Sulfur Detection at ppb Levels in Light Hydrocarbon Streams

Based on a New Super Permeable PLOT Column

Agilent Select Low Sulfur

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Sulfur compounds in refinery streams

Boiling point range of the feedstock determines presence type of sulfurs

- **H_2S**
- **COS**
- **Mercaptans**
- **Thiophenes**
- **Disulfides**
- **Sulfides**

Sulfur compounds even at < 100ppb level

- Poison Ziegler-Natta, Metallocene catalysts
- Drastically reduce the polymer yield of polyolefin feeds

Propylene, polypropylene

Sources of Propylene for polypropylene feed

- Refinery Fluidized Catalytic Cracking (FCC) byproduct
- Ethylene Cracking Furnaces, byproduct of ethylene production
- Propane catalytic dehydration

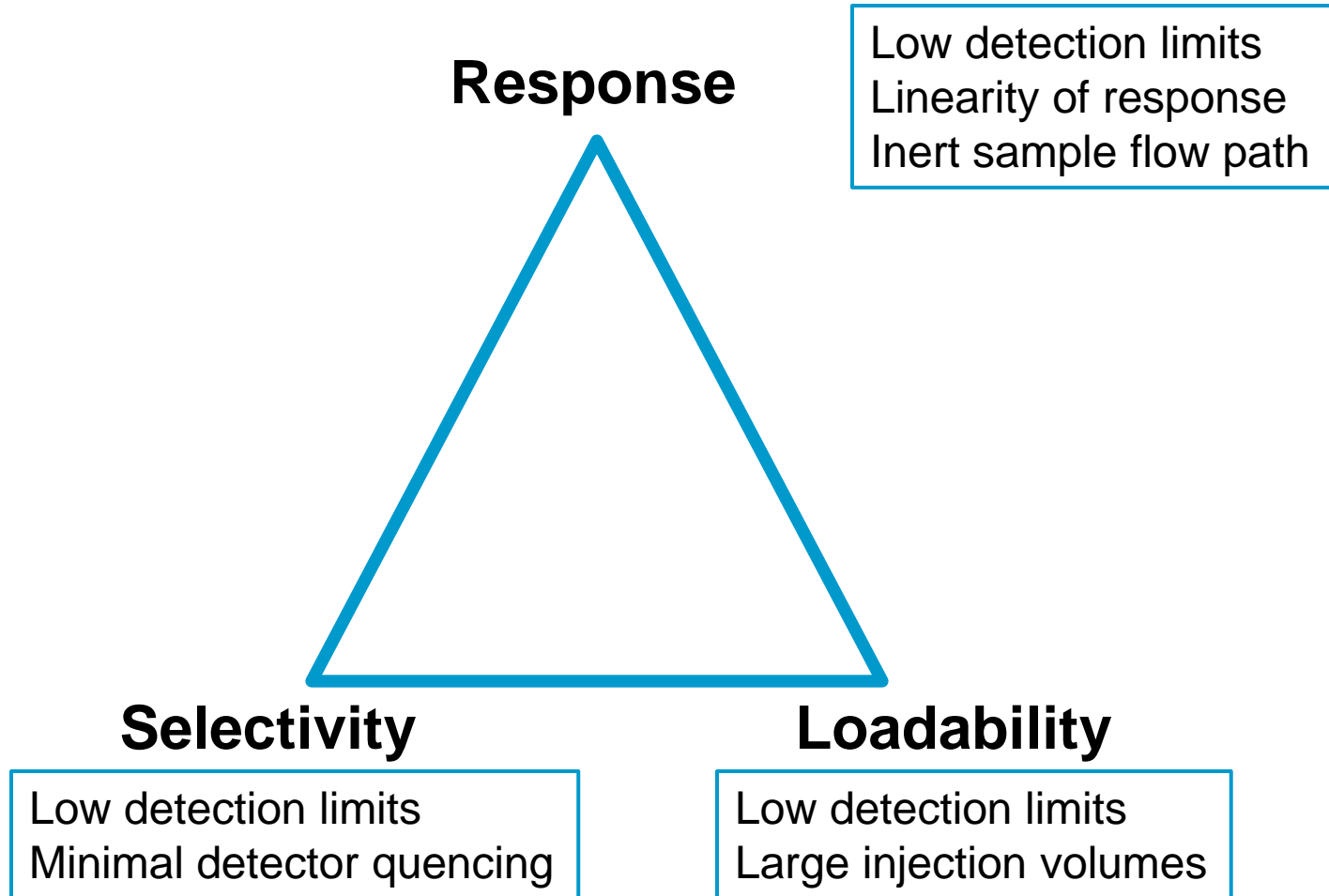Refinery FCC byproduct is by far the largest source

Ethylene, Propylene Matrix

Low ppb level detection of H2S, COS, Mercaptanes

The major challenges:

- Absorption of H2S and mercaptanes on active surfaces
  - Stability of calibration standards
  - Sample introduction path
  - Possible GC column absorption

- Sensitive sulfur specific detection required
  - Pulsed Flame Photometric Detector (PFPD)
  - Sulfur Chemiluminescence Detector (SCD)
  - Atomic Emission Detector (AED), limited sensitivity
  - Quenching due to co-eluting hydrocarbon species, matrix
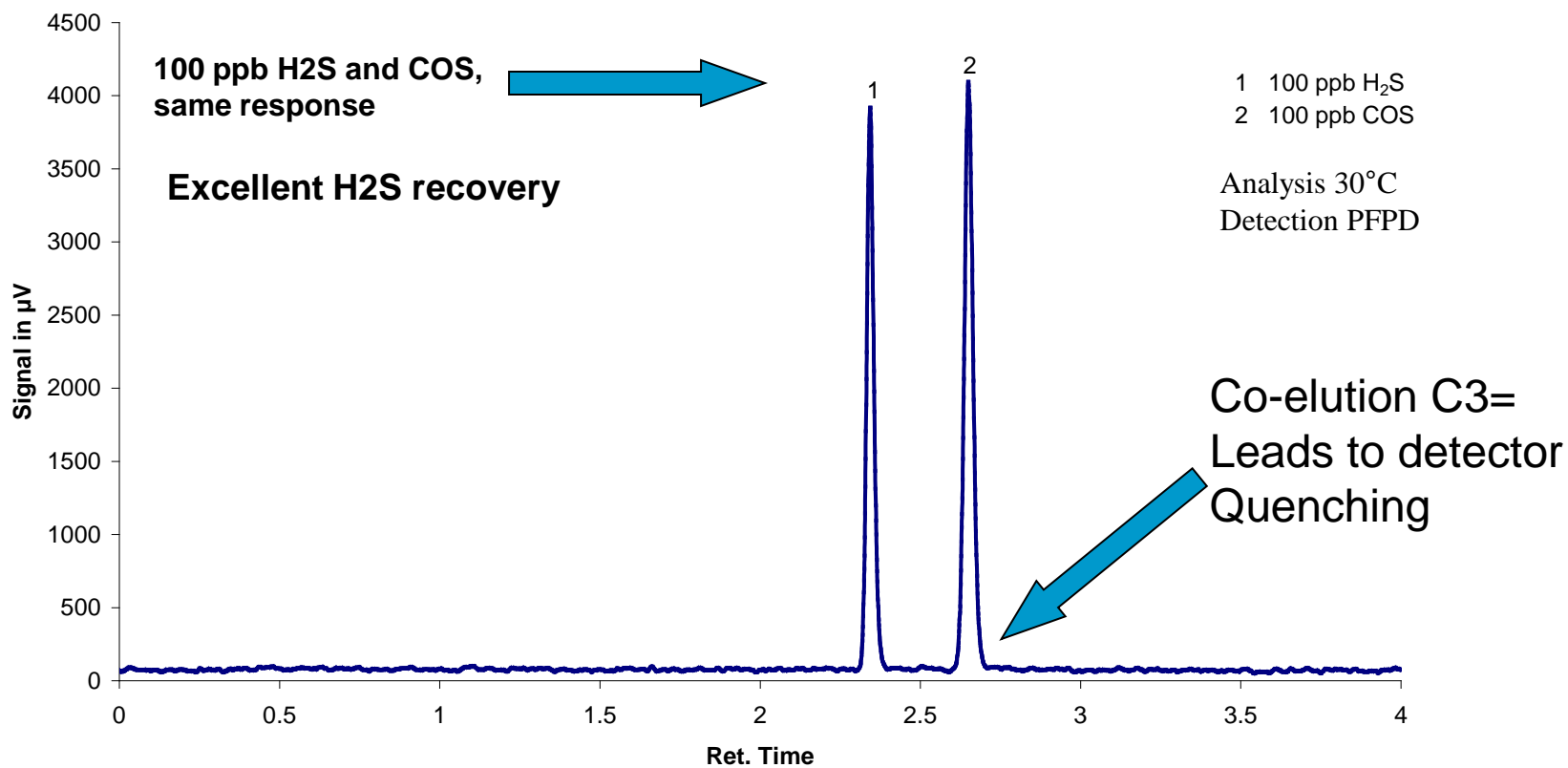
What is needed of GC column for Sulfur Analysis?

Response

Low detection limits
Linearity of response
Inert sample flow path

Selectivity

Low detection limits
Minimal detector quencing

Loadability

Low detection limits
Large injection volumes

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Requirements GC Columns for Sulfurs

Which columns are available?

Excellent H2S response, poor selectivity

PDMS , 30m x 0.32mm x 5μm

100 ppb H2S and COS, same response

Excellent H2S recovery

1 100 ppb H_2S
2 100 ppb COS

Analysis 30°C
Detection PFPD

Co-elution C3=
Leads to detector
Quenching

Excellent selectivity, poor response

Porous Silica 30m x 0.32mm

1. 100 ppb COS
2. 100 ppb H2S
3. Propane (matrix)
4. Methylmercaptane

Analysis 100°C
Detection PFPD

< 60% H₂S recovery
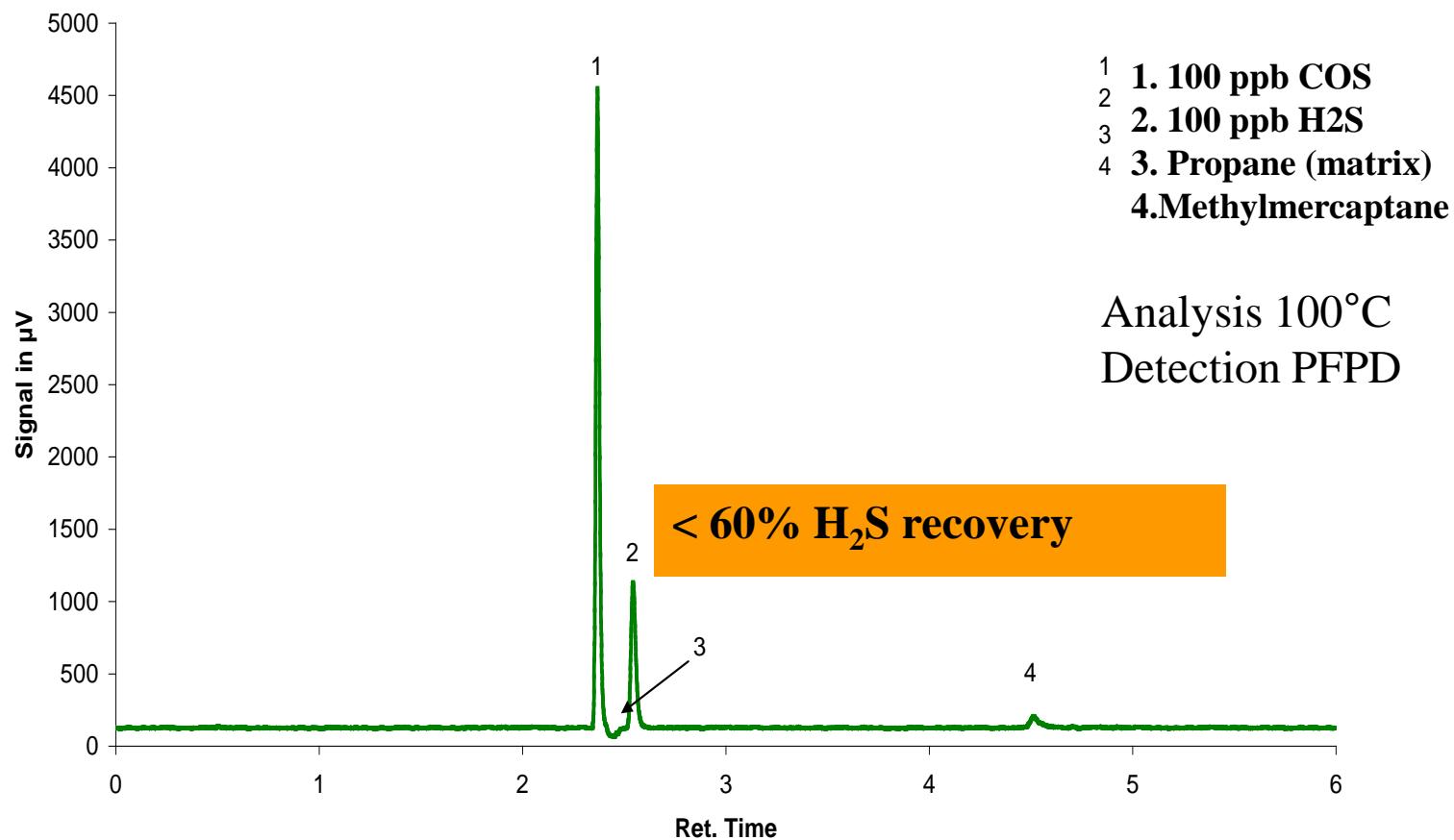
Current GC column materials for H$_2$S/COS

Non-Polar Liquid Phase, PolyDimethylSiloxanes, Thick film 5µm

- Highly inert column with excellent H$_2$S responses
- Not selective, COS/propylene co-elutes, detector quenching

Porous polymer PLOT columns

- Absorption of H2S at low ppm levels
- H2S/COS and propylene well separated

Porous Silica, PLOT columns

- COS/ethylene,propylene well separated
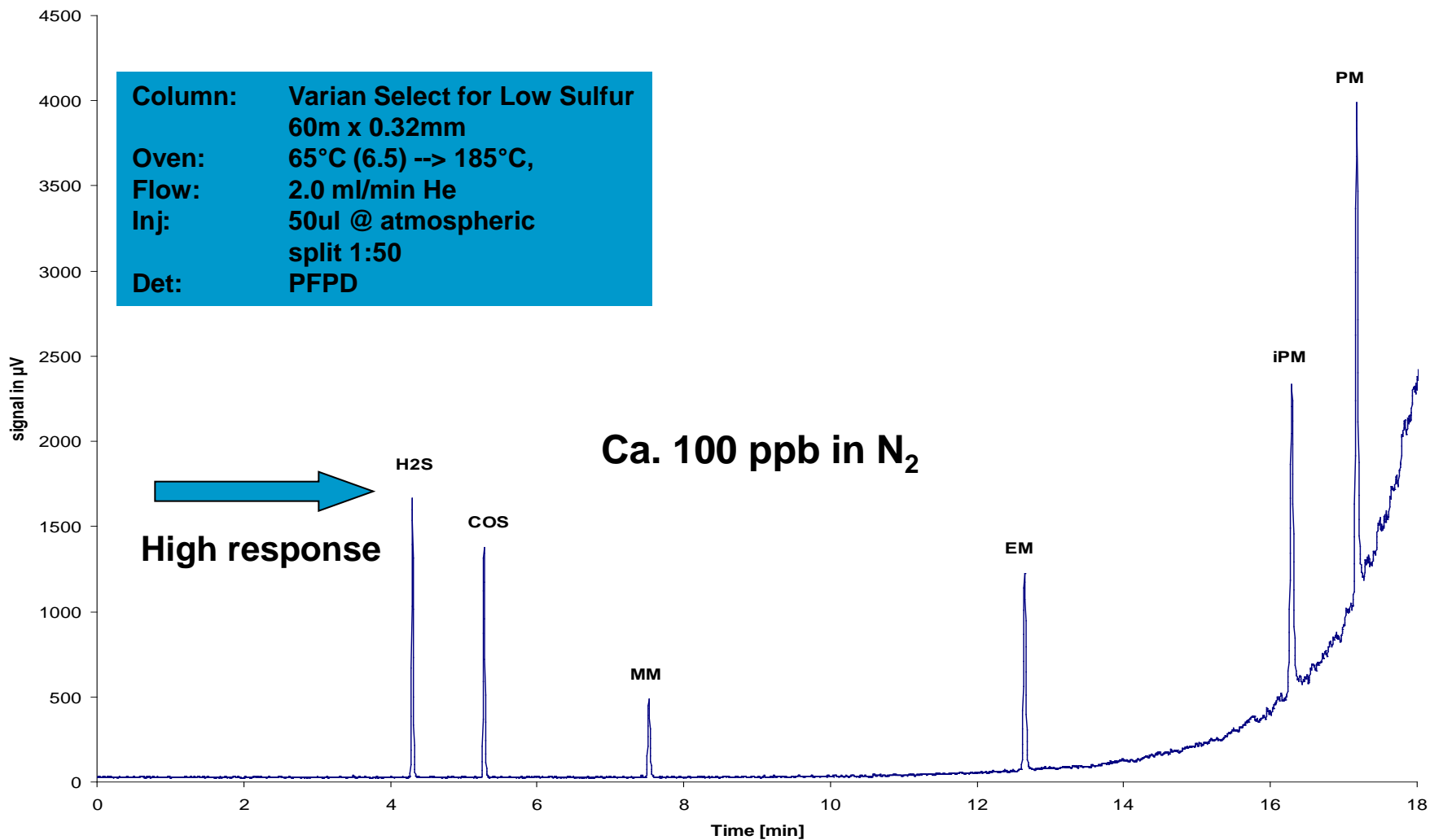- H2S/ethylene, propylene well separated
- Absorption of H2S at low ppb levels

All these columns either exhibit a poor selectivity or a poor H2S response
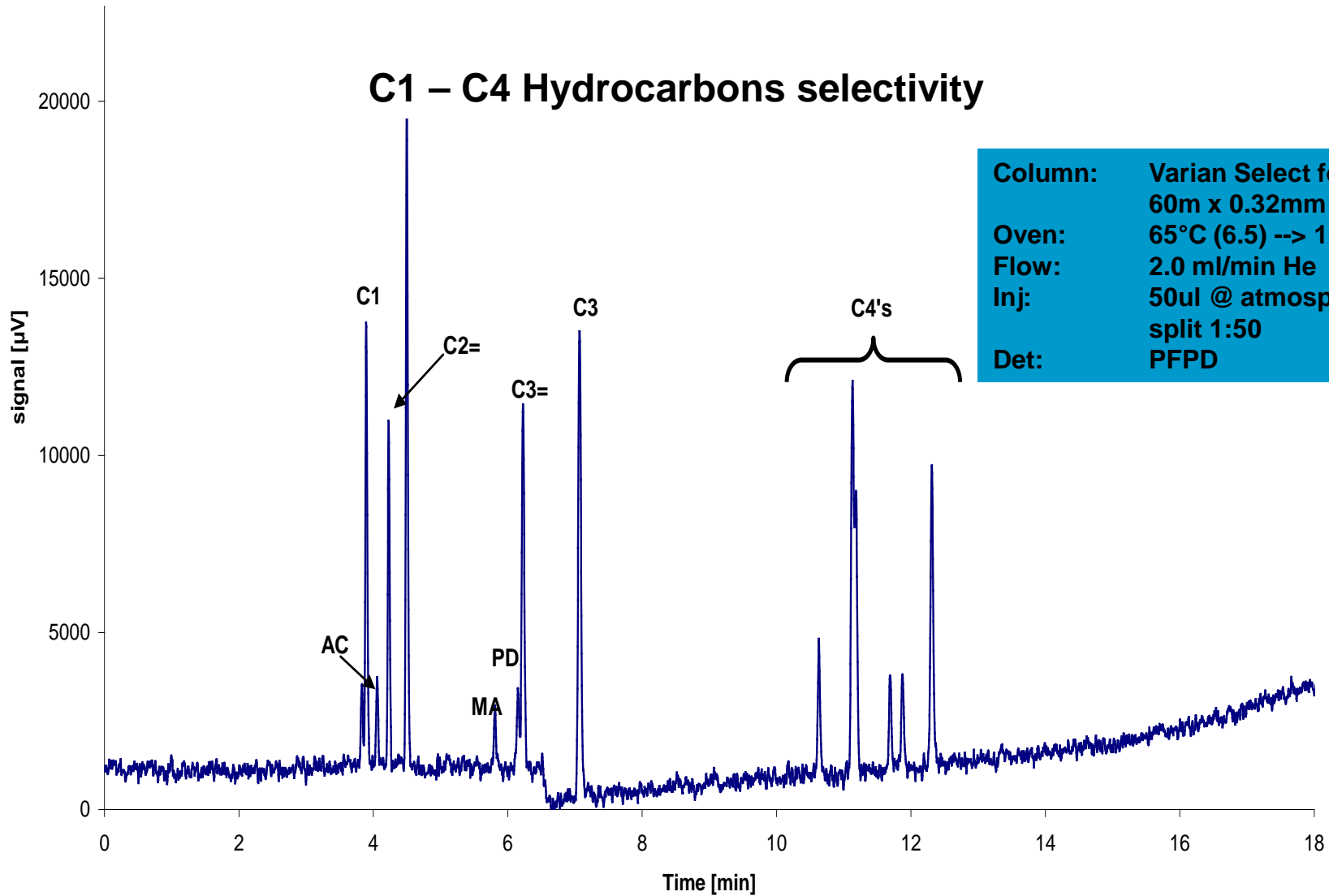
Agilent J&W Select for Low Sulfur

Agilent J&W Select for Low Sulfur

- Near 100% recovery for H_2S at ppb levels
- Excellent sulfur selectivity for propylene matrices
- Excellent prospects for ethylene matrices
- PFPD, SCD, AED Compatible

- Porous Layer Open Tubelar (PLOT) column
- Super Permeable & Porous Stationary Phase
  - proprietary material
- Zero particle loss
- Dimension 60m x 0.32mm

Varian Select for Low Sulfur

Column: Varian Select for Low Sulfur
           60m x 0.32mm
Oven: 65°C (6.5) --> 185°C,
Flow: 2.0 ml/min He
Inj: 50ul @ atmospheric
           split 1:50
Det: PFPD

Ca. 100 ppb in N_2

High response

Peaks: H2S, COS, MM, EM, iPM, PM

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Hydrocarbon elution profile on Select for Low Sulfur

C1 – C4 Hydrocarbons selectivity

Column:	Varian Select for Low Sulfur
	60m x 0.32mm
Oven:	65°C (6.5) --> 185°C,
Flow:	2.0 ml/min He
Inj:	50ul @ atmospheric
	split 1:50
Det:	PFPD

Sulfurs & HC's on Select Low Sulfur

Select Low Sulfur - 60m*0.32mm
Overlay of H$_2$S, COS and Methyl mercaptan with hydrocarbons

Conditions:

Column:	Select Low Sulfur, 60m x 0.32mm
Temperature:	65°C
Carrier Gas:	Helium, constant flow 2 mL/min
Injector:	200°C
Detector:	PFPD
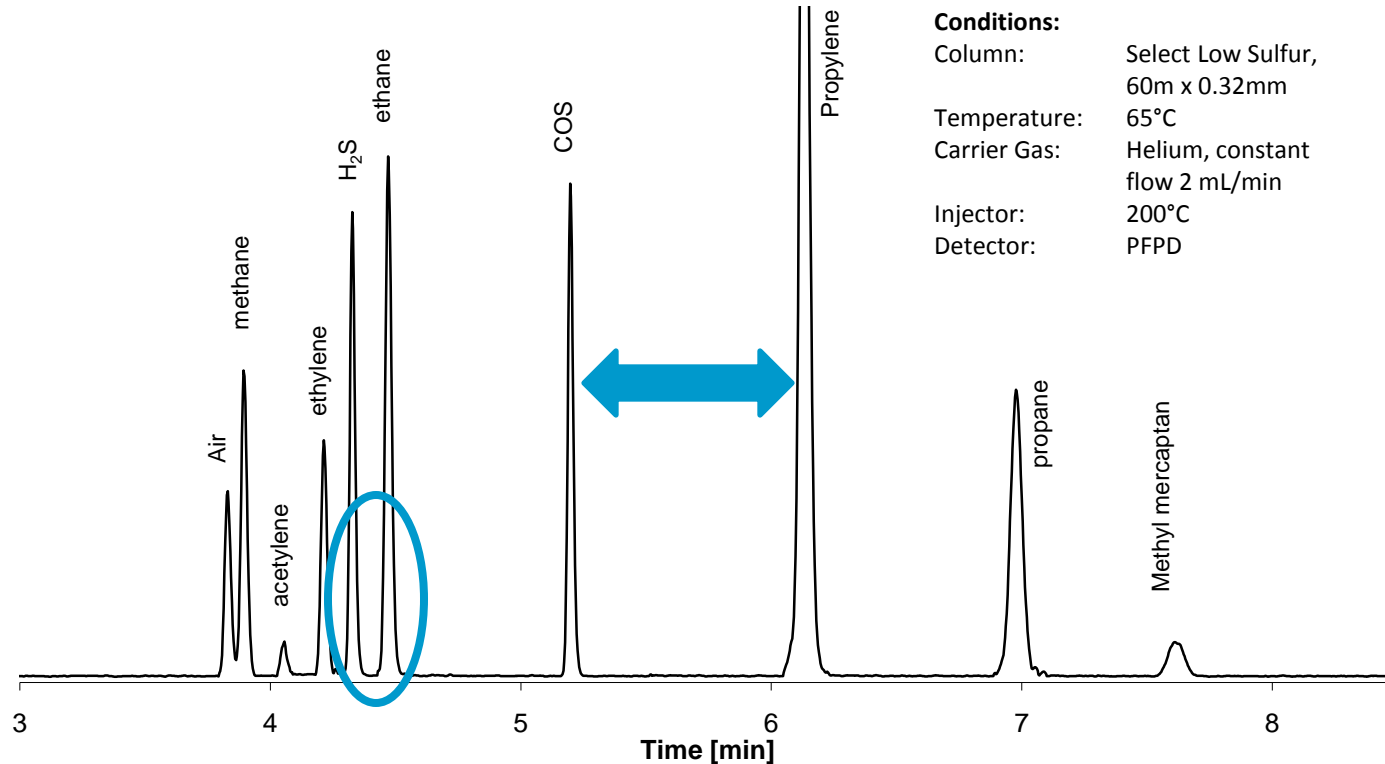
Excellent separation COS/Propylene

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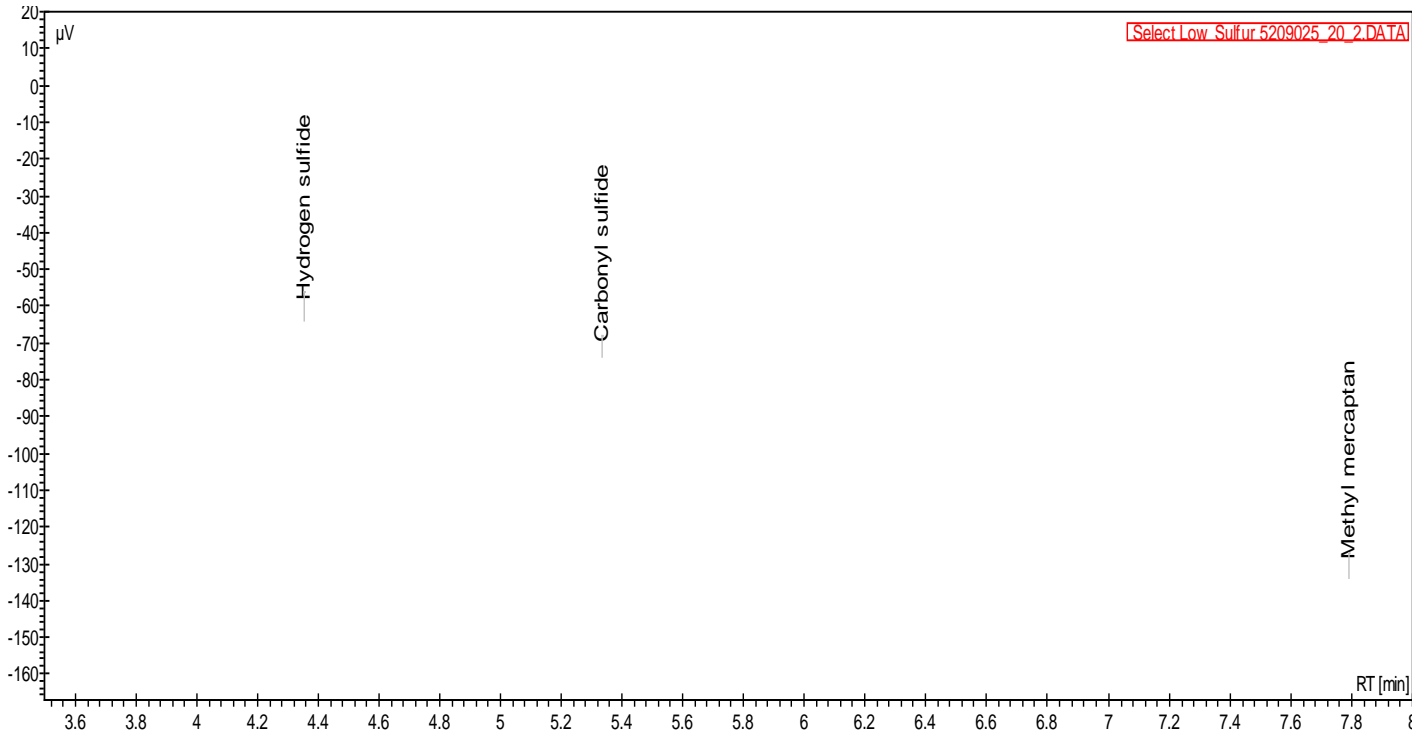
Column Selectivity & Loadability

H$_2$S, COS and Methyl mercaptan in Propylene matrix
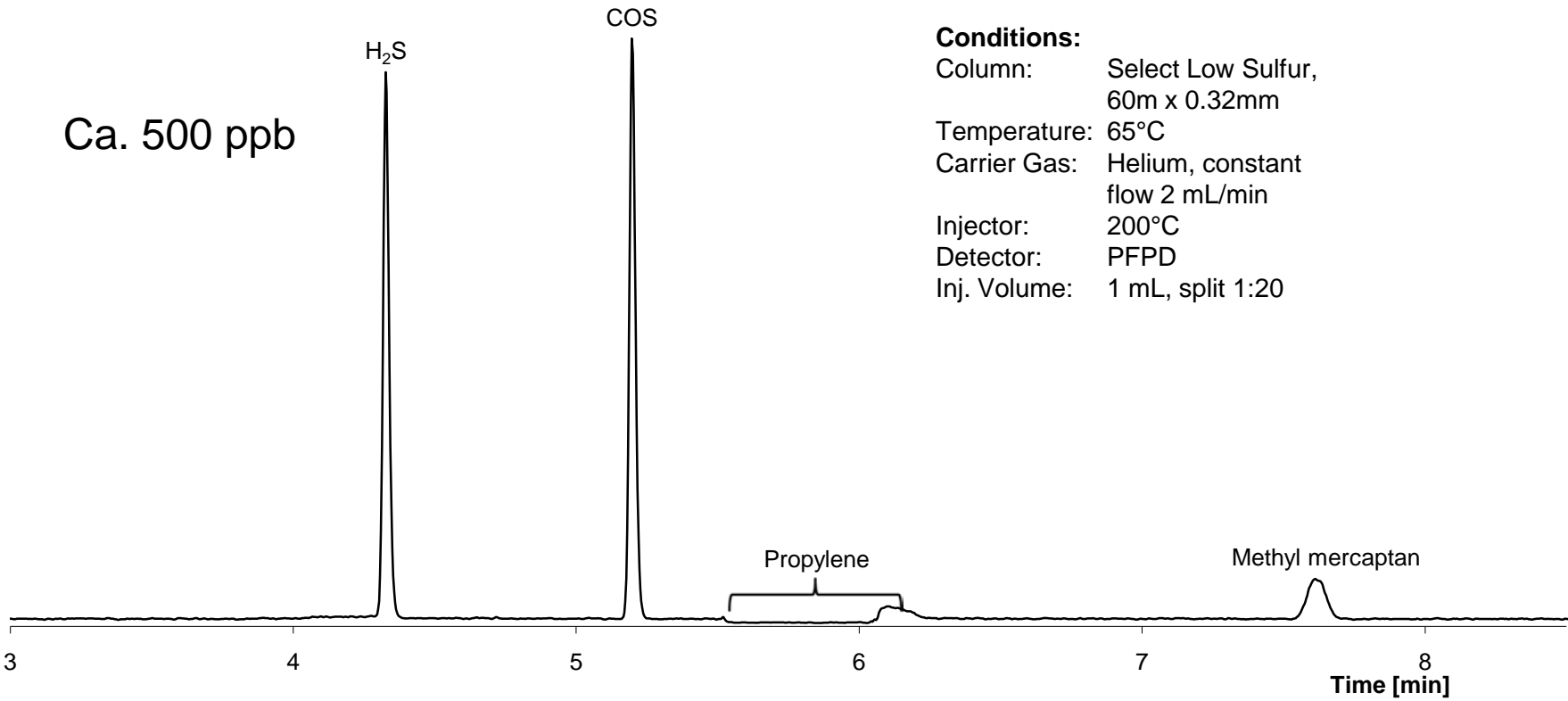
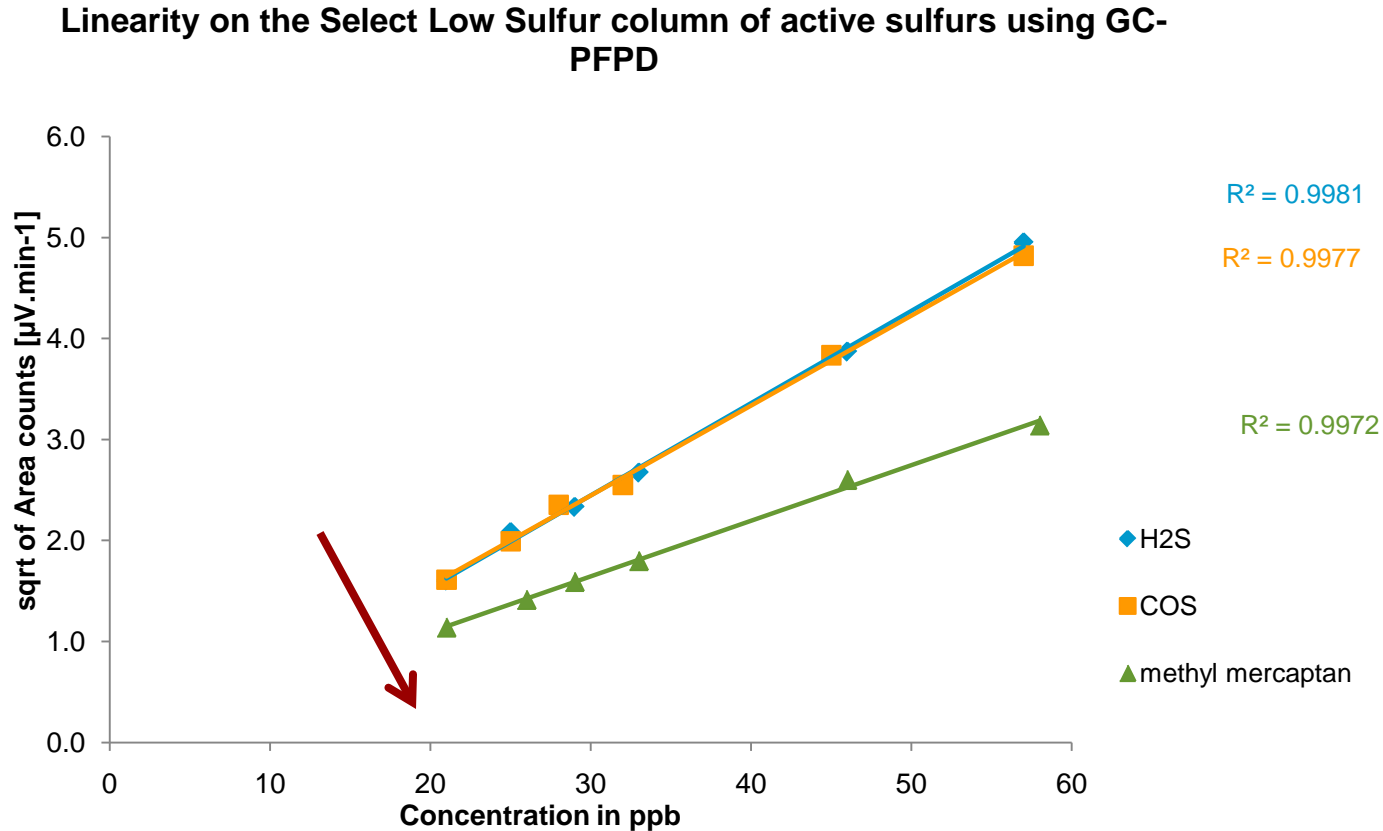Ca. 500 ppb

Conditions:
Column: Select Low Sulfur,
               60m x 0.32mm
Temperature: 65°C
Carrier Gas: Helium, constant
               flow 2 mL/min
Injector: 200°C
Detector: PFPD
Inj. Volume: 1 mL, split 1:20

Low PPB Sulfur Levels

Chromatogram of H$_2$S with calculated ppb concentration of 21 ppb:

Linearity on Select Low Sulfur
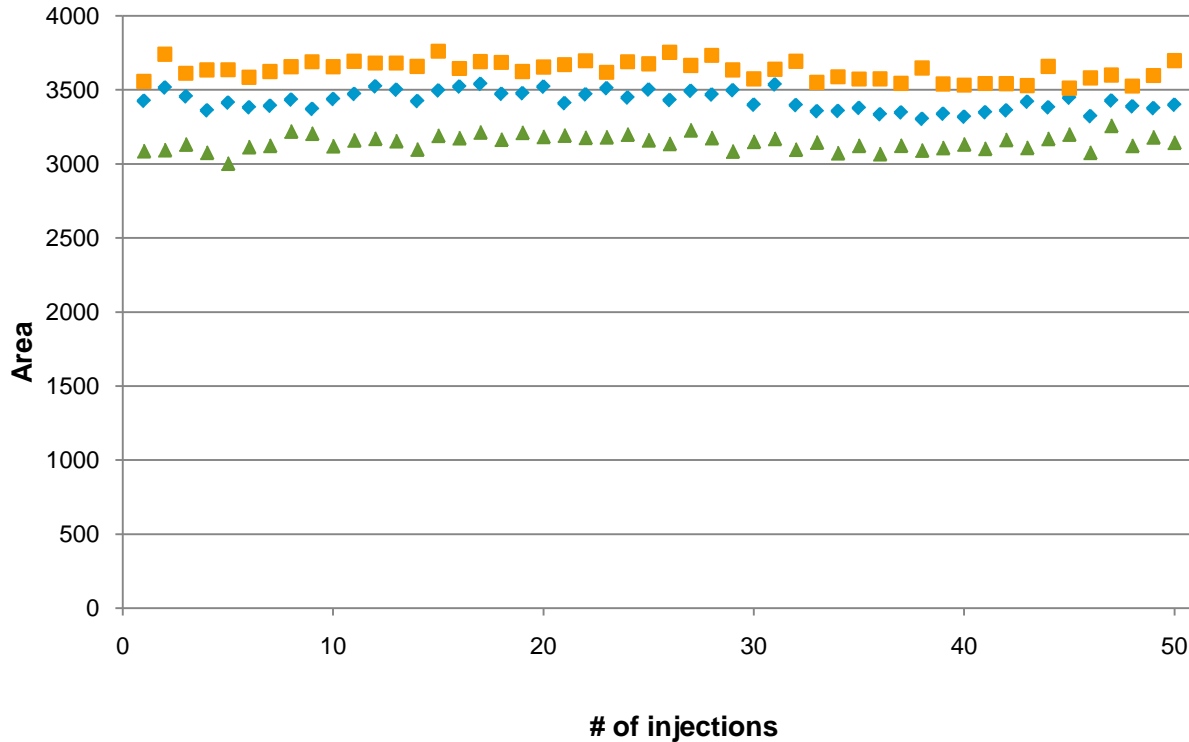
Linearity on the Select Low Sulfur column of active sulfurs using GC-PFPD

Sample: gas mixture of H_2S (11.4 ppm), COS (11.3 ppm) and MM (11.6 ppm) in N2.
Sample loop: 1 ml, Variable split ratio's (1:40 – 1:110)

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Repeatabilty on SCD

H2S, COS and MM on Select Low Sulfur using SCD

60 pg on column

Legend:
- ◆ H2S
- ■ COS
- ▲ Methyl mercaptan

	Average area	st dev Area	% RSD
H2S	3426	65	1.9%
COS	3631	65	1.8%
MM	3146	50	1.6%
recovery	94%		

Conditions:
Column: Select Low Sulfur, 60m x 0.32mm
Temperature: 50°C for 8 minutes, with °C/min to 185°C for 10 minutes
Carrier Gas: Helium, constant flow 2 mL/min
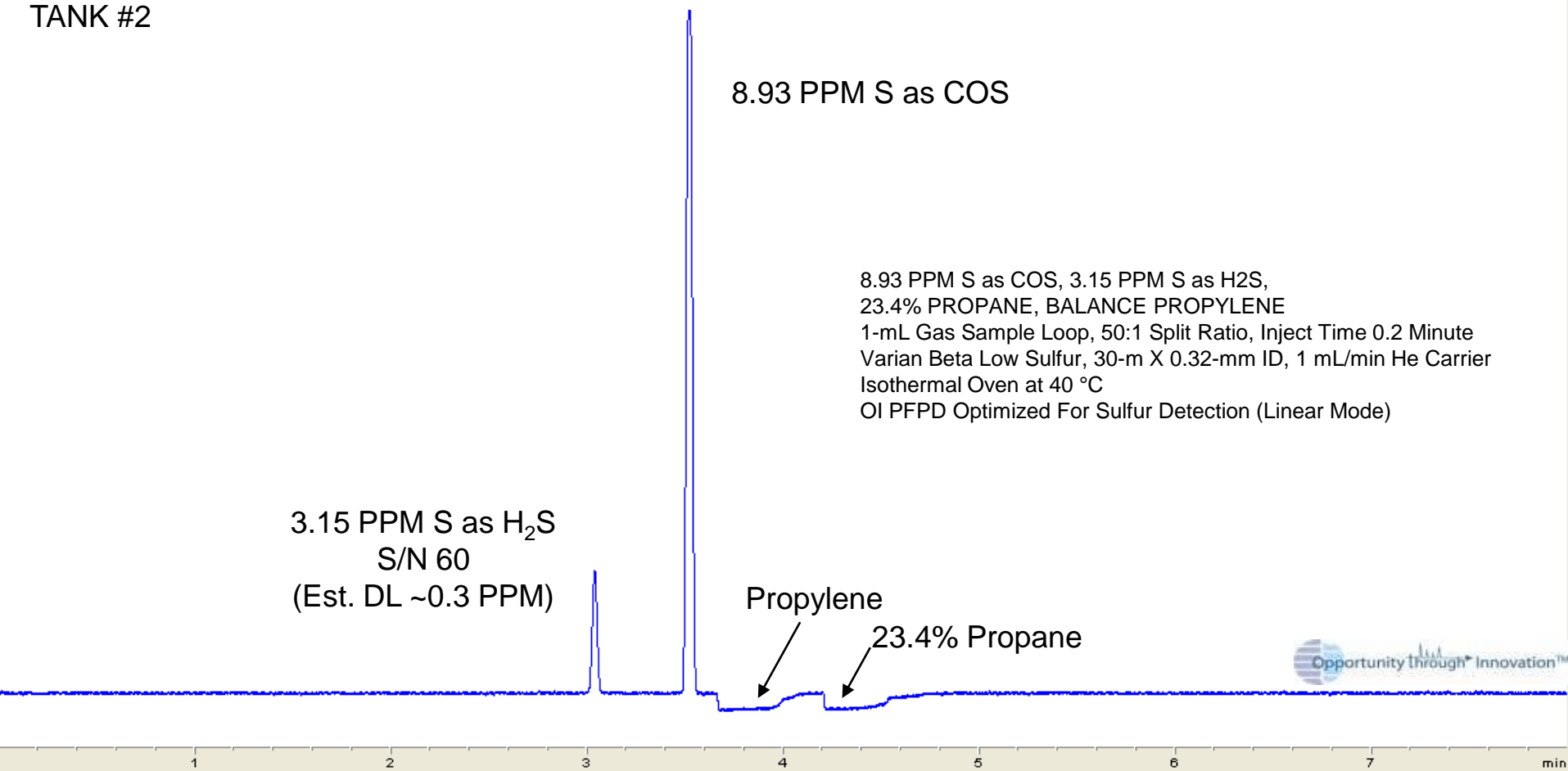Injector: 200°C
Detector: SCD, base temperature 200°C, burner temperature 800°C, oxidizer 65 mL/min, hydrogen 40 mL/min
Sample: 250ul, split 1:60, 11 ppm

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Sulfurs in Propane/propylene matrix

TANK #2

8.93 PPM S as COS

8.93 PPM S as COS, 3.15 PPM S as H2S,
23.4% PROPANE, BALANCE PROPYLENE
1-mL Gas Sample Loop, 50:1 Split Ratio, Inject Time 0.2 Minute
Varian Beta Low Sulfur, 30-m X 0.32-mm ID, 1 mL/min He Carrier
Isothermal Oven at 40 °C
OI PFPD Optimized For Sulfur Detection (Linear Mode)

3.15 PPM S as H$_2$S
S/N 60
(Est. DL ~0.3 PPM)

Propylene

23.4% Propane

Opportunity Through Innovation™

Courtesy: Laura Chambers, OI Analytical

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Sulfurs in Ethane/Propane/Propylene matrix

TANK #3

9.93 PPM S as COS

9.93 PPM S as COS, 3.63 PPM S as H2S,
20.7% ETHANE, 1% PROPYLENE, BALANCE PROPANE
1-mL Gas Sample Loop, 50:1 Split Ratio, Inject Time 0.2 Minute
Varian Beta Low Sulfur, 30-m X 0.32-mm ID, 1 mL/min He Carrier
Isothermal Oven at 40 °C
OI PFPD Optimized For Sulfur Detection (Linear Mode)

20.7% Ethane

3.63 PPM S as H$_2$S
S/N 50
(Est. DL ~0.3 PPM)

1% Propylene
Propane

Opportunity Through Innovation™

Courtesy: Laura Chambers, OI Analytical

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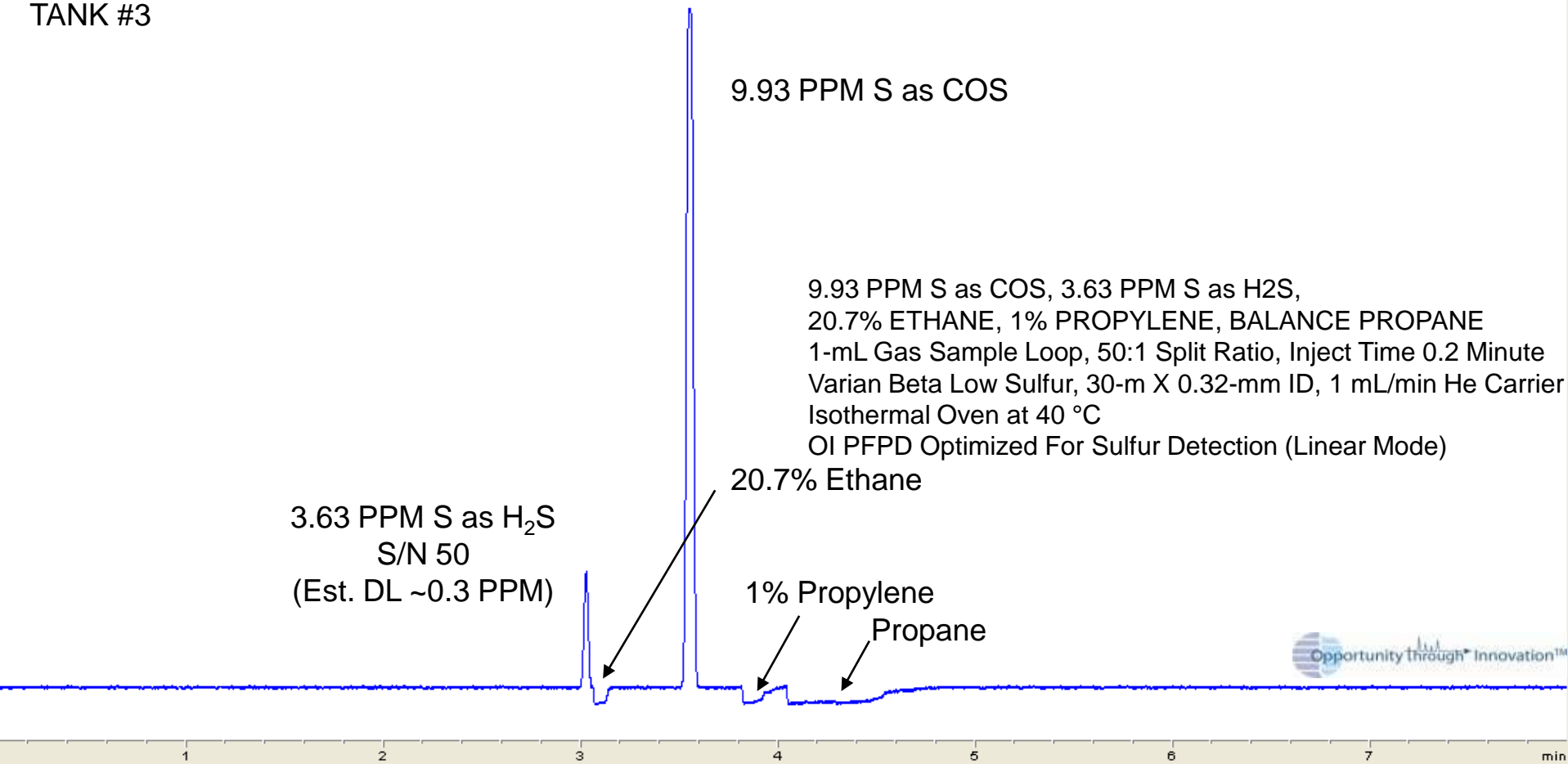
Conclusions

Agilent J&W Select for Low Sulfur

- Linear response H_2S, COS and MM at 20 – 200 ppb level

- One dimension, 60m x 0.32mm

- Best accuracy and repeatability

- Low ppb H_2S detection limits in propylene

- Mechanically stable PLOT column, zero particle loss

- Introduction December 2010, tentative

Acknowledgement

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