



Determination of Sulfur and Nitrogen Distributions for Fuel Processing

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Petroleum Sulfur Source & Issues

- **Heteroatoms present in Crude Oil**
 - Sulfur
 - Nitrogen
 - Oxygen
- **Environmental Issues**
 - tailpipe emissions
- **Refiner Issues**
 - product specifications
 - corrosion
 - catalyst poison

Fuel Regulations Allowable Sulfur

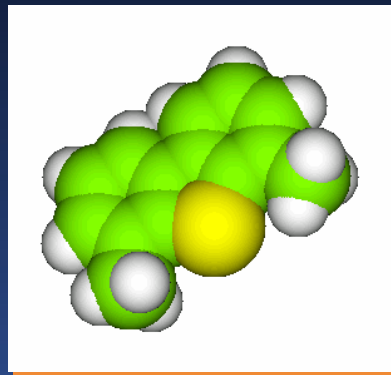
Country & Product	Target level	Year
United States Gasoline	30 ppm	2005
US Diesel	15 ppm	2006
US off-road diesel	500 ppm	2007
	15 ppm	2010
EU Gasoline	50 ppm	2005
EU Diesel	50 ppm	2005

Analytical Characterization Solution

■ GC-AED

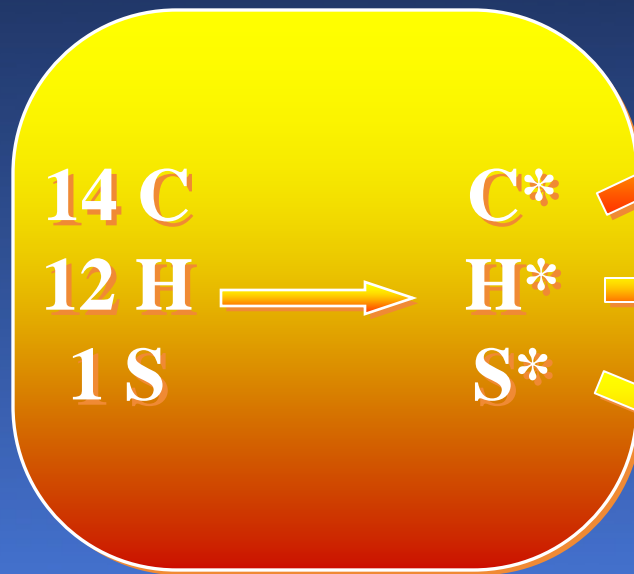
- **Chromatographic column separation of heteroatomic species followed by elemental detection.**

Atomic Emission Detector



GC separation

Helium
Plasma
(~ 24eV)



	179
	193
	248
C	264
	496
	834

	486
H	656

S	181
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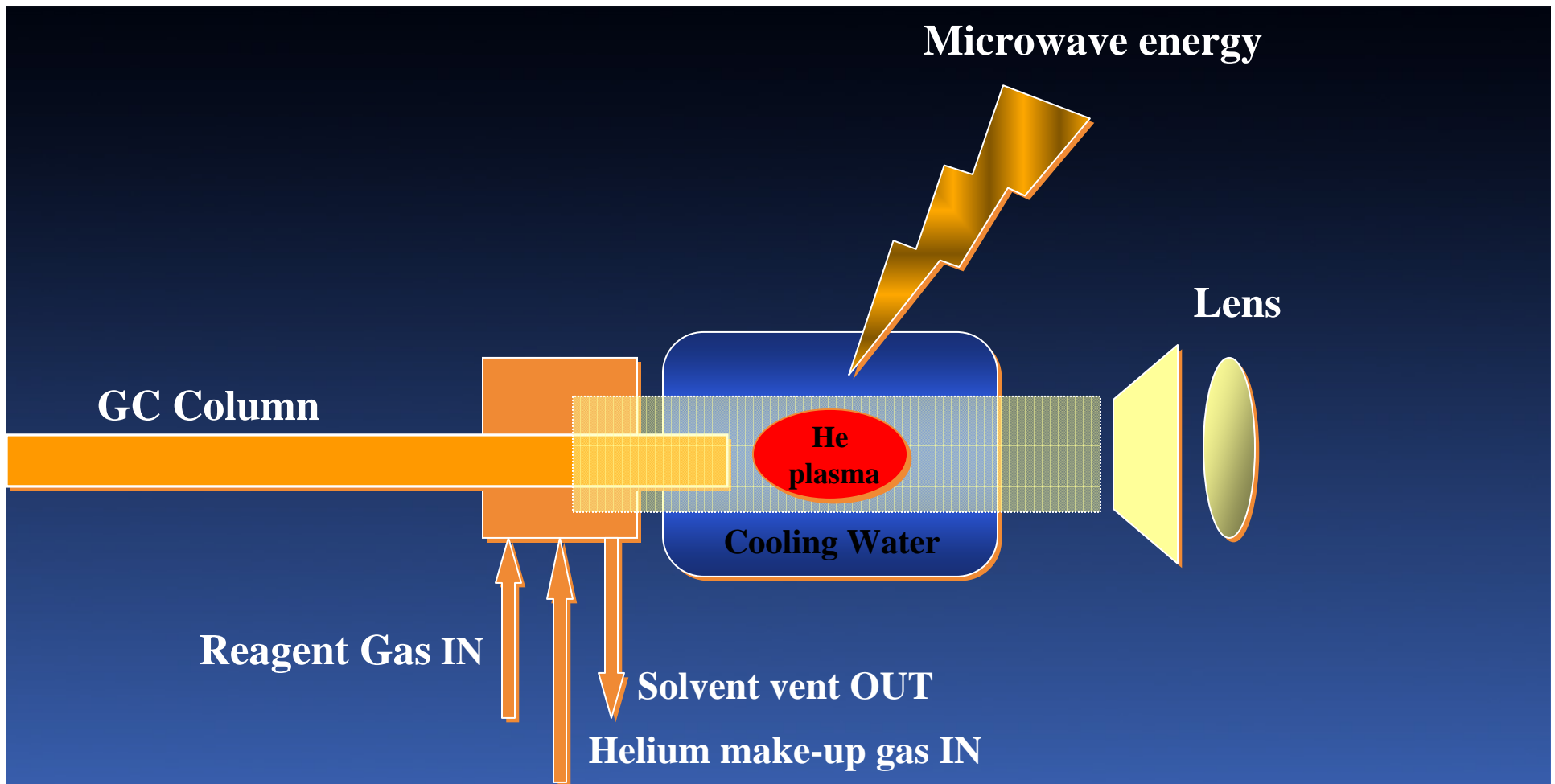
Emission

Atomization

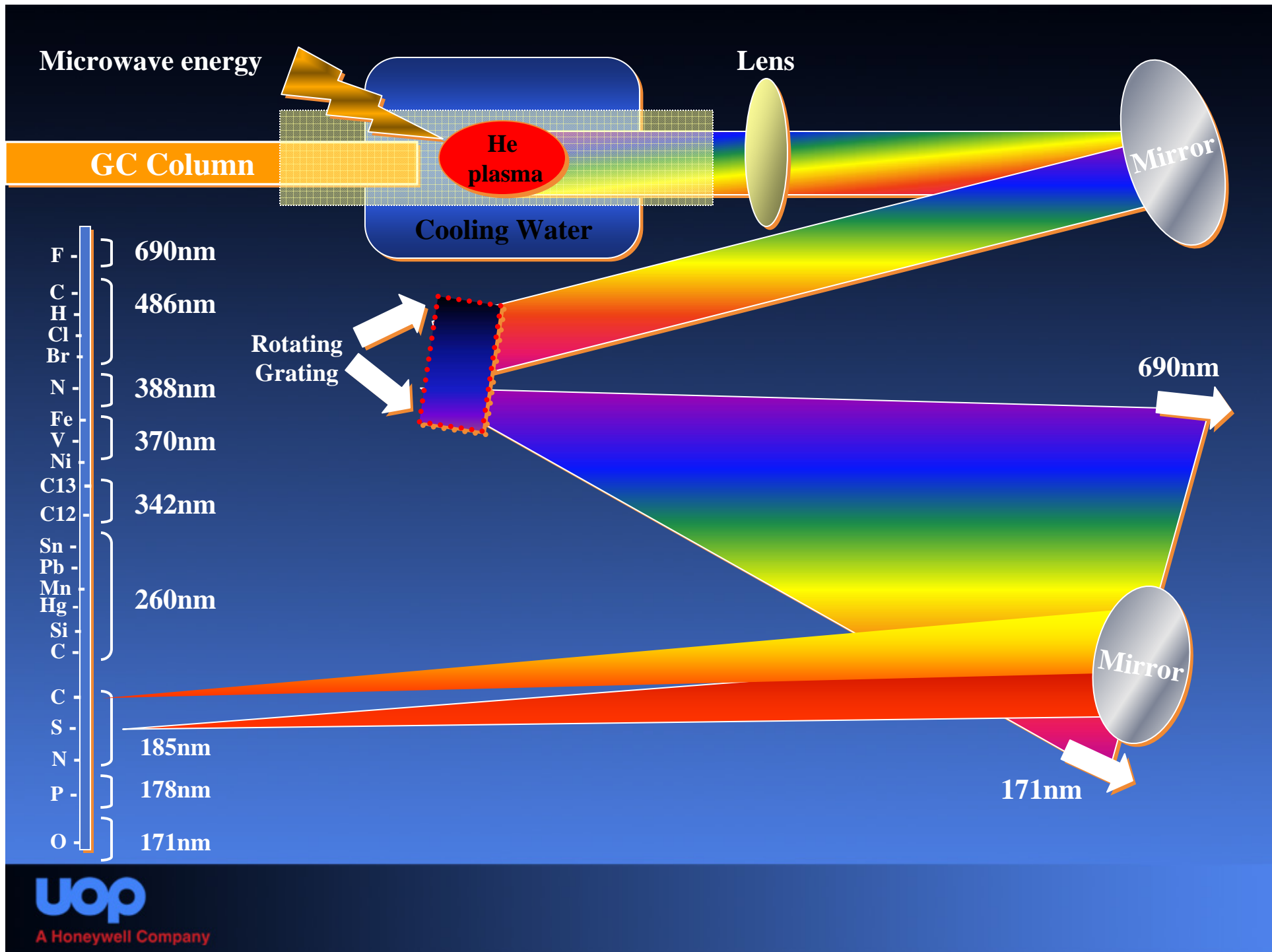
Excitation



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- **Oxygen** - *CO bands for carbon detection - reduce carbon black formation*
- **Hydrogen** - *Decreases discharge tube wall effects*
- **10% CH₃ in N₂** - *CO band for oxygen detection*
- **100 % CH₃** - *CN band for selective nitrogen detection - N 388*





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Case #1

■ Issue

- **Hydroprocessing: Sulfur removed by conversion to hydrogen sulfide (H₂S)**
 - added hydrogen breaks carbon-sulfur bonds & saturates remaining hydrocarbon chains
 - need to link process conditions to sulfur conversion and distribution

■ Analytical Solution

- **GC-AED analysis used to track processing chemistry**

Sulfur Species Reactivity

Sulfur Species

Thiophenes

Benzothiophenes

Non-Thiophenes

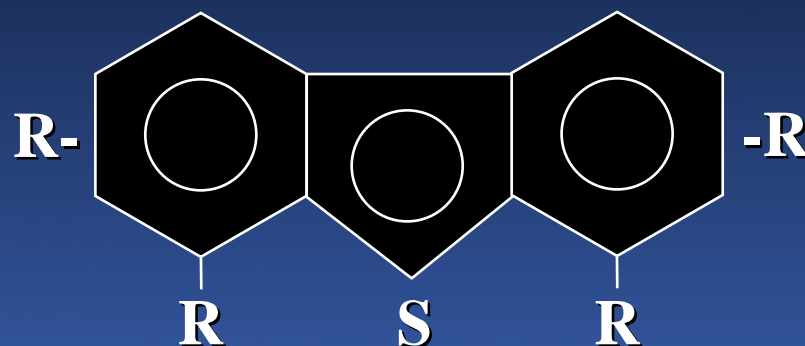
Dibenzothiophenes

Mono-Beta-Dibenzothiophenes

Di-Beta-Dibenzothiophenes

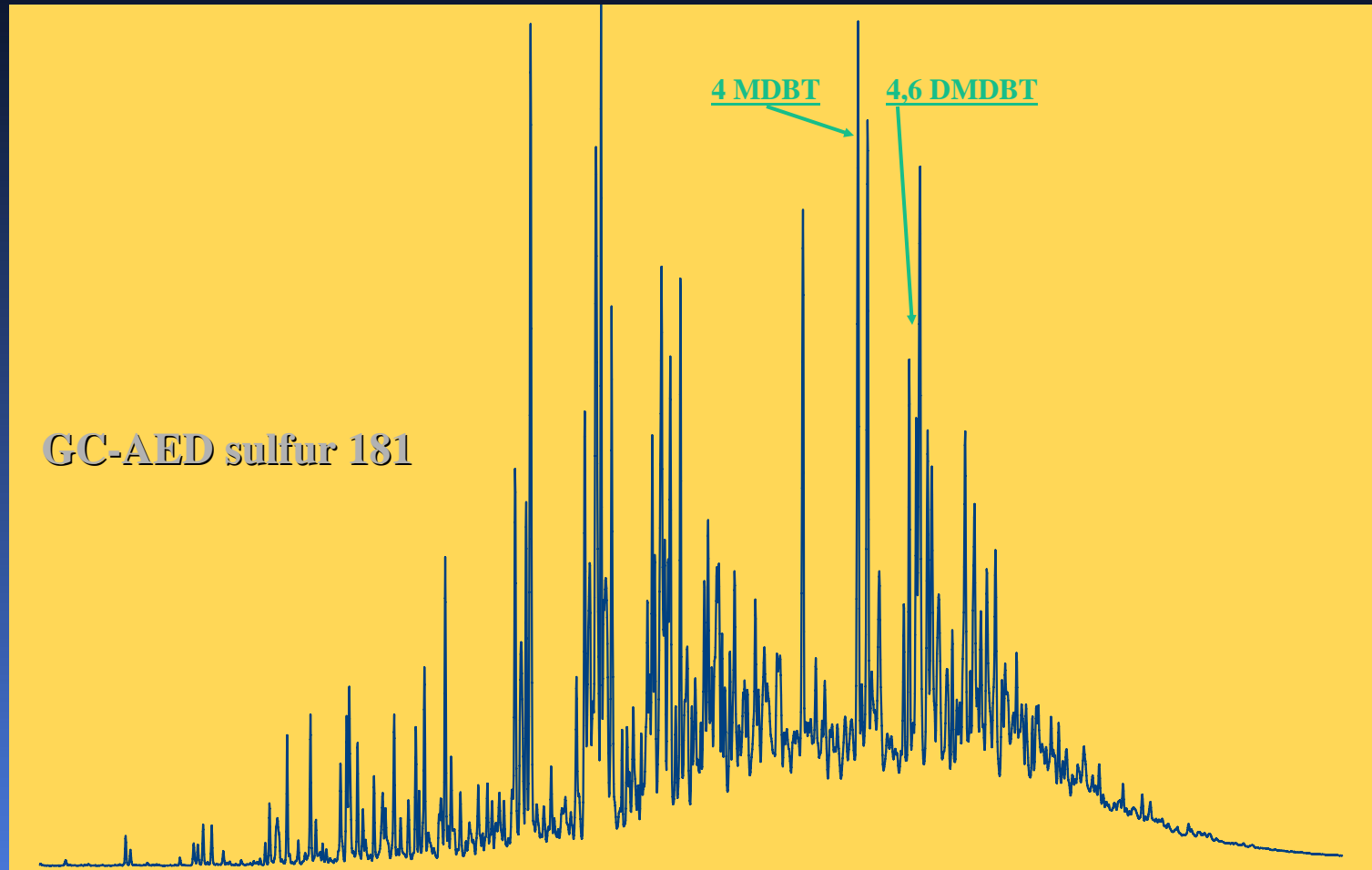
Reactivity

Most Difficult Species



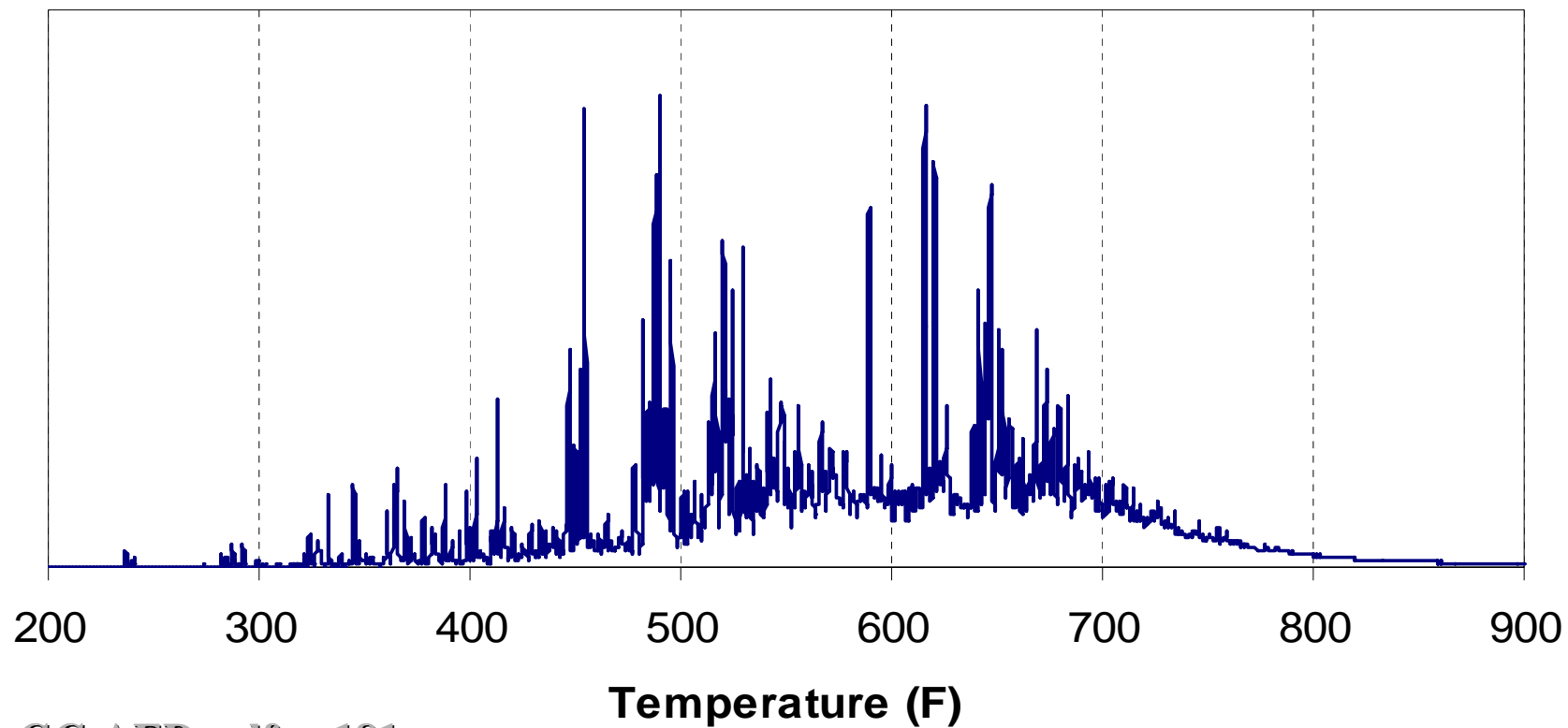
*Beta substituted-Dibenzothiophene
Family*

High Sulfur Feed



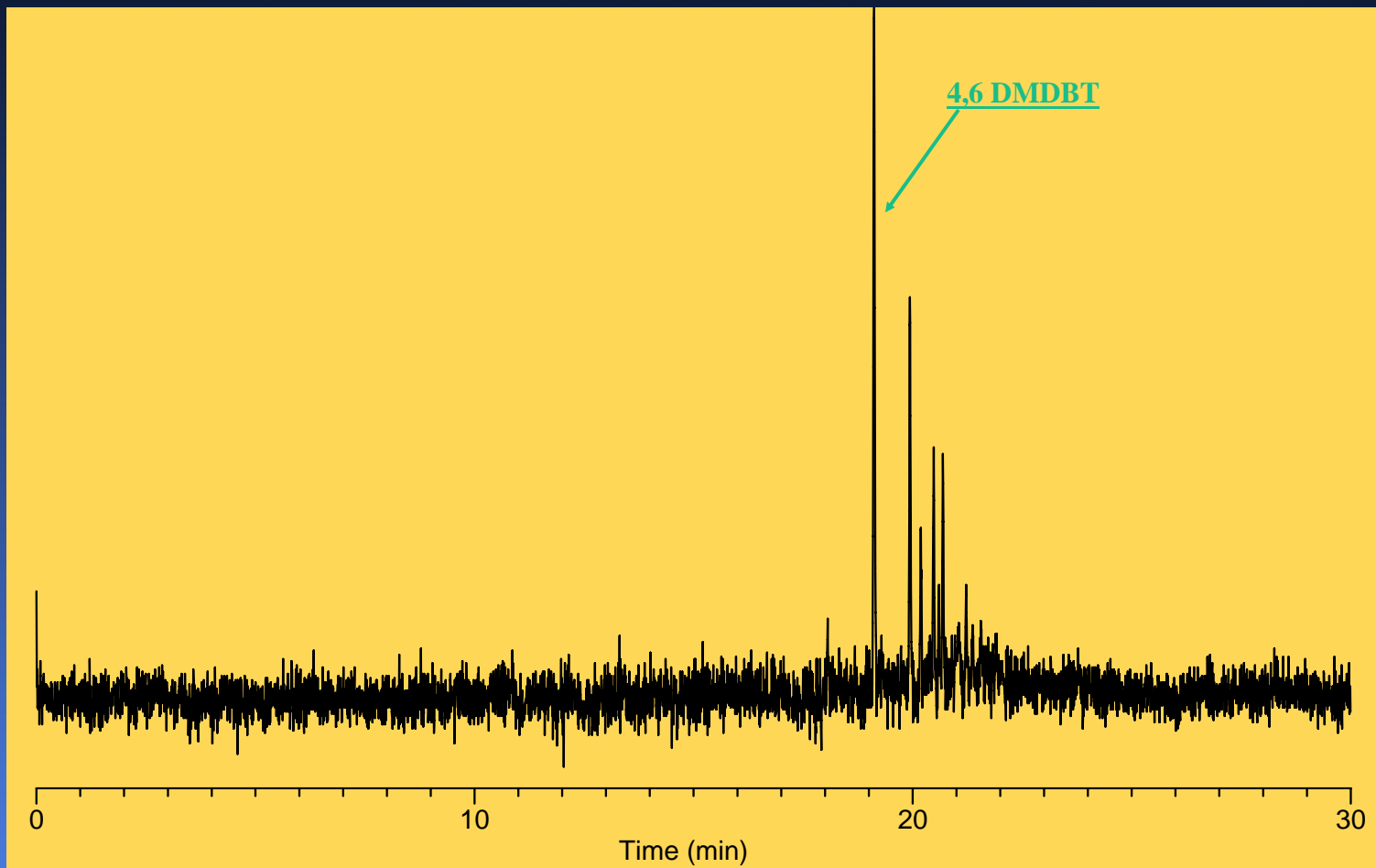
High Sulfur Feed

Sulfur 181



GC-AED sulfur 181

ULSD



Case #2

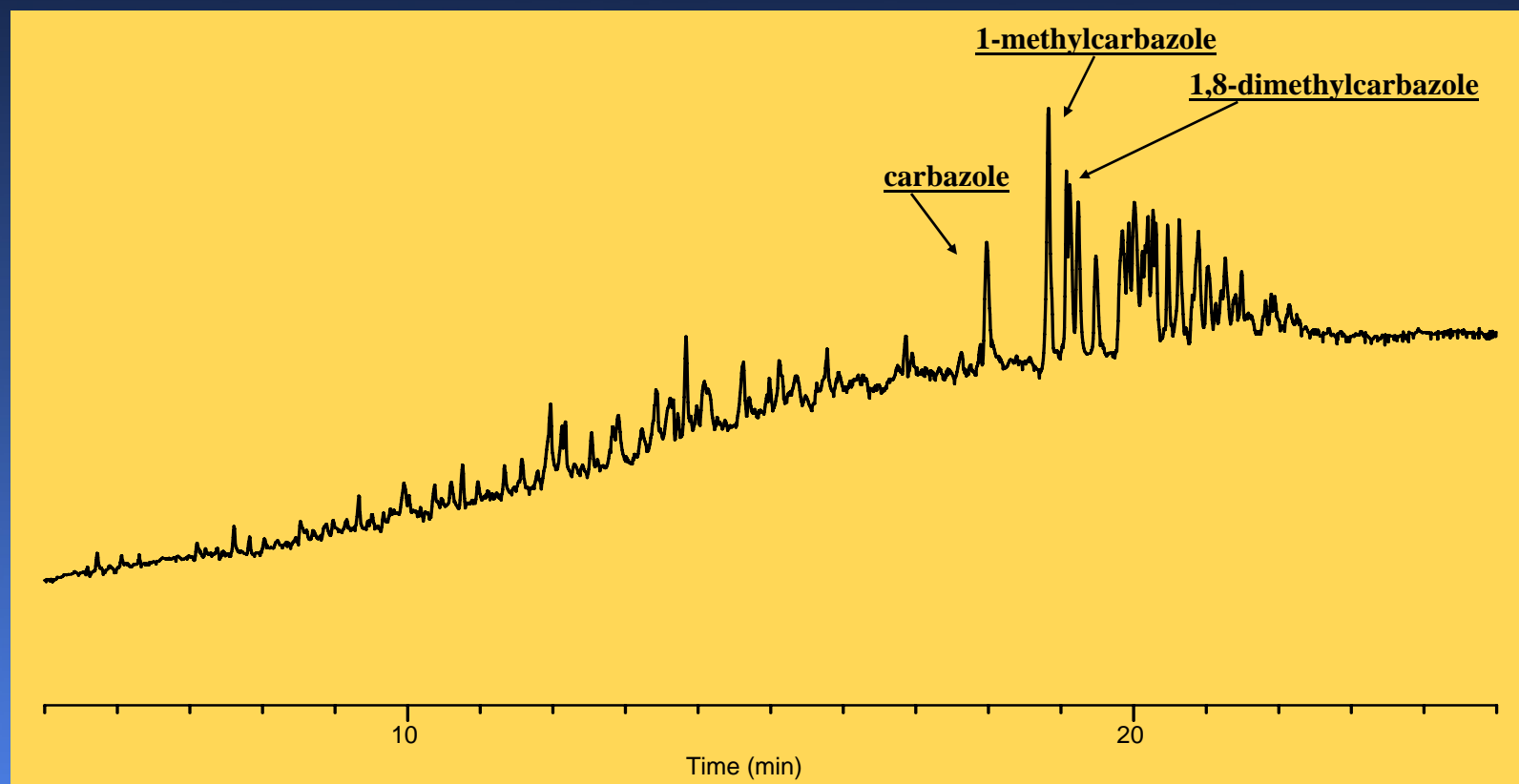
■ Issue

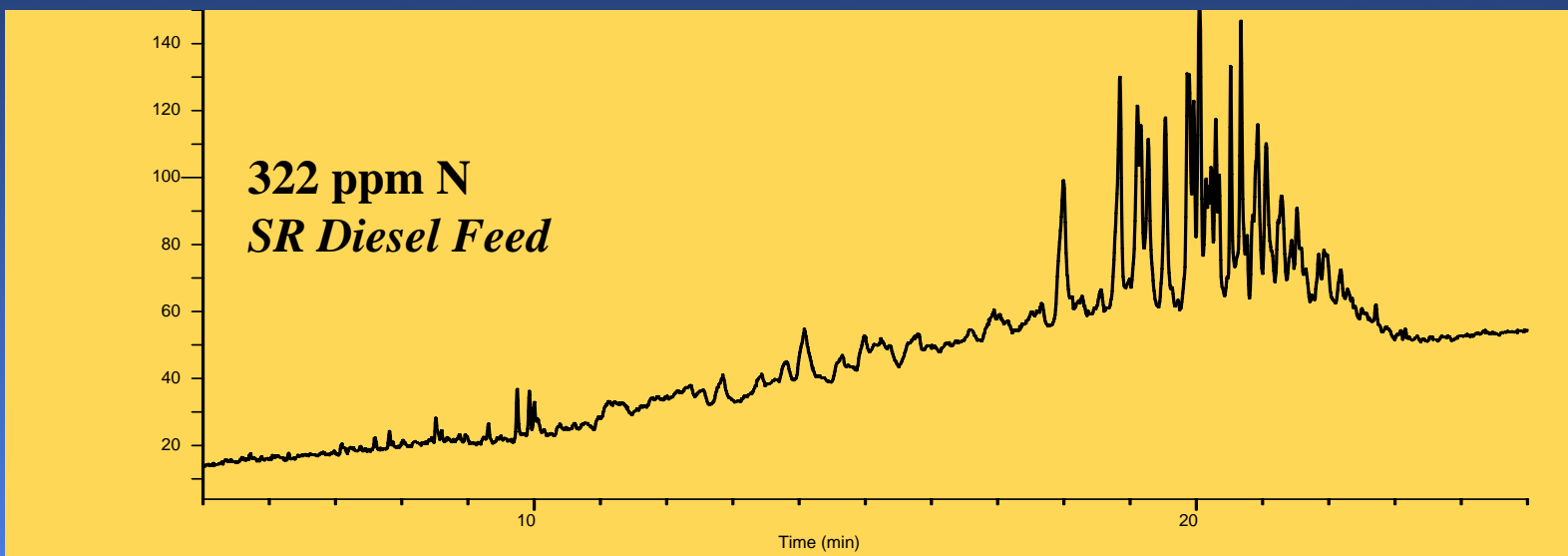
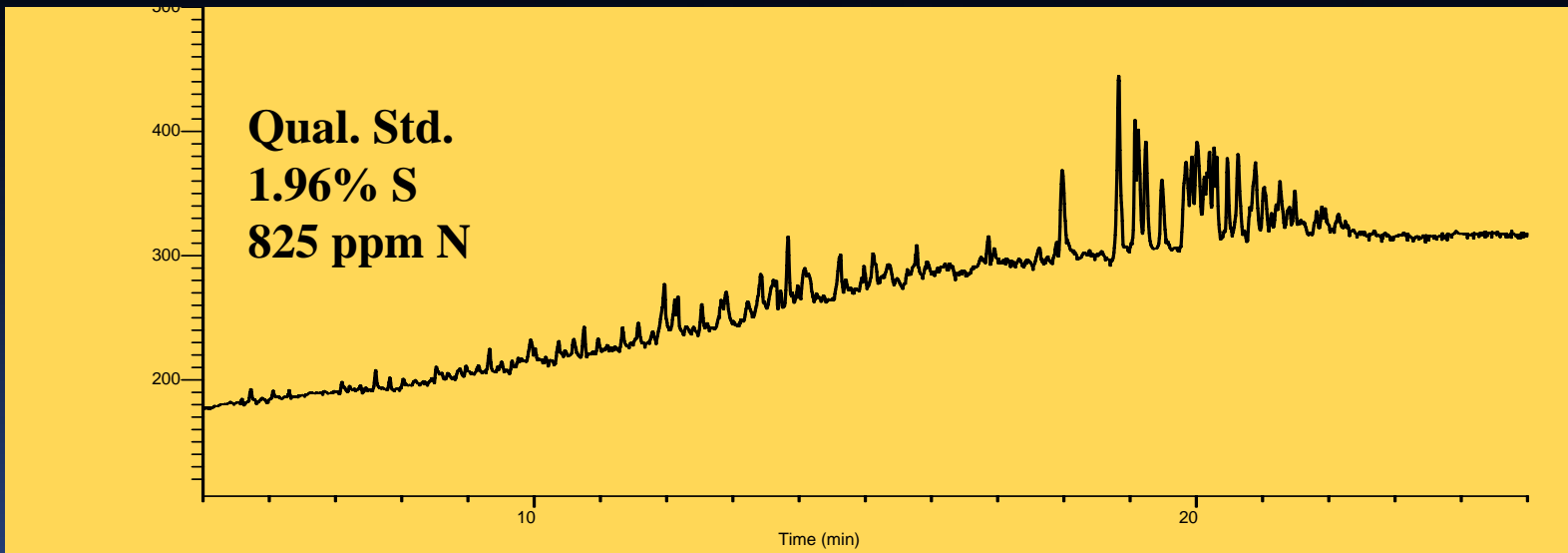
- Hydroprocessing: Nitrogen is removed by conversion to ammonia (NH_3)
 - Nitrogen requires about 4x hydrogen as the equivalent sulfur removal
 - Nitrogen inhibition of desulfurization
 - Some feeds harder to process than others

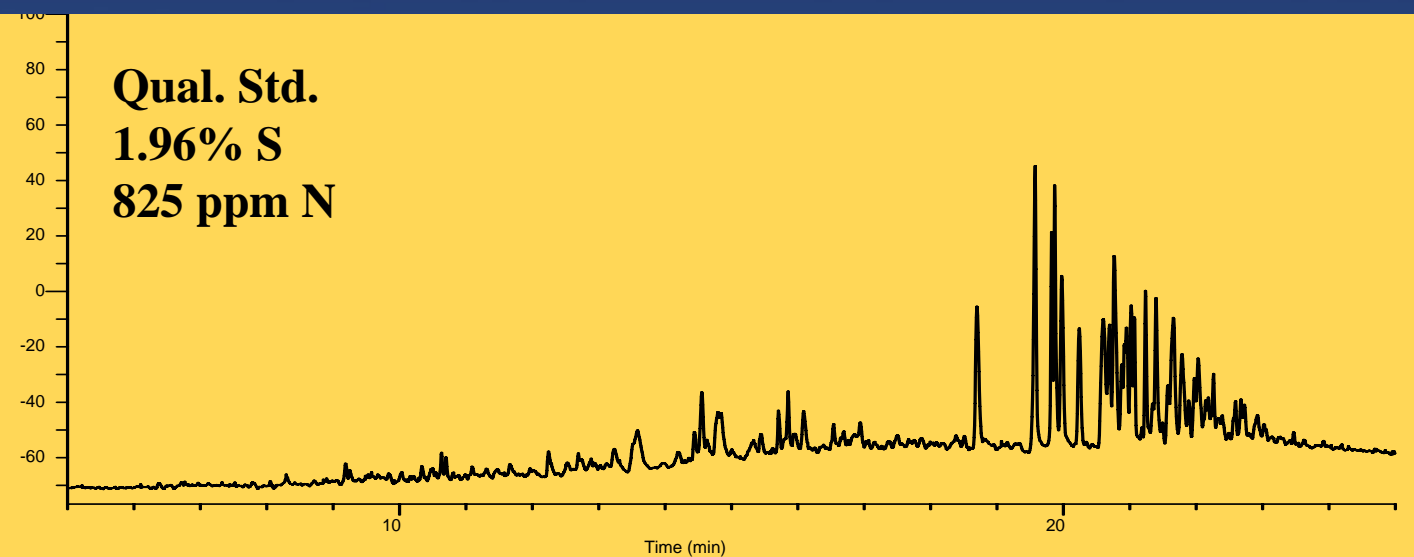
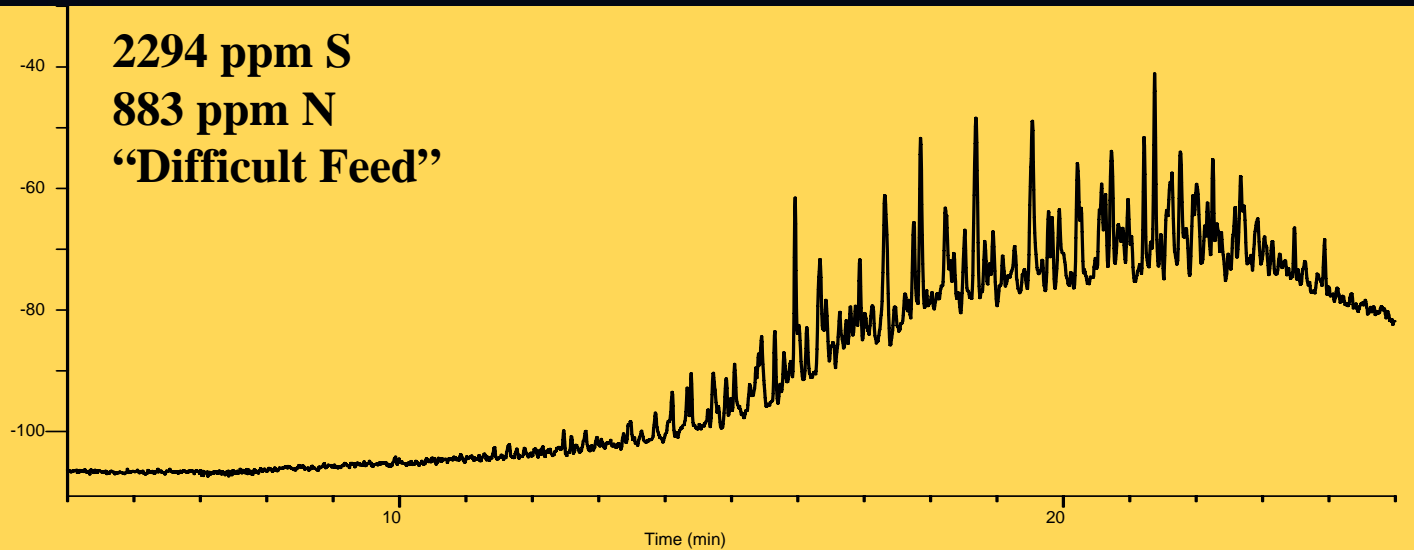
■ Analytical Solution

- GC-AED analysis used to track processing chemistry

Qualitative Std *825 ppm N*

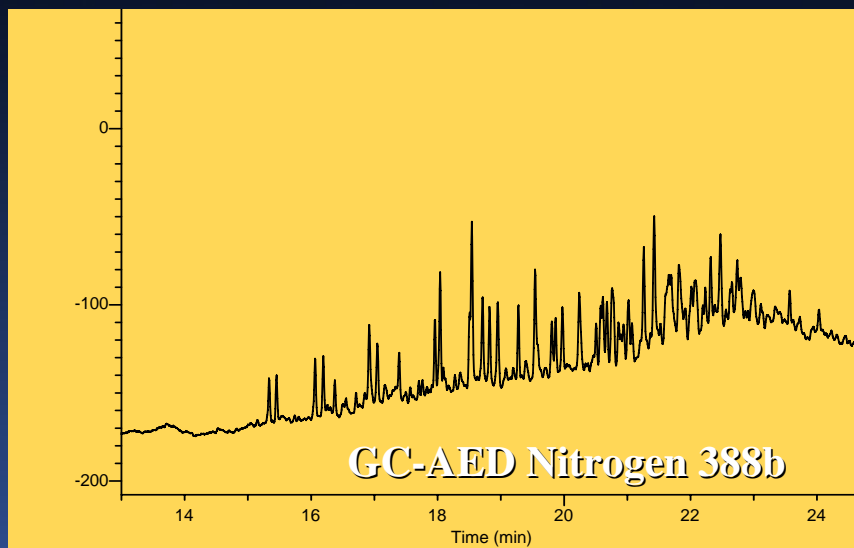




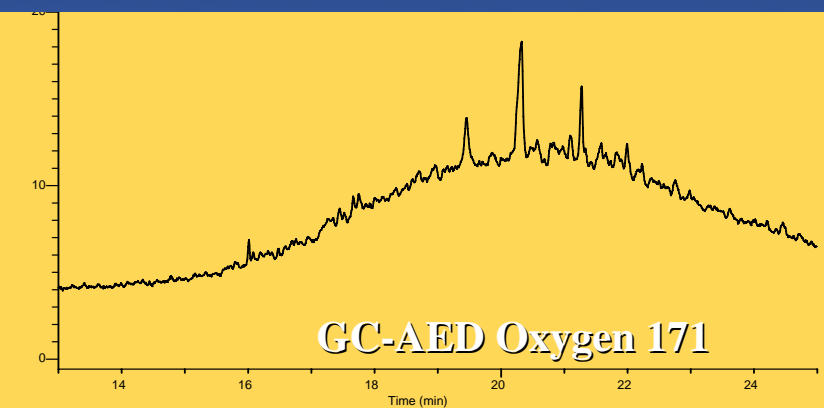
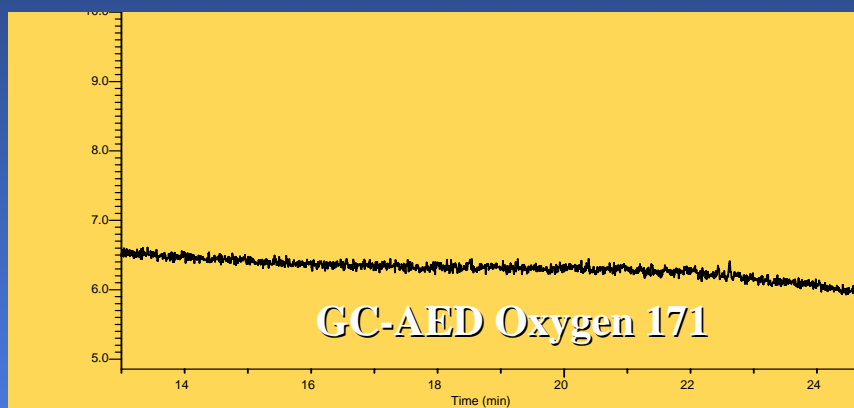
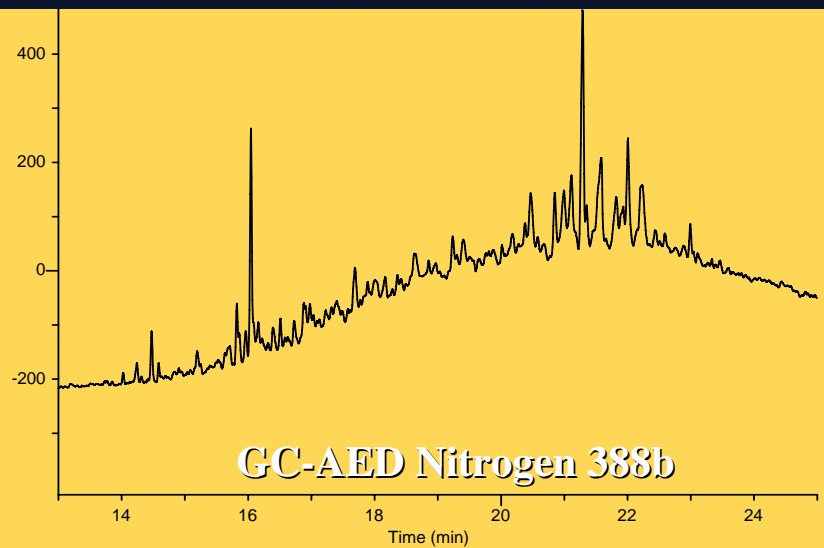


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**“Difficult Feed”
LC Fraction #3 (2.87%)**



**“Difficult Feed”
LC Fraction #4 (2.28%)**



Case #3

■ Issue

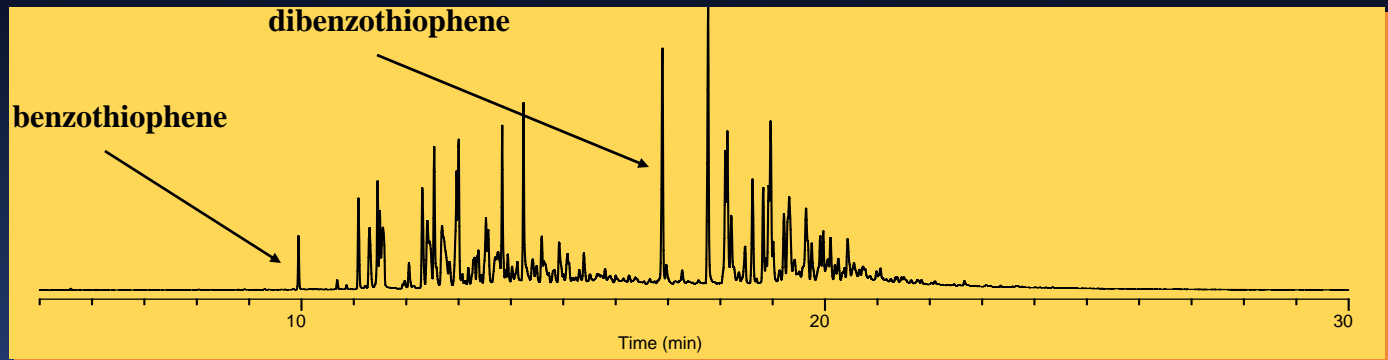
- **Oxidative Diesel Desulfurization: Sulfur is removed by reacting sulfur containing compounds with oxygen to form sulfones**
- **Adsorbent used to remove sulfones**

■ Analytical Support

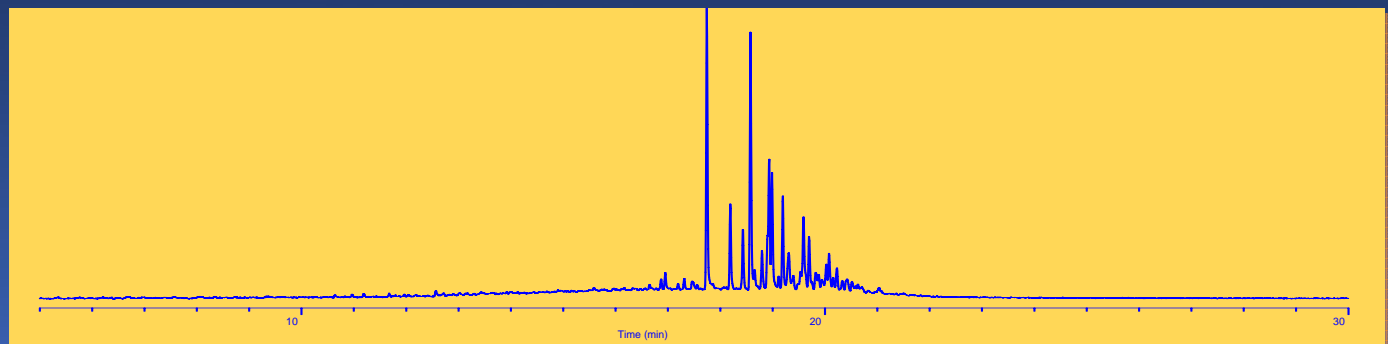
- **GC-AED used to track conversion**

GC-AED

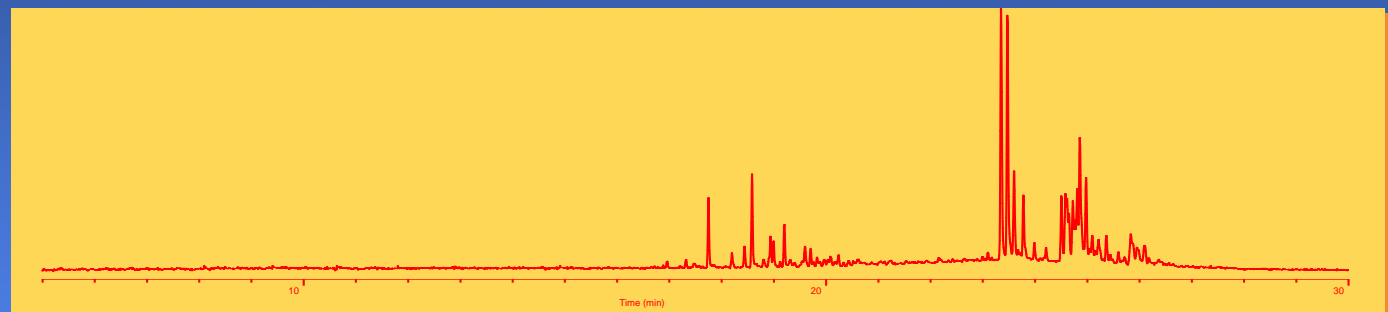
NIST 1624C
Sulfur 181



Diesel
Sulfur 181

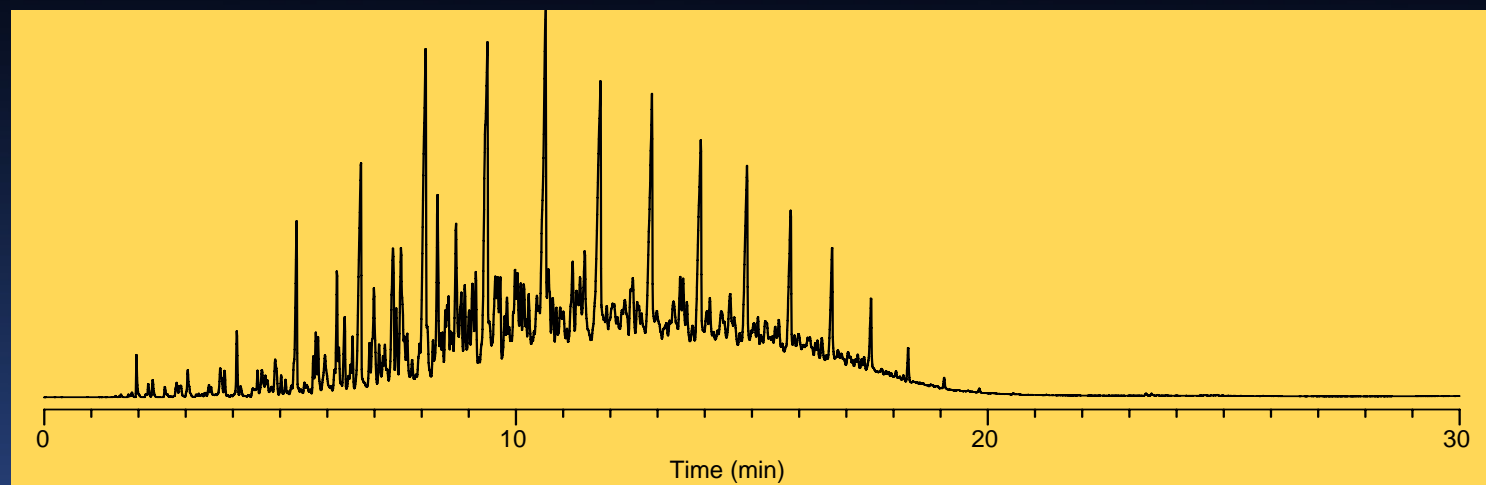


Oxidized Diesel
Sulfur 181

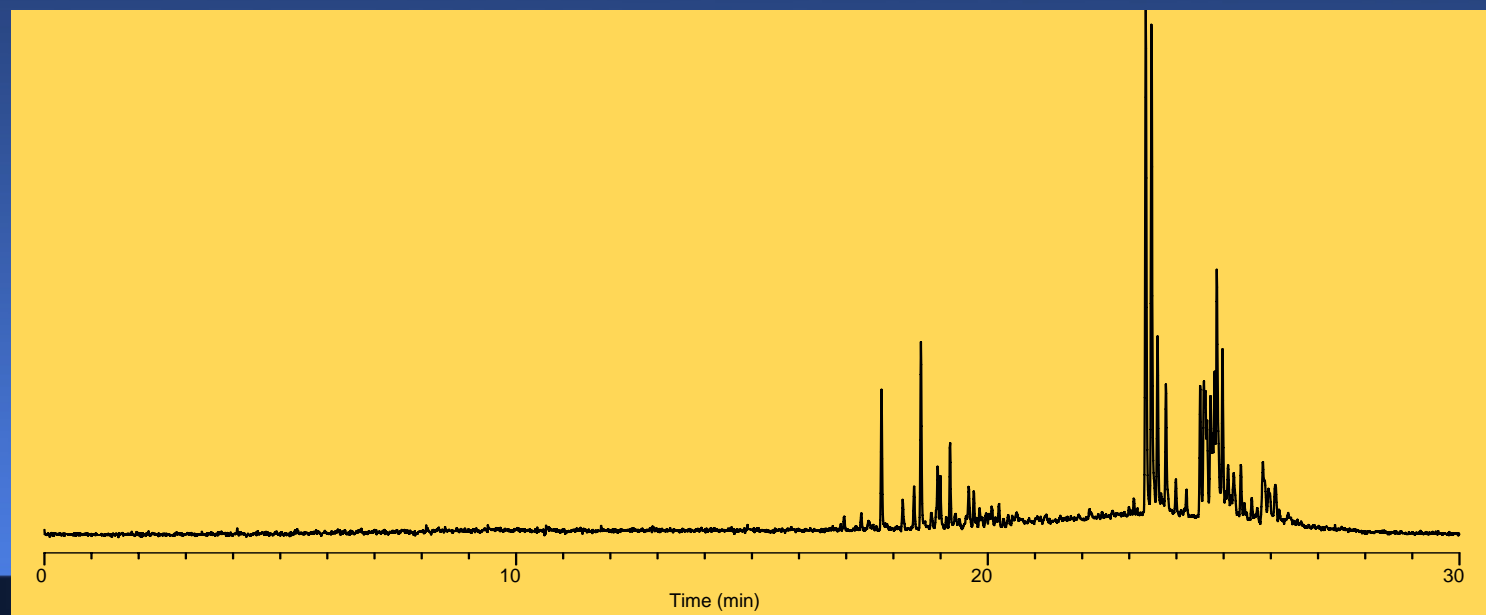


GC-AED

Oxidized Diesel
Carbon 179



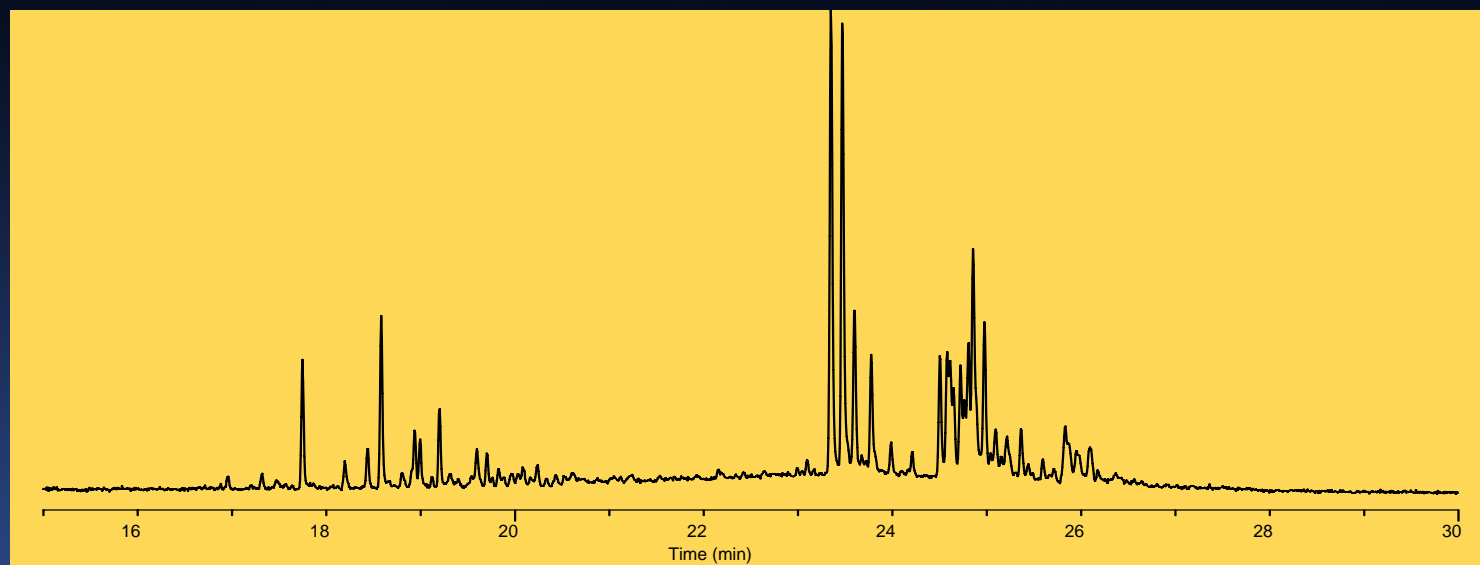
Oxidized Diesel
Sulfur 181



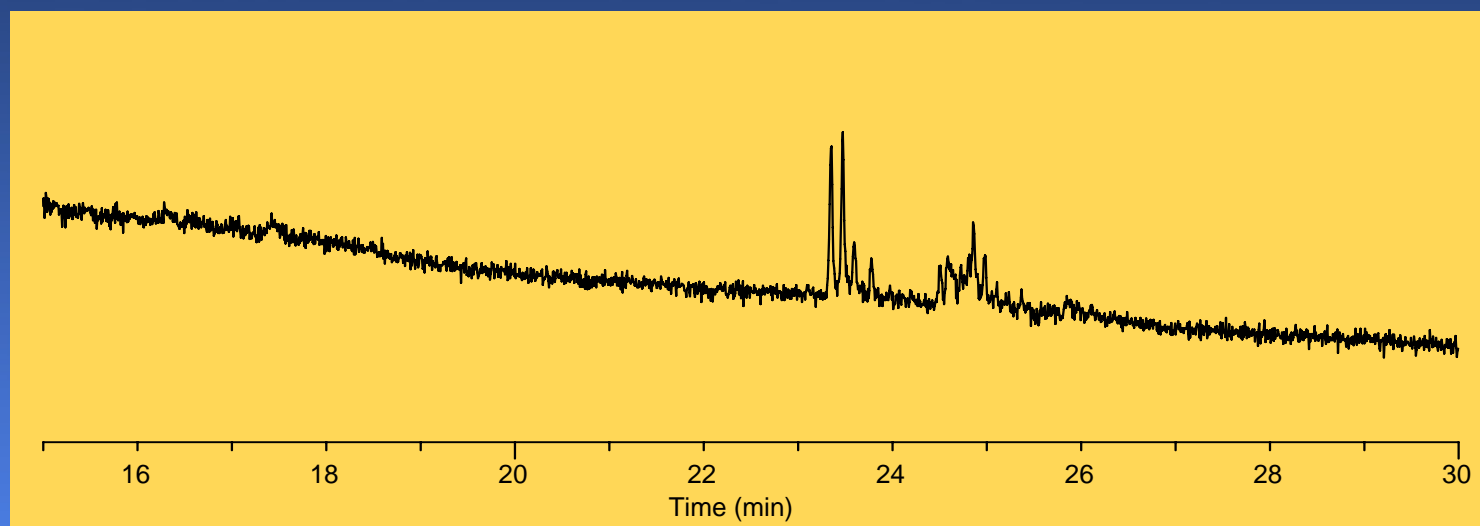
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GC-AED

Oxidized Diesel
Sulfur 181



Oxidized Diesel
Oxygen 171



Conclusions

- GC-AED is a powerful tool for the analysis of heteroatoms in petroleum samples
- Having information on only 1 heteroatom is insufficient for determining process performance of a feedstock in hydroprocessing