

# Improvement of Trace Level Sulfur Analysis in Refinery, Beverage and Environmental Applications

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## Introduction

Applications involving sulfur compounds

Challenges associated with Sulfur analysis

Solutions

Chromatograms

Conclusions

## Refinery/Petrochemical

- Impurities in Propylene and Ethylene
  - ◆ Catalyst poison
- Sulfur Content of fuels
  - ◆ Increased regulations, credits, mandatory limits
- Natural Gas/Refinery Gas
  - ◆ Quality Control, Safety (odorants)

## Beverages

- Sulfur Content of Carbon Dioxide
  - ◆ Safety, Taste, Quality Control
- Sulfur Content of Beer/Wine
  - ◆ Taste, Quality Control

## Environmental

- Stack Gas emissions monitoring, Sulfurs
  - ◆ Odor, Health
- Volatile Organics in Air, indoor/outdoor
  - ◆ Odor, Health, Safety

## Challenges

- Adsorption of Hydrogen Sulfide  $H_2S$ 
  - ◆ Very rapid on carbon and iron containing surface
- Reactivity of Mercaptans
  - ◆ Mercaptans convert to disulfides in contact with carbon

## Challenges

- Most sampling and transfer equipment is manufactured from steel.
  - ◆ Gas Sampling Cylinders
  - ◆ Fittings
  - ◆ Tubing
  - ◆ Analytical Instrument inlet and detectors systems

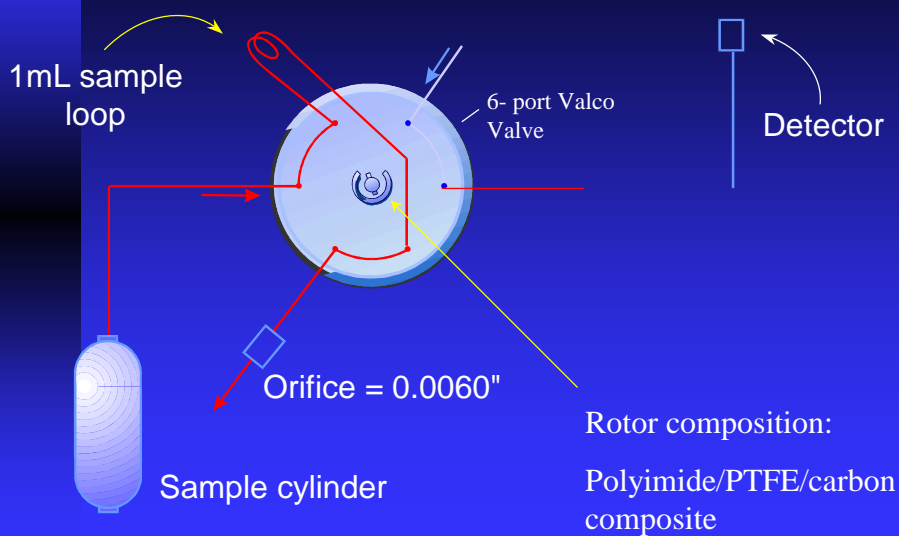
## Solutions for Transfer and Storage Equipment

- Deactivated Glass
- Teflon lined
- Sulfinert

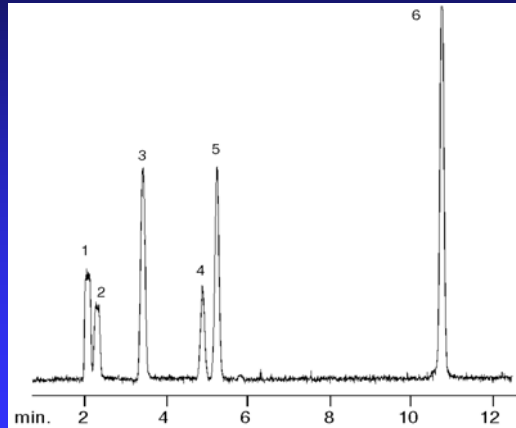
## Sulfinert™ Coating

- Covers all exposed surface area
- Physical Barrier preventing interaction of surface and samples
- Proven to 1ppb holding of reactive sulfurs

## Chromatographic System



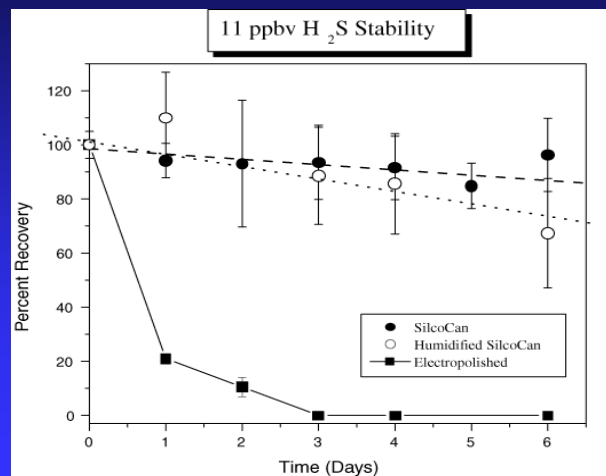
## Test run: Sulfurs at 60ppb



1. hydrogen sulfide
2. carbonyl sulfide
3. methyl mercaptan
4. ethyl mercaptan
5. dimethyl sulfide
6. dimethyl disulfide

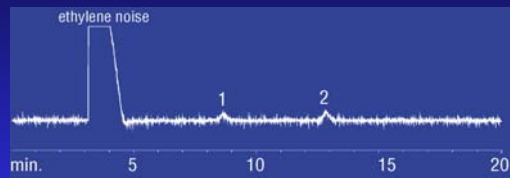
Rtx-1, 60m, 0.53mm ID , 7um

## 11ppb H<sub>2</sub>S Stability Coated Vs. Non-Coated cylinder

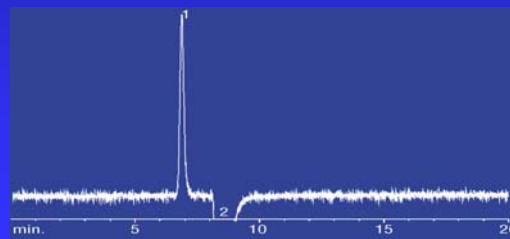




## Polymer grade Ethylene and Propylene impurities



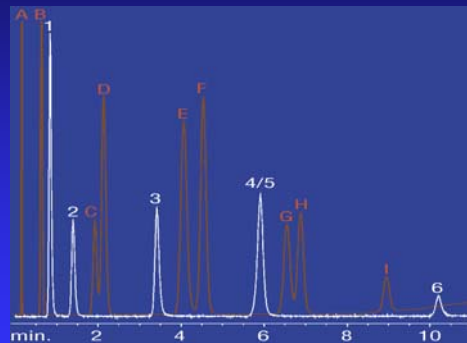
1. hydrogen sulfide  
20ppb
2. carbonyl sulfide  
20ppb



1. carbonyl sulfide  
20ppb
2. propylene interference

Rt- XL Sulfur  
Micropacked column

## Sulfurs and Hydrocarbon Natural Gas / Refinery Gas



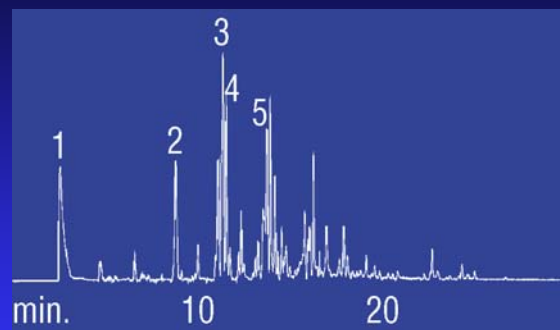
Rt-XL Sulfur  
Micropacked

50ppb each

1. hydrogen sulfide
2. carbonyl sulfide
3. methyl mercaptan
4. ethyl mercaptan
5. dimethyl sulfide
6. dimethyl disulfide

- A. methane
- B. ethane
- C. propylene
- D. propane
- E. isobutane
- F. butane
- G. isopentane
- H. pentane
- I. hexane

## Sulfur in Naptha by AED



500ppm Total Sulfurs

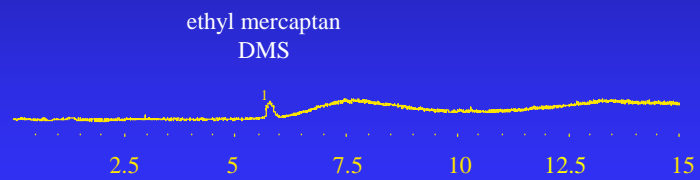
30m, 0.32mm ID, 4.0um Rtx-1

1. hydrogen sulfide
2. thiophene
3. 2-methylthiophene
4. 3-methylthiophene
5. 2-ethylthiophene  
+ alkylthiophenes



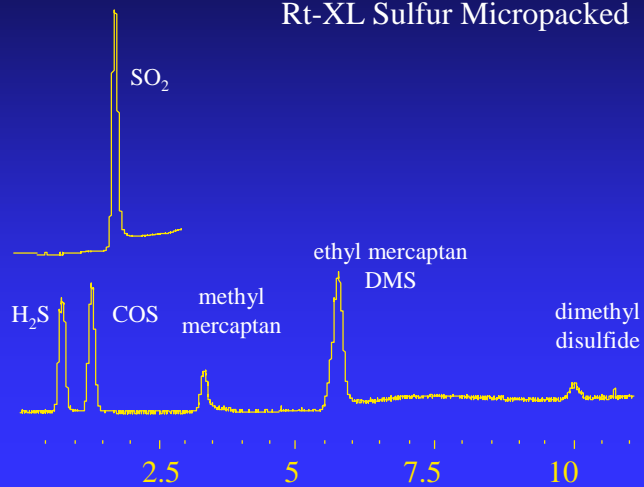
# Beverage Grade CO<sub>2</sub> blank

Rt-XL Sulfur Micropacked



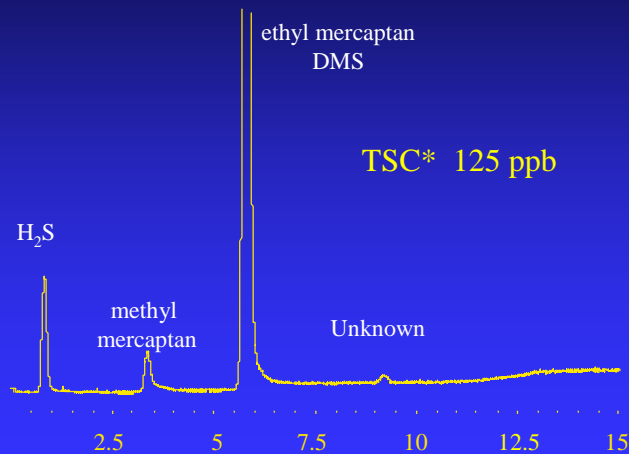
# 20 ppb sulfur and SO<sub>2</sub> in CO<sub>2</sub> Standard

Rt-XL Sulfur Micropacked



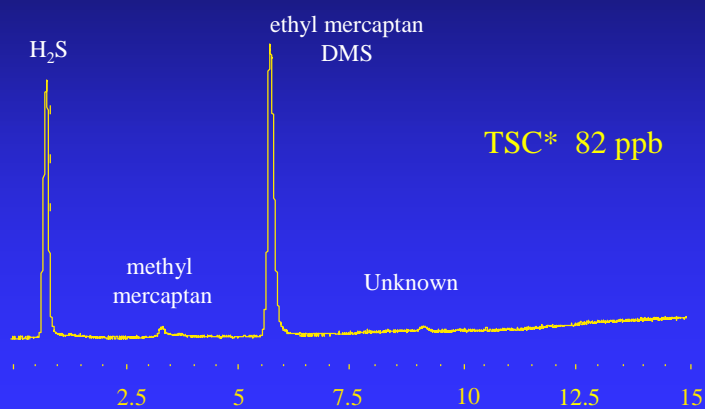
## Headspace sample: Brand "A" Beer

Rt-XL Sulfur Micropacked



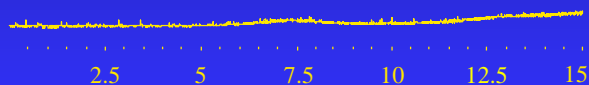
## Headspace sample: Brand "B" Beer

Rt-XL Sulfur Micropacked



## Headspace sample: Top brand Cola

Rt-XL Sulfur Micropacked



## Additional compounds benefiting from passive sample pathways

- Organo-phosphorous pesticides
- Chlorinated pesticides
- Chemical Warfare Agents (S and P containing)
- Brominated and chlorinated hydrocarbons

## Conclusion

- Overcome challenges of sulfurs analysis
- Methodology starting to require the use of coated cylinders to insure sample integrity
- As detection systems improve need for passive coatings will expand.

## Acknowledgments

- Lou D'Agostaro of DCG Partnership 1 Ltd. of Pearland Texas for supplying us with the sulfur standards
- Don Pachuta of Airborne Labs International Inc., of Bridgewater New Jersey for carbon dioxide testing methods.