The Do's and Don'ts in the Analysis of Sulfur for Polyolefin Producers

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Agenda

- Introduction
- Ethylene and Propylene
  - ✓ Why is S so important?
  - ✓ What are the stakes?
- Sulfur Analysis
  - ✓ What are the issues?
  - ✓ Analytical Challenges
    - Standard preparation and shelf life
    - How to deliver S to the detector
    - Instrumentation
    - Sample handling
- Summary
- Conclusion

Introduction

- Benjamin Biela, Analytical Specialist
- Equistar Chemicals Analytical Services Laboratory
- Location: Channelview, Texas

Equistar Channelview Analytical Services Lab

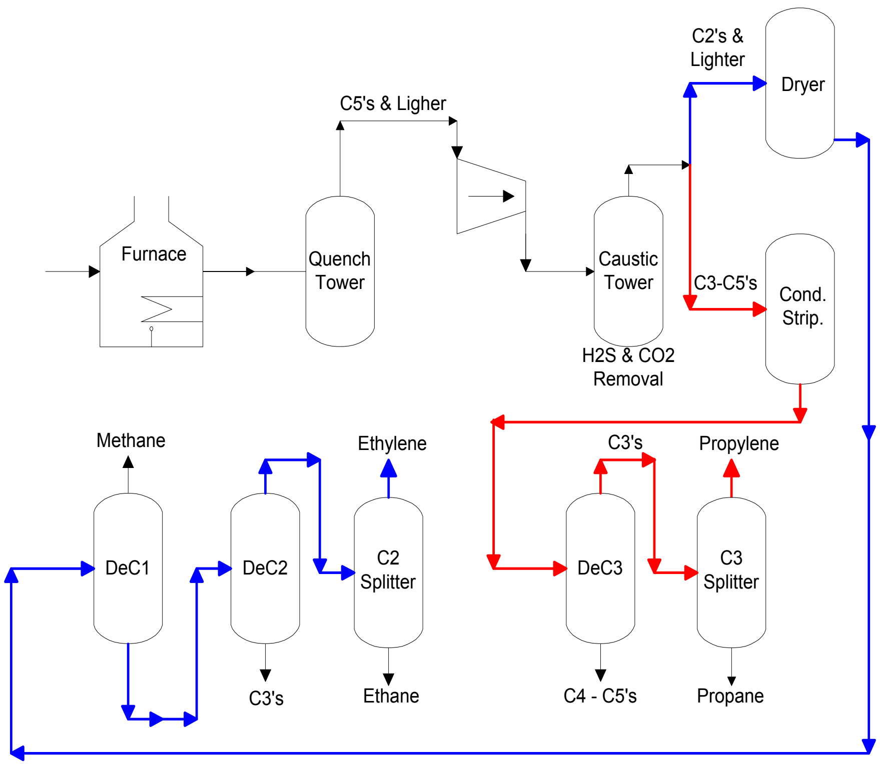
- Support 6 olefin plants producing the following products
  - ✓11.6 Billion lb/yr Ethylene
  - ✓5.0 Billion lb/yr Propylene
- Other products: Butadiene, Benzene, Toluene, Isoprene, Piperylene, Dicyclopentadiene, Alkylate, and Methanol

Sulfur Compounds - Polyolefin Catalyst Poisons

- ppb levels of sulfur compounds present in polyolefin feeds poison catalyst systems and drastically reduce polymer yield
- Reduced yields translate into lost profits **($$$)**
  - ✓ Millions of dollars / year
- Typical sulfur impurities
  - ✓ Ethylene
    - Hydrogen Sulfide (H_2S)
  - ✓ Propylene (Polymer Grade)
    - Carbonyl Sulfide (COS)
    - H_2S (Only during startup or unit upset)

Sulfur in Ethylene

- During steady state operation, sulfur in ethylene product is not normally an issue
- A cracked gas compressor surge or trip sometimes results in a caustic wash system upset allowing carbon dioxide and hydrogen sulfide to enter the ethylene splitter and ethylene product



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Sulfur in Propylene

- In the cracking furnaces, most (70 >90%) of the inlet COS is converted to H_2S
- Caustic wash towers do not remove a significant amount of COS
- The majority of COS exiting the cracking furnaces will enter the C3 splitter and exit with the propylene product
- A major unit upset or start-up condition could result in a trace amount of H_2S entering the C3 splitter and exiting with the propylene product.

Impact of S on Polymer Yield

Polypropylene Yield Data: Ziegler Natta Catalyst
Poison Level for Indicated Effect[1,2]

	Yield Loss		
Poison	5%	10%	20%
Carbonyl Sulfide	30	60	220
Hydrogen Sulfide	2800	3400	4600

1. *Equistar yield loss data*
2. *Poison level (ppb, wt) for indicated effect*

Specifications

- Poison levels for Metallocene catalyst: Propylene
  - ✓Acceptable maximum sulfur levels
    - Carbon Disulfide (CS_2): 50 ppb
    - Carbonyl Sulfide (COS): 10 ppb
    - Dimethyl Sulfide (C_2H_6S): 1 ppm
- Manufacturing specifications for polymer grade monomer
  - ✓Ethylene
    - Hydrogen Sulfide (H_2S): 50 wt. ppb
  - ✓Propylene
    - Carbonyl Sulfide (COS): 20 wt. ppb

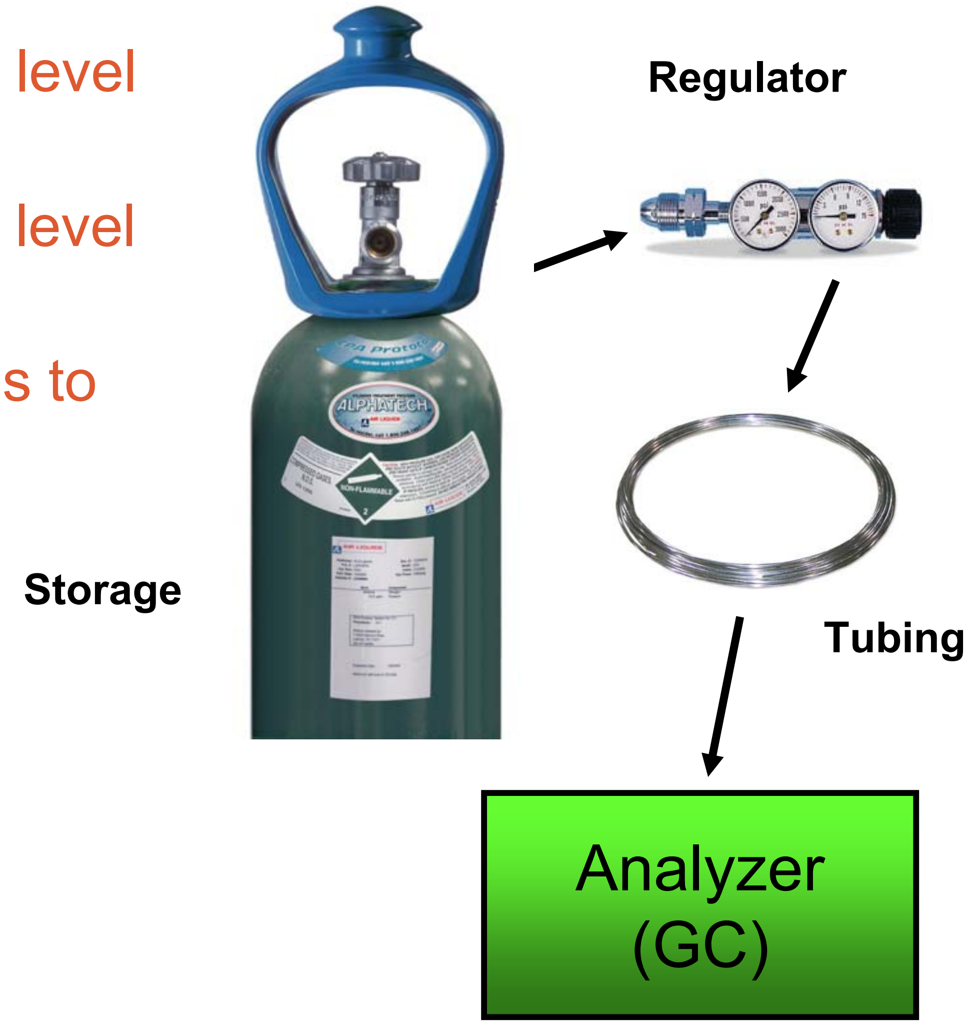
Analytical Challenges

- If no measurable sulfur response is noted at the analyzer, what does that mean?
  - ✓The hydrocarbon stream is free from S impurities
  - ✓"Purified" the hydrocarbon gas stream
    - Reacted out the S

- What are the issues to consider here?

Analytical Challenges

- Preparation of accurate ppb level sulfur standards
- Reasonable shelf life of ppb level sulfur compounds
- Delivery of sulfur compounds to the analytical instrument
  - ✓ Regulator
  - ✓ Tubing
- Analysis
  - ✓ Inlet system
  - ✓ Column



What Exactly is the Challenge?

- Accurate sulfur standards are now available
- Equipment to measure ppb S levels currently exists
- What about the rest of the story?
  - ✓Regulators
  - ✓Transfer tubing
  - ✓GC inlet system
  - ✓Column

→***How do these impact S analysis?***

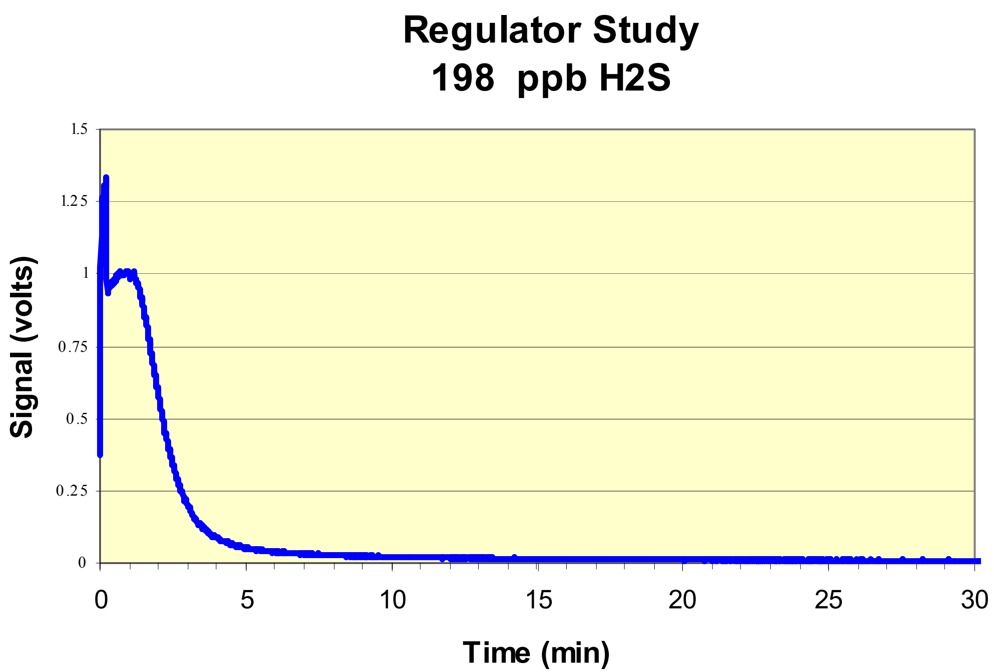
Summary: Storage

- Because of the long contact times associated with storage (minutes to years), any small reactivity of the sulfur compounds with the storage materials becomes critical
  - ✓ A shelf life study was performed with nominal 100 ppb H_2S in N_2 balance mixtures[1]
    - Excellent Materials
      - *Silcosteel™, Sulfinert ™*
        - » Bonded inert layer to surface of stainless steel
      - *ALPHATECH™ - Air Liquide America*
        - » Cylinder treatment process that yields a shelf life >1 year
    - Poor Materials
      - *Aluminum, Carbon Steel, Stainless Steel*

[1] *Benesch, R., Jacksier, T."The Preparation of Low Concentration Hydrogen Sulfide Standards" GCC 2002, paper 050*

Regulators

- Materials not as critical as for storage because of decreased contact times
  - ✓ A regulator comparison study was performed[1] with ppb H_2S in N_2
    - Stainless steel regulators work well once "passivated"
      - *Smaller volume SS regulators are preferred*
    - Materials with brass should be avoided at all costs
    - Sampling flow rates should exceed 100 mL/min



→Signal totally lost with utilization of incorrect regulator

[1] *Benesch, R., Haouchine, M., Tabert. B., Jacksier, T. "Low Concentration Hydrogen Sulfide Standards: Is it Possible to Obtain and Regulate at Concentrations below 100 ppb?" Abstract 40 Wednesday Oct 22nd Bluebonnet 9:20 am*

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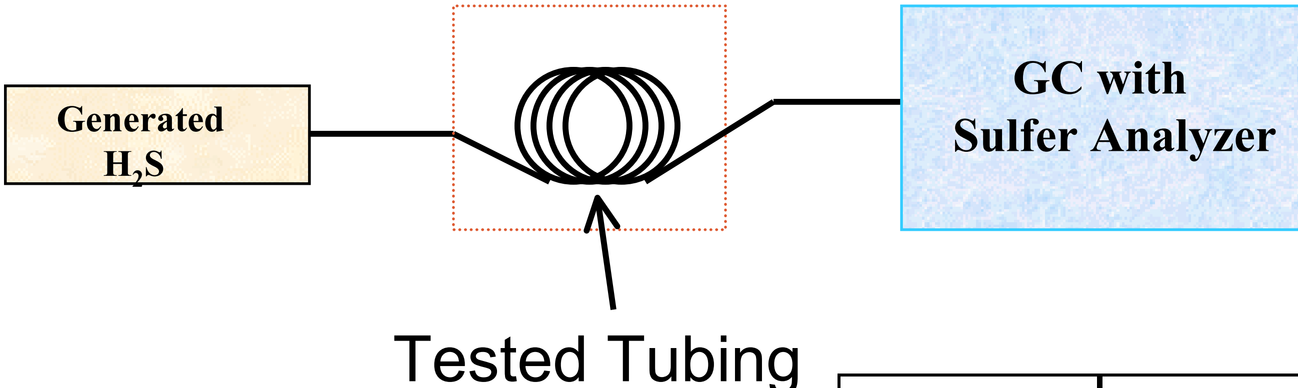
Tubing

- Materials are not as critical as for storage because of decreased contact time



- Tubing
  - ✓ Materials – Present in analysis systems
  - ✓ Sizes 1/4", 1/8", 1/16"

1/4 inch	1/8 inch	1/16 inch
Silcosteel™	Silcosteel™	Silcosteel™
Sulfinert ™	Sulfinert ™	Sulfinert ™
316 SS	316 SS	316 SS
3003 Alum.	3003 Alum.	x
6061 Alum.	x	x
FEP	FEP	x
x	PEEK	PEEK

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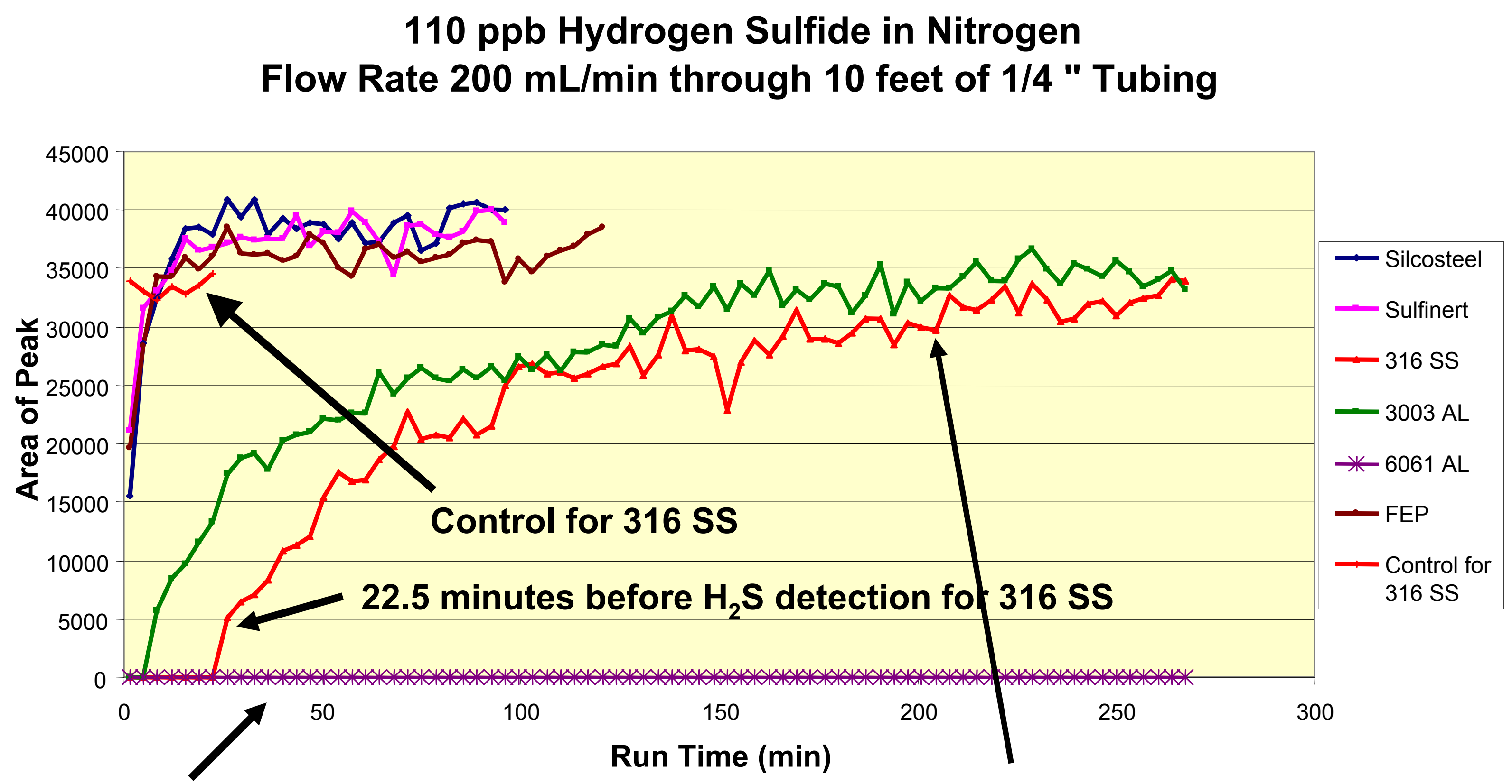
Procedure

- Control
  - ✓ Prior to testing – control experiments were run without the tubing to determine "control" signals
- Testing
  - ✓ Tubing piece attached and analysis started
    - Pretreatment of tubing
      - *Used "as is" from manufacturer*
      - *Left exposed to air until tested*
      - *No purging after attachment*
    - Analysis finished when signal approached control value

1/4 Inch Tubing



Surface of 6061 AL was very rough

> 200 minutes before control value was reached

→Residence time of the gas in the tubing < 1min

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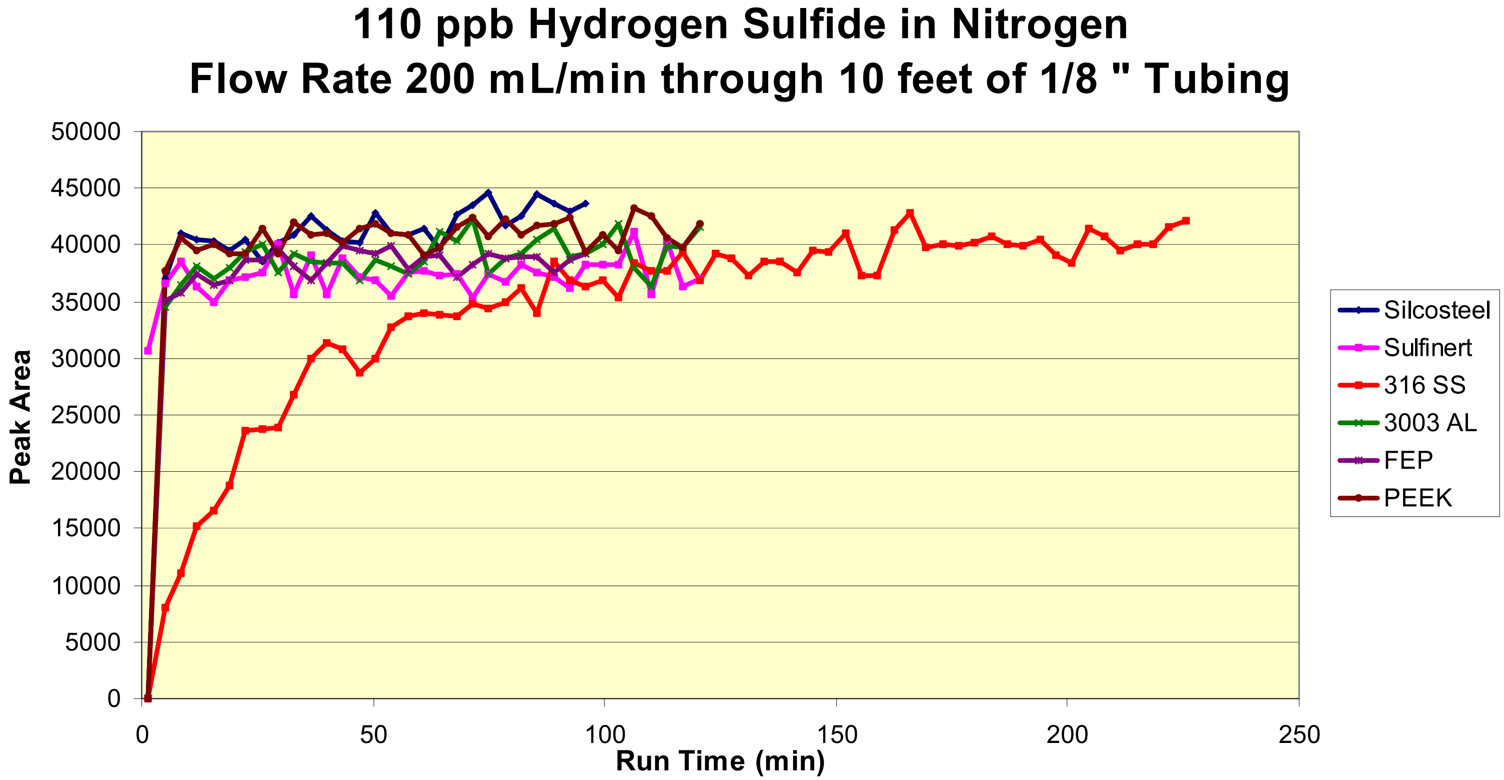
1/8 Inch Tubing



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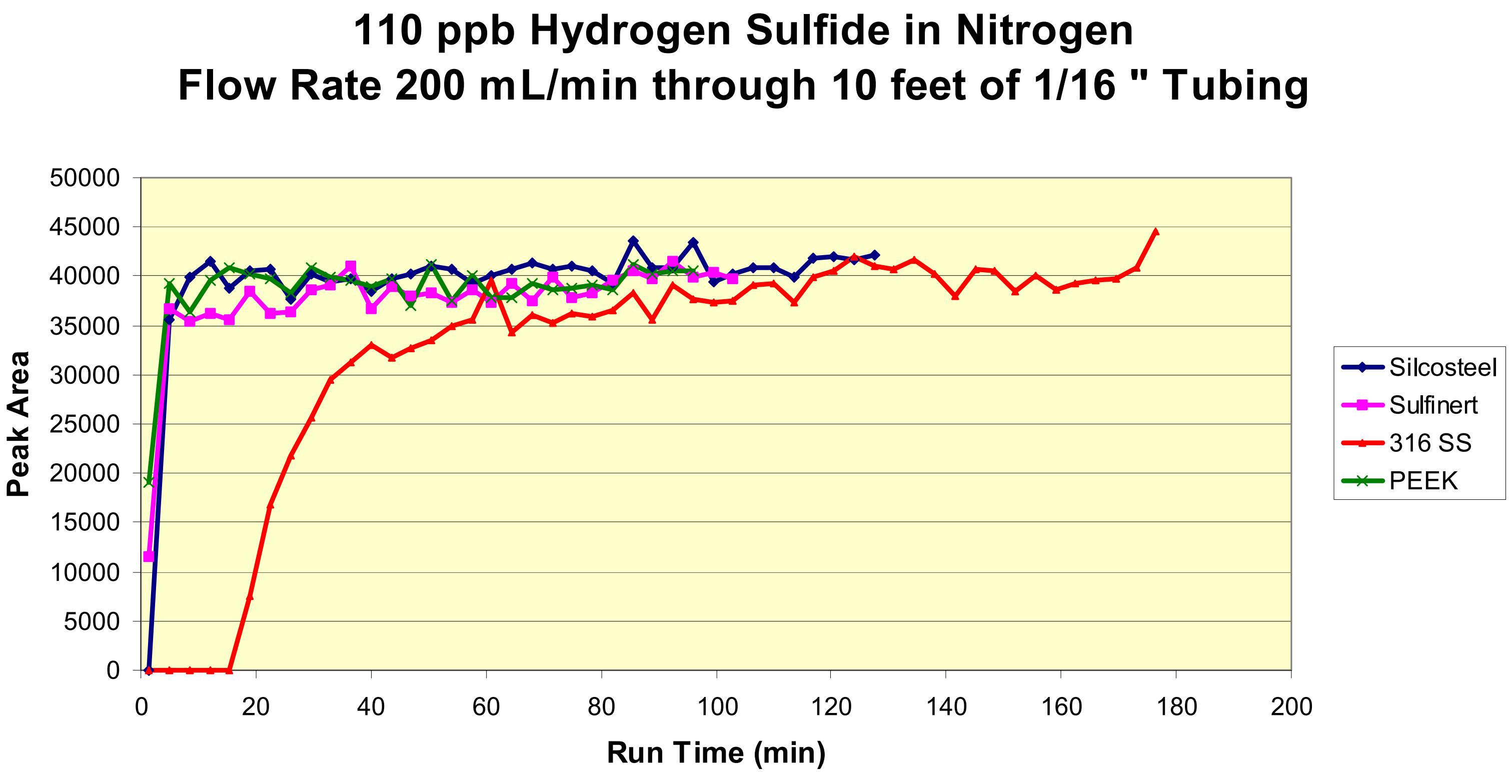
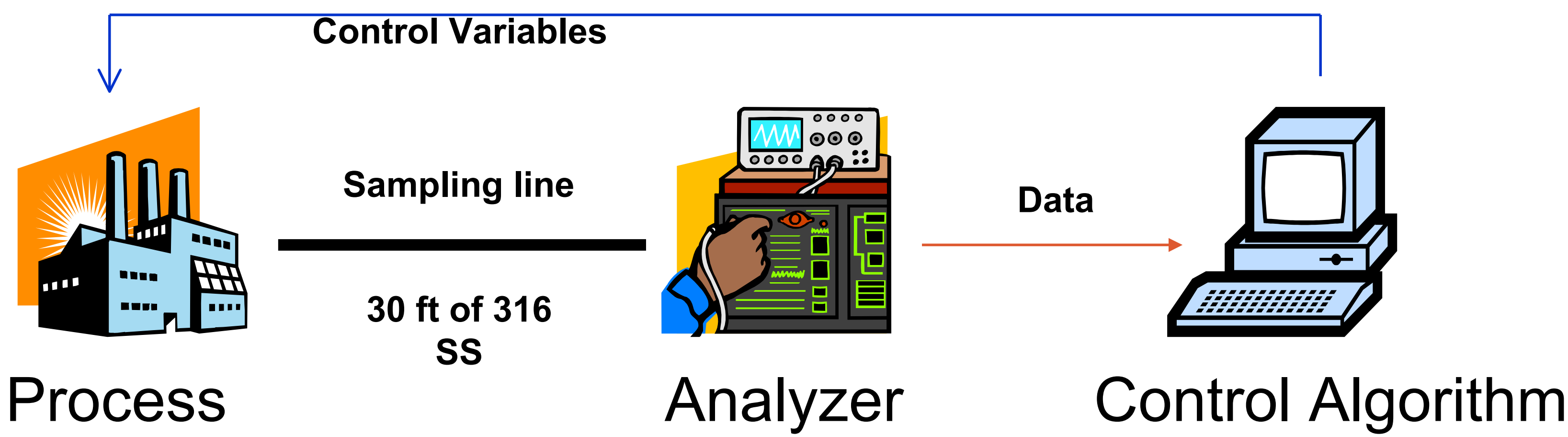
1/16 Inch Tubing



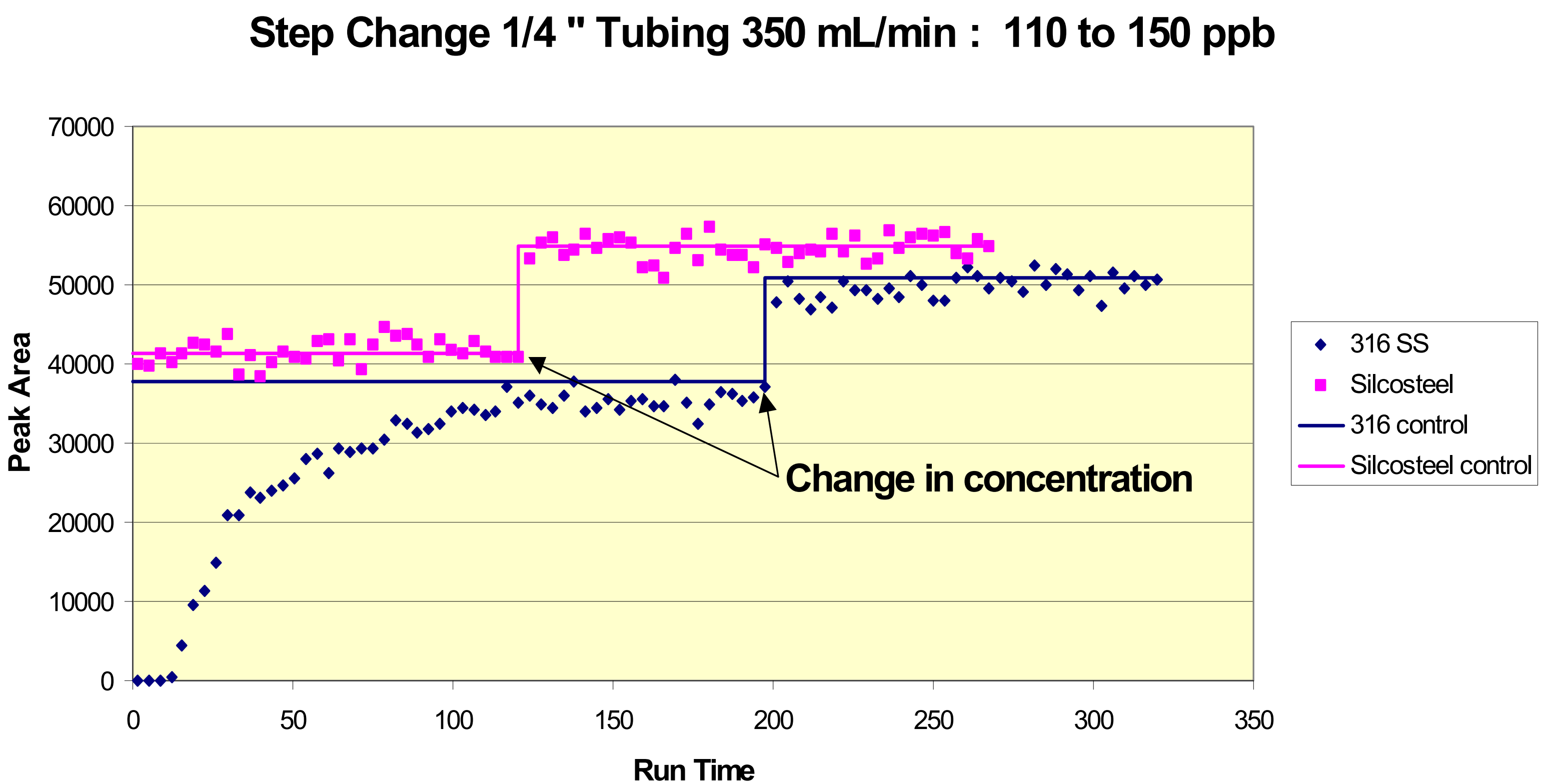
→ 1/16” SS is not EP and increased time for appearance of S signal maybe related to rougher tubing surface

Step Change in Concentration

- How will a change in the inlet concentration be observed in the outlet concentration?
  - ✓ Will there be a significant time delay in analysis?
    - For 316 SS, up to 200 minute delay per 10 ft of tubing
      - *Lead to process problems*



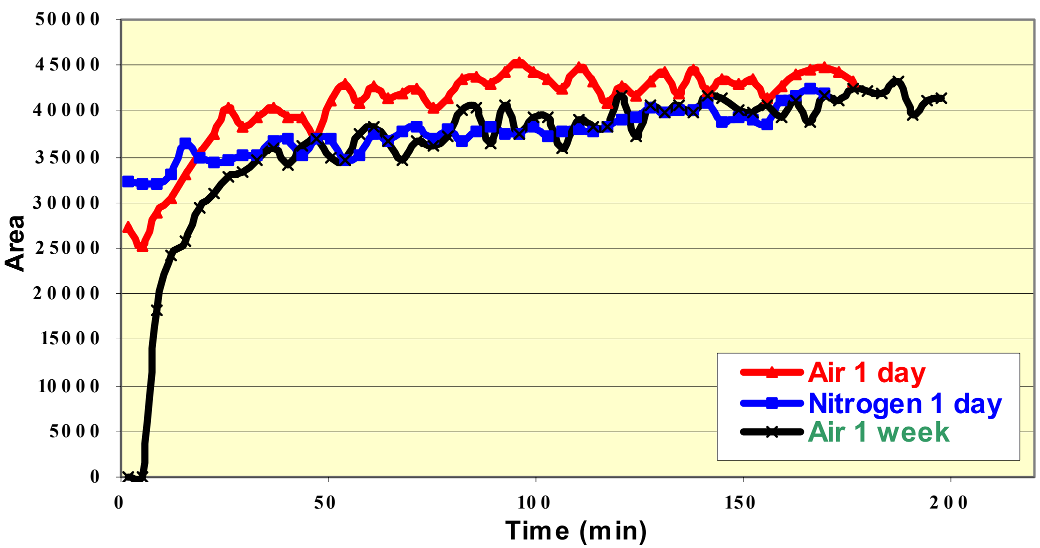
Step Change In Concentration



- ✓Silcosteel showed rapid increase
- ✓316 SS showed rapid increase once passivated

Passivation of SS

- Is the passivation of stainless steel permanent?
  - ✓Three pieces of 316 SS passivated and left to sit under different conditions
    1 - Exposed to N_2 for one day
    2 - Exposed to air for one day
    3 - Exposed to air for one week



✓After exposure – retested with 100 ppb H_2S in N_2 at 350 mL/min

✓Long exposures (> 1week) will require repassivation

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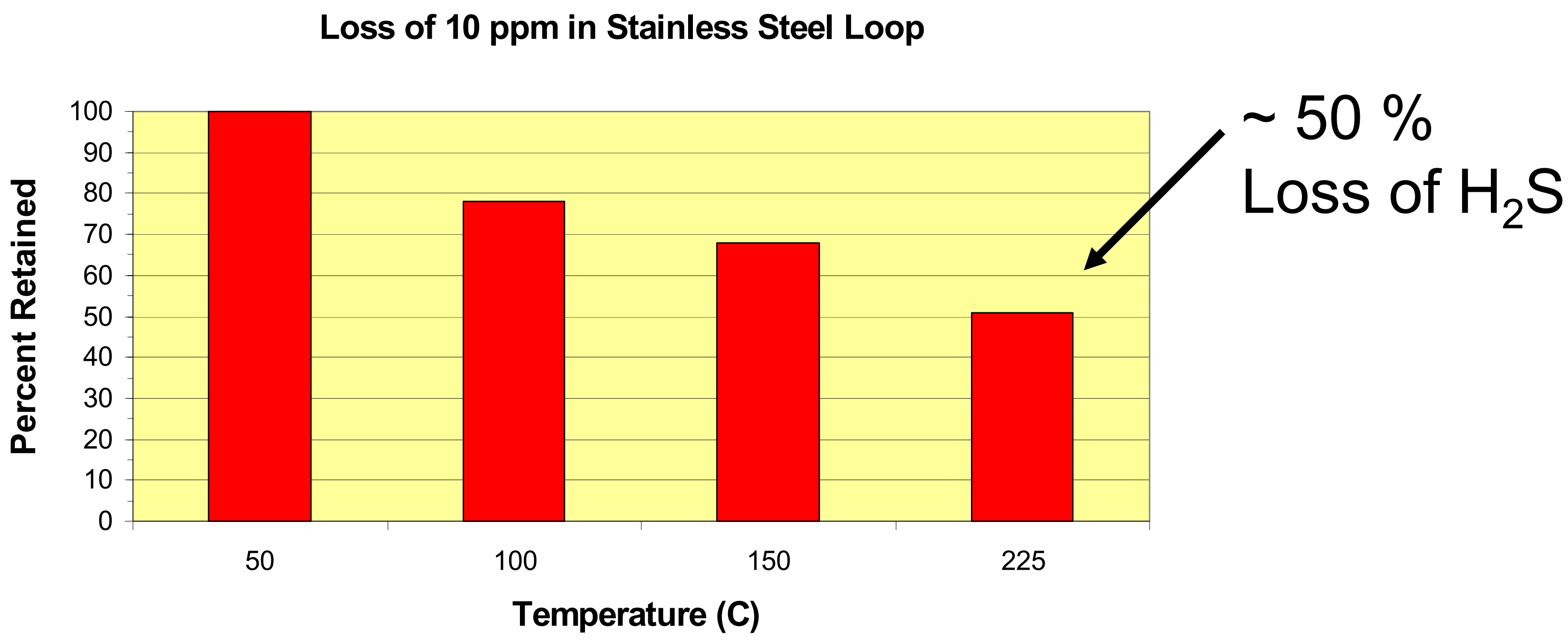
GC: Valve

- Loop materials
  - ✓ Stainless Steel - requires passivation
  - ✓ Silcosteel™, Sulfinert ™ - good material
- Temperature
  - ✓ Loops - often heated to prevent adsorption of compounds – how does this effect the reactive sulfurs – 2 concentration levels – 100 ppb and 10,000 ppb
    - Low concentration 100 ppb H_2S in N_2
      - *Silcosteel™ – no noticeable effects from 50 - 225 °C*
      - *Stainless steel – complete loss of signal when heated to temperatures above 100 °C, even after passivating*

GC: Sample Loop

- High concentrations 10 ppm
  - *Silcosteel™ - no noticeable effect 50 °C to 225 °C*
  - *Stainless Steel – loss of signal*



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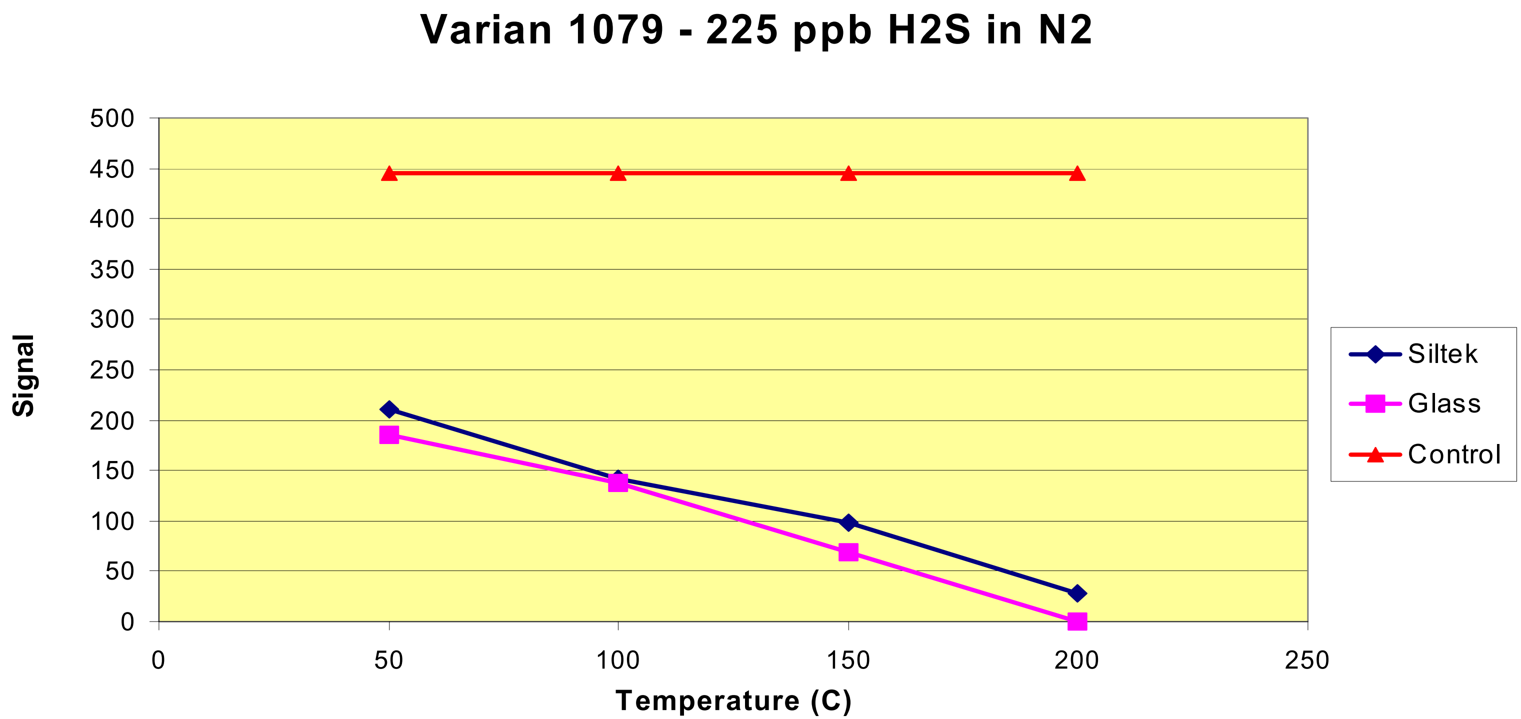
GC: Inlet

- On column injection is preferred because of minimal sample contact
- Inlets Tested – materials and temperature effects
  - ✓ Concentration tested – 225 ppb H_2S in N_2
    - Varian 1079
      - *Glass - insert*
      - *Siltek™ insert (Restek)*
    - Agilent Volatiles Interface

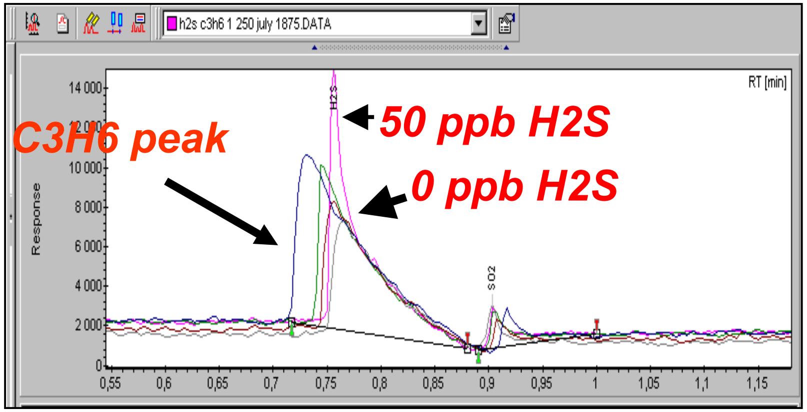
GC: Inlet



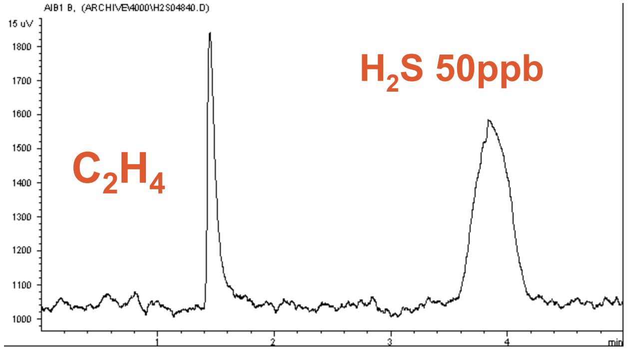
- ✓ "Control" determined by using a Silcosteel™ Tee as the inlet
- Volatiles Interface showed no temperature effects (Agilent)

GC: Columns

- Even though the SCD is "sulfur specific", high concentrations of olefins will produce peaks
- Hydrocarbon peaks <u>must</u> be separated from the S compounds[1]
  - ✓ Ethylene (& propylene) and H_2S coelute at temperatures above 0°C
  - ✓ Good separation at elevated temperatures with correct column selection



100 % dimethyl polysiloxane
split ratio 1:1
-50°C

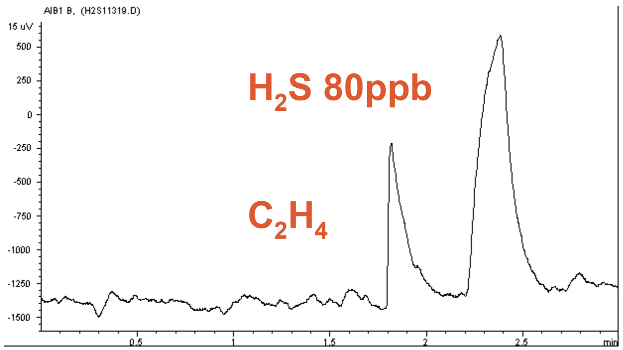


[1] *Grimberg, A., Benesch, R.,Haouchine, M., Richard, S., Coffre, E., Jacksier, T. "Analysis of Sulfur Compounds in Hydrocarbon Matrices", Pittcon 2002, paper 740-3.*

GC: Column

- Ethylene analysis
  - ✓ 100 % Dimethyl polysiloxane – often recommended for sulfur analysis
    - Coelution of ethylene and H_2S at non cryogenic conditions
  - ✓ Varian Silicaplot
    - Good separation
  - ✓ J&W Gas Pro
    - Good separation at temperatures >100°C

Gaspro column
split ratio 4:1
100°C



Summary

- Low concentrations of sulfur will poison Ziegler-Natta and Metallocene catalysts
- Store sulfur compounds in containers with Sulfinert, Silcosteel, or ALPHATECH™ surface treatment technology
- Low wettable surface SS regulators work well
  - ✓ "*Traditional*" SS regulators can be used if passivated and if the flow rate exceeds 100 mL/min
- Tubing should be Sulfinert, Silcosteel, or PEEK
- Column selection is critical for accurate analysis in hydrocarbon matrices
- Sample loop should be coated
- Utilization of "on column" or volatile interface for sample inlet

Conclusion

- Sulfur analysis is not trivial …the devil is in the details
  - ✓ Correct component selection is the hallmark for a successful analysis

- Feel sympathy for those who do trace level sulfur analysis

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