

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 organosulfur 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 NO_x gases, organosulfur compounds, polar organics like alcohols, esters, ethers, etc.
- Insoluble in acids like HCl and HNO₃
- 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
 - NO_x, 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 NO_x & 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 NO_x levels in study were 0.4ppm, 2ppm and 9.5ppm total

NOx Study Conditions

- 100' section of 1/4" SilcoNert 1000 (Silcosteel[®]) coated tubing used to transfer simulated exhaust streams
- Looking at recovery of components through the transfer system and relative standard deviation

NO_x-containing sample streams studied

- Variety of components and concentrations studied
- Each condition tested with 3 NO_x concentrations 0.4ppm, 2ppm and 9.5ppm total NO_x:
 - 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

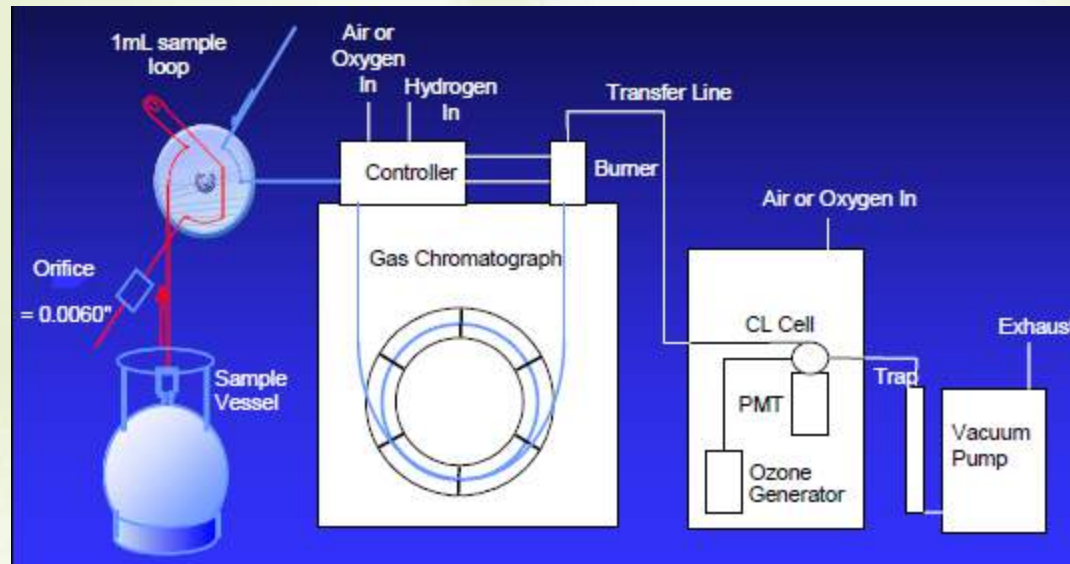
Results

- 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 CO₂, impurities in ethylene and propylene)

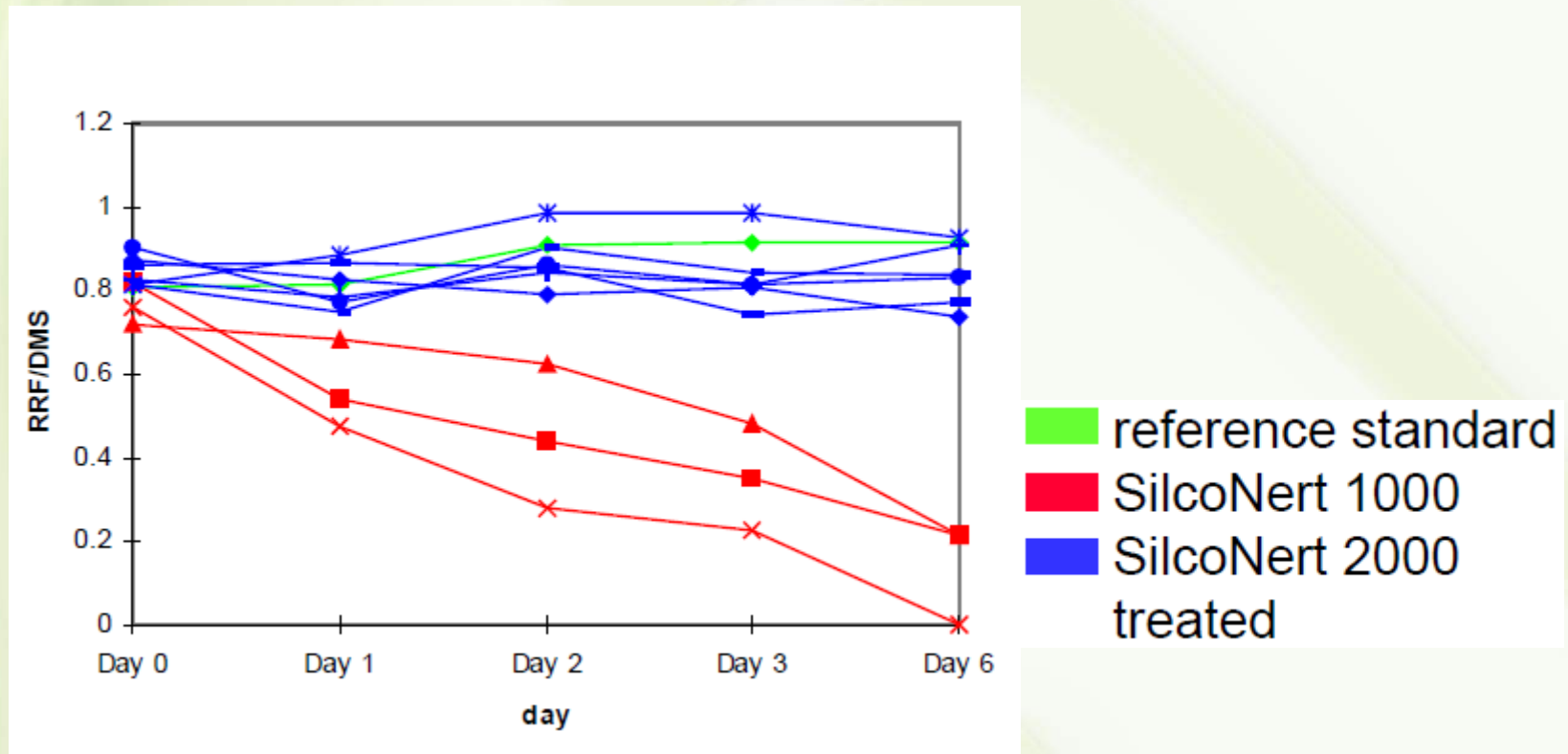
Block diagram of Analytical System



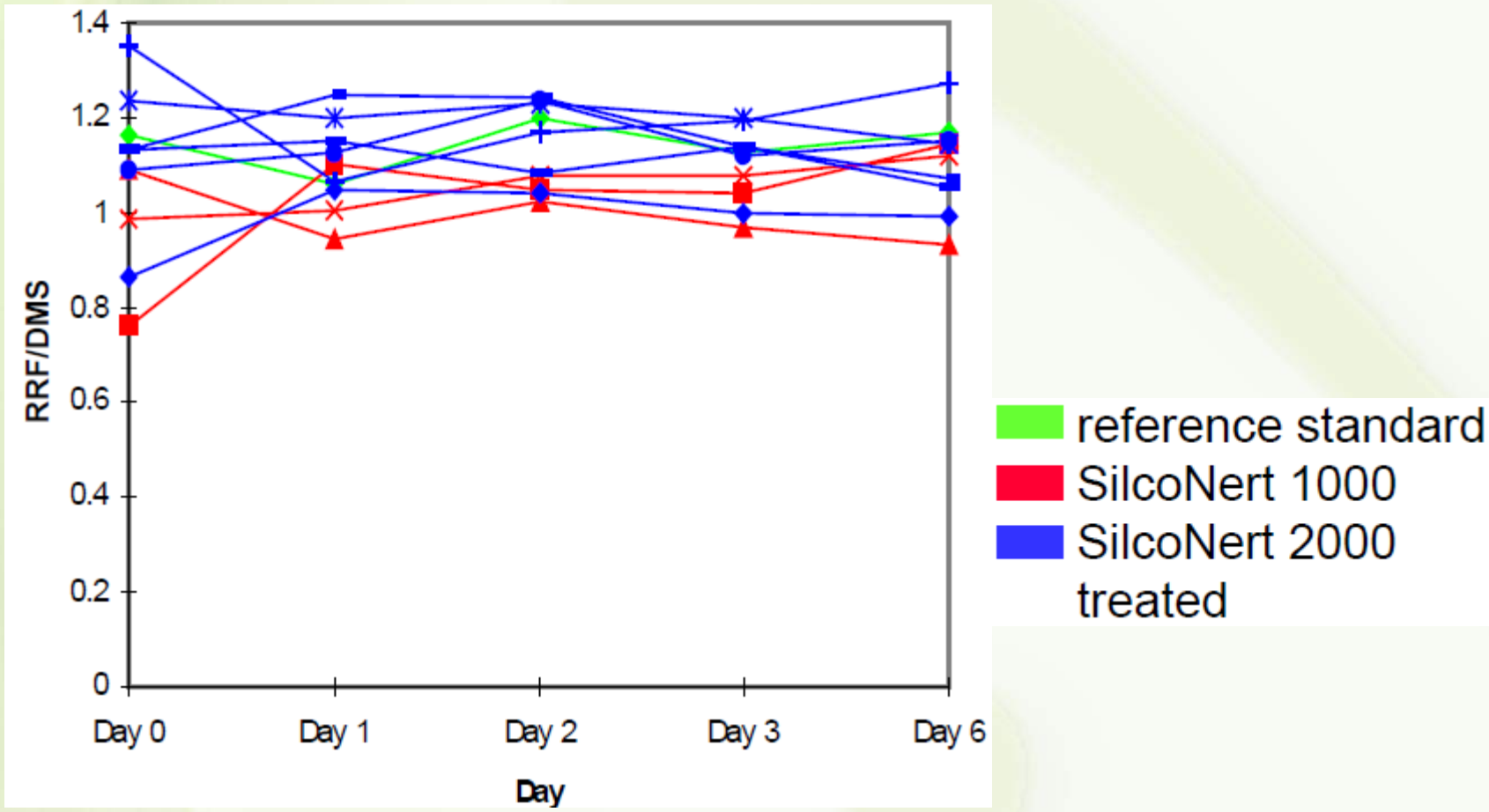
List of Sulfur Compounds

Compound Name	Formula	Conc (ppmv)	Conc (ppbv)	Conc as S (ppbv)
hydrogen sulfide	H ₂ S	105	11.51	10.83
carbonyl sulfide	COS	98	10.74	5.73
methyl mercaptan	CH ₃ SH	101	11.07	7.38
ethyl mercaptan	CH ₃ CH ₂ SH	101	11.07	5.71
dimethylsulfide	CH ₃ SCH ₃	99	10.85	6.81
dimethyl disulfide	CH ₃ SSCH ₃	100	10.96	7.46

H₂S at 11.51 ppbv



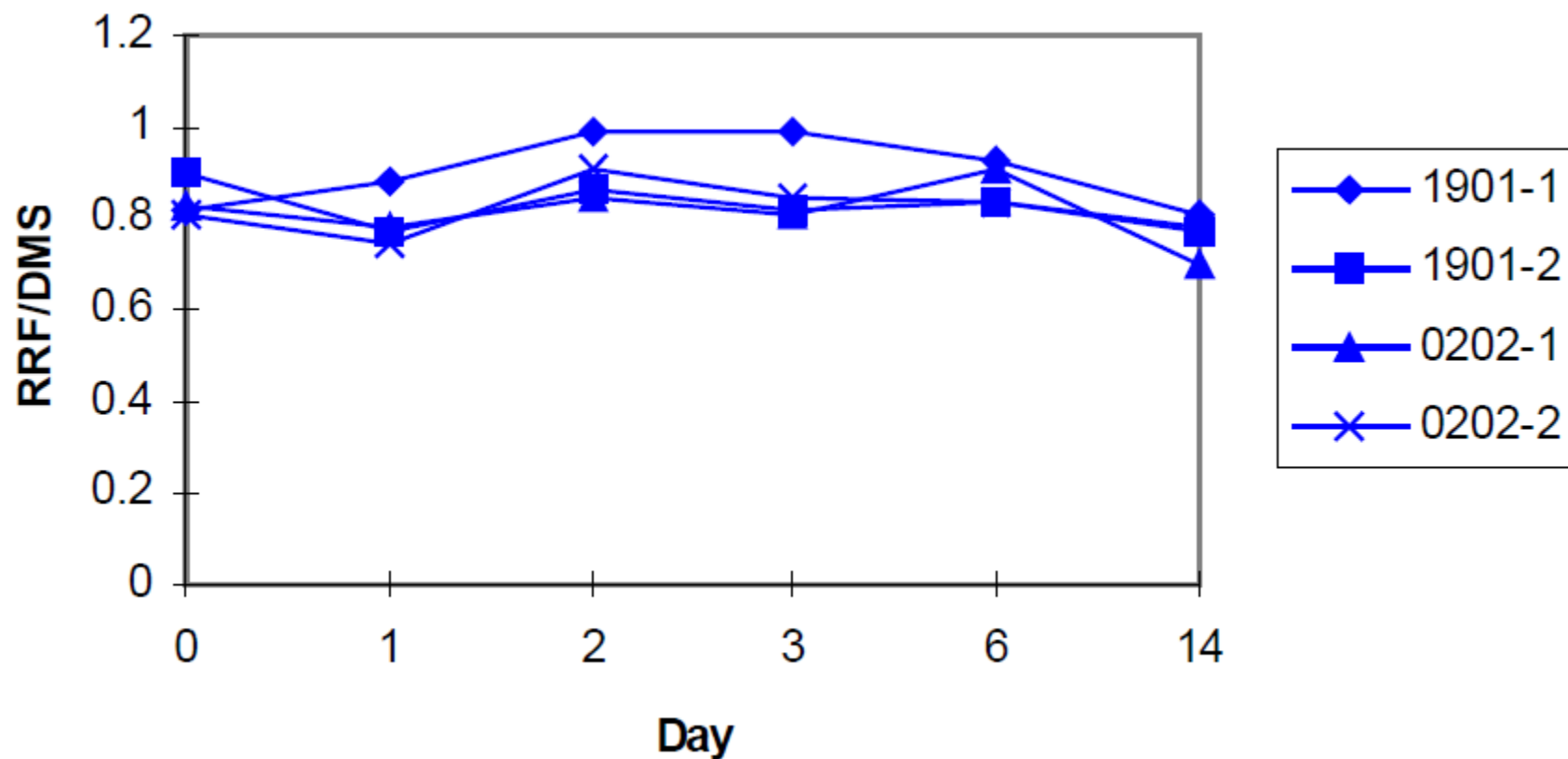
Methyl Mercaptan at 11.07ppbv



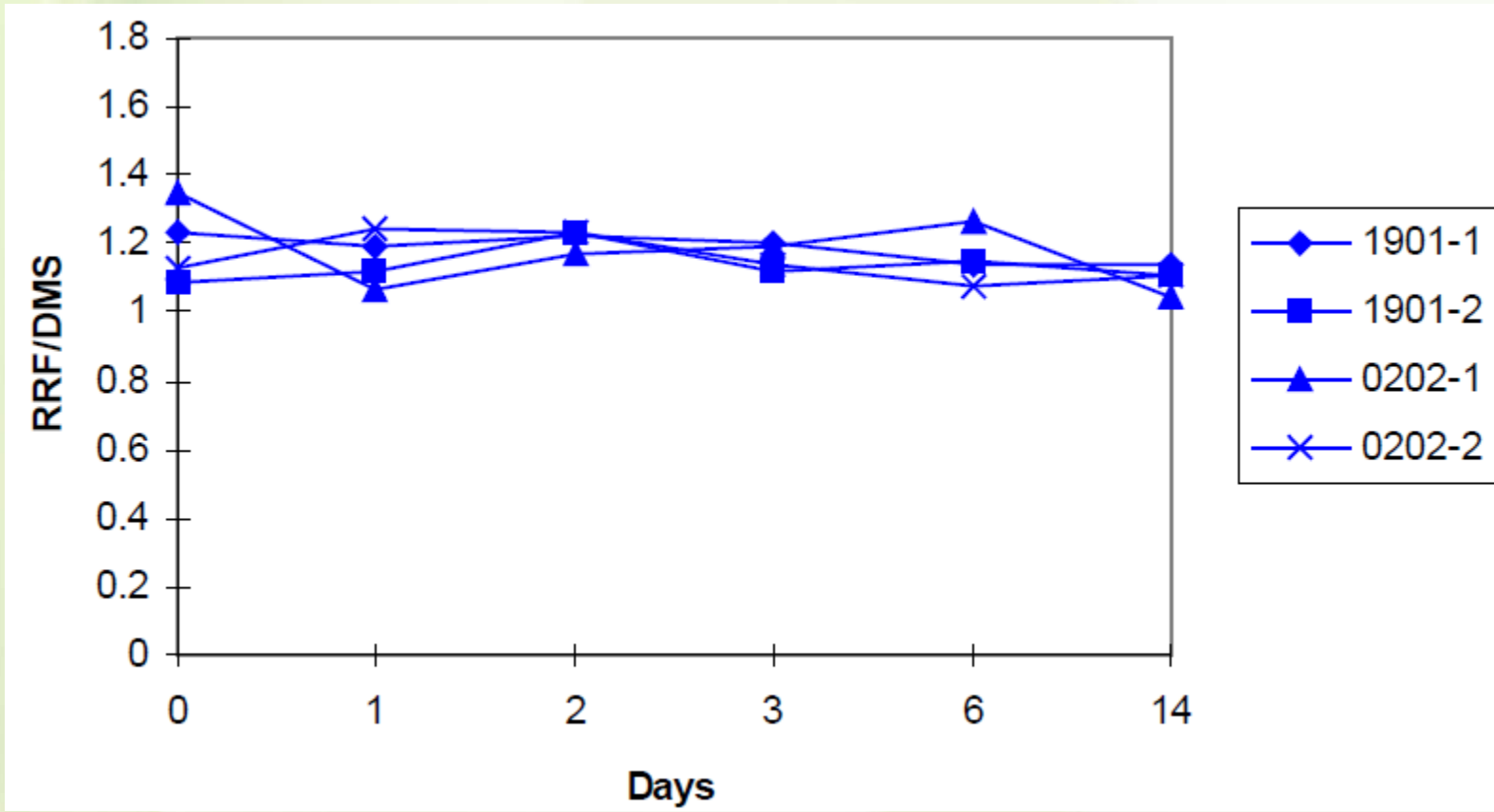
Extended Stability Study

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

H₂S at 11 ppbv for 14 days



Methyl Mercaptan 11.07 ppbv for 14 days

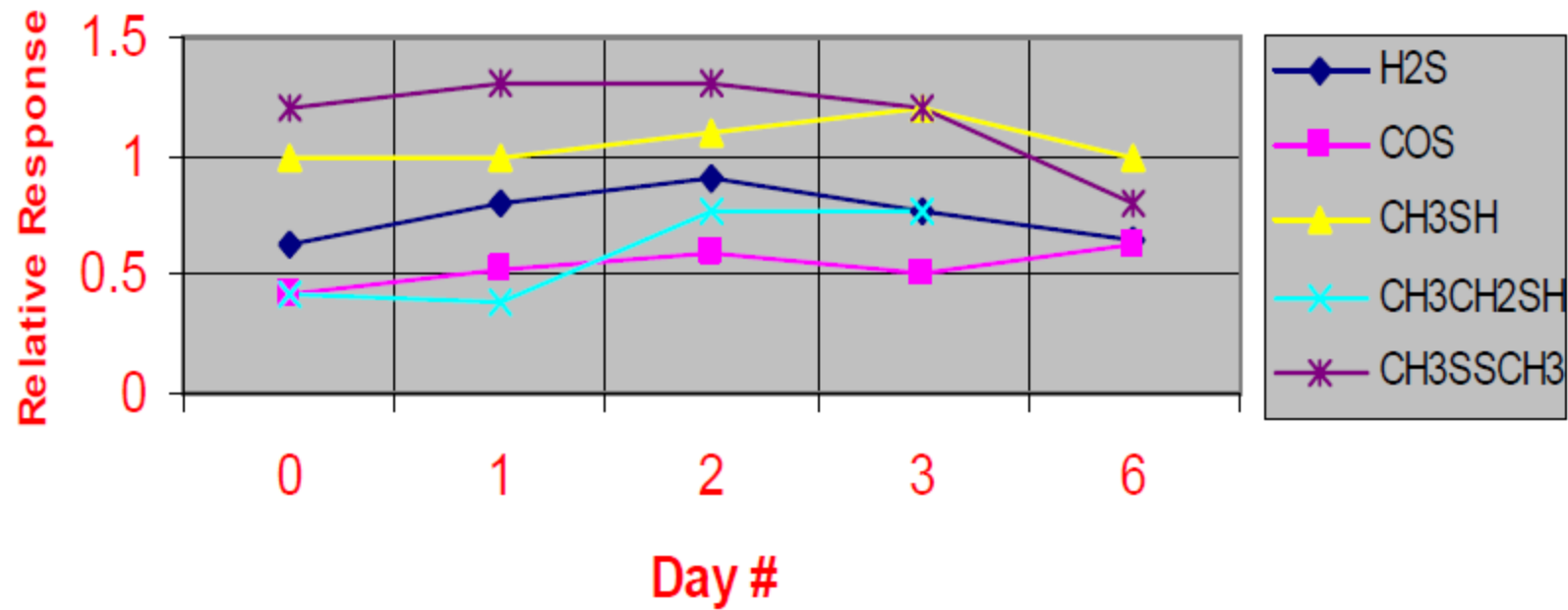


Can the SilcoNert 2000-coated vessels go to lower levels?

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

1.5ppbv organosulfur compounds in SilcoNert 2000-treated canisters

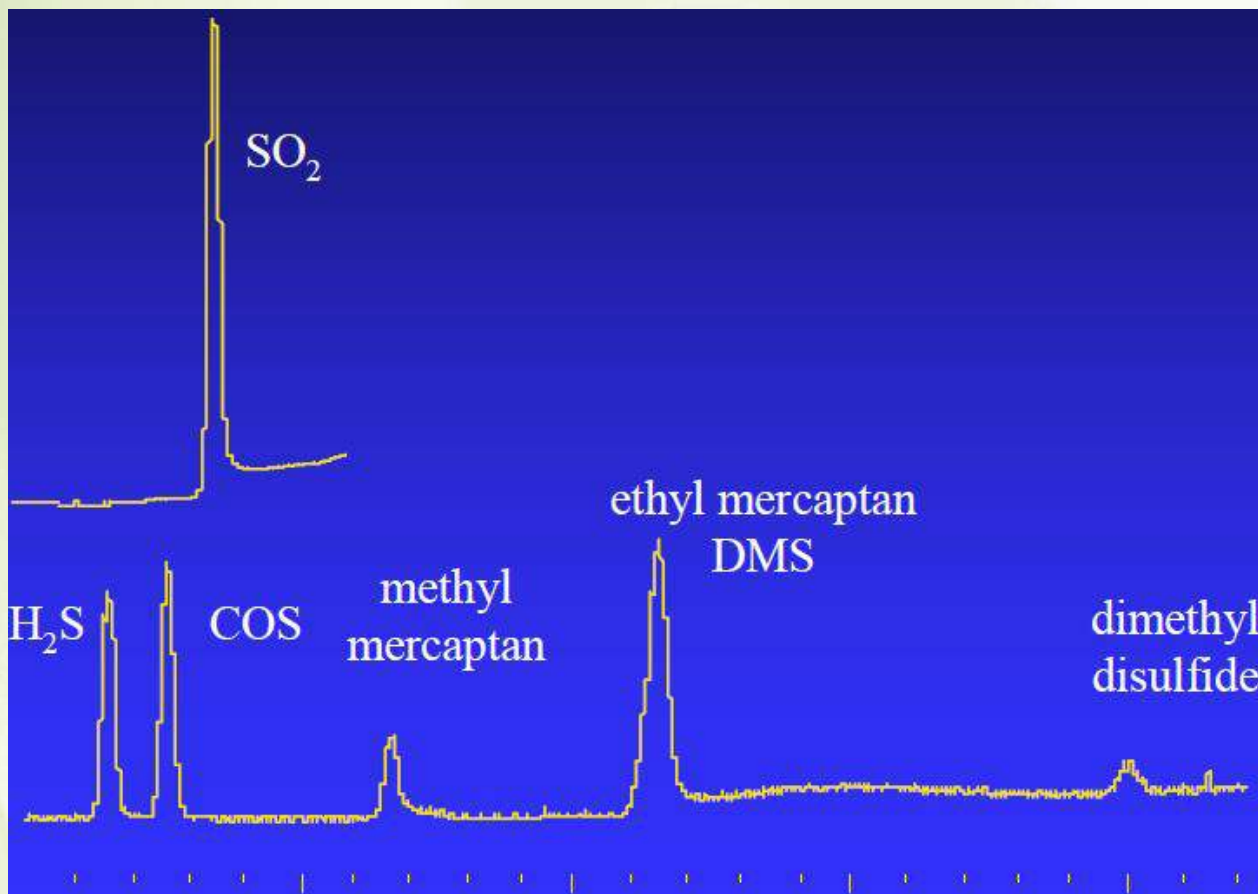
Sulfur Stability @ 1.5ppbv



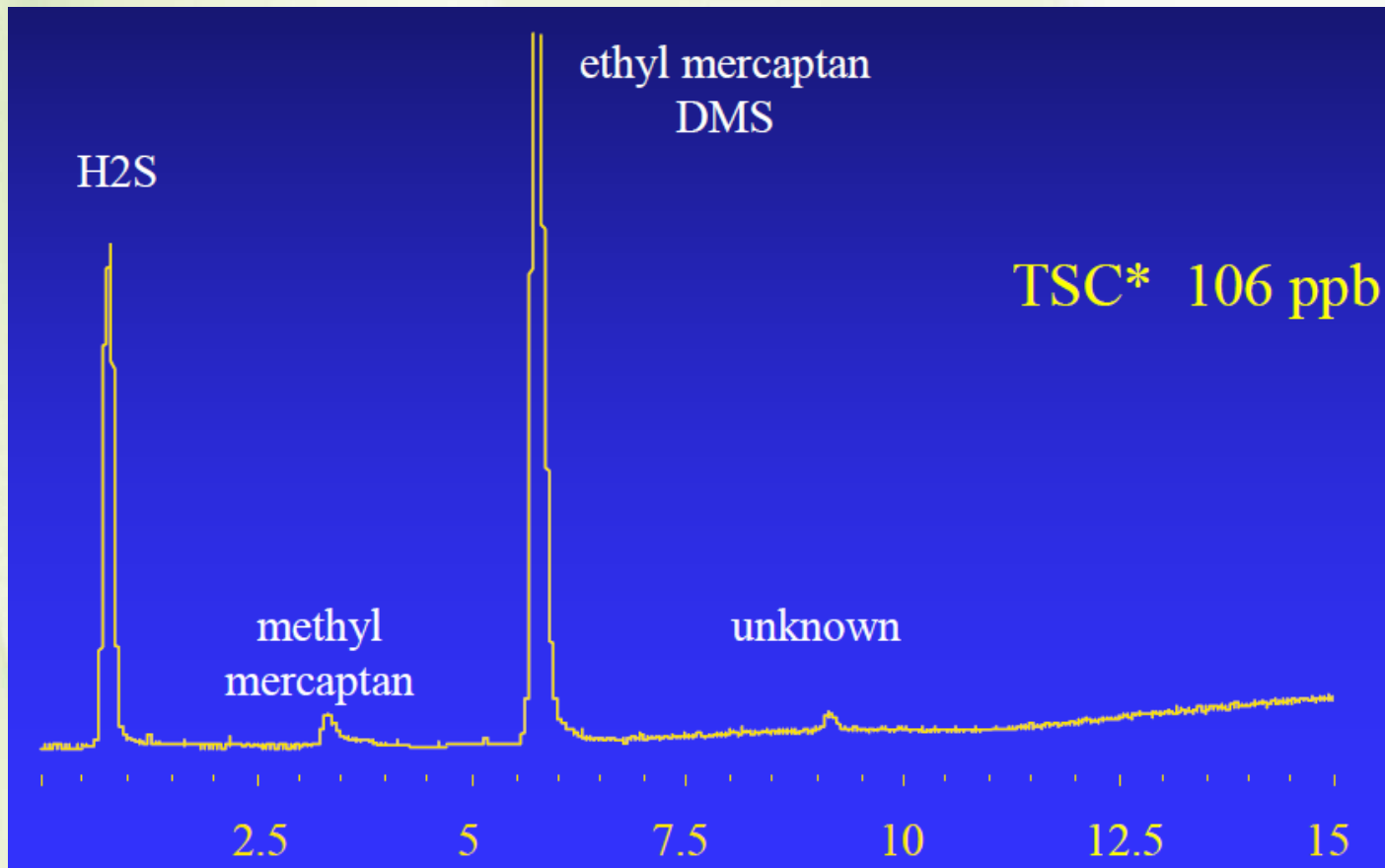
Example applications requiring SilcoNert treatment for optimal performance

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

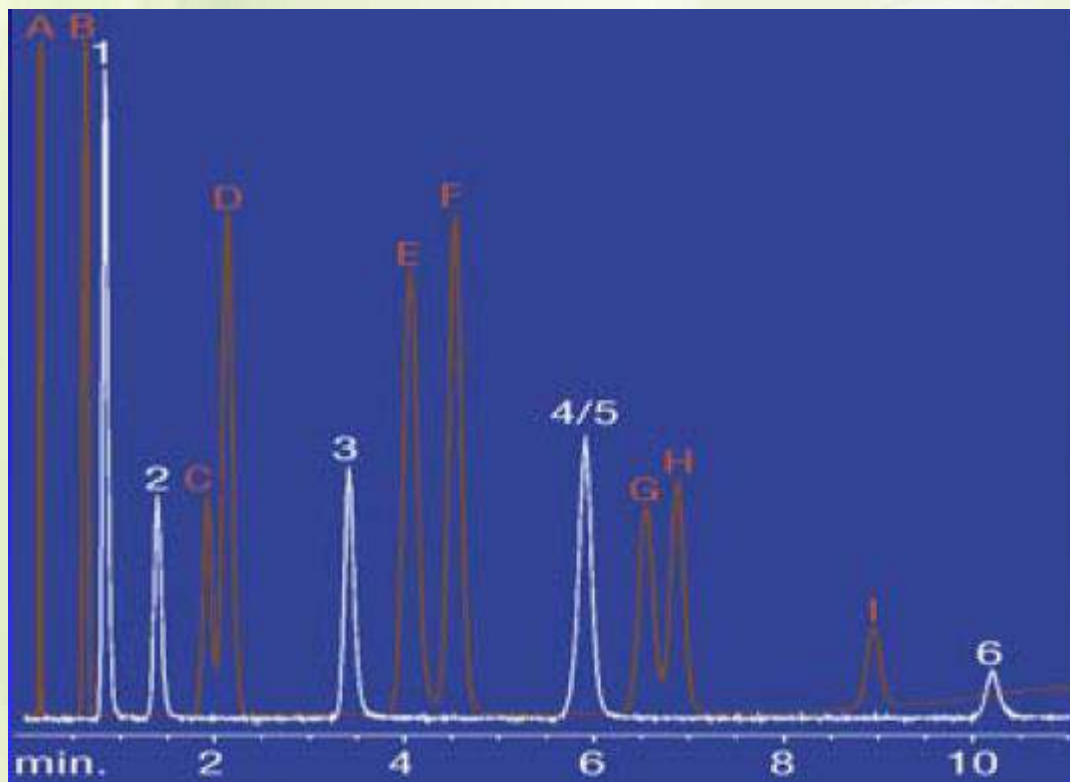
Beverage-grade CO2 20ppbv sulfur standard added



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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