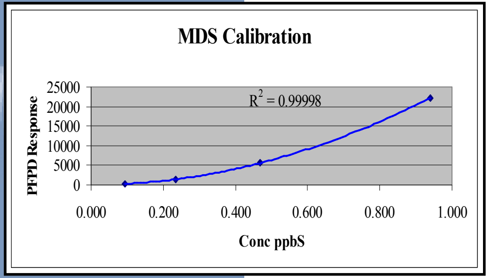


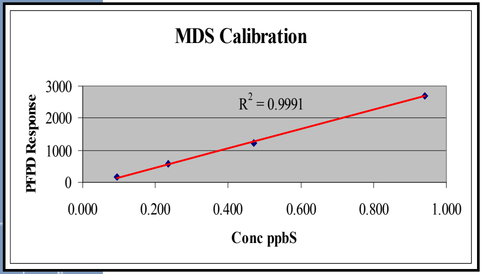


Opportunity through Innovation™

Calibration By Purge-and-Trap







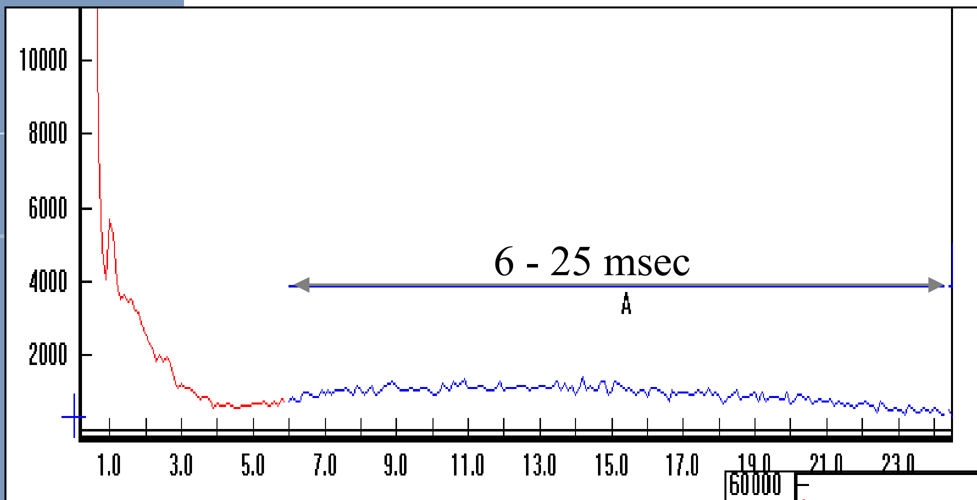
Compound	Cal Range (ppbS)	R^2 Quadratic	R^2 Linear
ETHIOL	0.52 – 10.4	0.9996	0.9994
ES	0.15 – 1.50	0.9996	0.9991
MS	0.12 – 1.16	1.000	0.9996
EMS	0.14 – 1.42	0.9998	0.9990
MDS	0.09 – 0.94	0.9998	0.9991
MTHIOAC	0.14 – 7.1	0.9998	0.9997
ETHDS	0.09 – 0.90	0.9990	0.9982
MTS	0.11 – 1.10	0.9998	0.9998
ETHIOAC	0.20 – 4.0	0.9990	0.9998

Questions #3 and #4
What is the dynamic range?
How do I calibrate the PFPD?

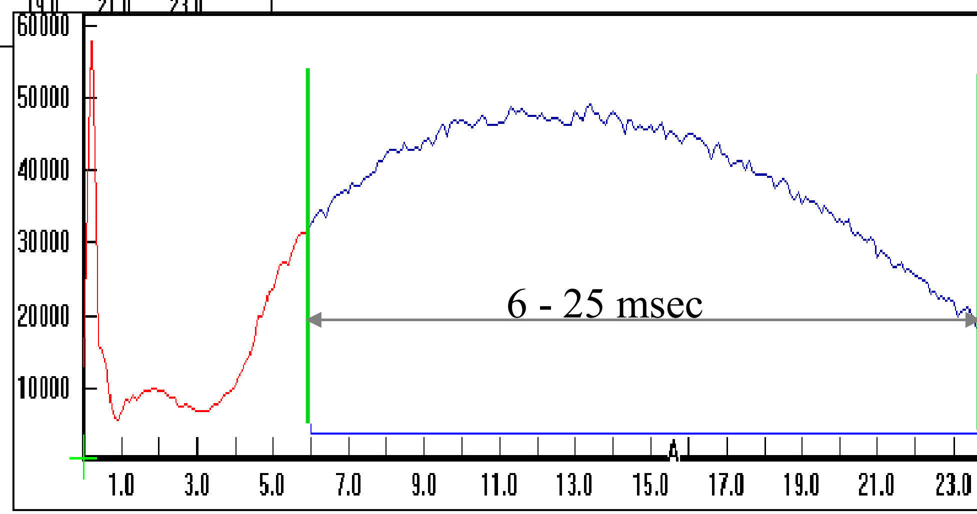
Calibration Thus Far

- Set lowest calibration point at ~1 pg S on column
- Sulfur emission saturates at ~100 pg S on column
  - Varies slightly depending on peak shape/width
- Linear or quadratic calibration possible throughout this range (~1 to 100 pg S on column)
  - User defined

Comparison of Sulfur Emissions

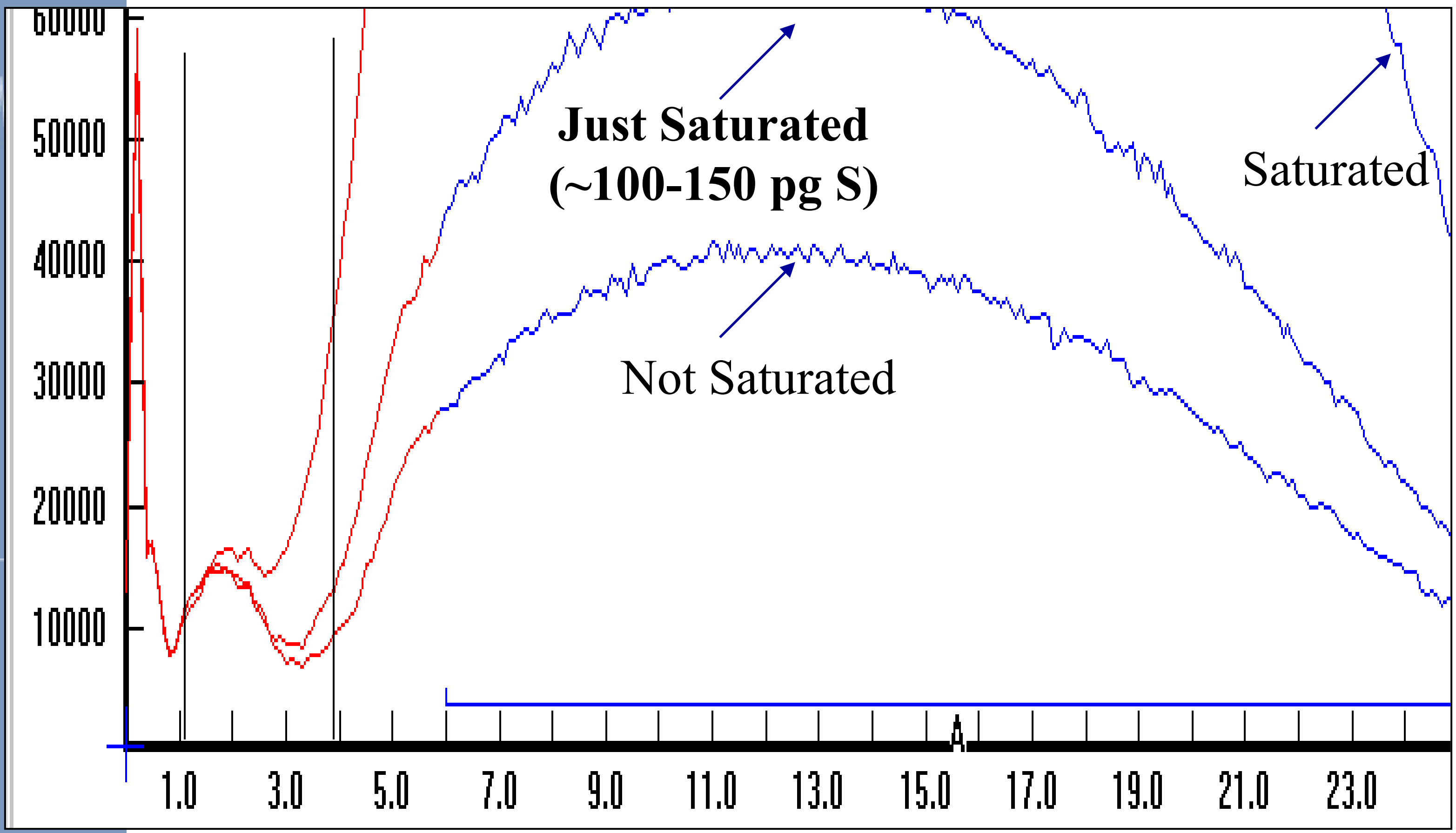


~20 pg S
on column

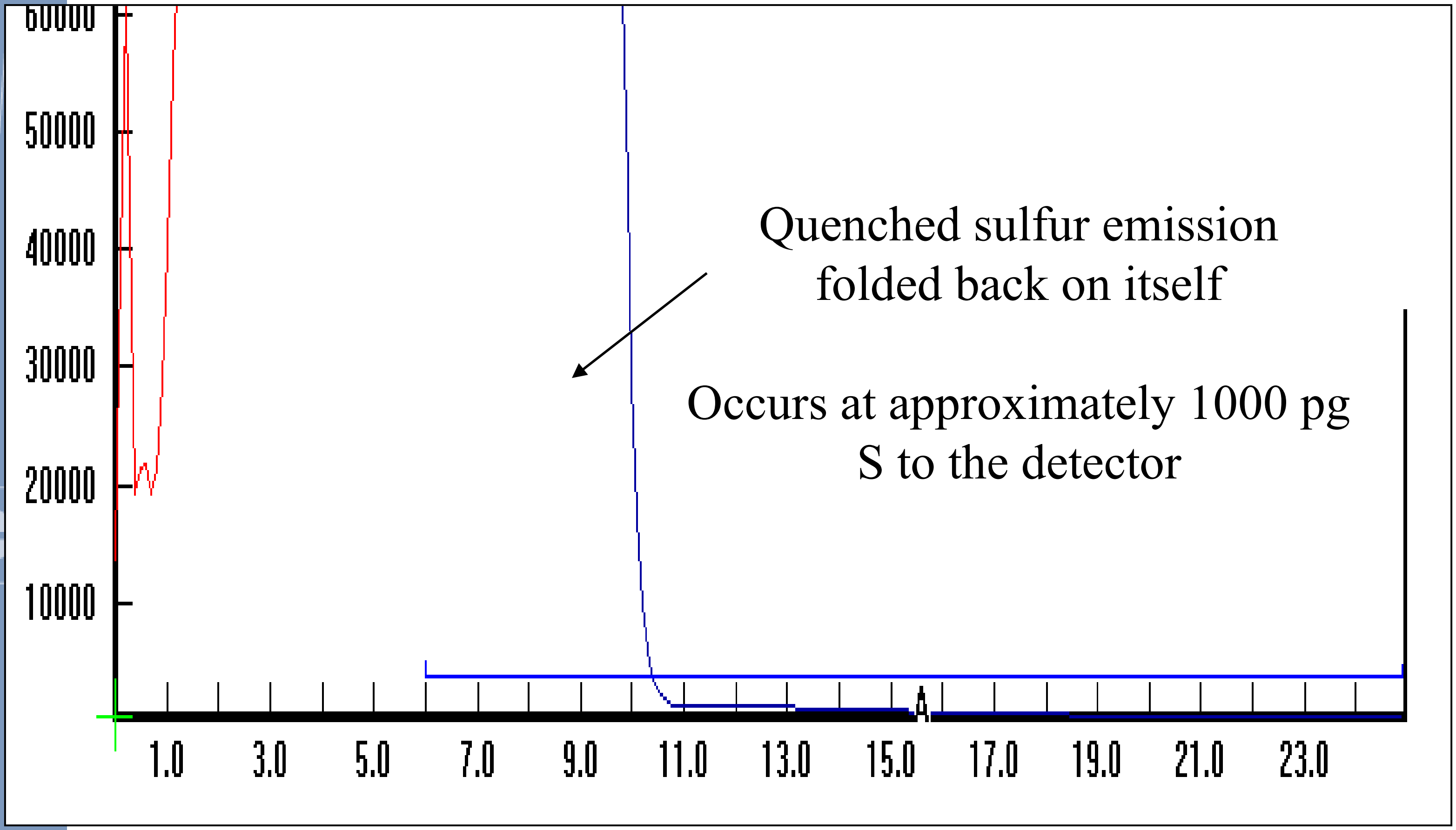


~100 pg S
on column

Saturated Sulfur Emission



Quenched Sulfur Emission



Extending the Dynamic Range

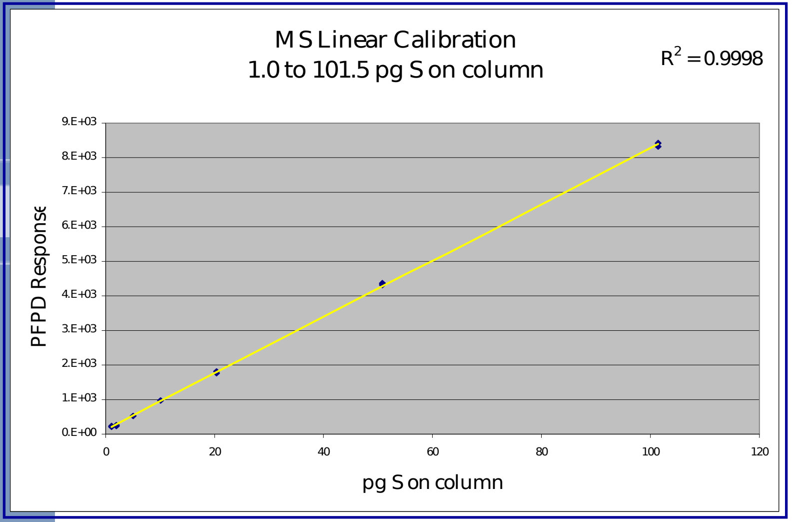
- Practical dynamic range is a little under 2 orders of magnitude using the “standard conditions”
- Can be extended using one of several techniques

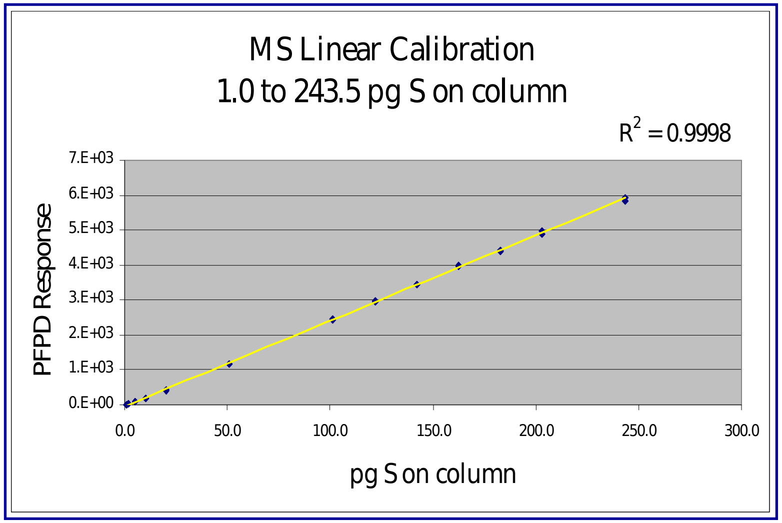
Technique #1

Increase Electrometer Range

Electrometer Range 10
1 to 102 pg S
$R^2 = 0.9998$

Electrometer Range 100
1 to 244 pg S
$R^2 = 0.9998$





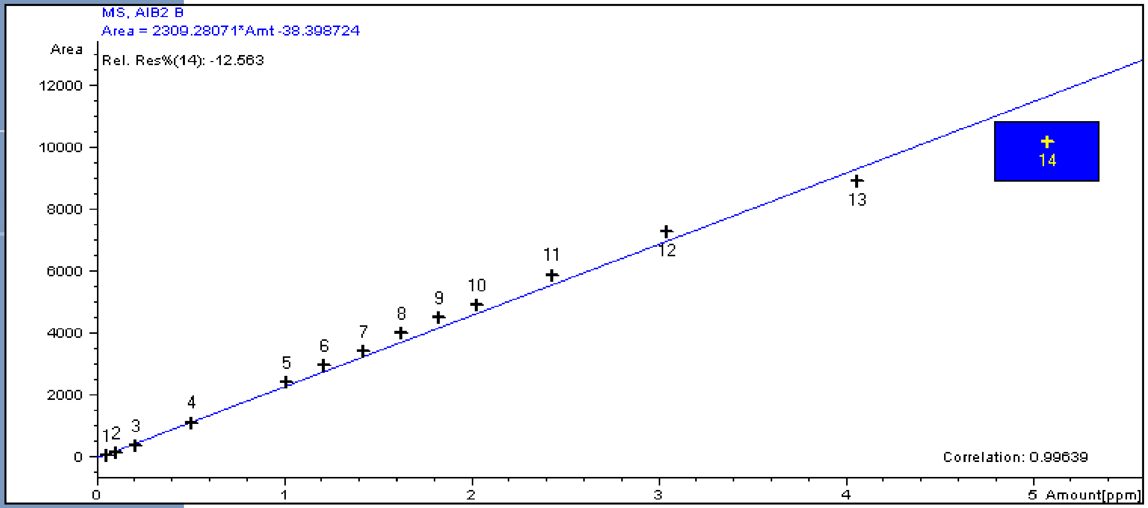
Technique #1: Pros and Cons

Pros	Cons
Easy	Less sensitive at low concentrations
Increases max from 100 pgS to ~250 pgS	
Linear or quadratic curve fit	

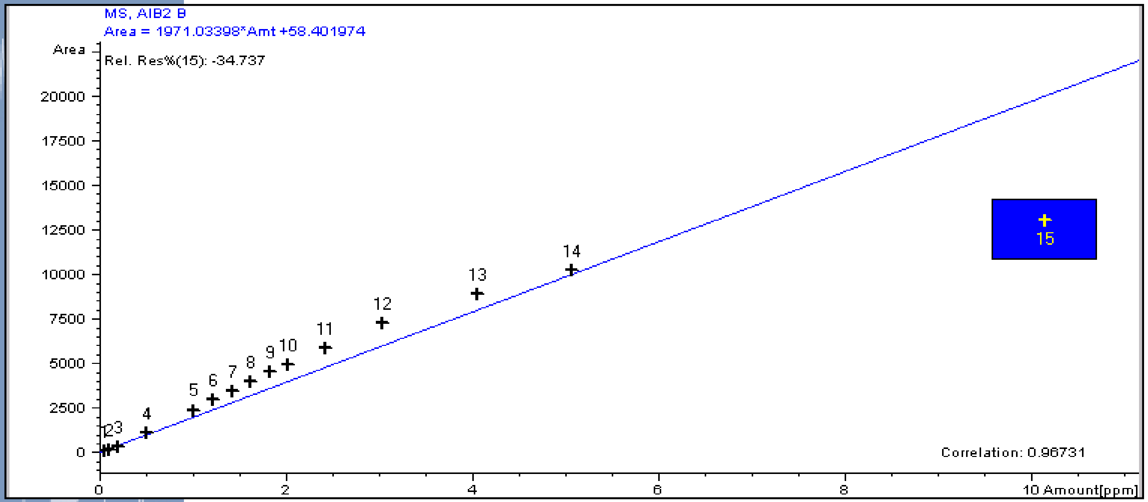
Technique #2

- Curve fit method
  - Use linear mode
  - Acquire data across entire range desired
  - Disregard emission saturation point
  - Use data handling software to find best curve fit

MS Calibration 1 pg to 1 ng Sulfur Using Chemstation Software

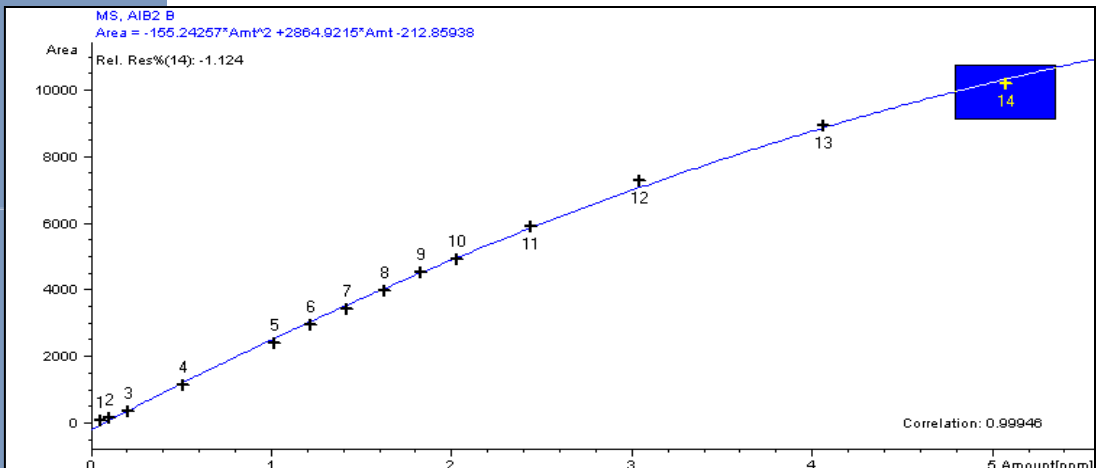


1 – 500 pg S
Linear Curve Fit
$R^2 = 0.99639$



1 – 1000 pg S
Linear Curve Fit
$R^2 = 0.9671$

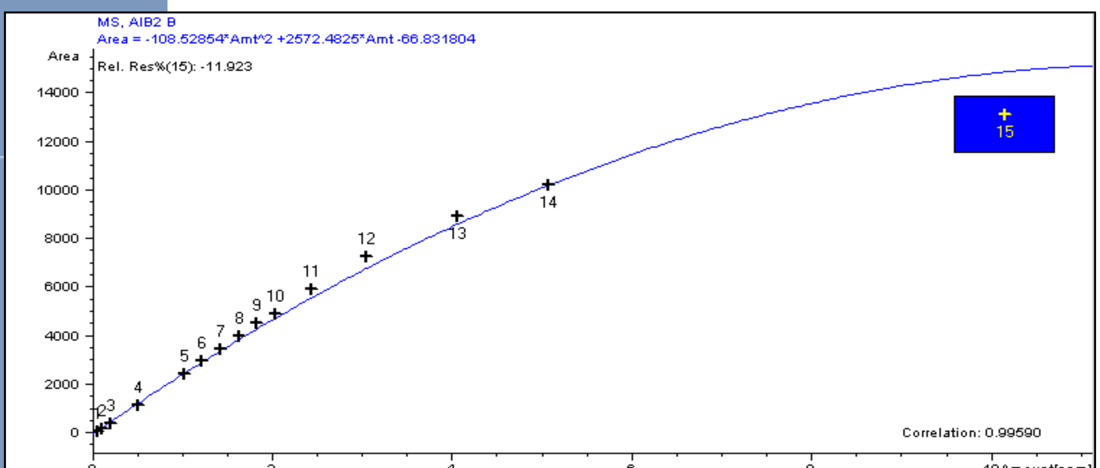
MS Calibration 1 pg to 1 ng Sulfur Using Chemstation Software



1 – 500 pg S

Quadratic Curve Fit

$R^2 = 0.99946$



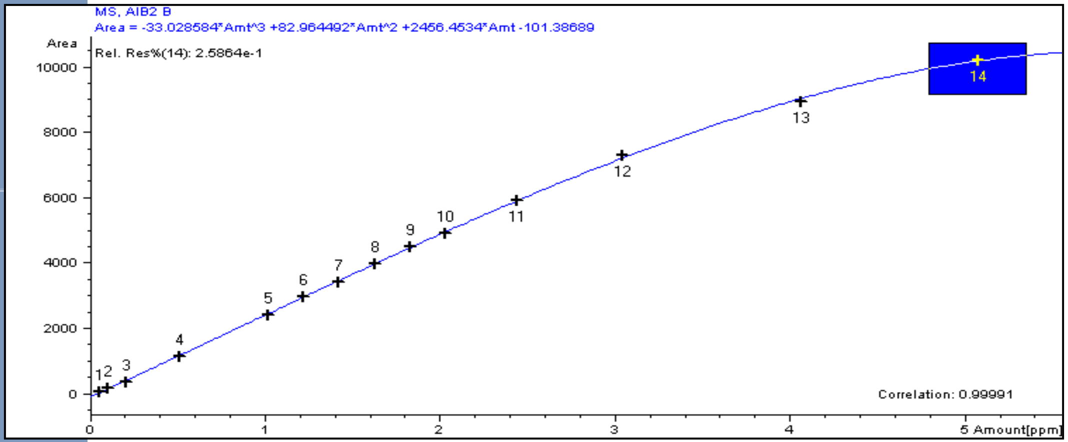
1 – 1000 pg S

Quadratic Curve Fit

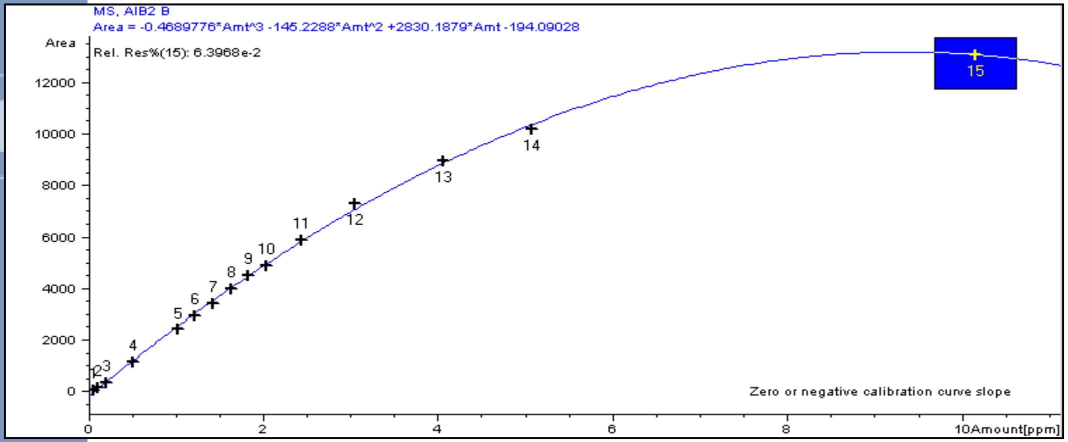
$R^2 = 0.99590$

Note: Using quadratic fit to the linear output

MS Calibration 1 pg to 1 ng Sulfur Using Chemstation Software

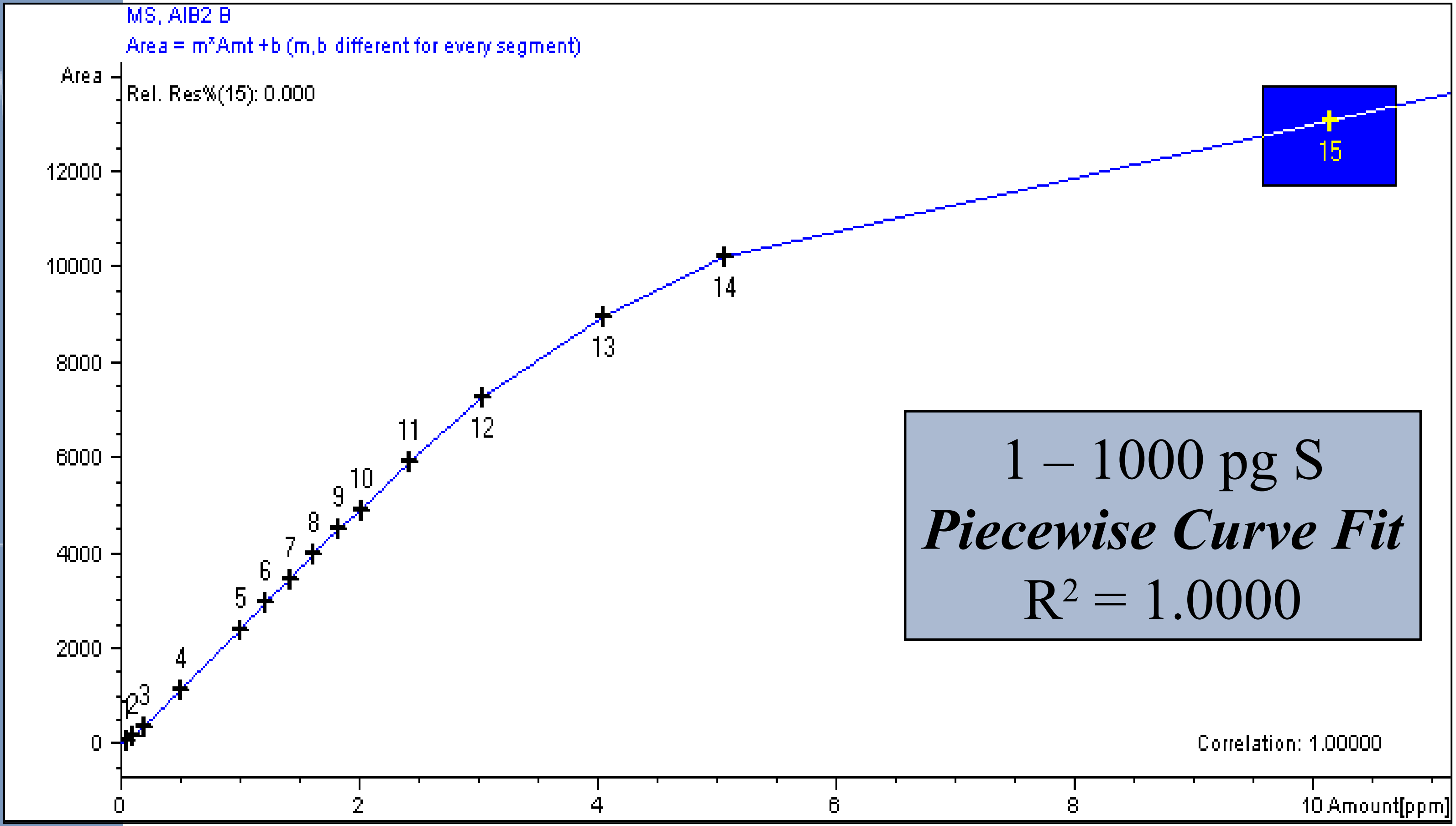


1 – 500 pg S
Cubic Curve Fit
$R^2 = 0.9991$



1 – 1000 pg S
Cubic Curve Fit
(Neg. slope)

MS Calibration 1 pg to 1 ng Sulfur
Using Chemstation Software

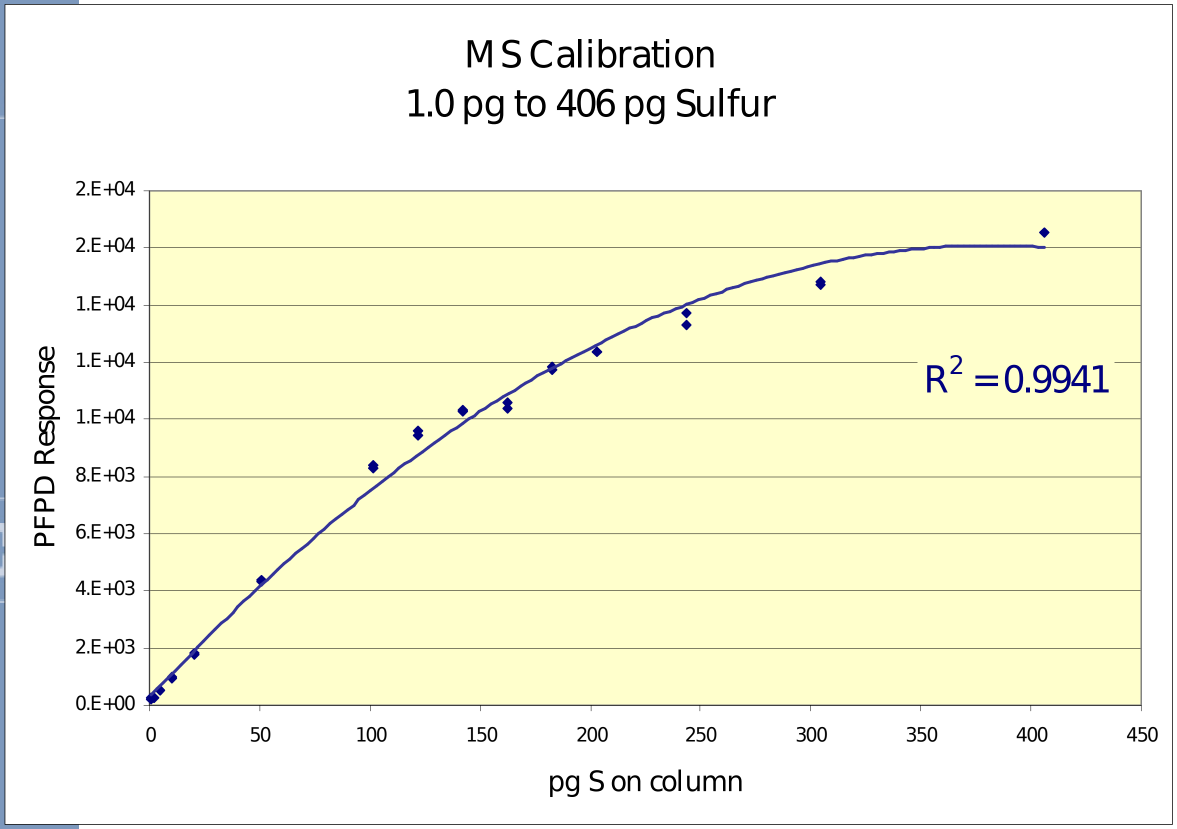


1 – 1000 pg S

Piecewise Curve Fit

$R^2 = 1.0000$

MS Calibration 1 to 400 pg Sulfur Using Excel Software



1 to 406 pg S
Power fit
$R^2 = 0.9941$

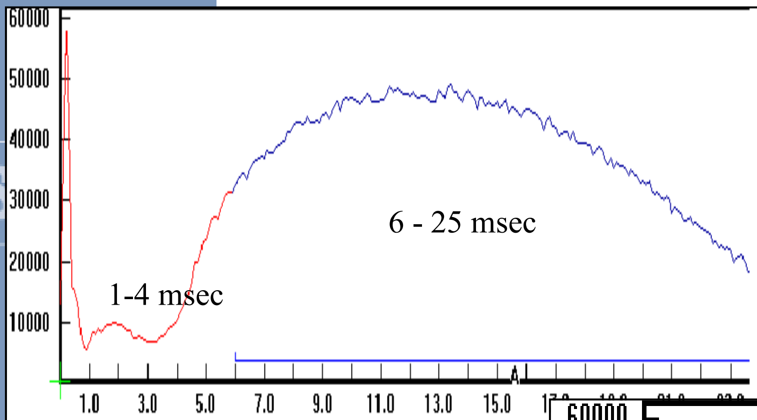
Technique #2: Pros and Cons

Pros	Cons
Easy	Not linear
Extends range up to 3 orders magnitude	Increased error near curve maximum (i.e. at a horizontal tangent)
Good to excellent curve fit every time	For some options requires more calibration points
Fully utilizes sophisticated software options	

Technique #3: Dual Gates

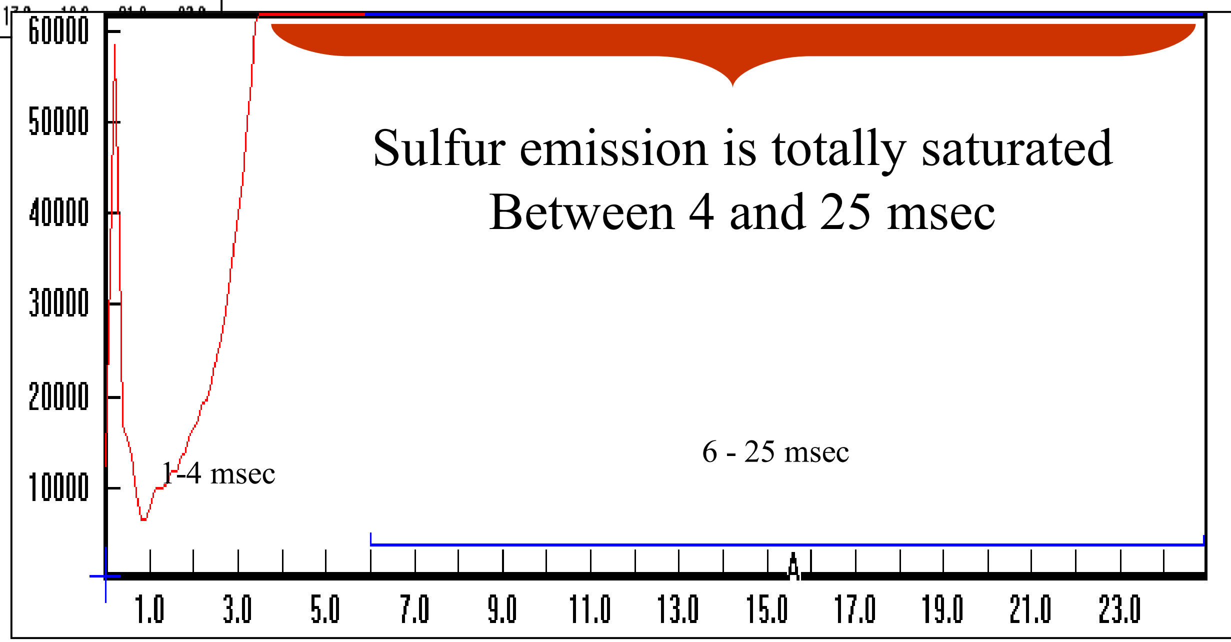
- Gate 1 = 6 - 25 msec
- Gate 2 = 1 - 4 msec
- Use Gate 1 for concentrations below the saturation point (~1 to 100 pg S)
- Use Gate 2 for concentrations above the saturation point (~100 pg to 1 ng)

Comparison of Sulfur Emissions

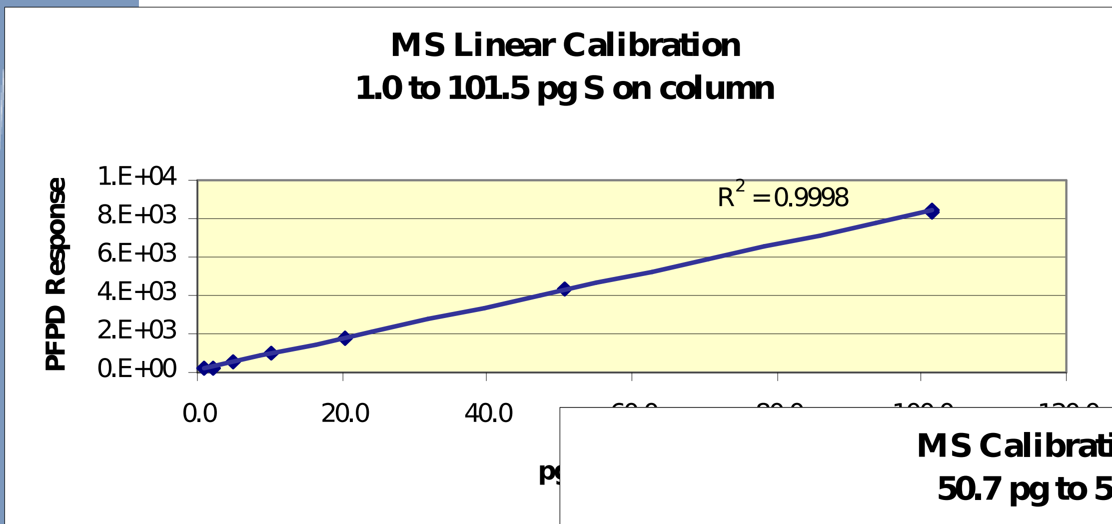


~100 pg S

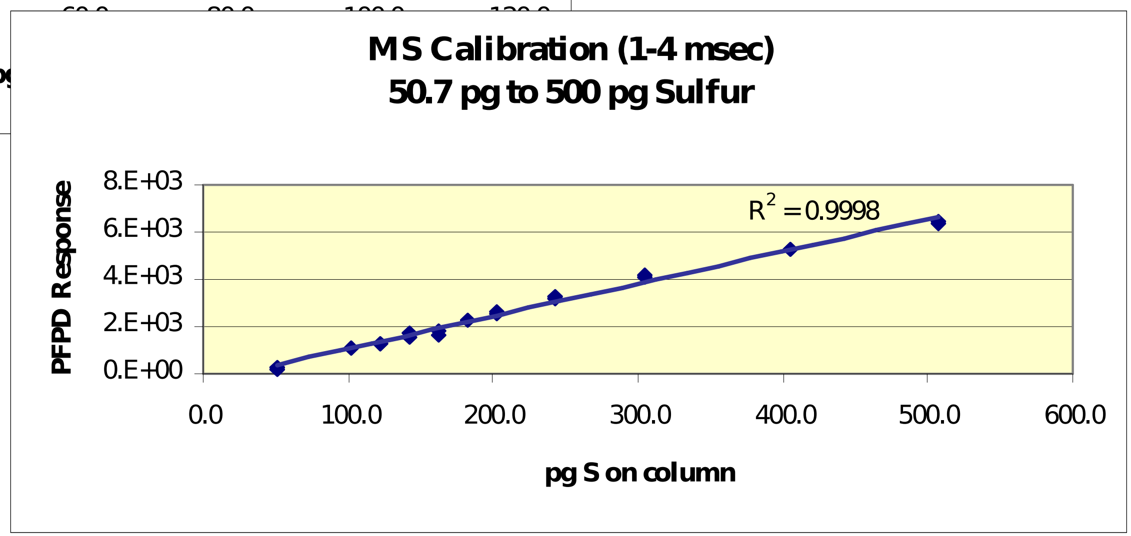
~1000 pg S



Extended Calibration Using Dual Gates

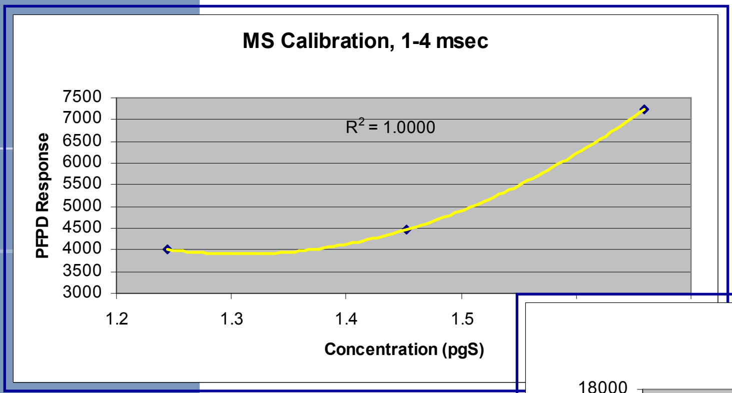


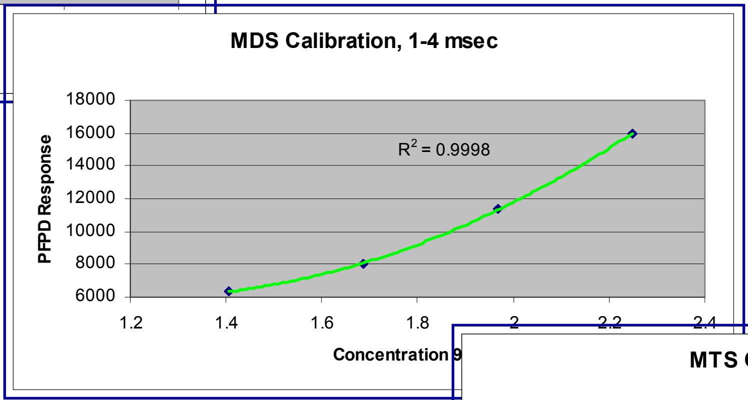
6-25 msec gate

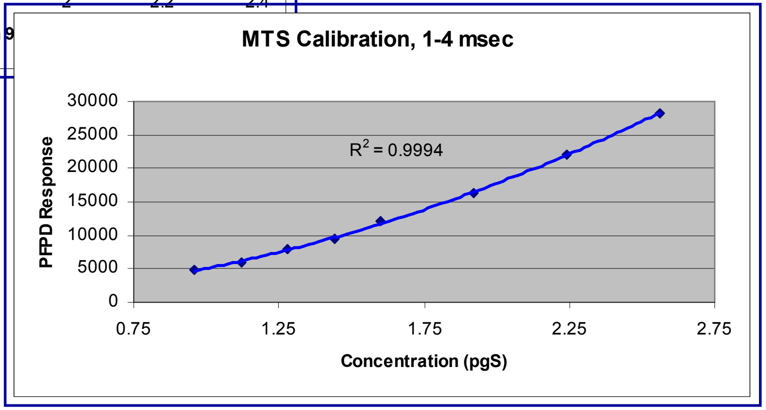


1-4 msec gate

Extended Calibration Using 1-4 msec Gate







MS R^2 = 1.000

MDS R^2 = 0 9998

MTS R^2 = 0 9994

Extended Range Using Dual Gate Settings

	Without Dual Gate	With Dual Gate
MS	1.0 – 103.7	1.0 pg – 1 ng
MDS	1.4 – 98.4	1.4 pg – 1 ng
MTS	1.6 – 64.1	1.6 pg – 1 ng

All concentrations in pg Sulfur on column

Technique #3: Pros and Cons

Pros	Cons
Extends range to full 3 orders of magnitude	More data "crunching" simplified with PFPD software
Accurate	Coeluting large HC peaks will cause errors
Linear or quadratic modes	Loss of selectivity with HC peaks must be considered

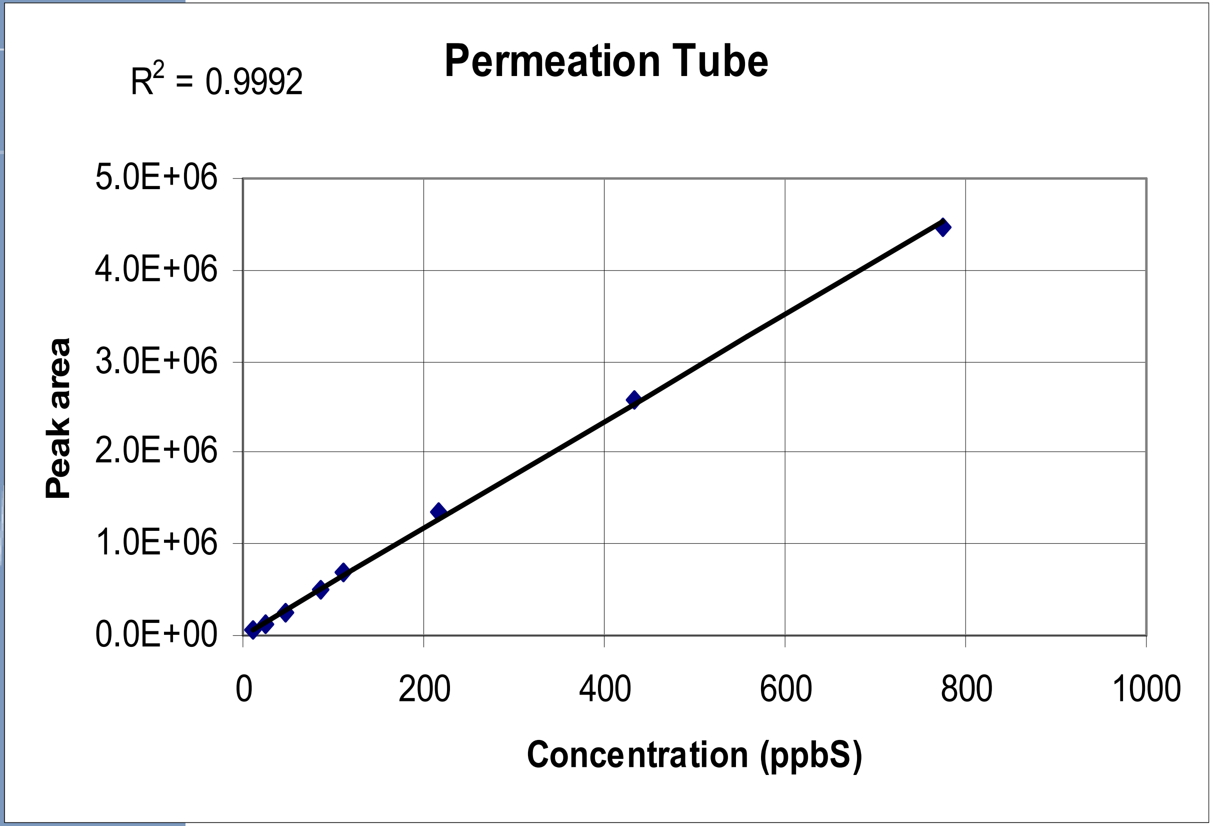
Method Development

- Measure PFPD detectivity at <1 pgS/sec
- Adjust method parameters for 1-2 pg S on column
  - Lowest instrument calibration point
- Select best calibration technique
  - ~1 to 250 pg S – Linear or Quadratic
  - ~1 to ~500 pg S – Curve Fit
  - ~1 to ~500 pg S – Dual Gate

Calibration Technique for Gas Sampling System

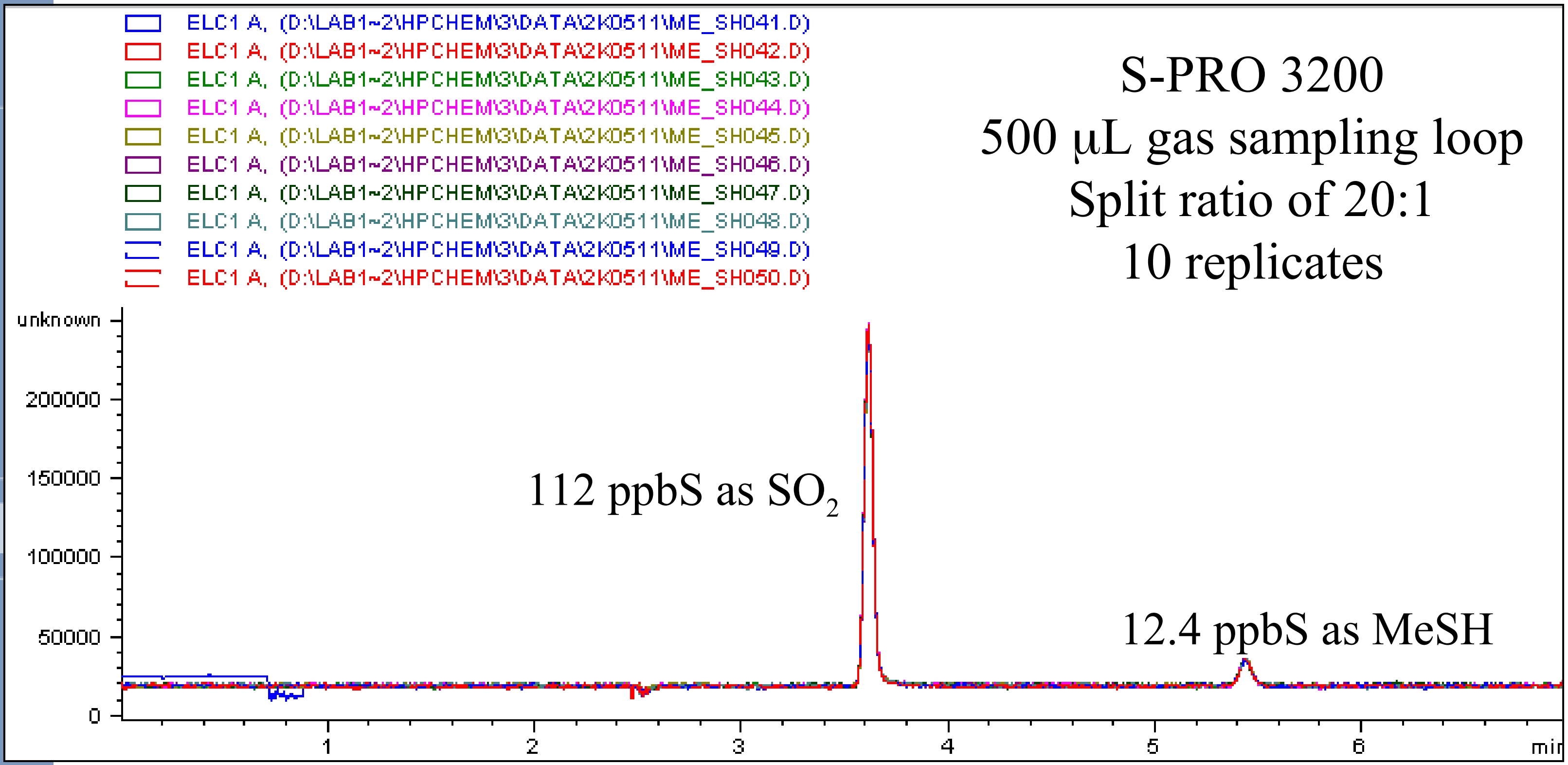
- Standard with two compounds at different concentrations (e.g. MeSH at 12.4 ppbS and SO_2 at 112 ppbS)
- Analyze at four levels (e.g. different gas flows)
- Generate eight-point curve based on amount of Sulfur

Calibration Curve Based on Sulfur



- 0.5-mL gas sample loop
- Split ratio 20:1
- PFPD in sulfur mode
- Linear calibration using peak areas
- 12.4 – 775.4 ppb S
- $R^2 = 0.9992$

MeSH and SO_2 in CO_2



Concentrations of MeSH and CO_2 Used for Calibration

SO_2 in CO_2		MeSH in CO_2	
Conc (ppb S)	% RSD (n = 10)	Conc (ppb S)	% RSD (n = 10)
112.0	0.99	12.4	2.71
216.8	1.54	24.1	2.35
432.8	1.88	48.2	2.59
775.4	1.02	86.4	0.88

Gas Sampling Technique Pros and Cons

Pros	Cons
Fast and easy	Peaks widths/areas must be the same
Equimolar response	Errors if peaks widths differ
Calculate total sulfur concentration	
Ideal for gas sampling system	

Question #5

Is the response equimolar?

Equimolar Sulfur Response

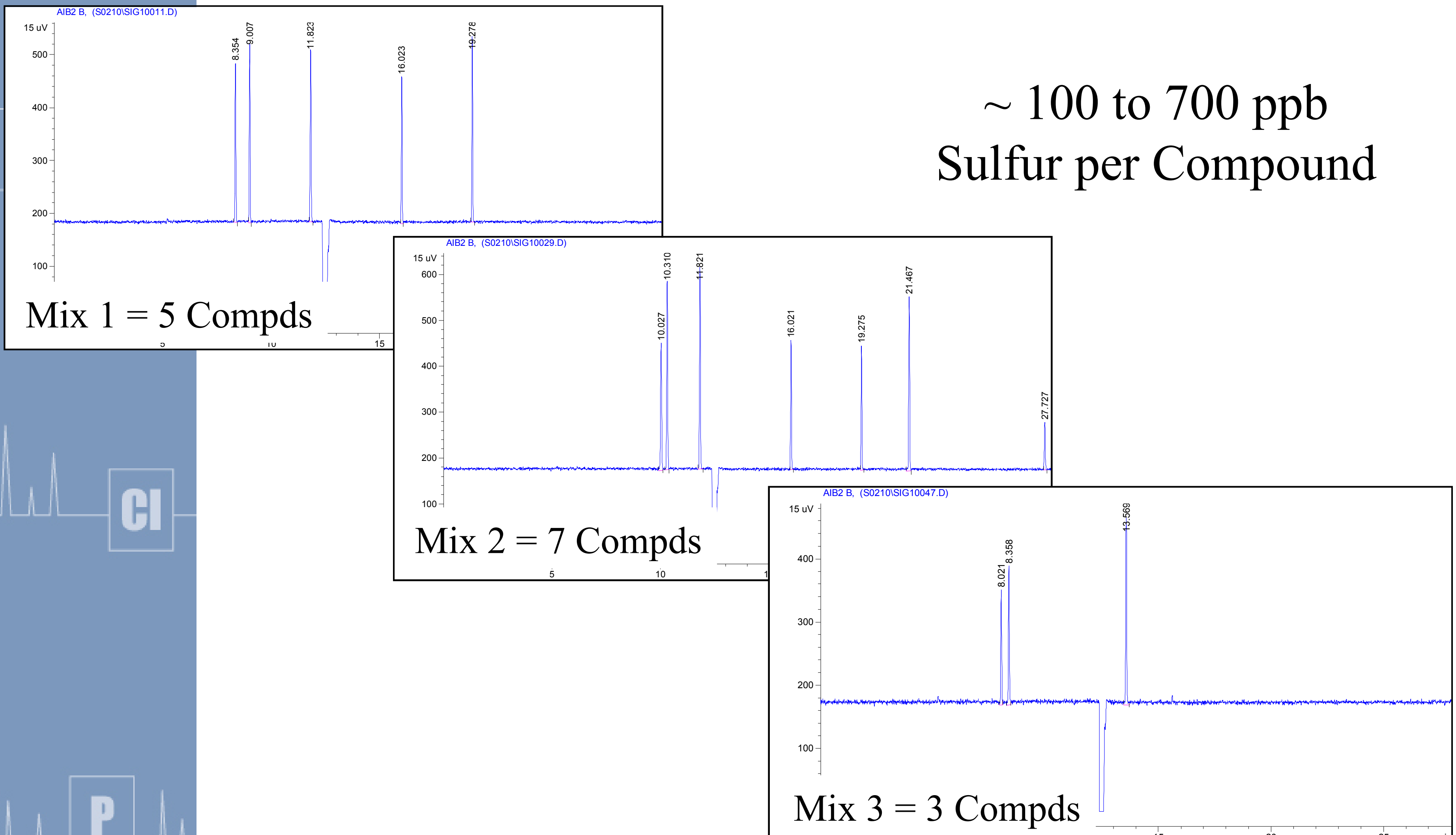
- Once the output signal has been linearized, sulfur response of the PFPD is equimolar
- “X” amount of sulfur at the detector will always produce “X” response
- Independent of sulfur environment
- Apparent non-equimolar responses are due to losses elsewhere in the system
  - Volatility
  - Reactivity (e.g. H2S)
- Phosphorus response is naturally linear and equimolar

Equimolar Response Sulfur

- 3 Mixes of sulfur compounds analyzed
- Volatile, so some compounds in 2 mixes
- Response factors calculated
- RF for all compounds very similar
- RF %RSD was < 4%

Chromatograms for 3 Mixes

~ 100 to 700 ppb
Sulfur per Compound



Sulfur Response Factors

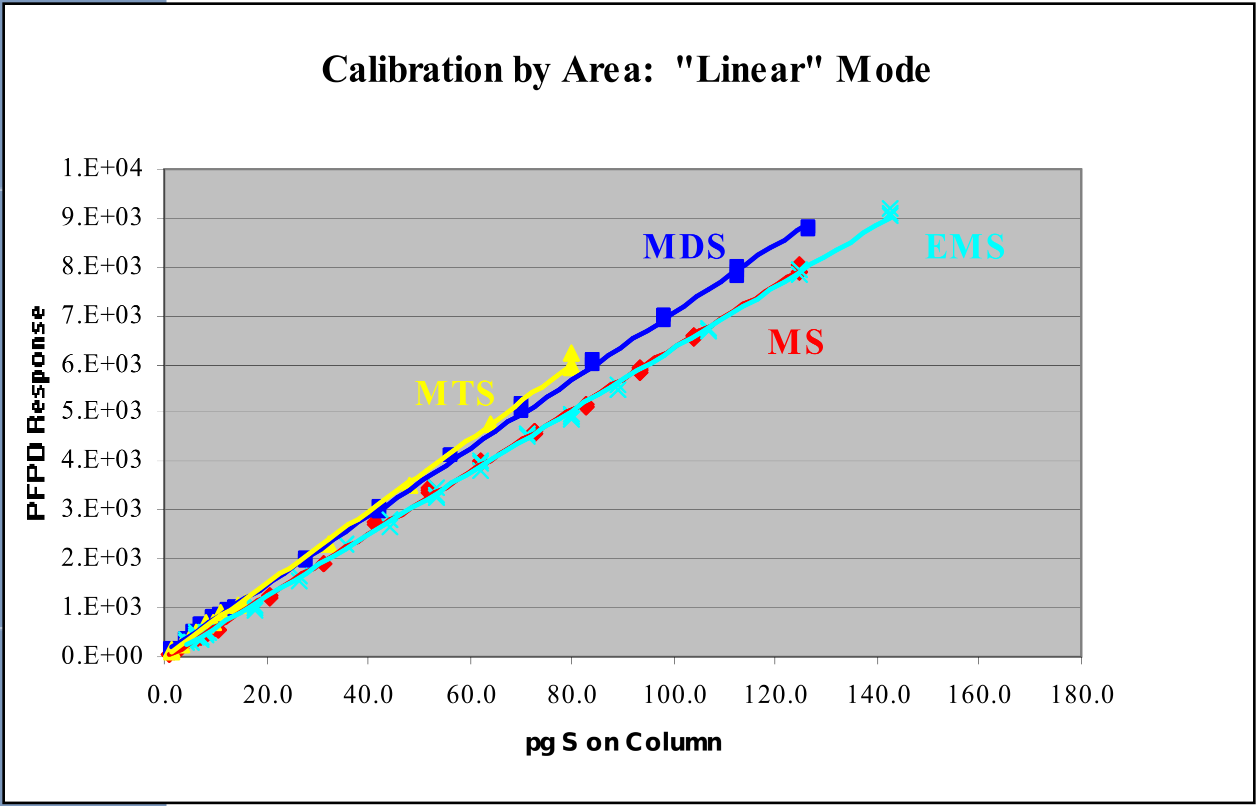
Mix 1 RFs	
Methyl sulfide	1.73
Carbon disulfide	1.80
Thiophene	1.87
Amyl sulfide	1.89
Heptyl mercaptan	1.97

Mix 2 RFs	
Methyl sulfide	1.80
Ethanethiol	1.79
Dimethyl disulfide	1.83

Mix 3 RFs	
2-Methylpropanethiol	1.91
1-Methylproanethiol	1.90
Thiophene	1.98
Amyl sulfide	1.83
Heptyl mercaptan	1.97
t-Butyl disulfide	1.86
1-Dodecanethiol	1.89

Average Sulfur RF = 1.87
RSD = 3.9%

Equimolar Sulfur Response



<u>Slope</u>

MS = 63.8

EMS = 63.6

MDS = 69.7

MTS = 74.5

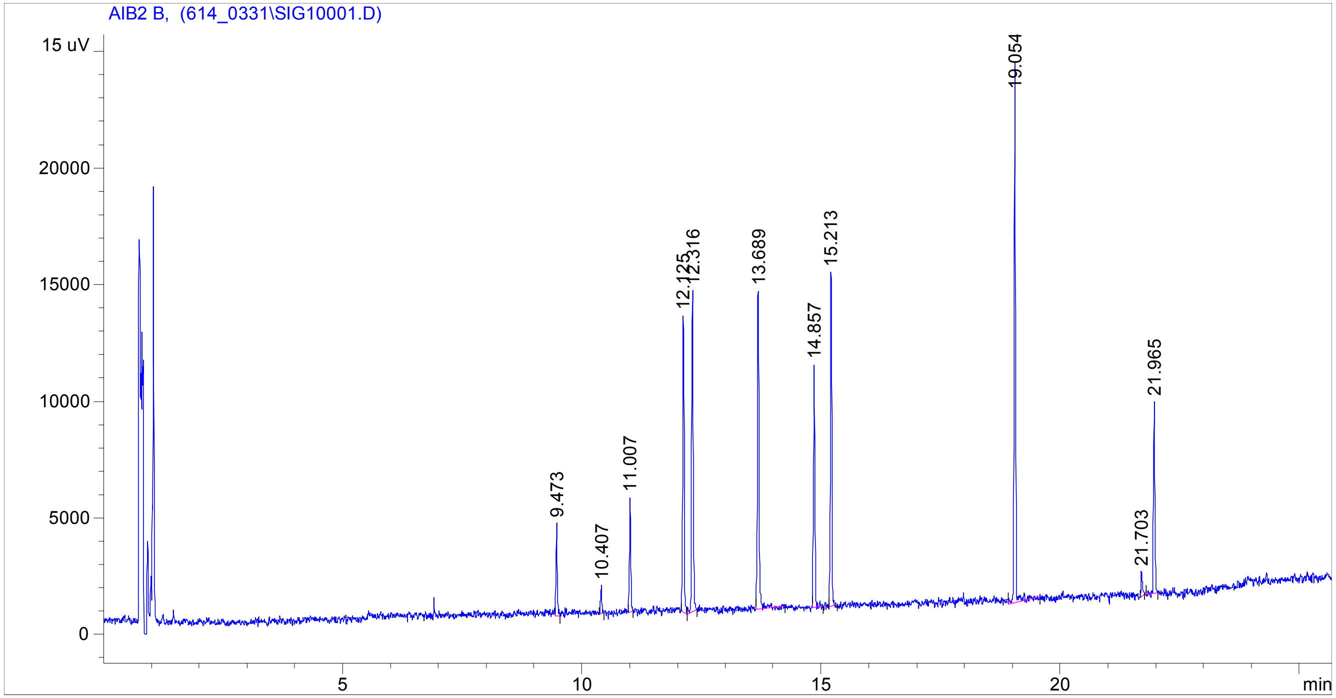
6.6% RSD

Volatile compounds have lower RFs due to losses

Equimolar Response Phosphorous

- 1 Mixes of phosphorous compounds
- Response factors calculated
- RF for all compounds very similar
- RF %RSD was < 10%

Phosphorous Mix Chromatogram



Phosphorous Mix = 9 Compounds

~ 3 to 20 pg Phosphorous per Compound

Phosphorus Response Factors

Phosphorus RFs	
Demeton O	2629
Demeton S	2622
Diazinon	2754
Disulfoton	2913
Parathion methyl	2890
Malathion	2631
Parathion ethyl	2708
Ethion	2574
Azinphos methyl	2057

Avg. Phos. RF = 2675
RSD = 9.6%

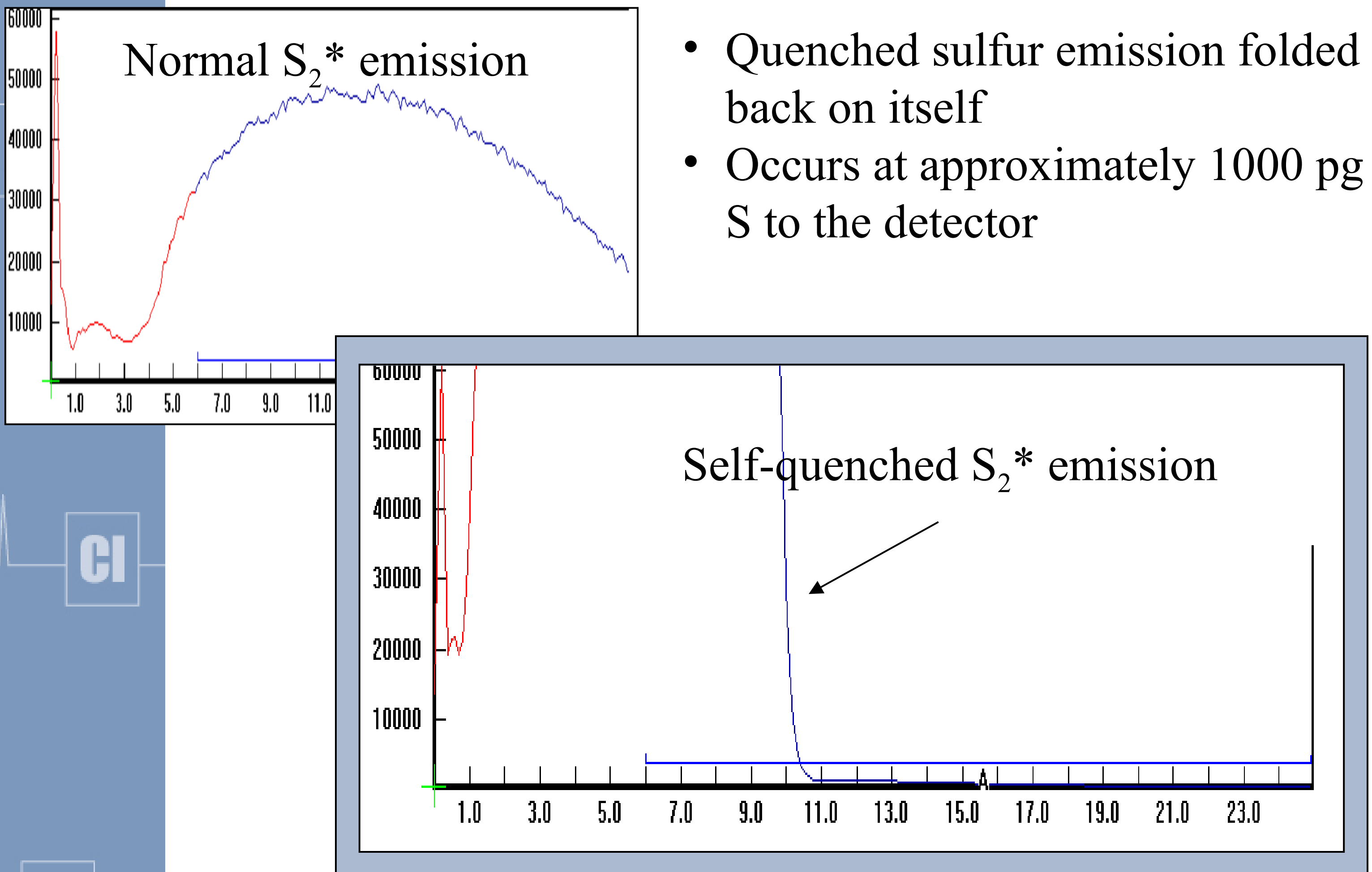
Question #6

What is "quenching"?

Sulfur Suppression Type #1

- Sulfur self-quenching occurs when very high concentration of sulfur within the combustor causes the S_2^* emissions to be self-absorbed, and never transmitted to the PMT
  - Starts at about 1000 pg S
- Easily adjusted for by reducing the amount of sulfur injected
  - Increase split ratio
  - Decrease injection volume

Self-Quenched Sulfur Emission

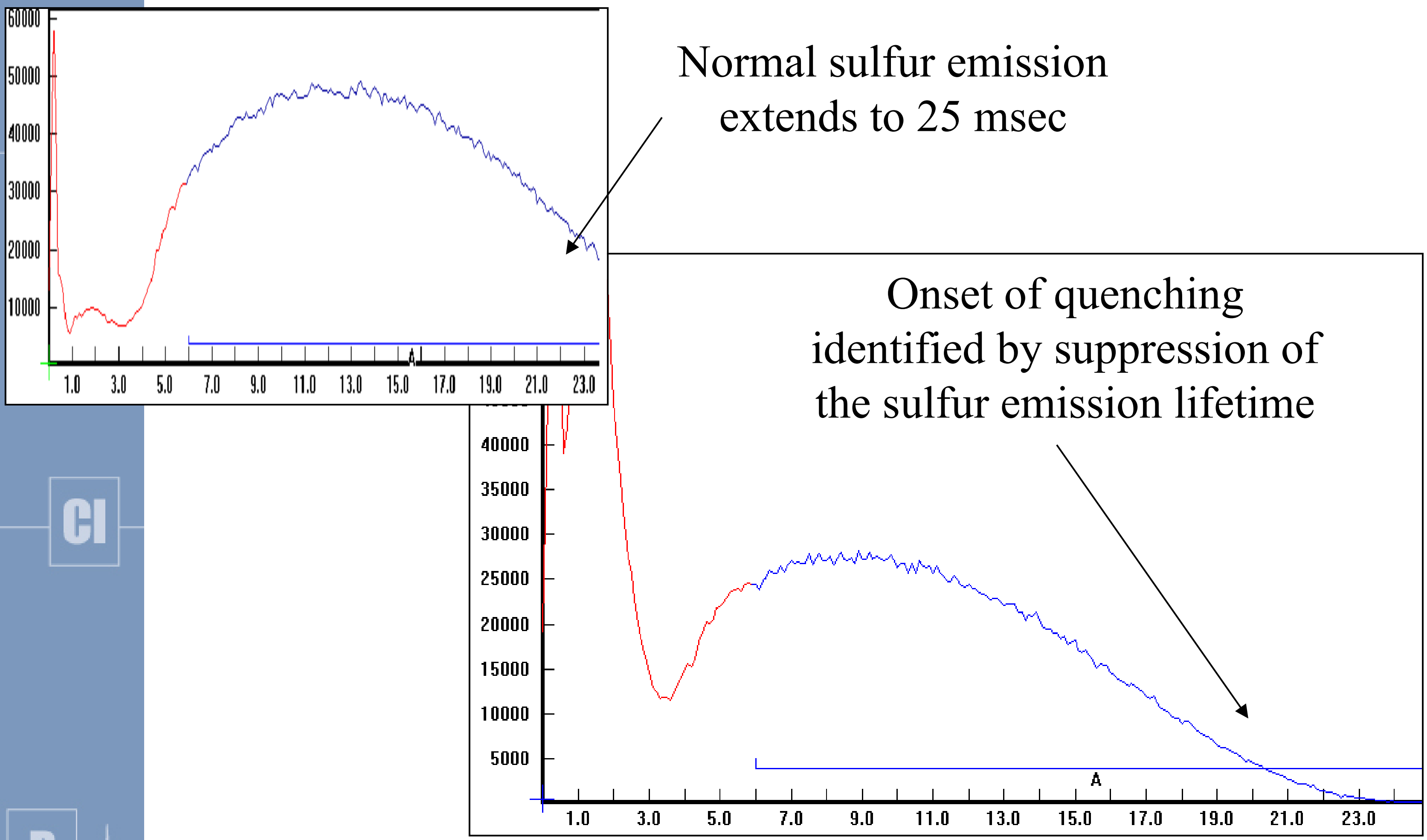


- Quenched sulfur emission folded back on itself
- Occurs at approximately 1000 pg S to the detector

Sulfur Suppression Type #2

- Sulfur suppression, aka “quenching”, results when high concentrations of HC cause competing reactions within the combustor, forming COS instead of S2*
- Shortens the lifetime of the sulfur emission
- Must have a very high concentration of hydrocarbon co-eluting with the sulfur peak for suppression to occur
  - Similar to temporary loss of signal with solvent front seen on other types of detectors

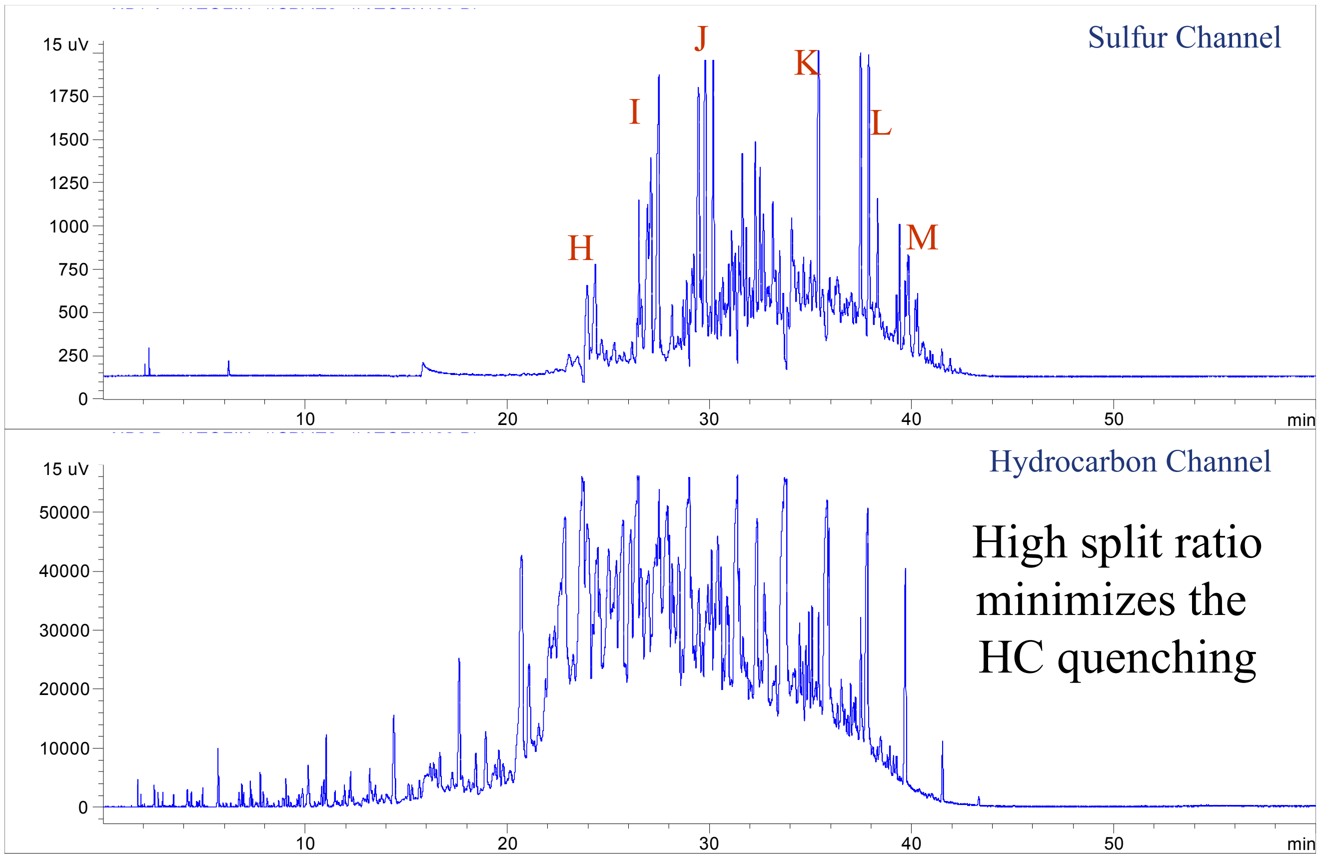
Onset of HC Quenching



Sulfur Suppression (cont.)

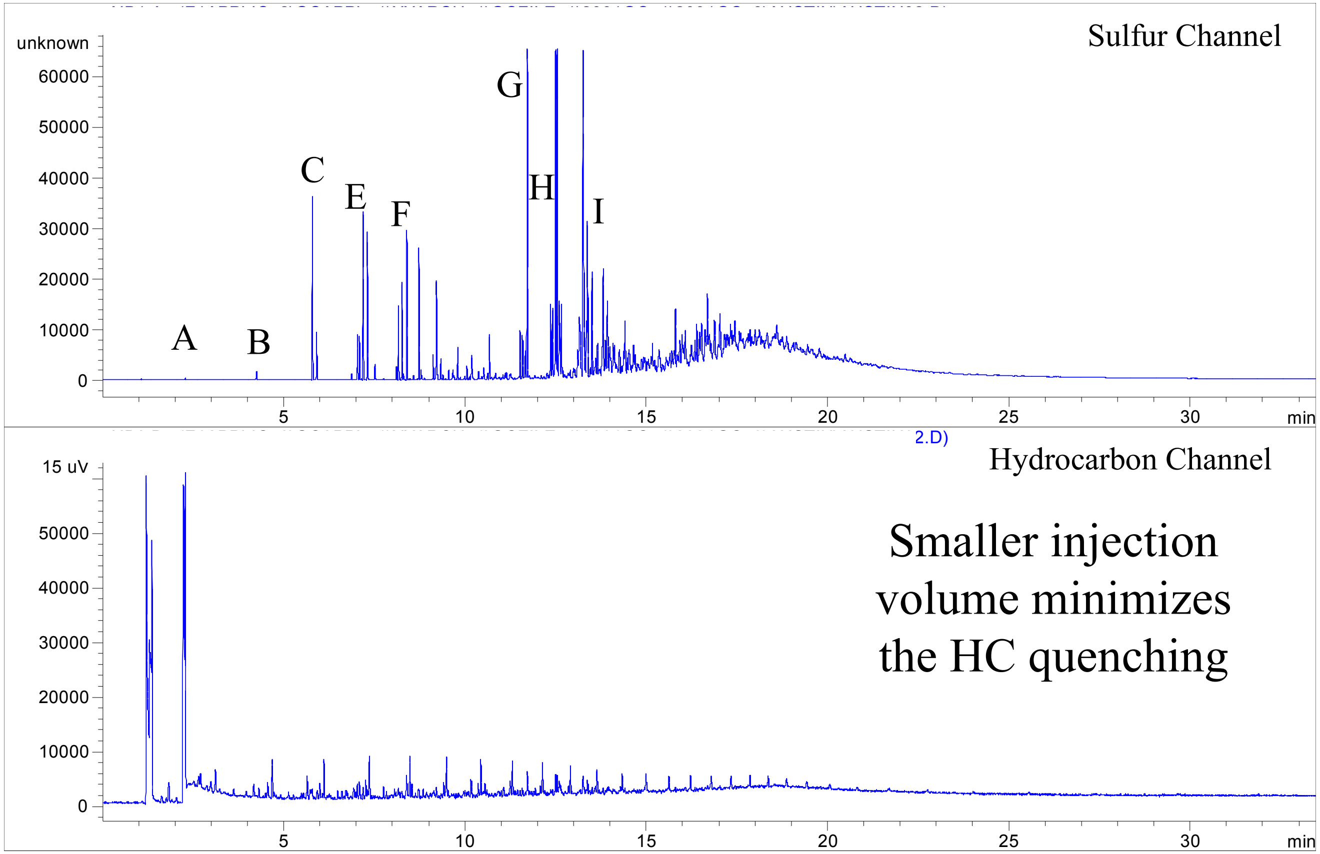
- Potential for suppression can be minimized by selection of proper application parameters
  - Split ratio
  - Injection volume
  - Dilution
  - Column selection and conditions
- Suppression is observable and identifiable on the PFPD's real-time emission display
  - Also can be saved for post-acquisition review (PFPDView)

Increase Split Ratio



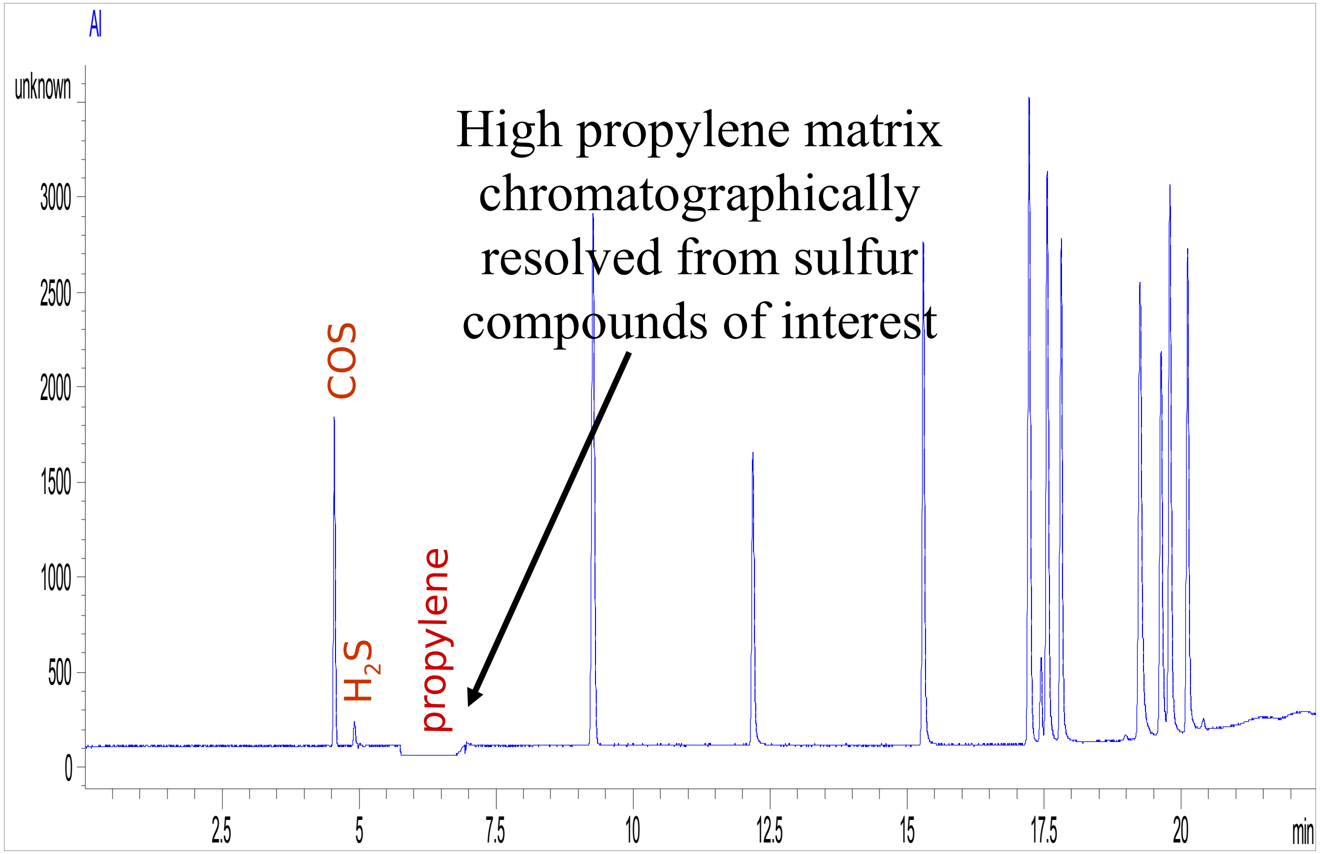
Diesel fuel with 0.15% total sulfur content
1 µL injection; split 250:1.

Reduce Injection Volume



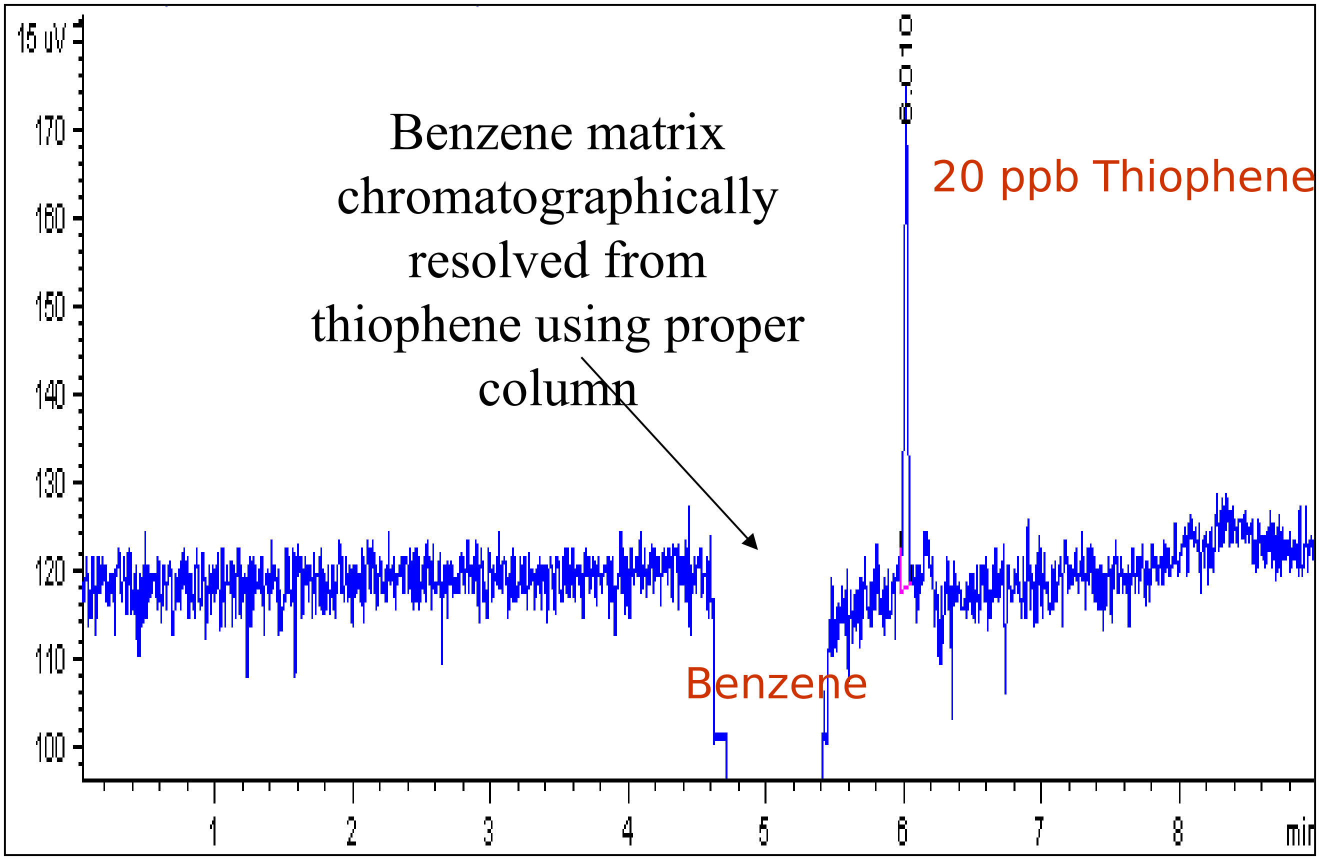
Light cycle oil with 610 ppm total sulfur content
0.3 µL injection; split 100:1.

Adjust Chromatography



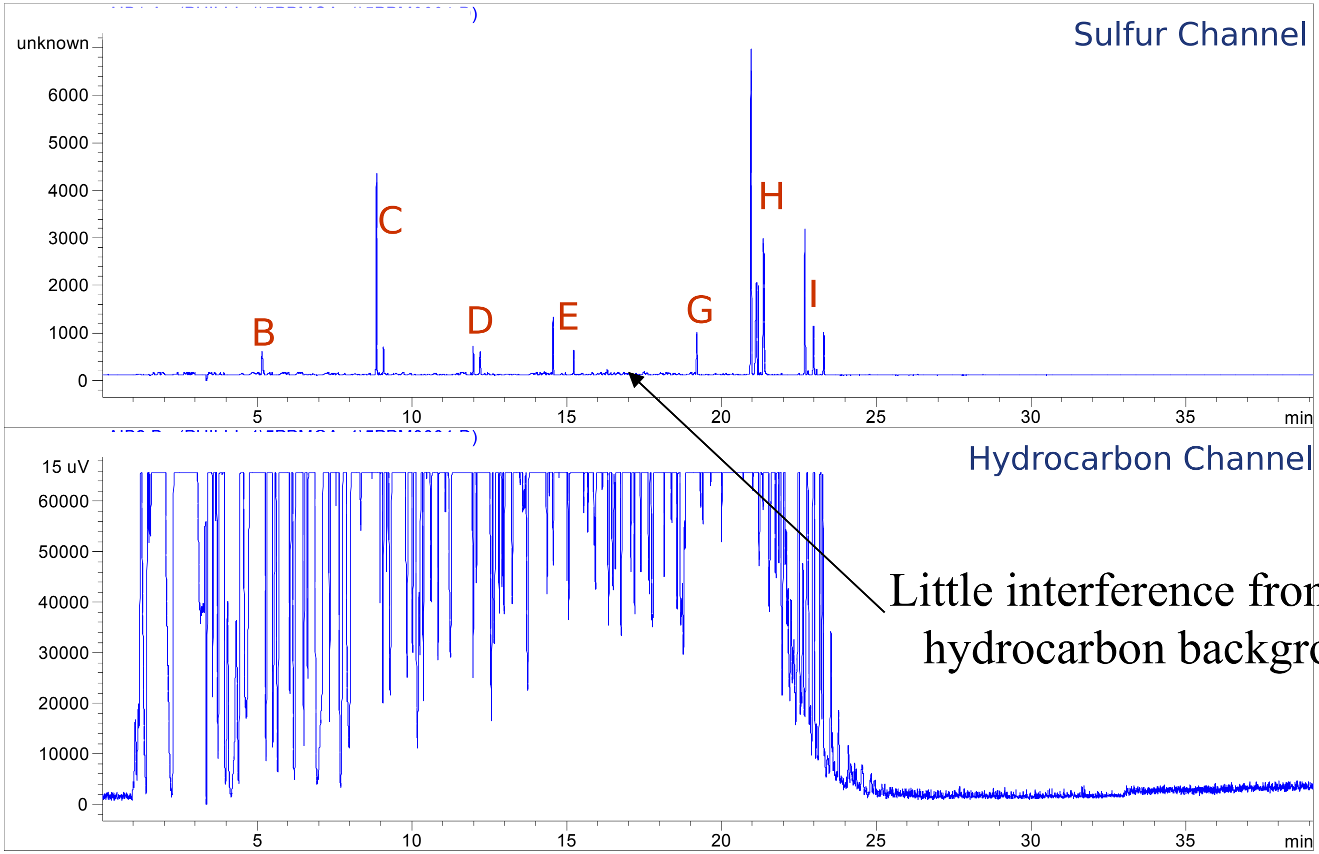
13 sulfur compounds in propylene at 1 ppm each

Adjust Chromatography



1 μL injection; split 3:1; DB-WAX column.

Adjust PFPD Conditions



Little interference from high hydrocarbon background

Gasoline with 5 ppm total sulfur content
1 μL injection; split 10:1.

End of Part 4