A Chromatographic View at Inert Coating of Components Used for Sample Transfer and Holding

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Application Note

Components that benefit from inert coatings

- Sample-holding vessels
- Valves and regulators
- Transfer tubing
- Vaporizing or flash chambers
- Reactors
- Tubing connectors and fittings

→ Anything that touches the sample

Introduction

- Physical properties of SilcoNert® 2000 (previously known as Sulfinert®)
- Chemical properties
- SilcoNert-treated GC liners
- Example of coated stainless steel used for sampling and storage of organsulfur compounds
- Corrosion resistance
- Reduction of carbon buildup using coated stainless steel components

Chemical properties of SilcoNert® 2000

- Amorphous silicon (a-Si) based
- Excellent inertness to NOx gases, organosulfur compounds, polar organics like alcohols, esters, ethers, etc.
- Insoluble in acids like HCl and HNO_3
- Highly soluble in caustic environments, pH >8 (use Dursan® for pH 0-14)

SilcoNert® 2000, continued

- Surface functionalization (hydrocarbons) in secondary and tertiary deposition processes
- Reduces effects of pin holes and porosity
- Creates ultra-inert surface capable of parts-per-trillion analysis of certain compounds

SilcoNert-coat any stainless steel, glass, high temperature alloy or ceramic parts that contact the sample flow path to guarantee reliable and accurate results.

Inlet Liner Deactivation

- Inertness for acids, bases, neutrals, pesticides
- Low bleed
- Thermal stability
- Durability
- Regeneration. Easily cleaned with simple solvent sonication
- Great for SemiVols+
- Re-deactivation service available

Physical properties of SilcoTek Coatings

- Durable and flexible
  - Can be bent to the specs of your system without damage to the layer
- Strong, intermolecular adhesion
- Non-permeable surface
- Stable to high temperatures (450° C +)

Processing Conditions

- Chemical vapor deposition (CVD)
- Applied to SS, nickel and chrome-containing alloys, ceramics, glass, etc.
- Caustic surface preparation to eliminate dirt, dust, grease or fingerprints
- Vacuum process
- Process temp: 400-450° C max.

When to use SilcoNert®

- Transfer and holding of adsorptive or reactive species like:
  - Sulfurs
  - NOx, stack gas monitoring
  - Alcohols
  - Pharmaceuticals
  - Explosives
  - Chemical weapons
  - VOCs
  - OP Pesticides and Chlorinated Pesticides
  - Herbicides
- All analytical instrument components used for low-level analysis

- Transfer of acidic corrosive media (use Dursan® for bases)
- In components used to transfer or contain hydrocarbon streams that are prone to “coking,” or carbon buildup.

Project Example: SilcoNert® 2000

- Need a treatment that prevents chemical adsorption on stainless steel surfaces for low-ppbv sulfur gases
  - Chromatographic sampling system
  - Containment vessels (high pressure vessels and air sampling canisters)
    - Provided by Restek® Corporation

Performance of SilcoNert® coating for transfer of NOx & Ammonia-containing streams

- Study conducted by University of California Center for Environmental Research and Technology (Oct. 2001)
- Focused on quantifying uncertainties in continuous emission monitoring systems
- Study tried to simulate exhaust gas
- Total NOx levels in study were 0.4ppm, 2ppm and 9.5ppm total

NOx Study Conditions

- 100’ section of ¼” SilcoNert 1000 (Silcosteel®) coated tubing used to transfer simulated exhaust streams
- Looking at recovery of components through the transfer system and relative standard deviation

NOx-containing sample streams studied

- Variety of components and concentrations studied
- Each condition tested with 3 NOx concentrations 0.4ppm, 2ppm and 9.5ppm total NOx:
  - Dry simulated exhaust
  - Wet (13% H2O) simulated exhaust
  - Wet (13% H2O) simulated exhaust + 6ppm ammonia
  - Wet (13% H2O) simulated exhaust + 10ppm ammonia
  - Wet (6% H2O) simulated exhaust
  - Wet (13% H2O) simulated exhaust + 10ppm ammonia

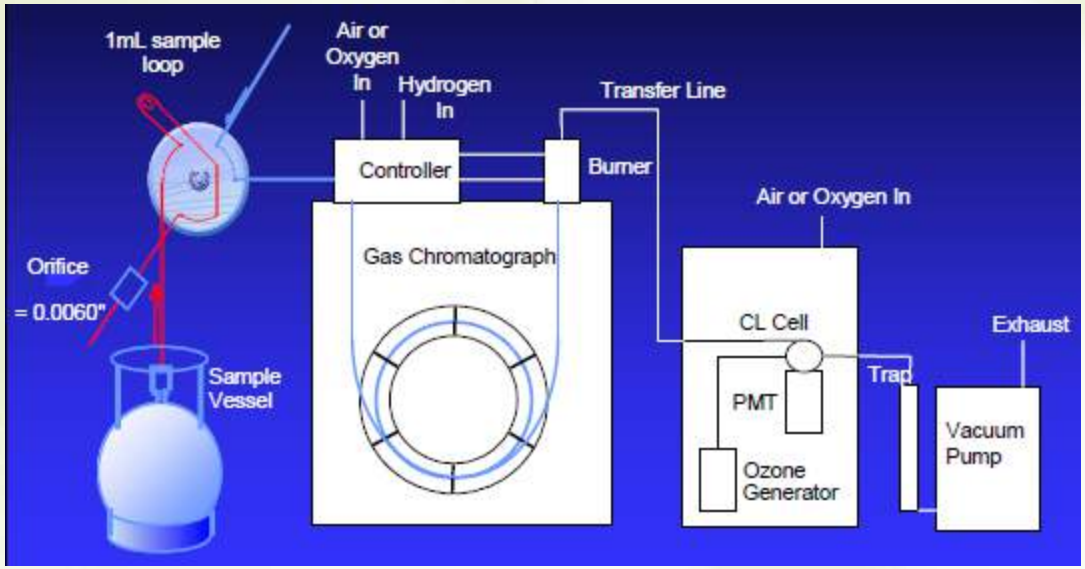
Results

- SilcoNert 1000-coated tubing showed good transfer of properties for entire experimental matrix
- Performed at the same level as PTFE-lined tubing
- Both performed better than a standard stainless steel transfer line
- Study noted that results warranted further study

Organosulfur Compounds

- Certain species adsorb to steel surfaces (e.g. hydrogen sulfide)
- Reactions can occur on a non-coated stainless steel surface (e.g. methyl mercaptan)
- Importance of accurate quantification (e.g. odorants, beverage grade CO_2, impurities in ethylene and propylene

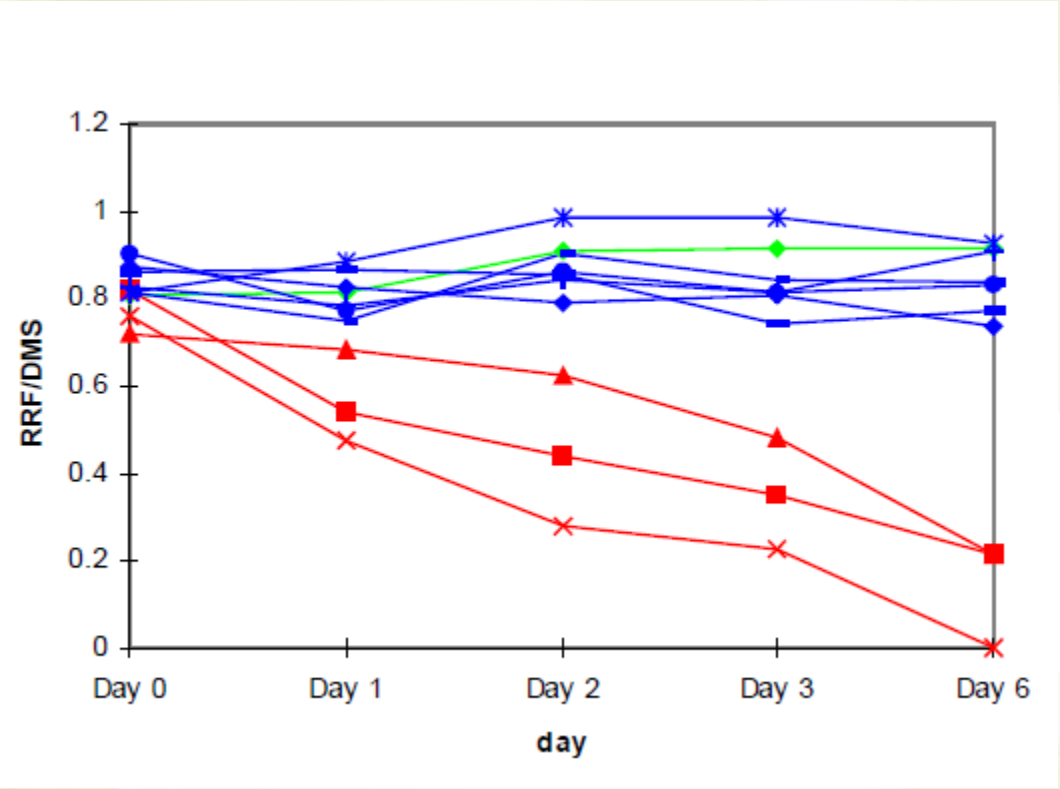
Block diagram of Analytical System



List of Sulfur Compounds

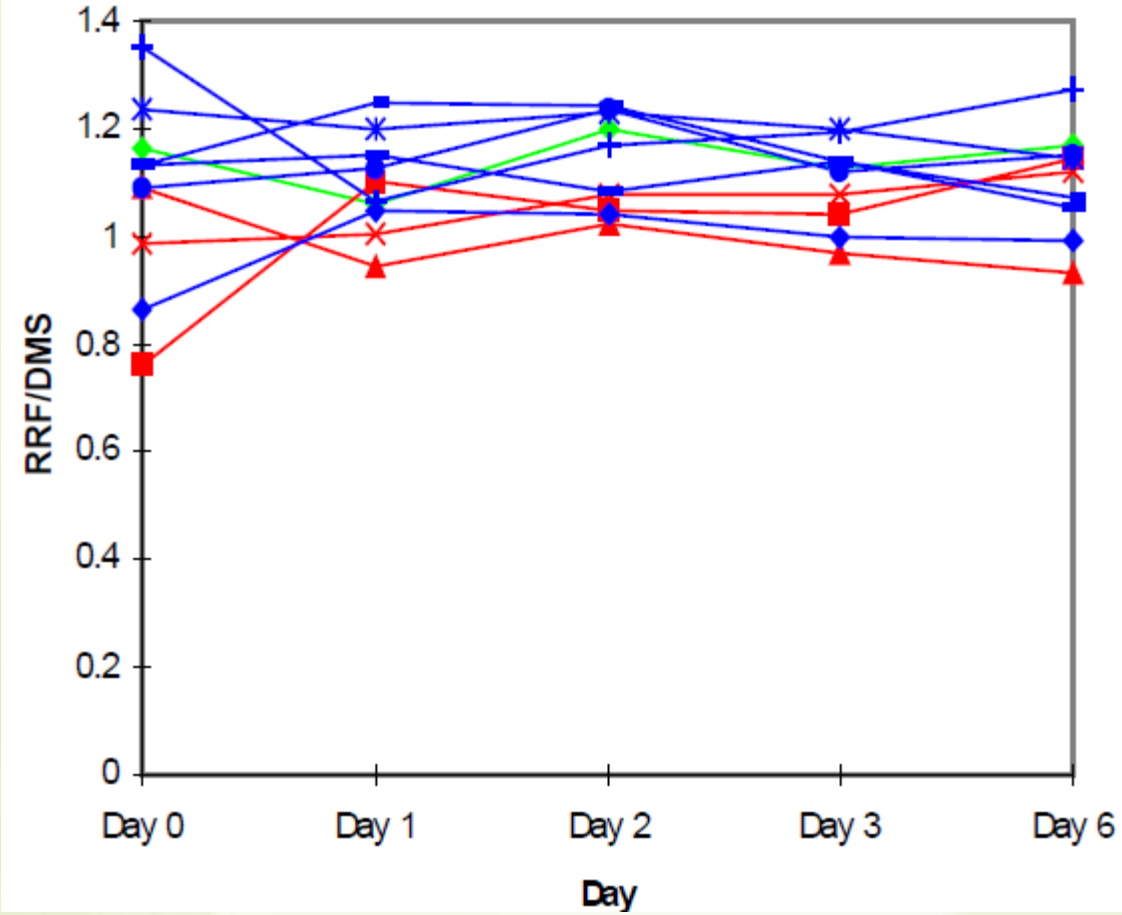
Compound Name	Formula	Conc (ppmv)	Conc (ppbv)	Conc as S (ppbv)
hydrogen sulfide	H2S	105	11.51	10.83
carbonyl sulfide	COS	98	10.74	5.73
methyl mercaptan	CH3SH	101	11.07	7.38
ethyl mercaptan	CH3CH2SH	101	11.07	5.71
dimethylsulfide	CH3SCH3	99	10.85	6.81
dimethyl disulfide	CH3SSCH3	100	10.96	7.46

H_2S at 11.51ppbv



reference standard
SilcoNert 1000
SilcoNert 2000 treated

Methyl Mercaptan at 11.07ppbv

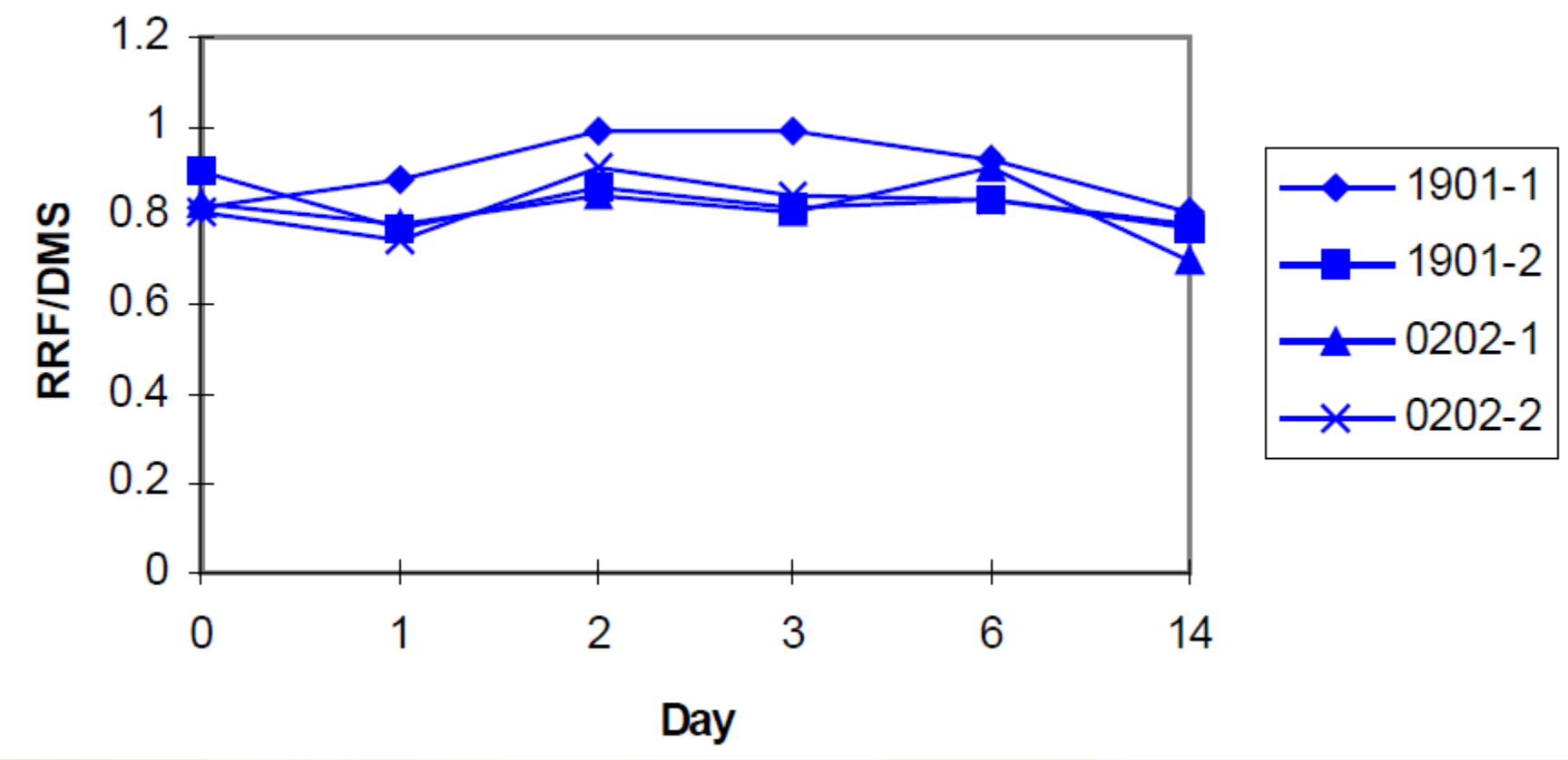


reference standard
SilcoNert 1000
SilcoNert 2000 treated

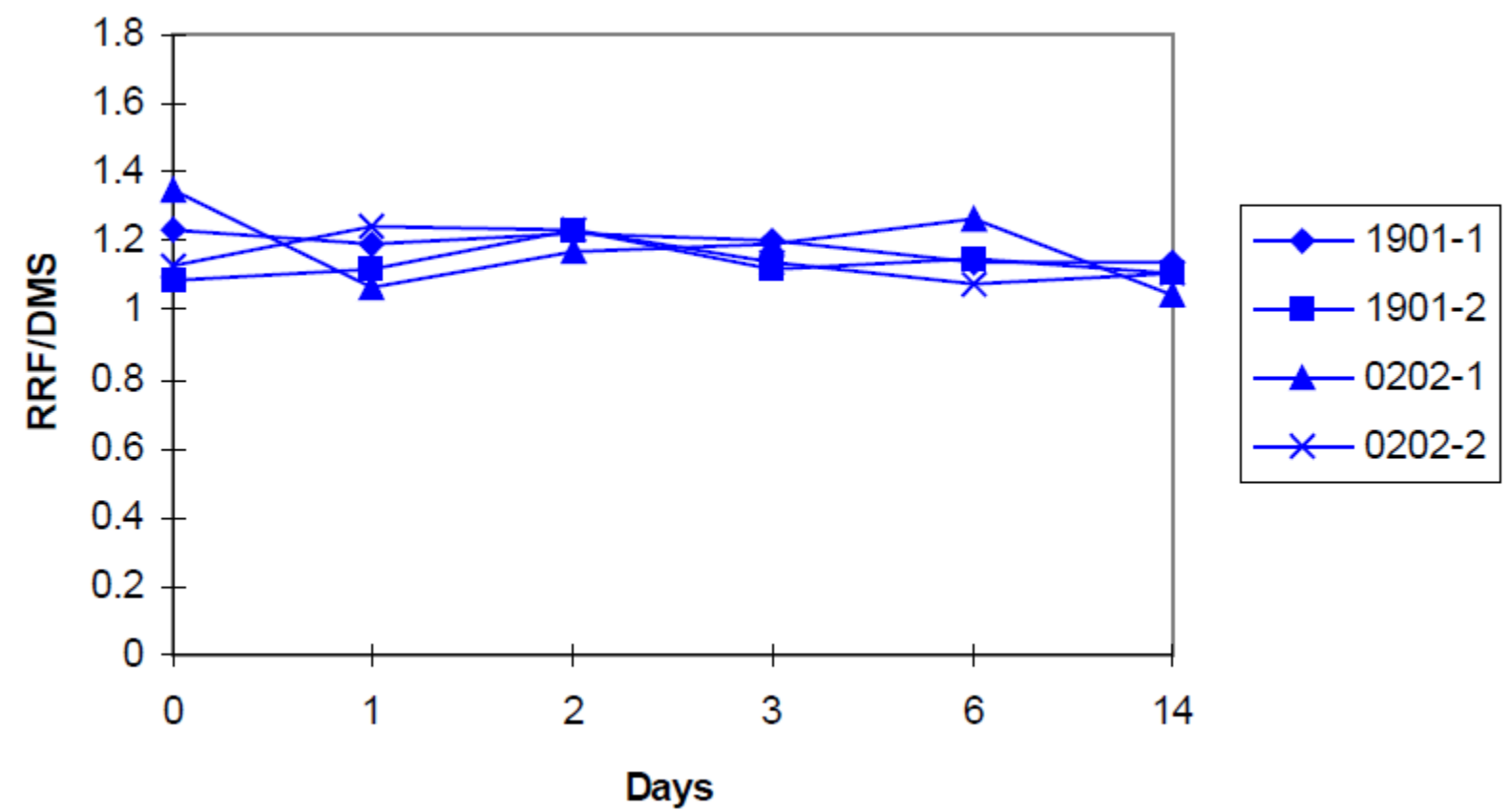
Extended Stability Study

- Is the SilcoNert® 2000 surface capable of storing 11ppbv sulfurs longer than 6 days?

H_2S at 11ppbv for 14 days



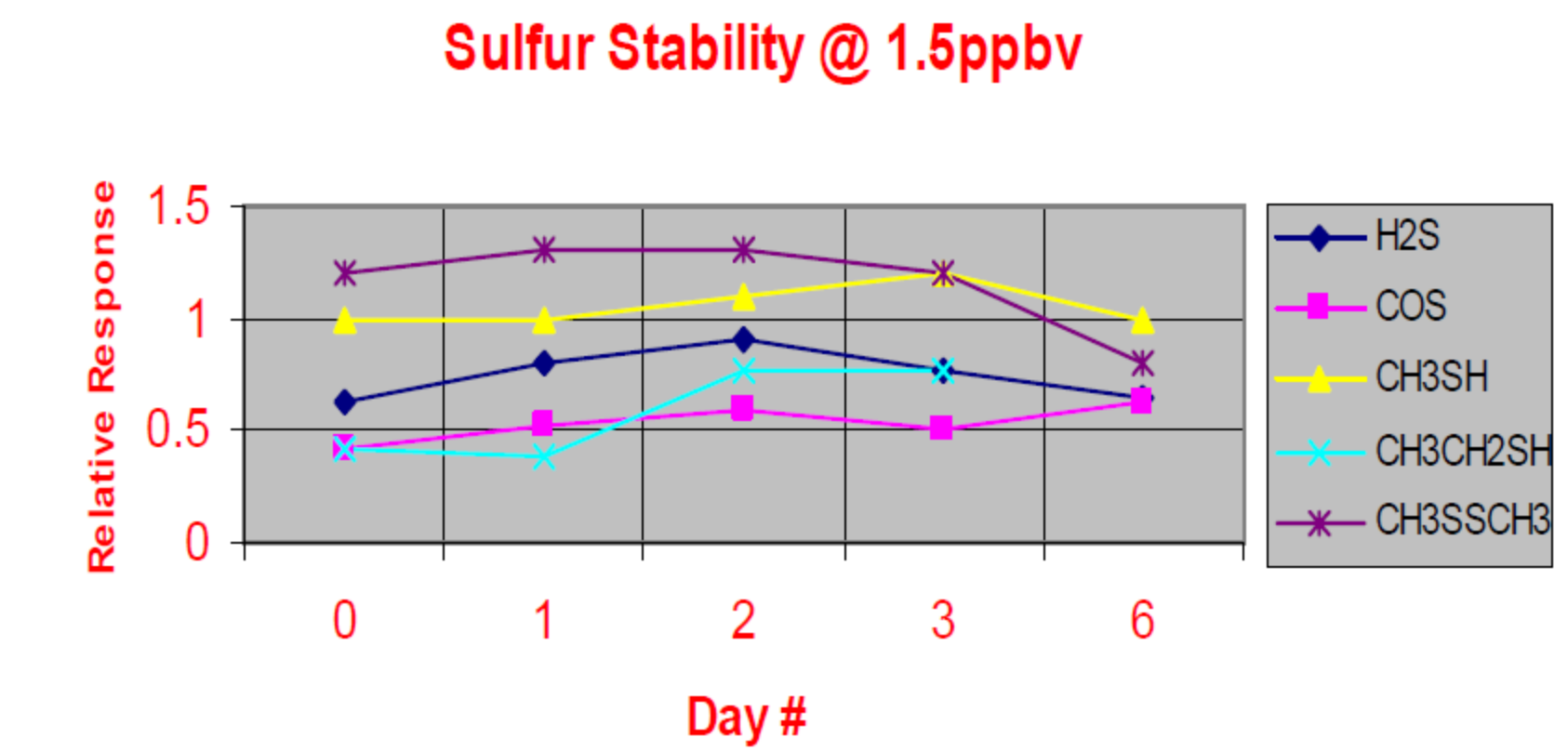
Methyl Mercaptan 11.07 ppbv for 14 days



Can the SilcoNert 2000-coated vessels go to lower levels?

- Is the SilcoNert® surface treatment stable for sulfurs at 1.5ppbv?

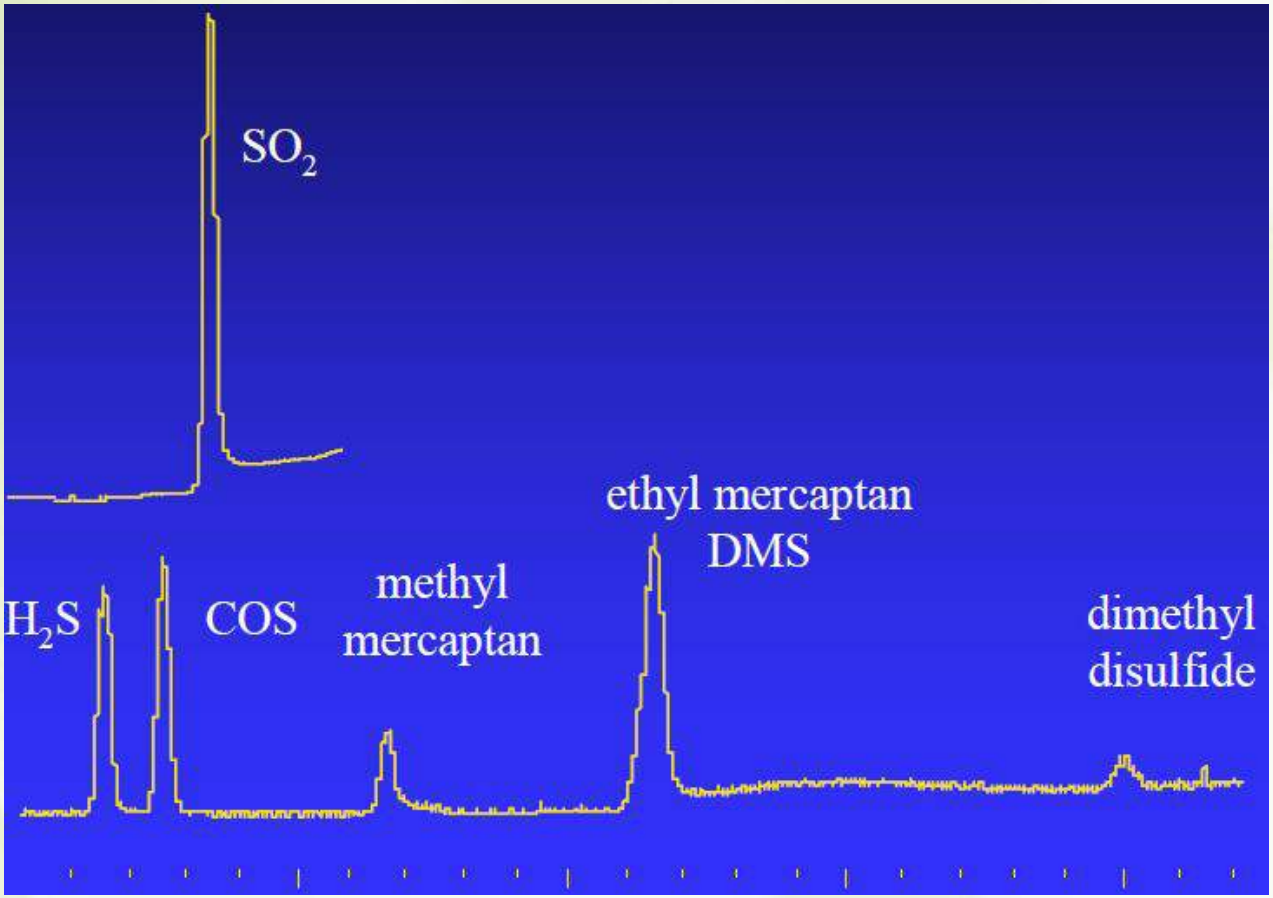
1.5ppbv organosulfur compounds in SilcoNert 2000-treated canisters



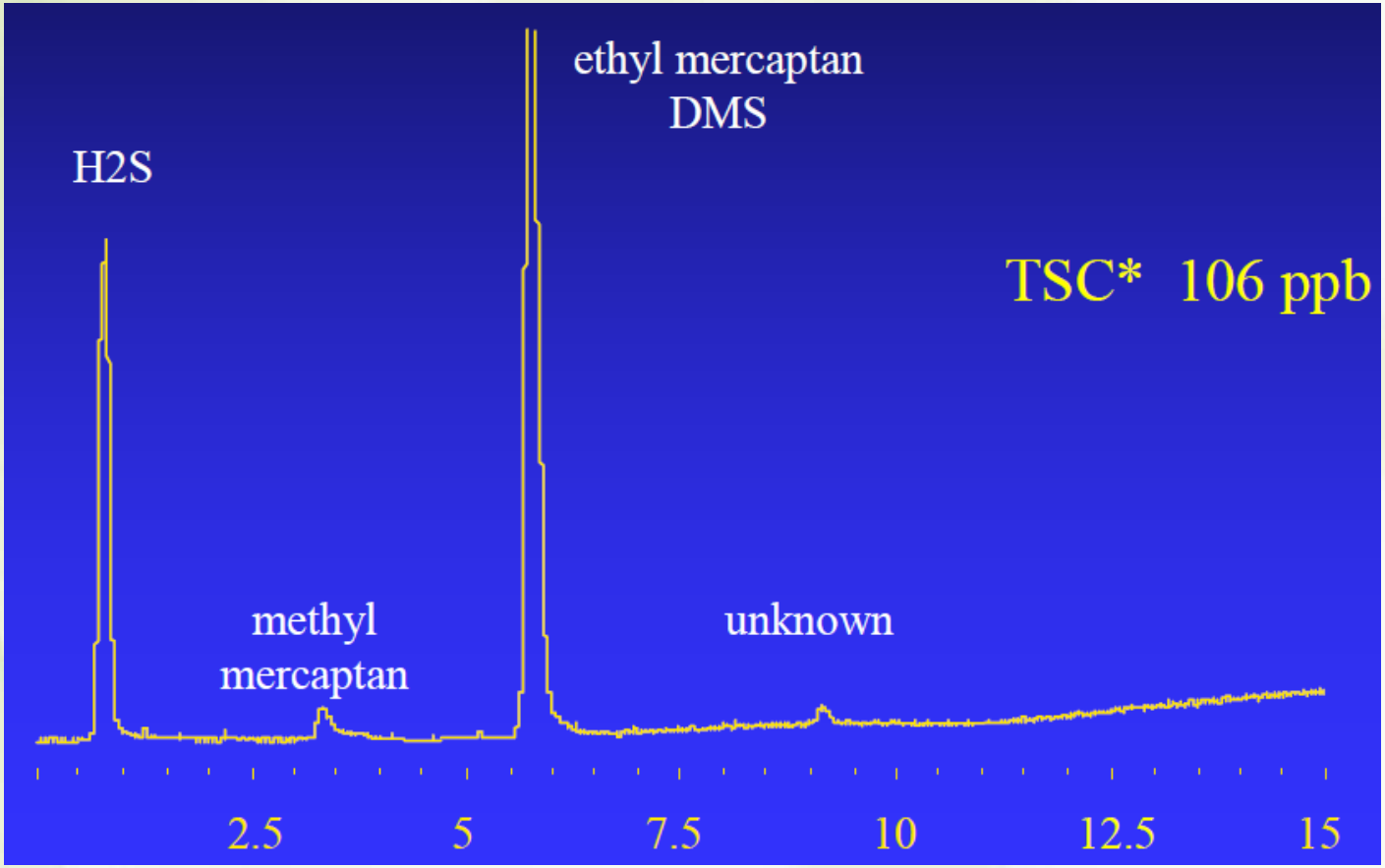
Example applications requiring SilcoNert treatment for optimal performance

- Testing of beverage-grade CO2 for organosulfur impurities
- Quality testing of beers, wines, and distilled spirits
- Evaluating natural gas / refinery gas

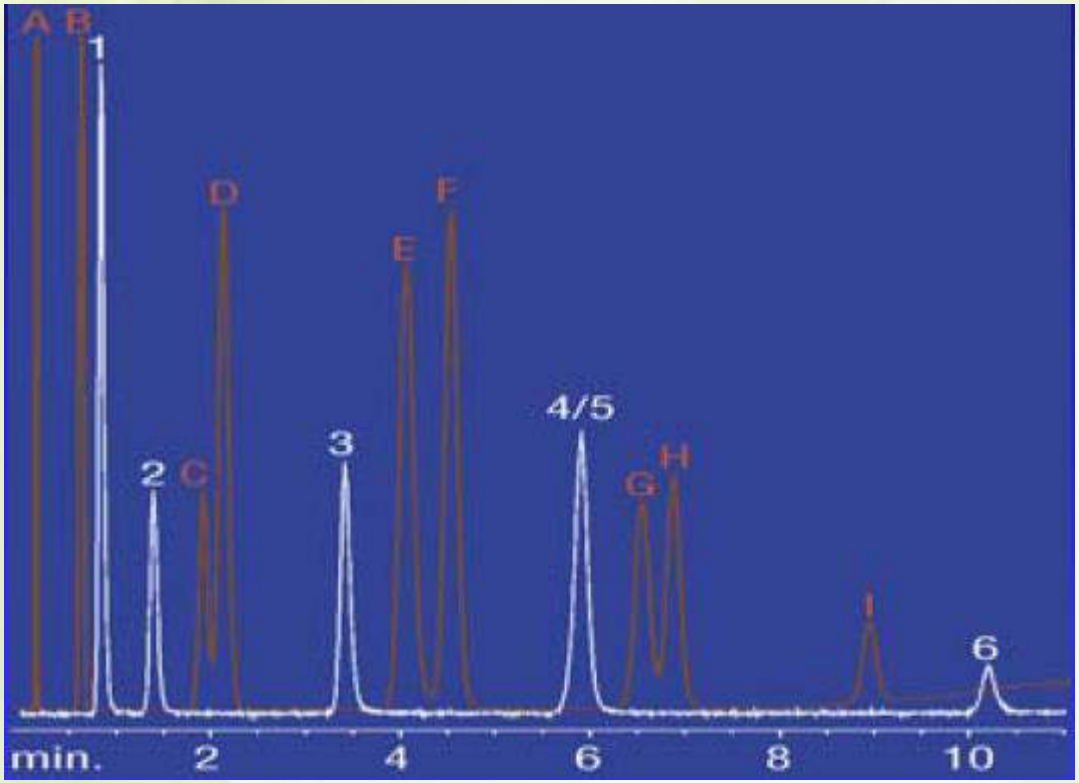
Beverage-grade CO2 20ppbv sulfur standard added



Typical run to determine beer's sulfur content



Sulfurs and hydrocarbon analysis of natural/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

Conclusions on stability of organosulfur compounds

- Surface treatments for steel surface allow low-ppbv containment, transfer, and subsequent analysis of sulfur gases
  - SilcoNert 1000: good for ppm levels
  - SilcoNert 2000: single ppb, high ppt levels

Advantages of inert coated steel components

- Sulfur-containing compounds; polar organic compounds
- Coat storage vessels and any stainless steel or glass component in the flow path
- Drastically improved durability compared to glass and PTFE linings
- Improved lifetimes and reduced diffusion compared to PTFE

Conclusion

- SilcoNert is an all-in-one solution for unmatched inertness in a sample flow path, existing or new
- Shielding exposed metal surfaces is critical
- Other coatings like Dursan® offer different properties depending on your application

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