Passivation of Components used for Sample Transfer and Holding

Gary A. Barone, David Smith, David Shelow

Restek Corporation
www.restekcorp.com

Components That Benefit from Inert Coatings

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

Restek Coating Solutions

- History of Restek passive coatings for sample pathways and sample chambers

- Silcosteel®, Sulfinert™ and Siltek™ Coatings

Introduction

- Physical Properties of Sulfinert™, Siltek™ and Silcosteel® coatings
- Chemical Properties
- Siltek™-treated Liners for Gas Chromatographs
- 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 Inertness Properties of Silcosteel® Coating

- Silicon based
- No reactivity to organosulfurs compounds
- No reactivity or adsorption of polar organic compounds such as alcohols, esters, ethers, etc.,.
- Some flaws such as pin-holes and porosity created during coating process
- Insoluble in acids such as HCl, HNO_3, and H_2SO_4
- Highly soluble in caustic environments, pH>8

Chemical Properties of Sulfinert™ Coating

- Silicon Based Coating; non-reactive
- Initial processing similar to Silcosteel® process
- Secondary and Tertiary coatings applied to reduce effects of pin-holes and porosity
- Improved performance for transfer & storage of organosulfur compounds
- Improved resistance to caustic environments pH=10


Sulfinert™
Patented passivation treatment
that provides a durable,
thermally-stable and highly
inert surface

Siltek™ Deactivation

- Inertness for acids, bases, neutrals, pesticides (developed for pesticides analysis)
- Low bleed
- Thermal stability
- Durability (acids, bases, water)
- Regeneration. Easily cleaned with simple solvent sonication.
- Siltek™ for SemiVols+

Physical Properties of Restek Coatings

- Durable and flexible
- Strong adhesion to substrate
- Non-permeable surface
- Stable to high temperatures

Processing conditions for Restek Coatings

- Chemical vapor deposition
- Applied to stainless steels, carbon steels, high nickel containing alloys of steel, ceramics and glass
- Clean-room process, any oils or dust reduce coating quality
- Vacuum process. Uses either vacuum chambers or connections to items capable of holding vacuum
- Processing temperature of 400^{o}C

When to use Coatings

- Transfer and holding of adsorptive or reactive species such as:
  - Sulfurs
  - Alcohols
  - Pharmaceuticals
  - Explosives
  - chemical weapons
  - VOC’s
  - OP Pesticides and Chlorinated Pesticides
  - Herbicides
- All Analytical Instrument components used for low-level analysis

When to use Coatings

- Transfer of corrosive materials such as HCl, nitric acid, and sulfuric acid
- In components used to transfer or contain hydrocarbon streams that are prone to “coking”

Examples

- Siltek™-treated glass inlet liners; reduce breakdown and improve durability
- Project review detailing the storage and transfer of organosulfur containing streams
- How far can we go?
- Other applications benefiting from Sulfinert™-treated components

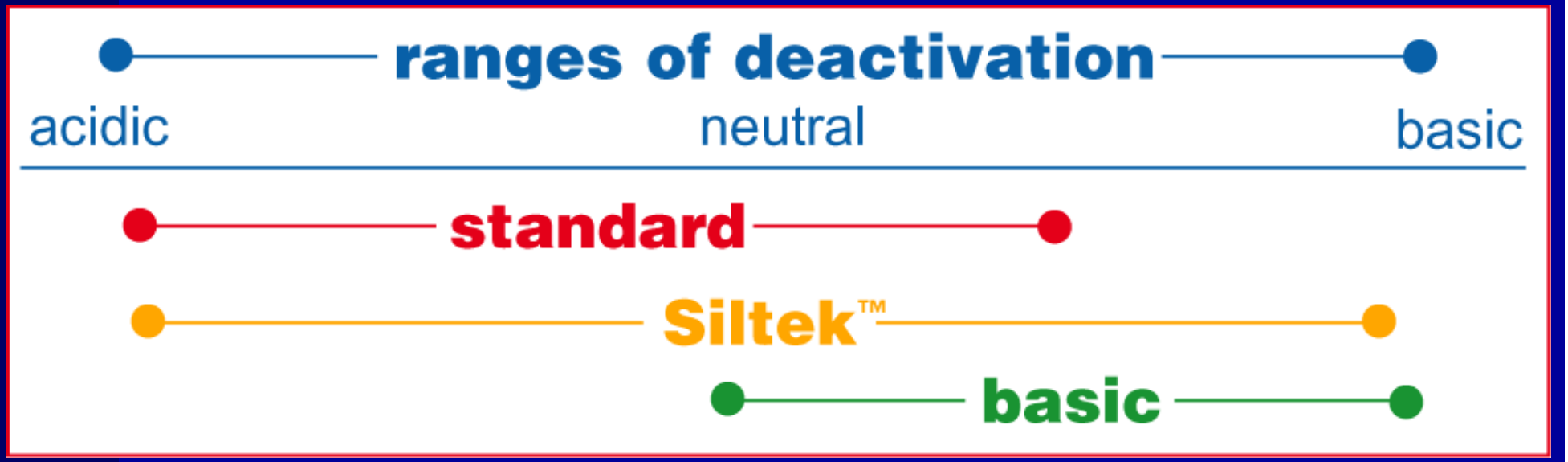
Siltek™-treated Inlet Liners

Restek
www.restekcorp.com

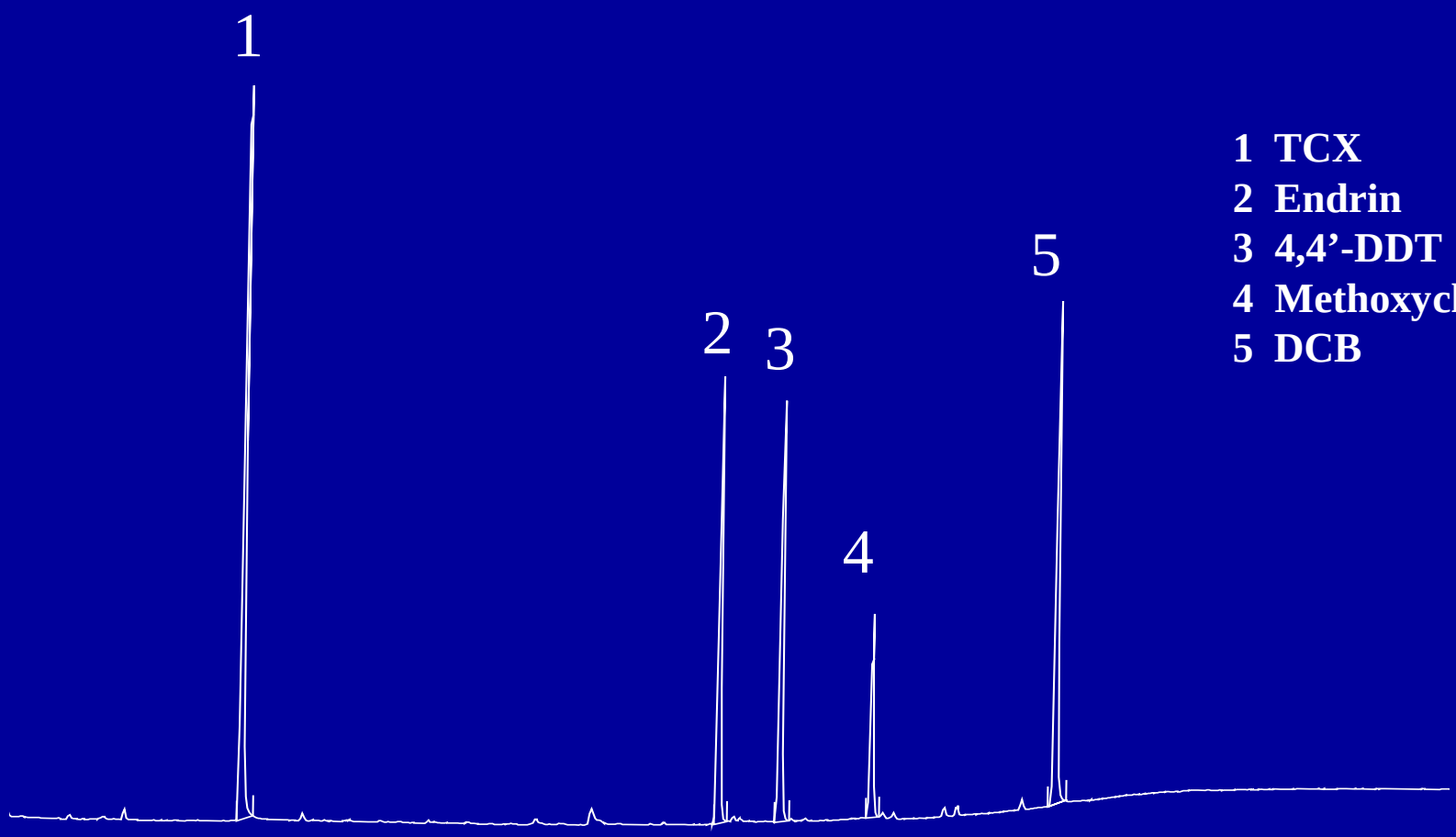
Siltek™ Deactivation

- Surface modification, not deactivation “layer”
  - Does not require existing silanol groups (ie. can be applied to glass, metal, ceramic)
- Higher level of inertness for Endrin
- More resistant to acid or base attack
  - Stays inert for longer time
- Easily cleaned
  - Solvent rinsing usually acceptable

Siltek™ Offers Extended Use Range



Excellent Performance: 1.5% Endrin Breakdown



1 TCX
2 Endrin
3 4,4’-DDT
4 Methoxychlor
5 DCB

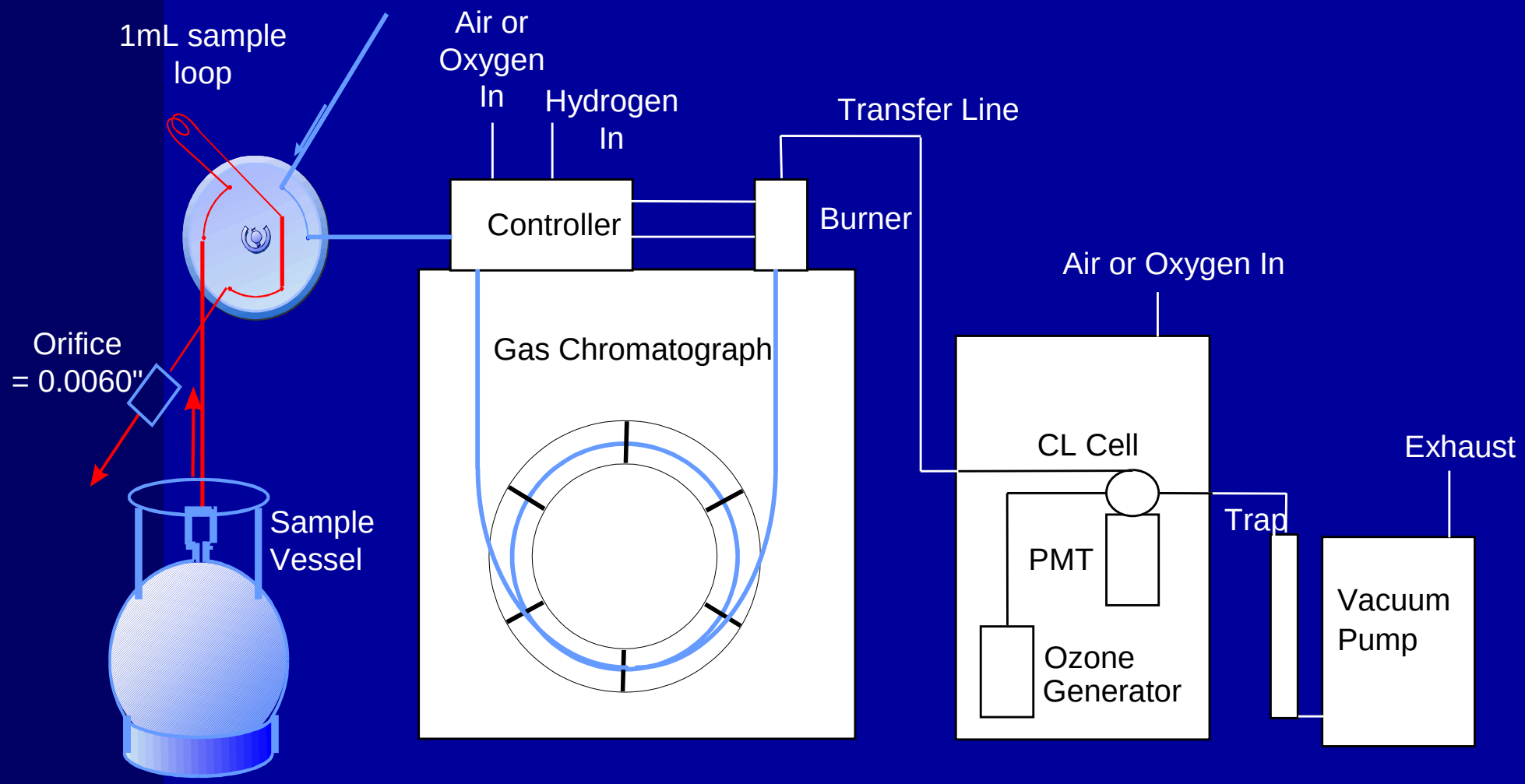
Project Example: Sulfinert™

- To create passivation processes for stainless steel surfaces which will allow the analysis of low- ppbv sulfur gases
  - Chromatographic sampling system
  - Containment vessels (high pressure vessels and air sampling canisters)

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 quantitation (e.g., odorants, beverage grade CO_2, impurities in ethylene and propylene)

Block diagram of Analytical System

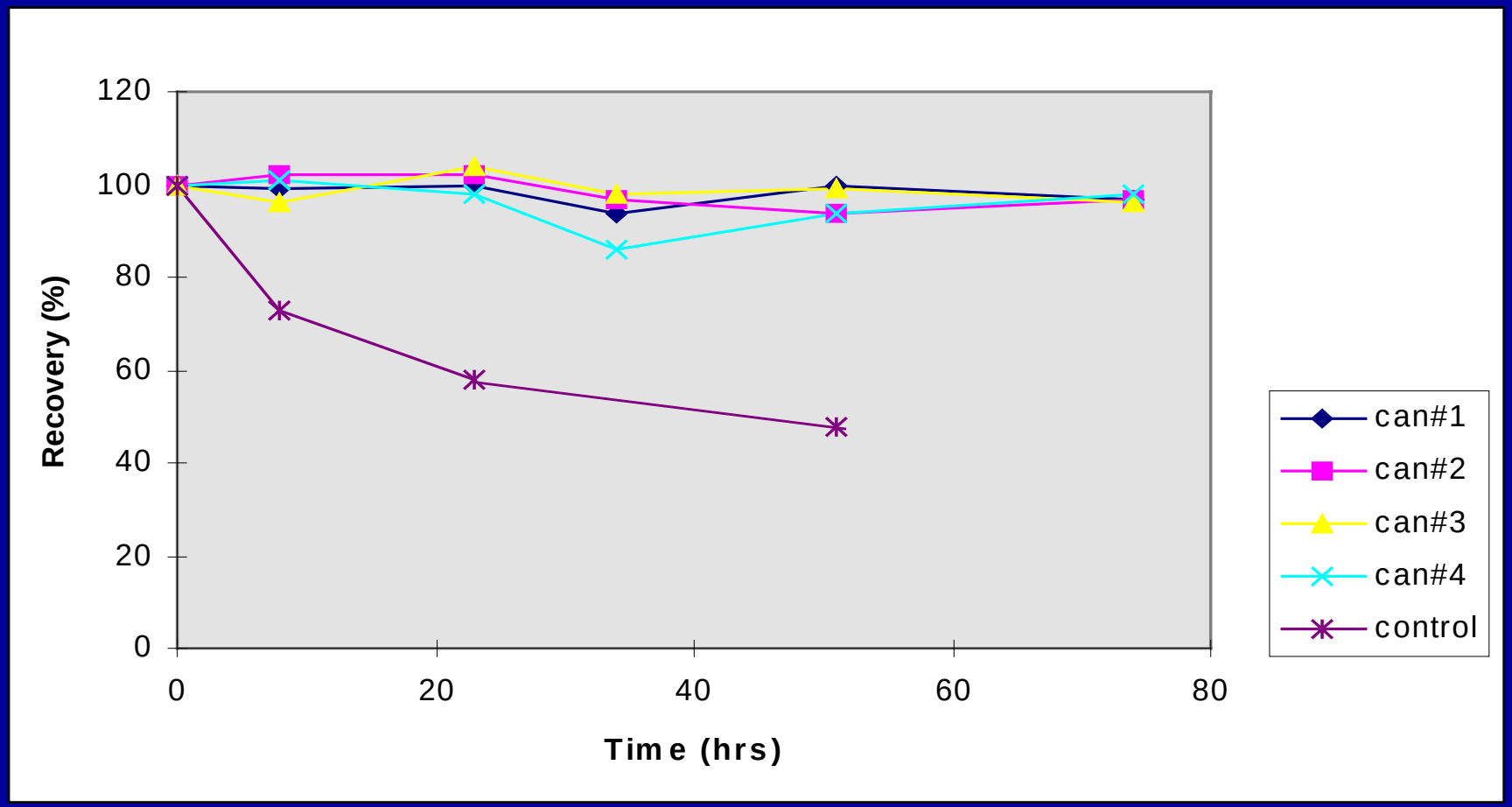


Restek
www.restekcorp.com

Sulfur Compounds Investigated

Compound	Formula	Stock conc. (ppmv)	Standard conc. (ppbv)	Standard conc. as S (ppbv)
hydrogen sulfide	H_2S	100	60	56
carbonyl sulfide	COS	100	60	30
methyl mercaptan	CH_3SH	100	60	40
ethyl mercaptan	CH_3CH_2SH	100	60	30
dimethyl sulfide	CH_3SCH_3	100	60	30
dimethyl disulfide	CH_3SSCH_3	100	60	40

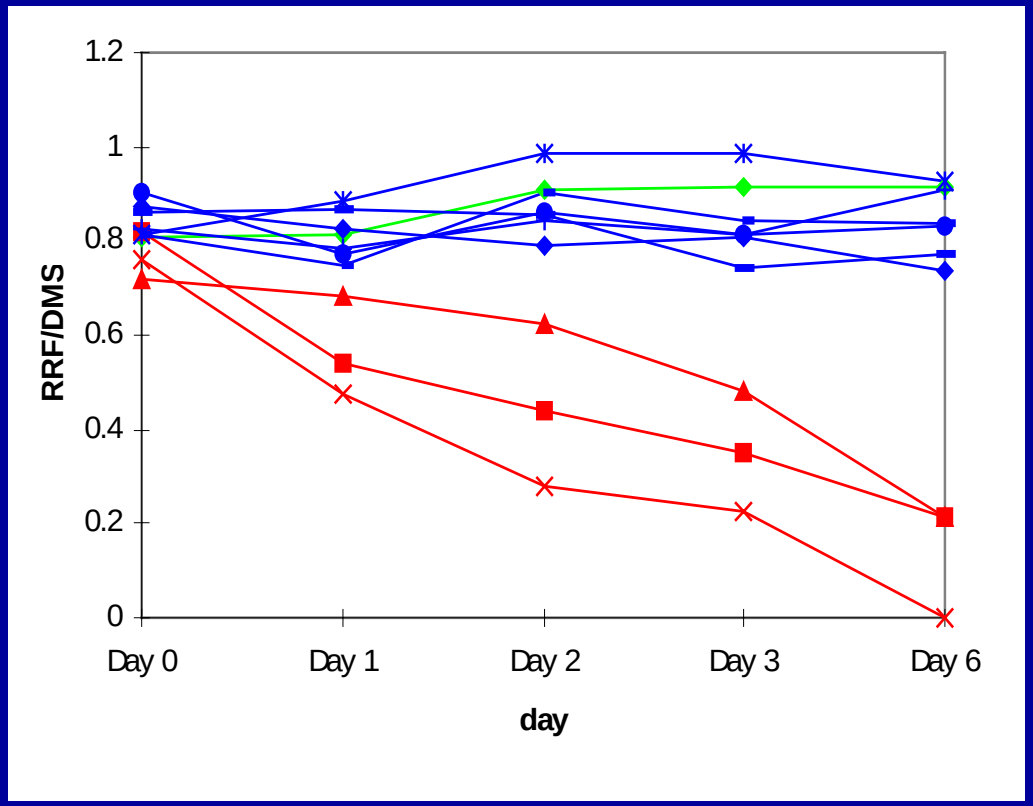
Methyl Mercaptan Stability



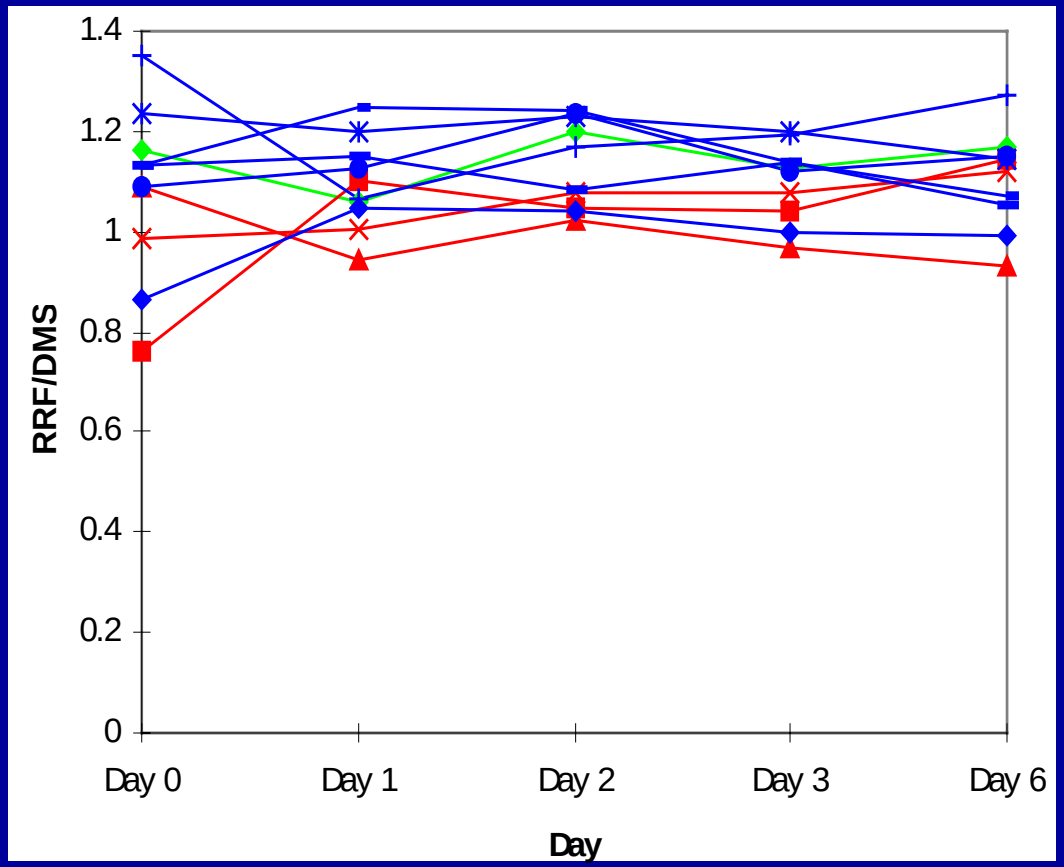
List of Sulfur Compounds

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



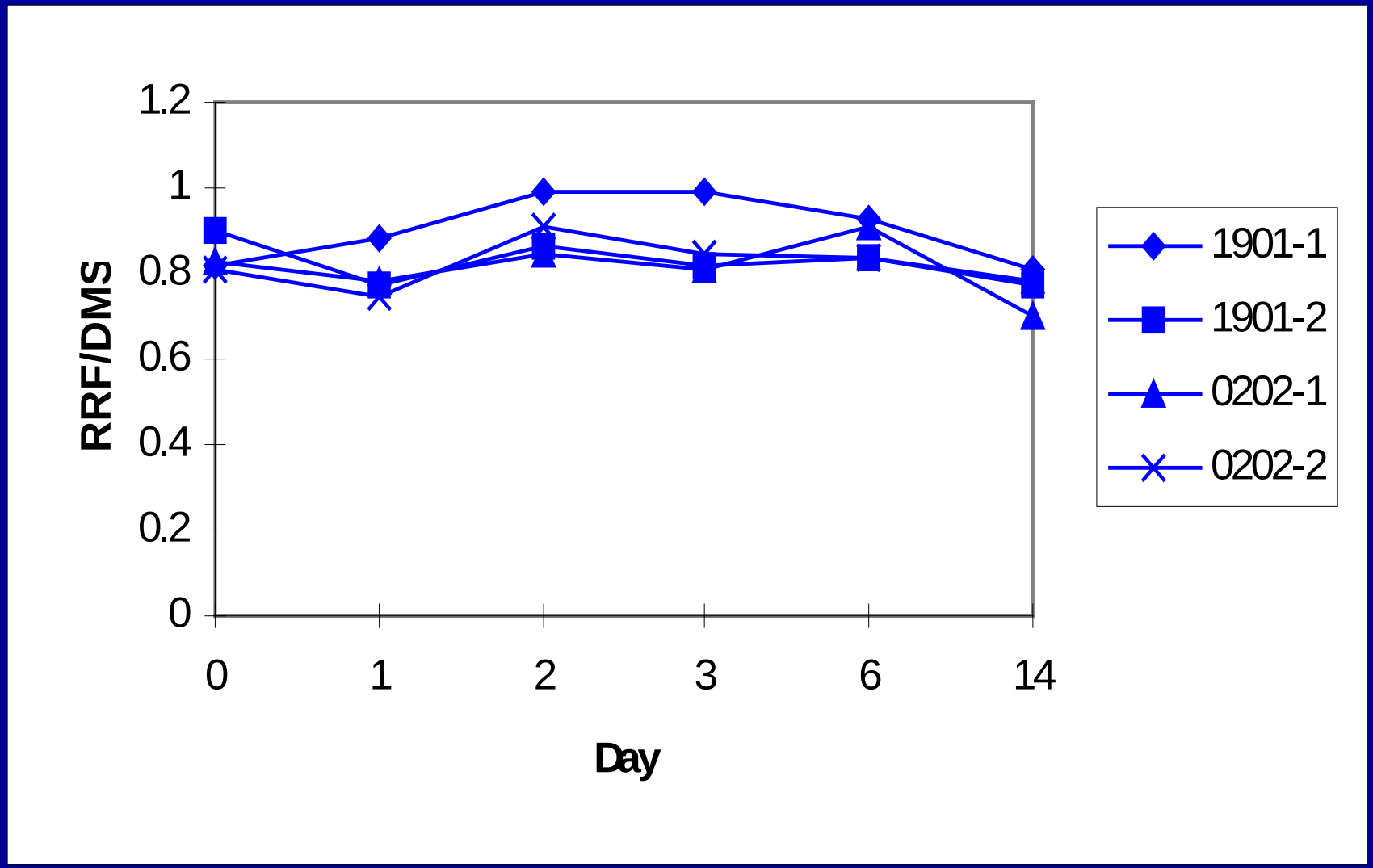
Methyl Mercaptan at 11.07ppbv



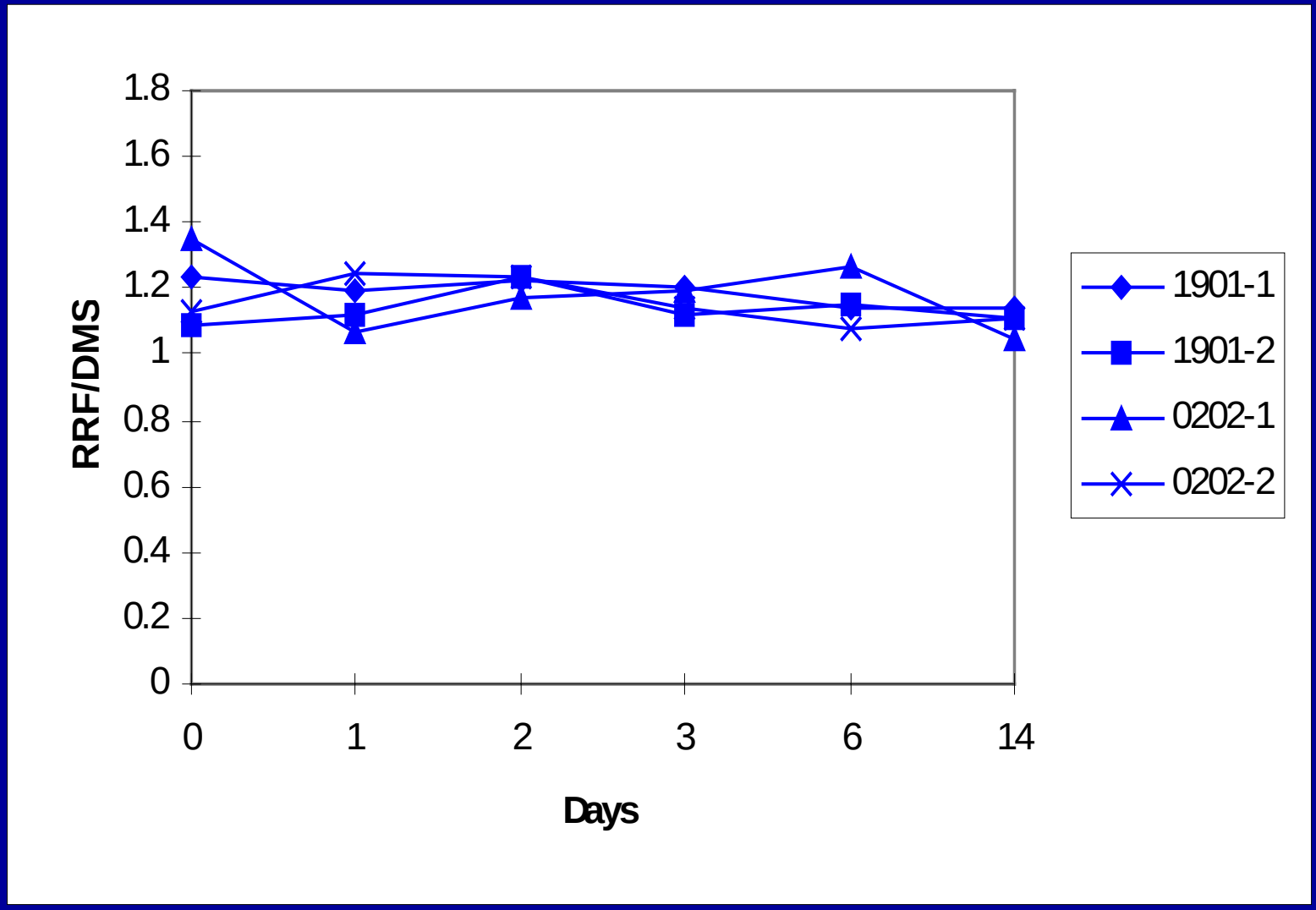
Extended Stability Study

- Is the Sulfinert™ surface capable of storing 11ppbv sulfurs longer than 6 days?

H_2S at 11ppbv for 14 days



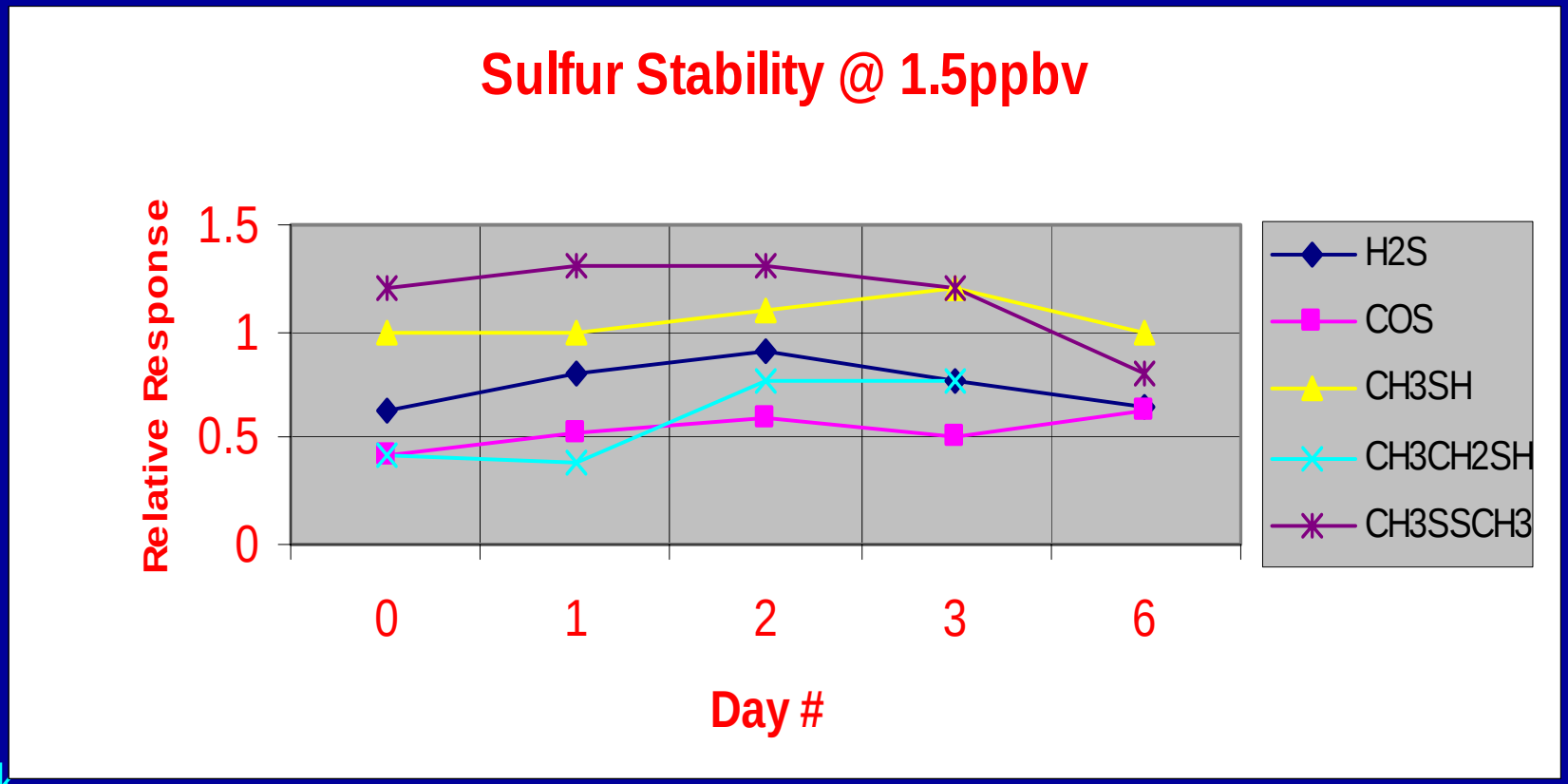
Methyl Mercaptan 11.07 ppbv for 14 Days



Can the Sulfinert™ coated vessels go to lower levels?

- Is the Sulfinert™ surface treatment stable for sulfurs at 1.5ppbv?

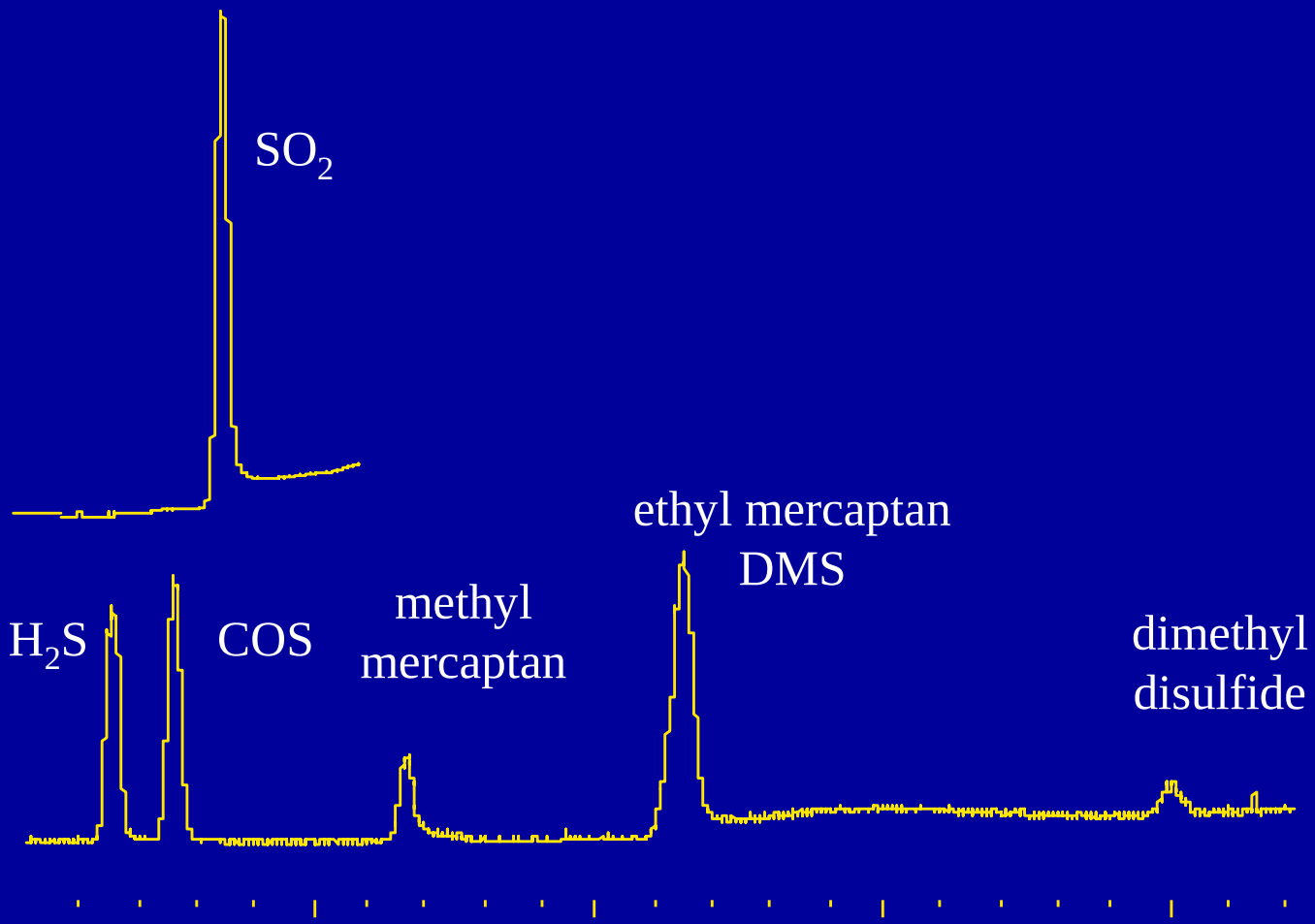
1.5ppbv organosulfur Compounds in Sulfinert™-treated Canisters



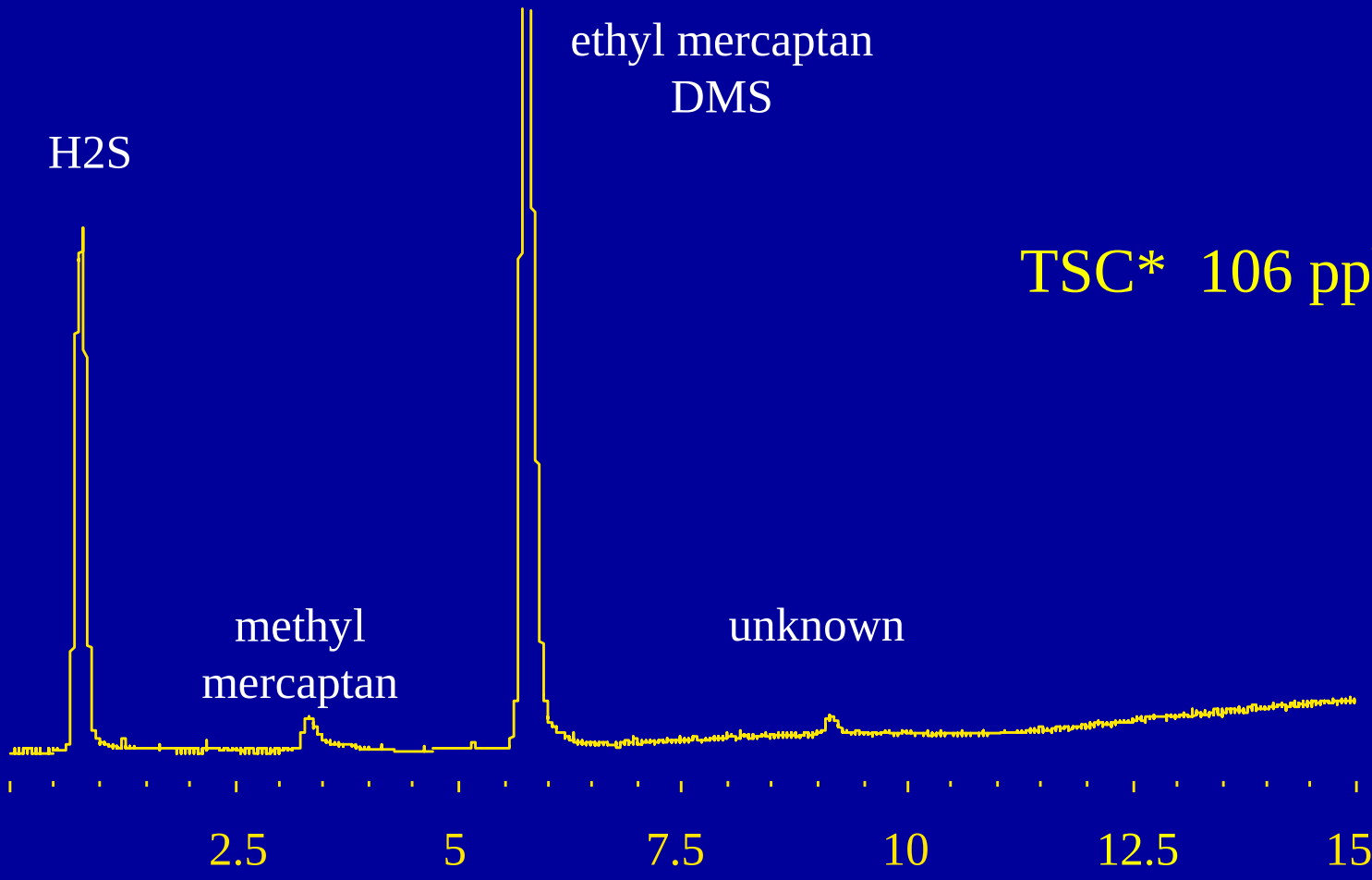
Example Applications Requiring Sulfinert™-Treatment for Optimum Performance

- Testing of Beverage Grade CO2 for organosulfur impurities
- Quality testing of Beers/Wines/Distilled Spirits
- Natural Gas / Refinery Gas

Beverage Grade CO2
20ppbv Sulfur standard added

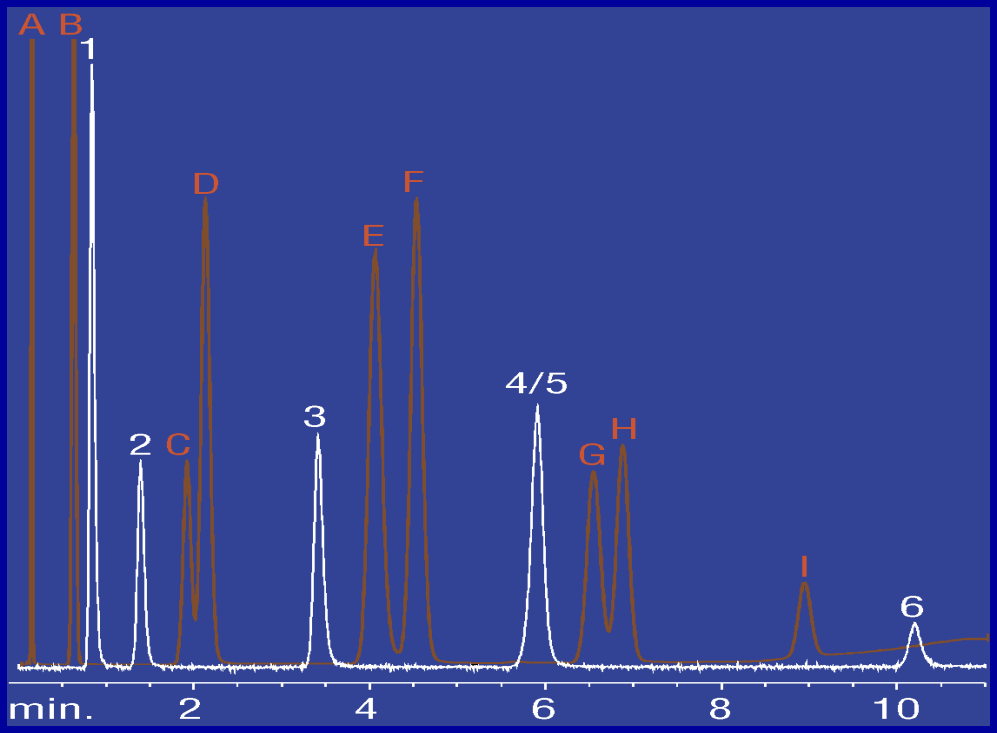


Typical Run to Determine Sulfur Content of Beer



TSC* 106 ppb

Sulfurs and Hydrocarbon analysis of Natural Gas / Refinery Gas



50ppb each

Rt-XL Sulfur Micropacked

Restek
www.restekcorp.com

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 Organo-sulfur compounds

- Surface treatments for steel surface allow low-ppbv containment, transfer and subsequent analysis of sulfur gases
  - Silcosteel® coating good for ppm levels
  - Improved performance to single ppb levels using Sulfinert™
- Future directions include testing Sulfinert™ in a broader array of applications

Coating Resistance to Acids

- Good resistance to HCl using Silcosteel®-AC coating
- Initial data: 14 fold increase in resistance to 37% HCl of a coated vs. non-coated metal coupon
- Currently undertaking a program to quantify and graph resistance to acids

Silcosteel® Coating as a Coking Inhibitor

- Studies being conducted by The Pennsylvania State University in conjunction with Wright Patterson Air Force Base
- Focus on jet fuels, JP-8
- Initial Data indicates tailored Restek coatings reduce deposits by 12-fold
- Silcosteel®-coated metal surfaces inhibit catalytic deposition from thermal decomposition of jet fuel

Advantages of Inert, Coated Steel components

- Sulfur-containing compounds; polar organic compounds
- Coated storage vessels and any steel component in flowpath
- Improved durability compared to glass linings
- Improved lifetimes and reduced diffusion compared to Teflon linings

Conclusion

- Consideration in sample flowpath construction
- Importance of shielding exposed metal surfaces
- Usefulness and advantages of using inert, coated components to reduce corrosion and carbon buildup