# Restek Corporation Performance Coatings

Restek
Performance
Coatings

# Restek Corporation Background

- Established in 1985 as gas chromatography supplies company
- Currently $25M+ annual revenue, double-digit growth 16 of 18 years
  - GC columns and consumables
  - Chemical standards
  - LC columns and consumables
  - Air analysis canisters and supplies
  - Performance Coatings Division

# Performance Coatings Background

- Began with tubing in 1987
- Stand-alone parts in 1993
- Initial goal to impart the inertness of glass on a steel surface (Silcosteel®)
- New surfaces in 1997 expanded applicability and performance (Siltek™)
- Patent protection
- Concerted development effort launched in 2002

# What can we coat?

- Tubing:
  - 0.004” to 0.5” ID
  - 2000+ ft. continuous lengths
- Complex geometry parts (inside and out)
  - Fittings, valves, frits, custom parts
  - Largest vessel: 1’ ID x 4’ cylinder w/ 10” opening
- Substrates
  - Stainless steels, steels, alloys, glass, ceramics

# What can't we coat?

- Nickel (most high-performance alloys will coat)
- Aluminum*
- Copper
- Brass
- Gold, Silver-plated components
- Magnesium
- Elastomers

*heat-dependent

# Basic Manufacturing Process

- Receive items
- Document – digital, customer contact
- Clean
  - Standard:  caustic ultrasonic bath, 2 systems
  - Custom:  solvation via other means
- Process
  - Vacuum
  - 400ºC
  - Chemical vapor deposition, silicon-based
- Clean
- Document – digital, customer contact
- Pack, ship

# Application Areas

- Analytical (passivation): Silcosteel®, Siltek™, Sulfinert™
  - Transfer lines
  - Instrumentation parts
  - GC consumables
- Anti-Coking: Silcosteel®-AC
- Anti-Corrosion: Silcosteel®-CR
- Ultra-High Vacuum: Silcosteel®-UHV


Coating Appearances:
Silcosteel ®
Sulfinert™
Siltek™

# Coating Appearances (cont.)

# New Process Oven

# More Parts


# Inertness

- Application:  Reduce activity of substrate (ie., stainless steel) to minimize adsorption of compounds
- Coated system products deliver better reproducibility and accuracy by reducing hold-up of active compounds
- List of some active compounds:  Hydrogen Sulfide, Nitrous Oxides, Mercury, Alcohols, Aldehydes, Ketones, etc.,.

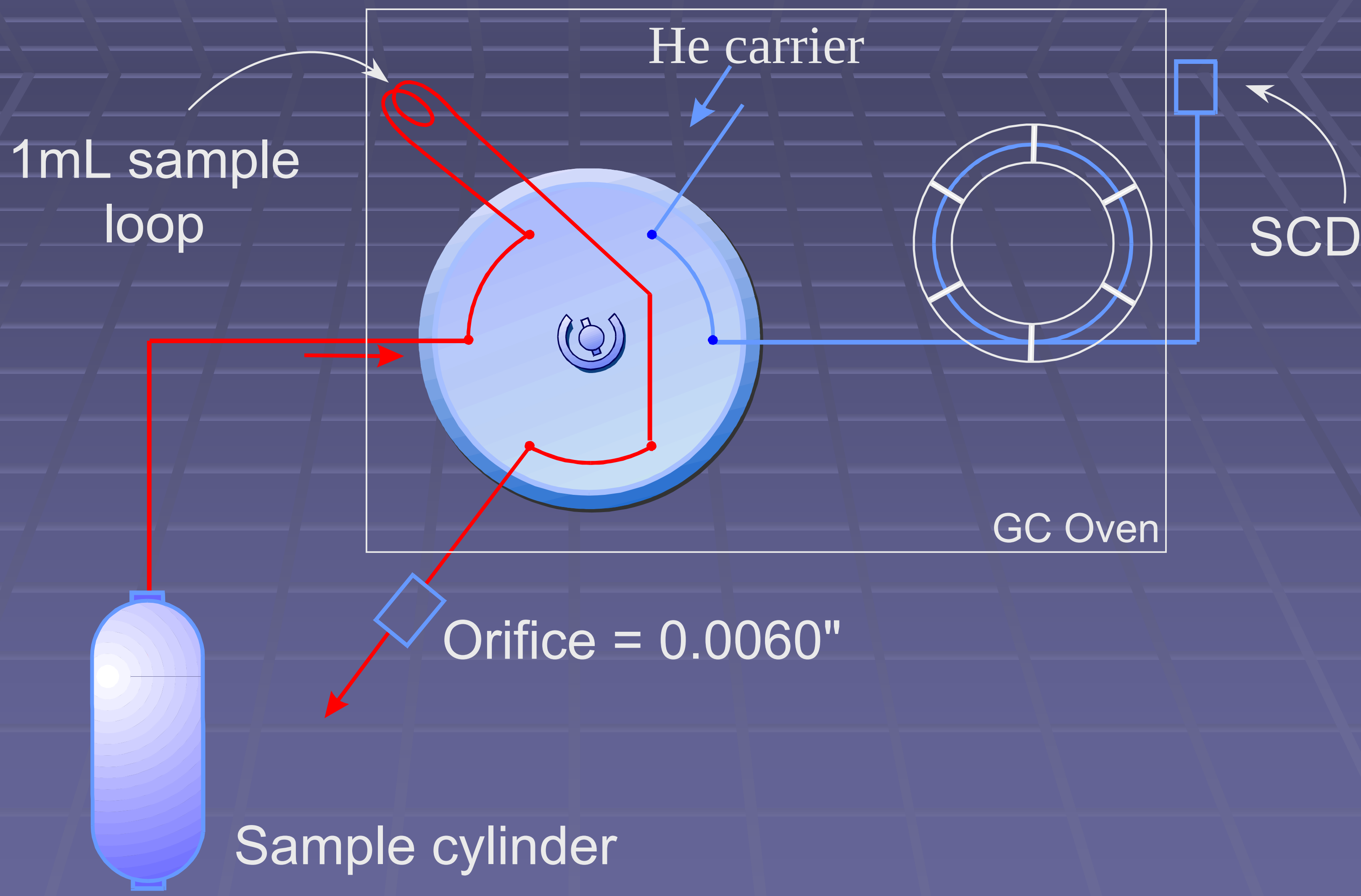
# Project Objective

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

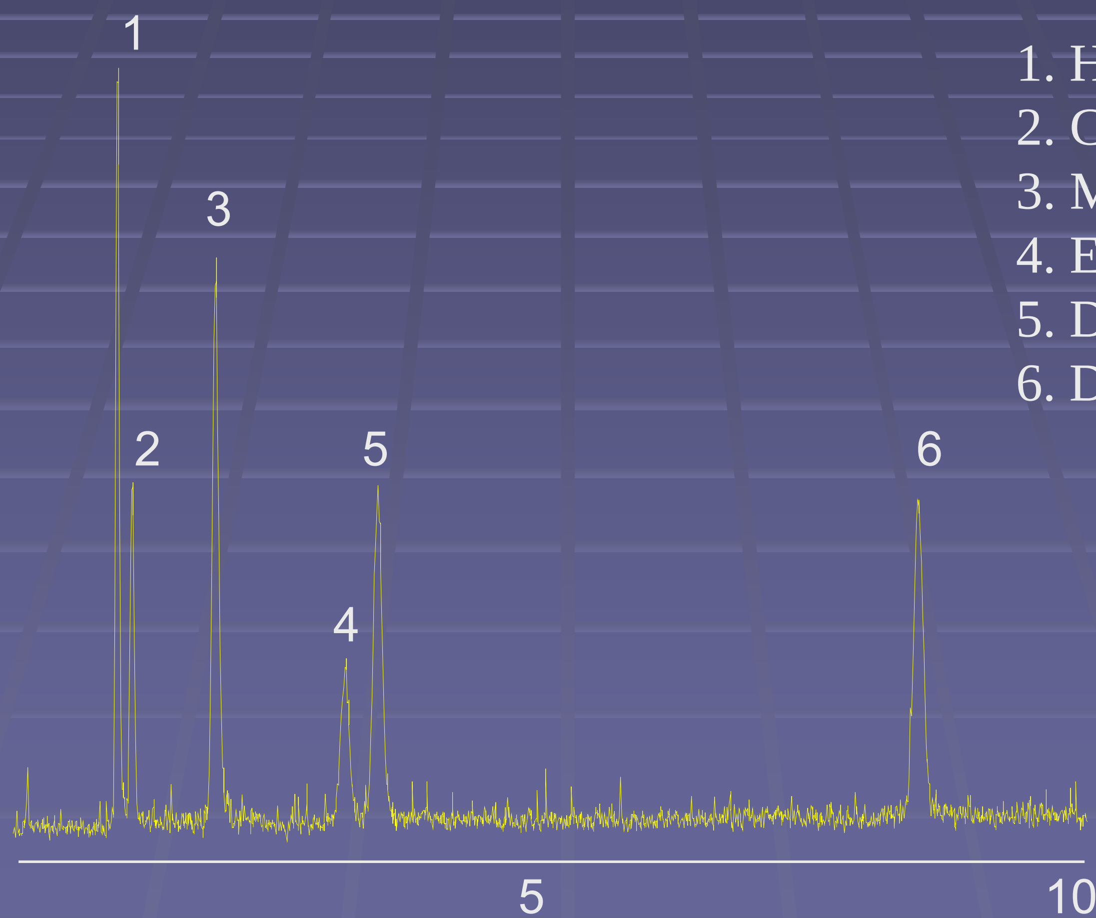
# Testing System for Sulfur Gas Storage & Transfer

- Sulfinert™-deactivated sample cylinders with Sulfinert™ sample valves
- Sulfinert™-deactived sampling system (transfer line, sampling valve, 1ml sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard

# Complete Sulfur Analysis System



# 11ppbv Sulfur Standard




1. $H_2S$
2. COS
3. Methyl Mercaptan
4. Ethyl Mercaptan
5. Dimethyl Sulfide
6. Dimethyl Disulfide

Rtx-1 60m x 0.53mm, 7.0µm

# List of Sulfur Compounds

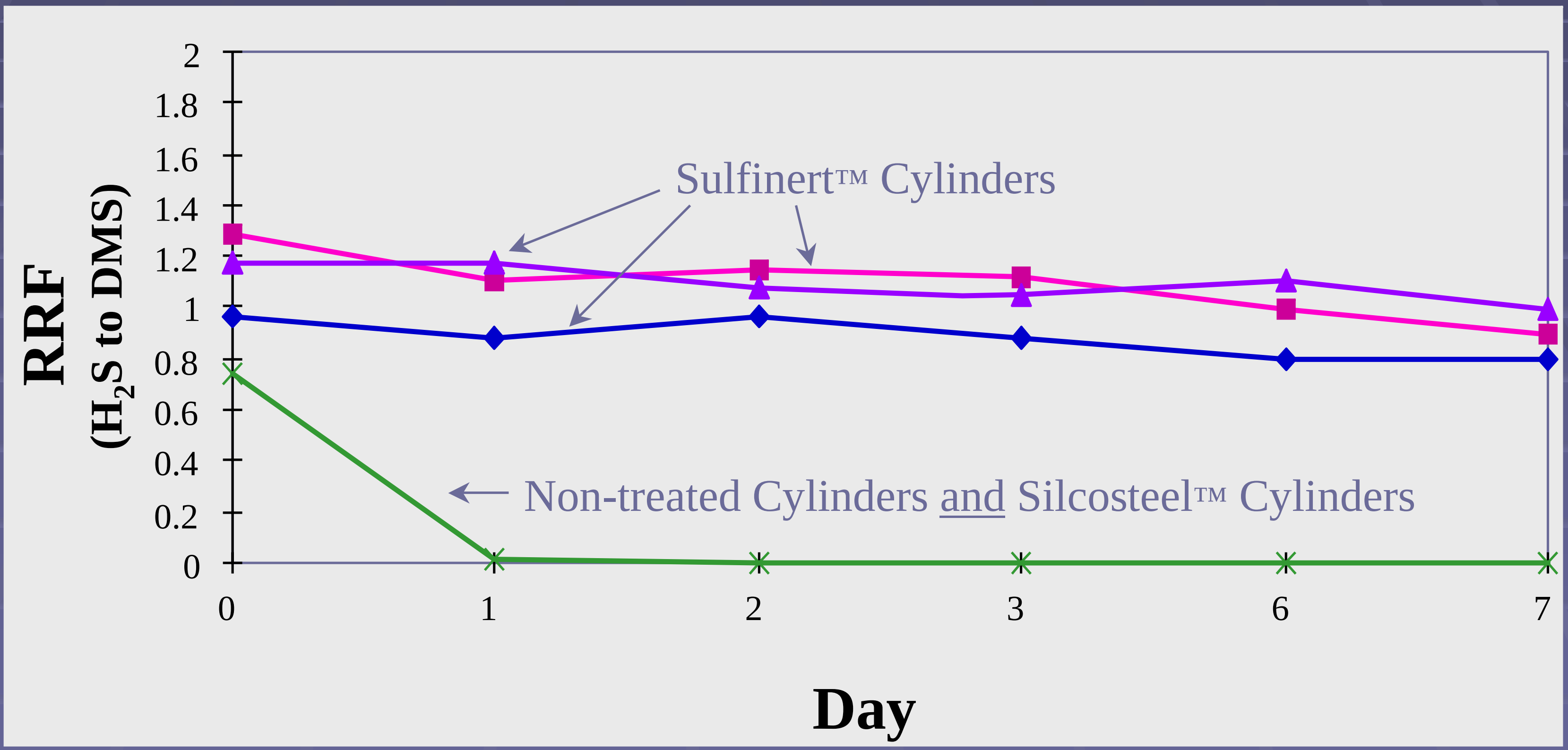
| | | Conc | Conc | Conc as S |
|---|---|---|---|---|
| Compound Name | Formula | (ppmv) | (ppbv) | (ppbv) |
| hydrogen sulfide | H2S | 105 | 11.51 | 10.83 |
| carbonyl sulfide | COS | 98 | 10.74 | 5.73 |
| methyl mercaptan | CH3SH | 101 | 11.07 | 7.38 |
| ethyl mercaptan | CH3CH2SH | 101 | 11.07 | 5.71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

# System Repeatability

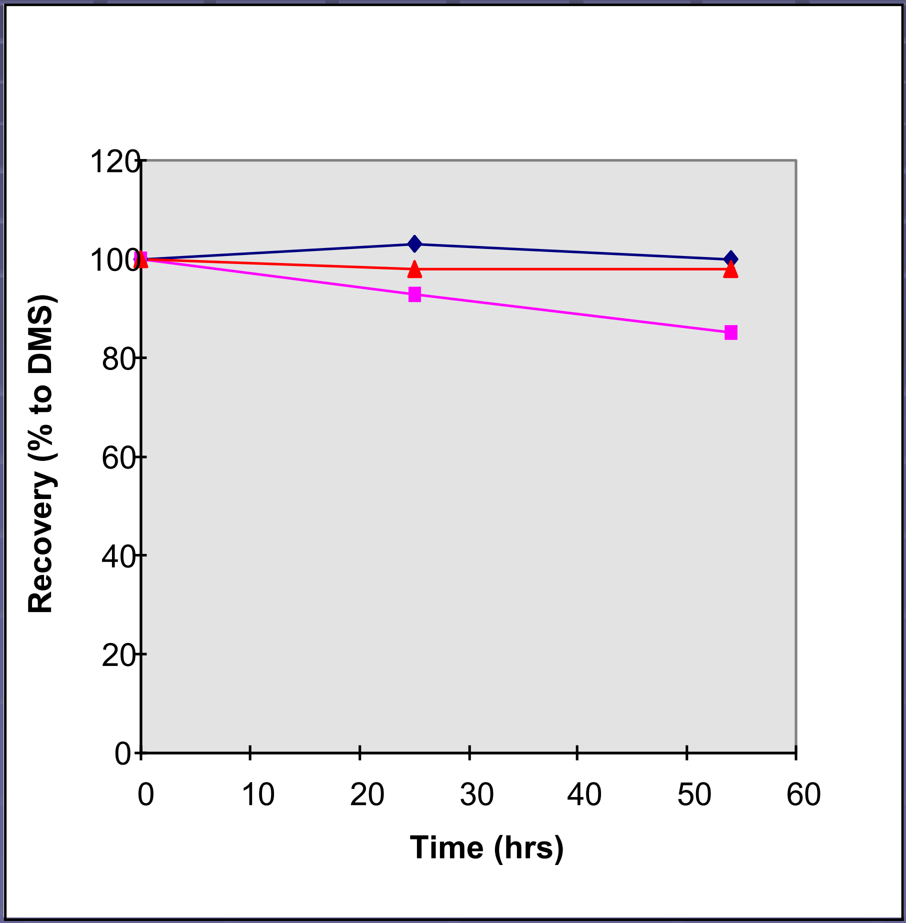
| Compound Name | %RSD |
|---|---|
| hydrogen sulfide | 2.2 |
| carbonyl sulfide | 4.2 |
| methyl mercaptan | 2.0 |
| ethyl mercaptan | 8.7 |
| dimethylsulfide | 3.3 |
| dimethyl disulfide | 9.2 |

n=7

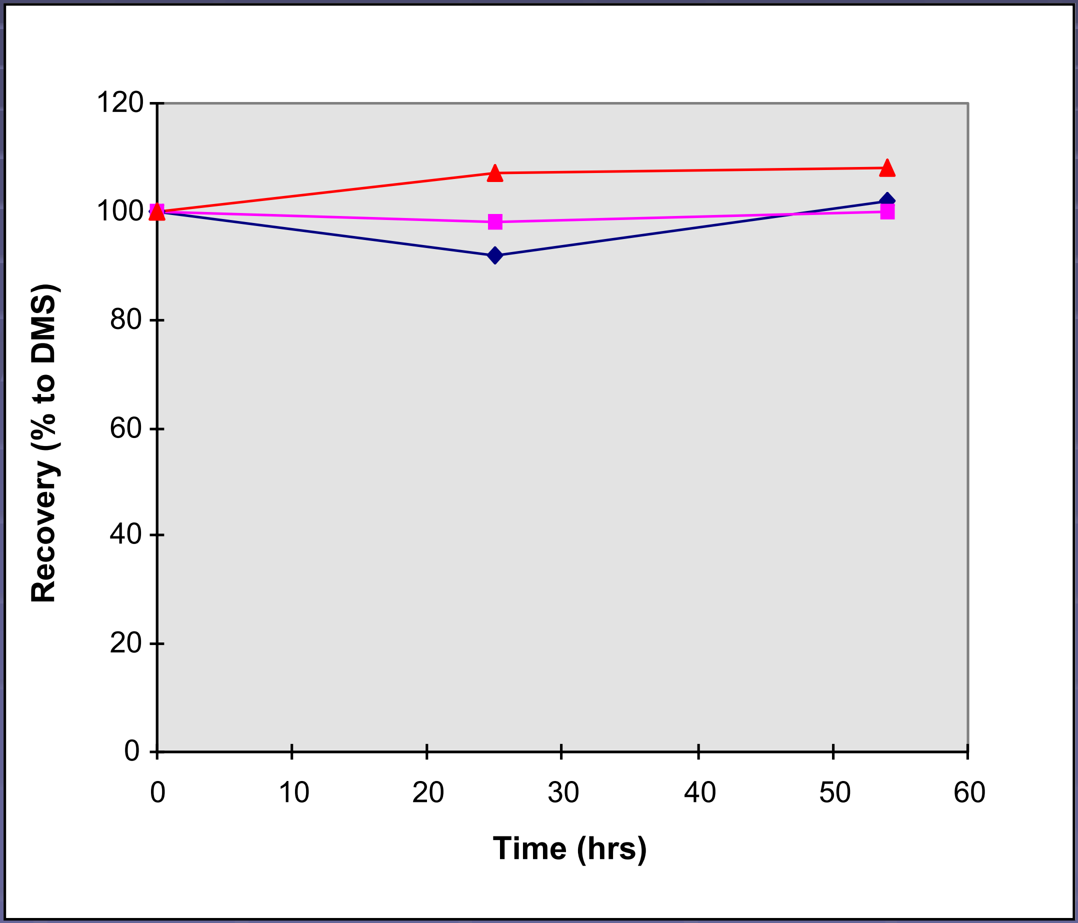
# 17ppbv $H_2S$ Containment in 500ml Cylinders



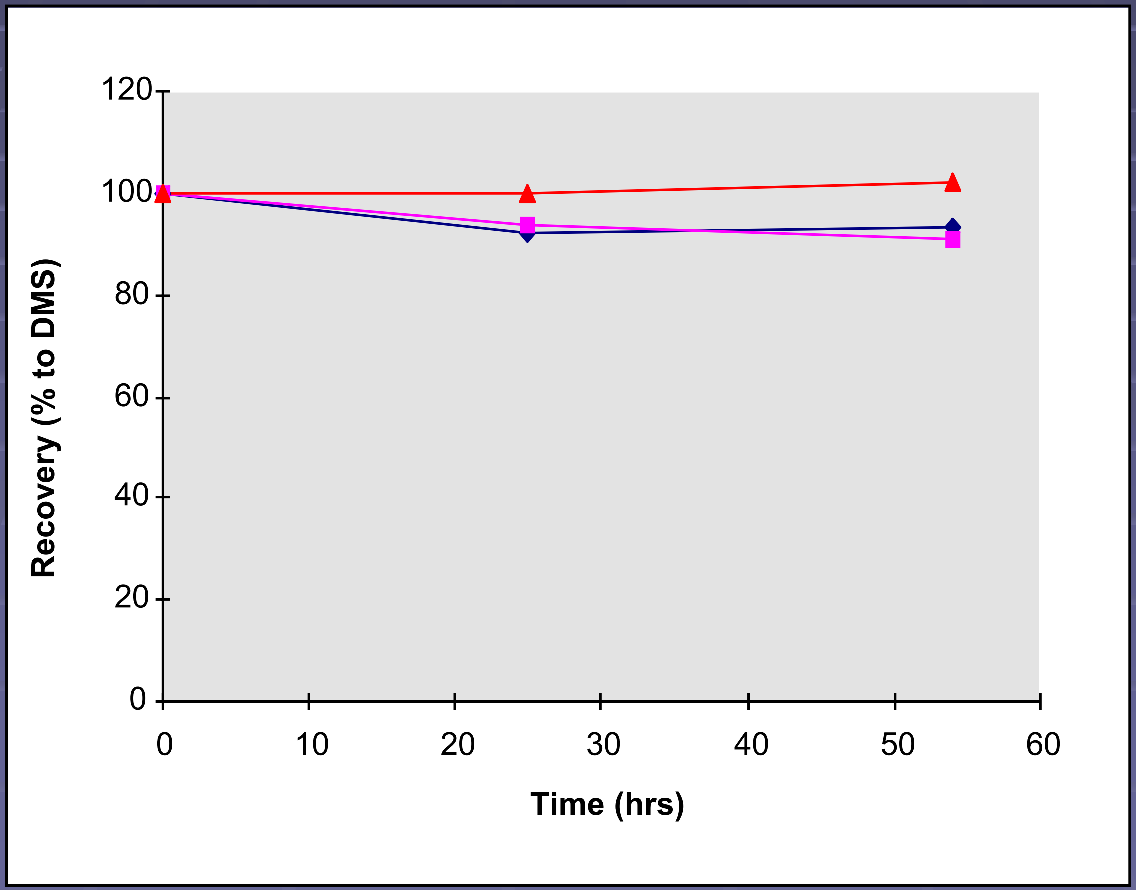
# $H_2S$ at 27.57ppbv in 300ml Sulfinert™ Cylinders



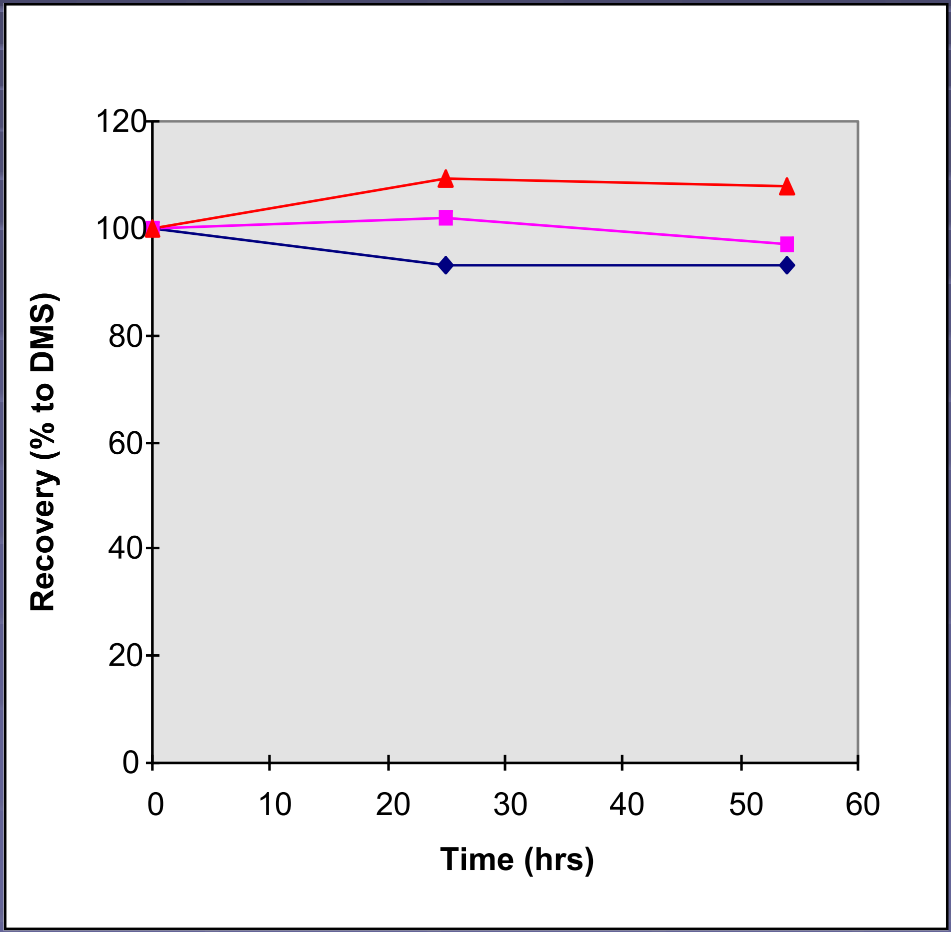
# COS at 14.59ppbv in 300mlSulfinert™ Cylinders



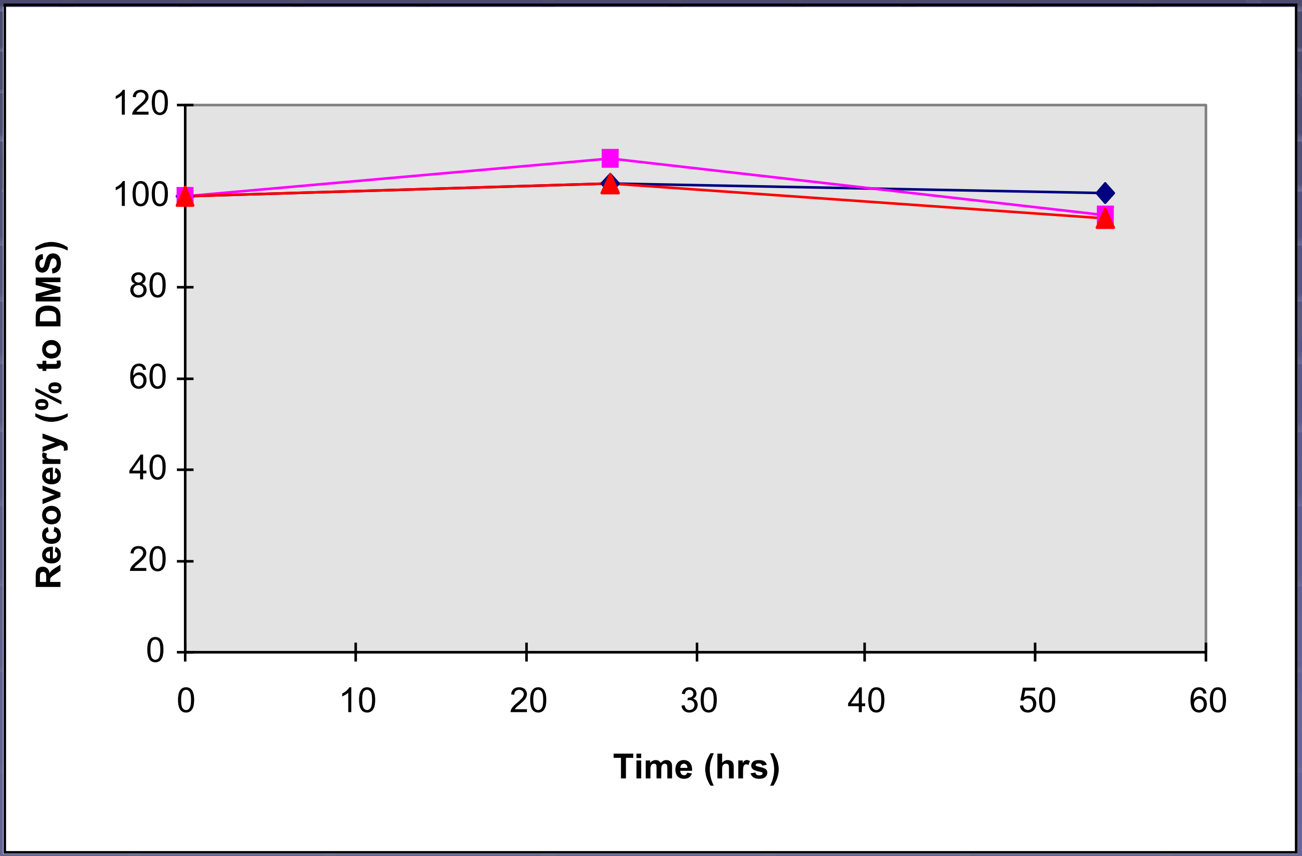
# Ethyl Mercaptan at 14.53ppbv in 300ml Sulfinert™ Cylinders



# Methyl Mercaptan at 18.8ppbv in 300ml Sulfinert™ Cylinders



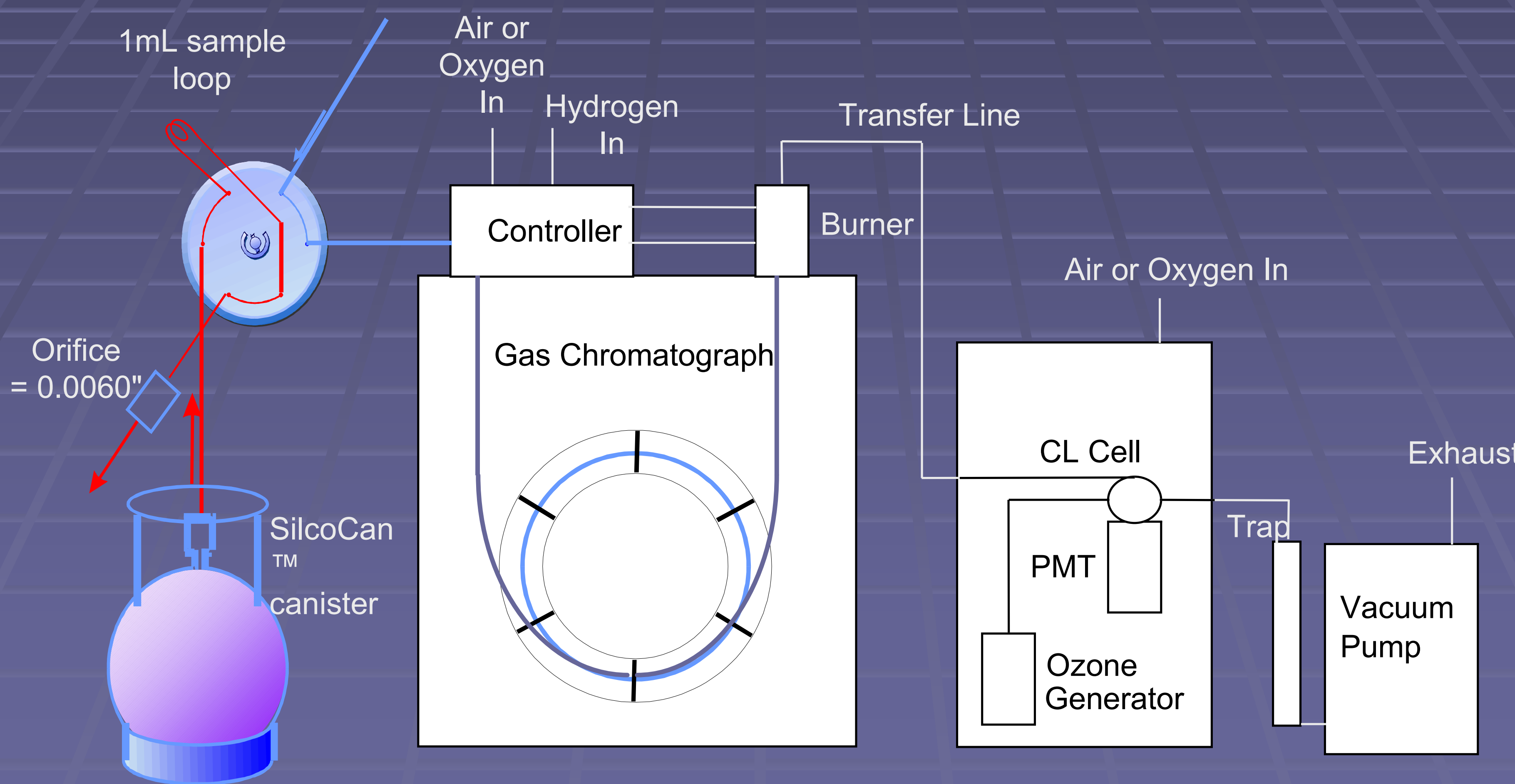
# Dimethyl Disulfide at 18.99ppbv in 300ml Sulfinert™ Cylinders



# Ambient Air Sampling Canisters Objective

- **Demonstrate suitability for storage of low level (1-20ppbv) sulfurs in SilcoCan™ canisters.**

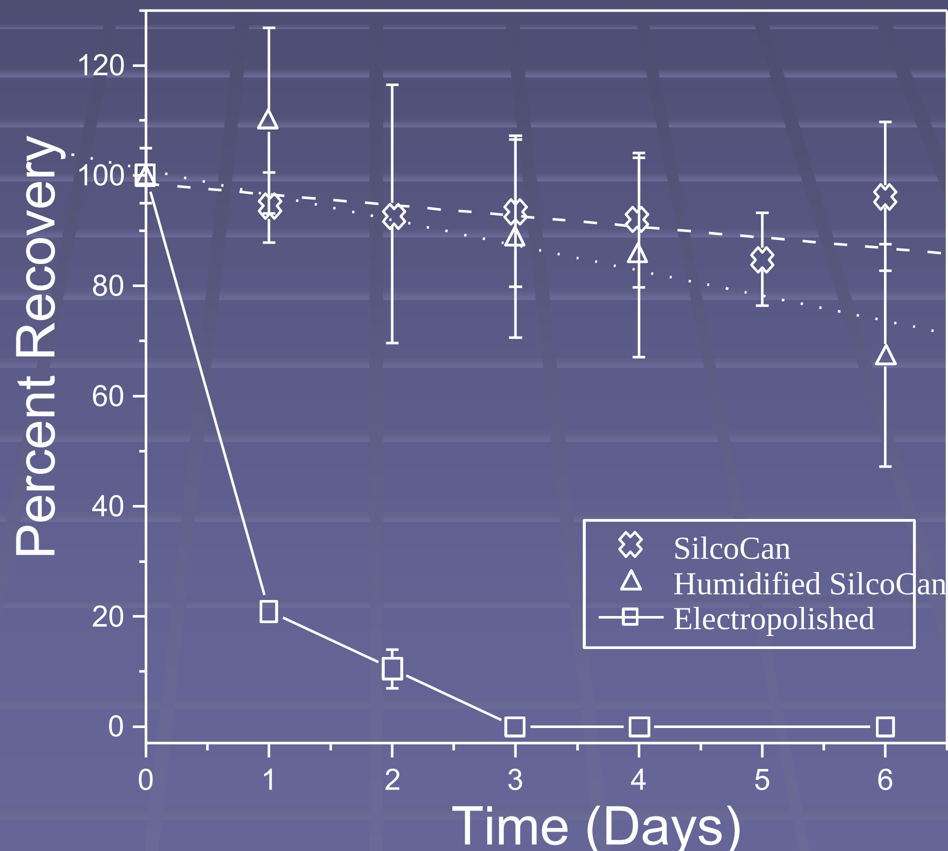
# Block diagram of Analytical System



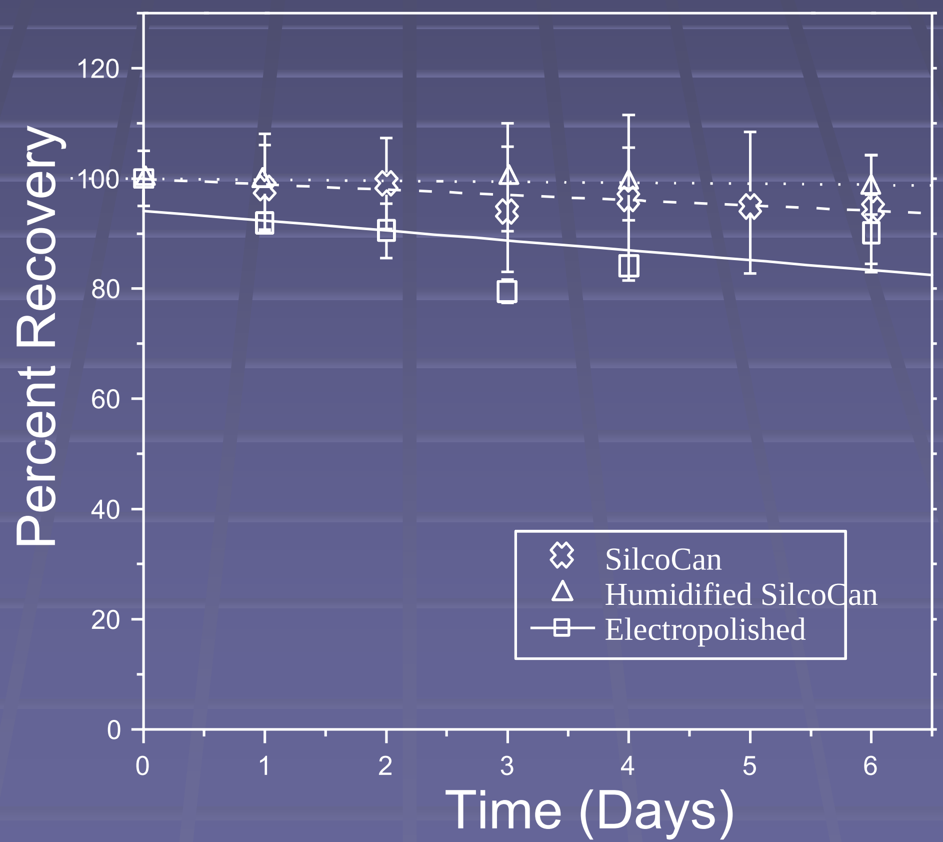
# Stability Study Test

- **11ppbv**
- **6 days stability study**
- **Reference std is at 55ppbv**
- **Dimethyl sulfide as internal standard**
- **SilcoCans (n=18)**
- **Humidified (rh=50%) SilcoCans (n=5)**
- **Electropolished Cans (n=2)**

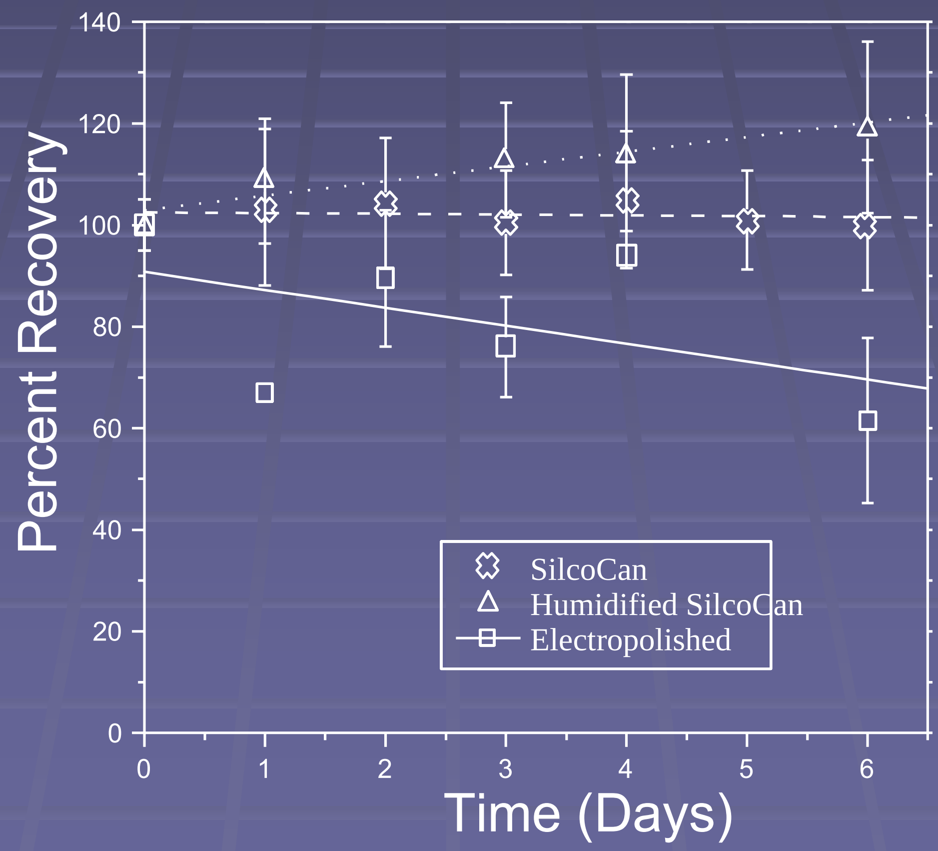
# $H_2S$ at 11ppbv in 6l Air Sampling Cans



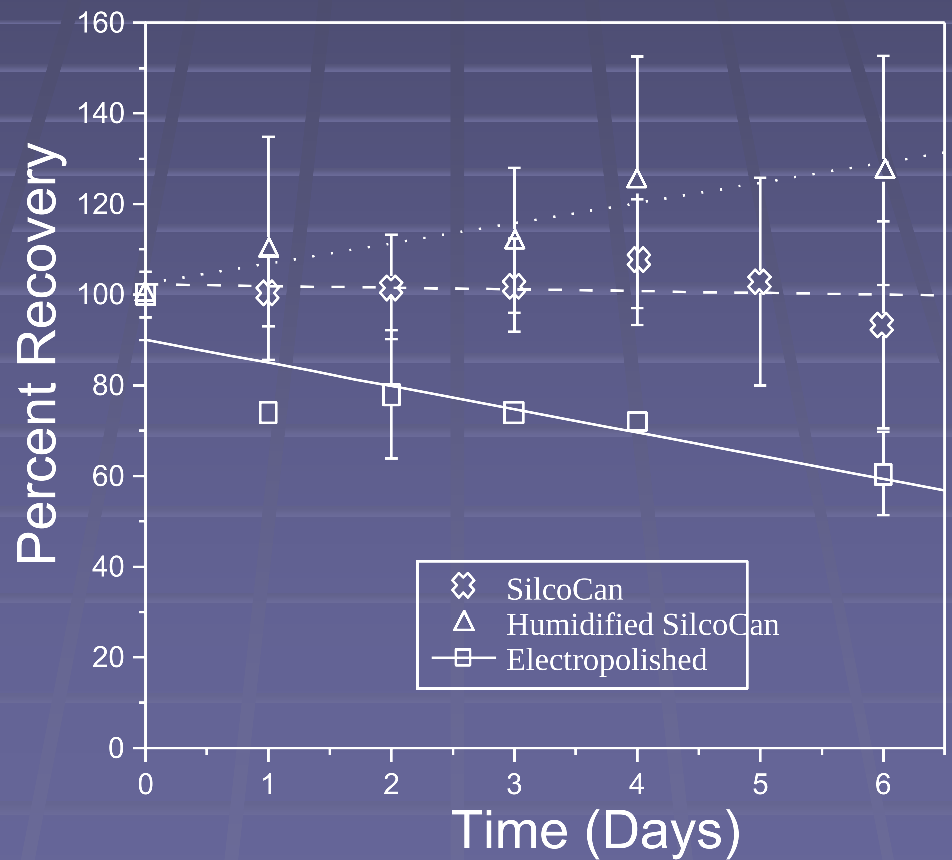
# COS at 10ppbv in 6l Air Sampling Cans



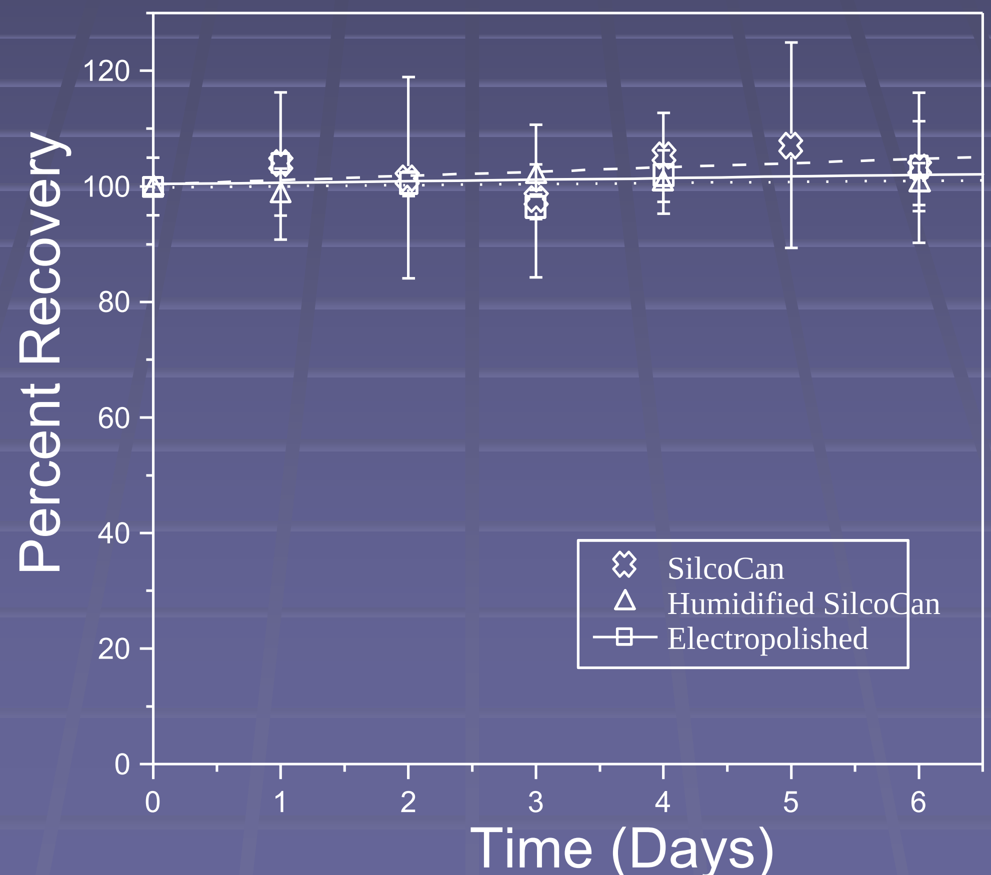
# Methyl Mercaptan at 11ppbv in 6l Air Sampling Cans



# Ethyl Mercaptan at 11ppbv in 6l Air Sampling Cans



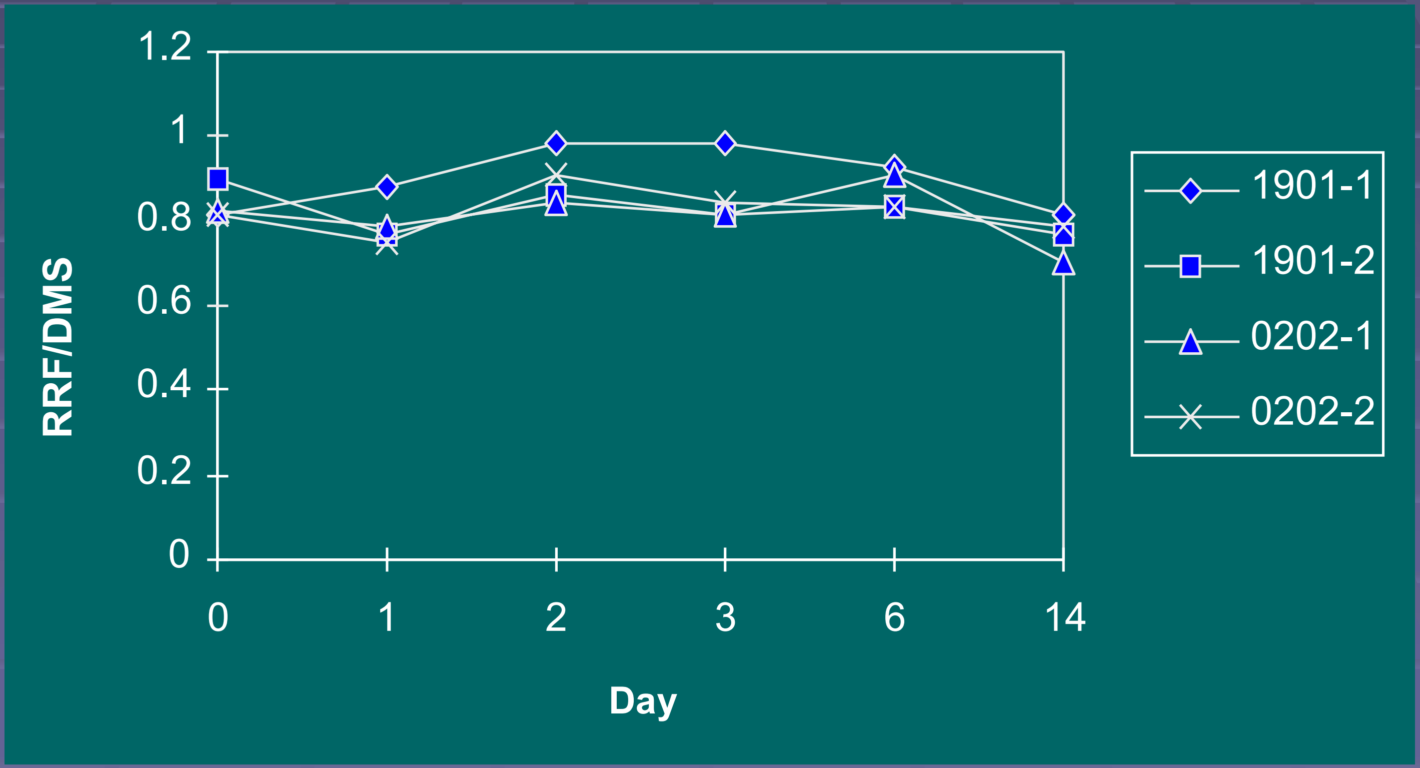
# Dimethyl Disulfide at 11ppbv in 6l Air Sampling Cans



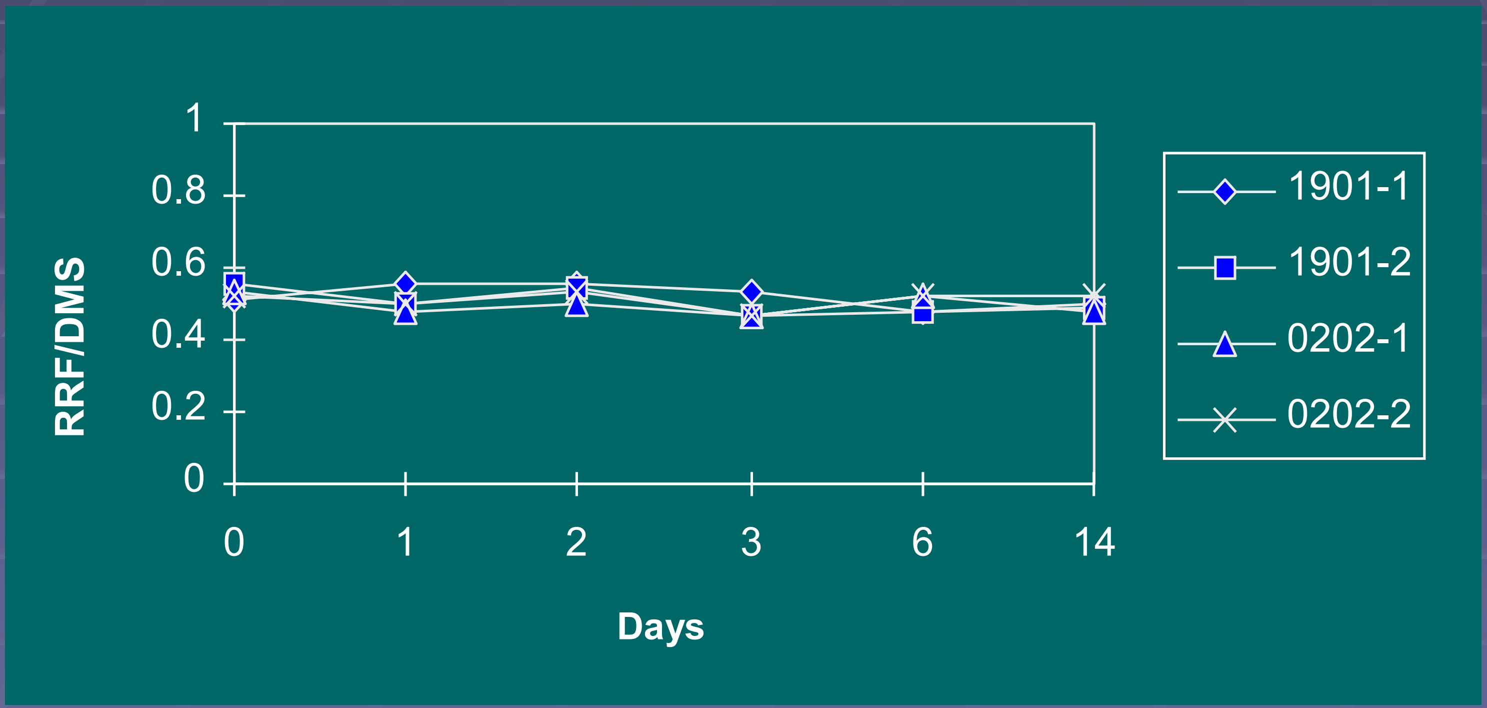
# Extended Stability Study

- **Is the SilcoCan capable of storing 11ppbv sulfurs longer than 6 days?**
- **Tested 4 SilcoCans on Day 14**

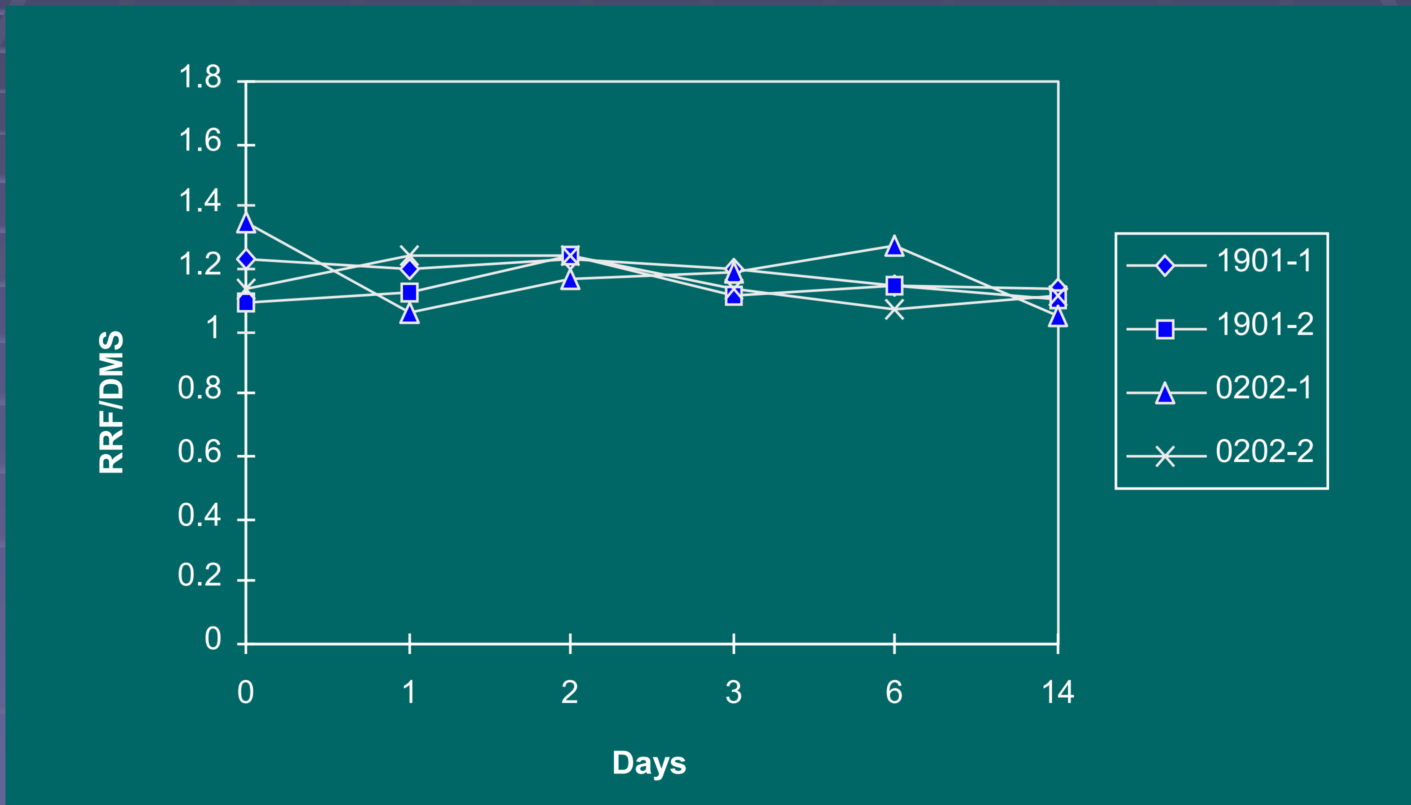
# $H_2S$ at 11ppbv for 14 days



# COS at 10ppbv for 14 Days



# Methyl Mercaptan 11ppbvfor 14 Days



# Performance of Silcosteel® Coating for transfer of $NO_x$ & Ammonia containing streams

- Study conducted by University of California Center for Environmental Research and Technology (October 2001)
- Study 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
- Dry, wet, and with ammonia

# $NO_x$ Study Conditions

- 100’ section of ¼” 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%H20) Simulated Exhaust
  - Wet (13% H20) Simulated Exhaust + 6ppm Ammonia
  - Wet (13% H20) Simulated Exhaust + 10ppm Ammonia
  - Wet (6% H20) Simulated Exhaust
  - Wet (6% H2O) Simulated Exhaust + 10ppm Ammonia

# Results from Study

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

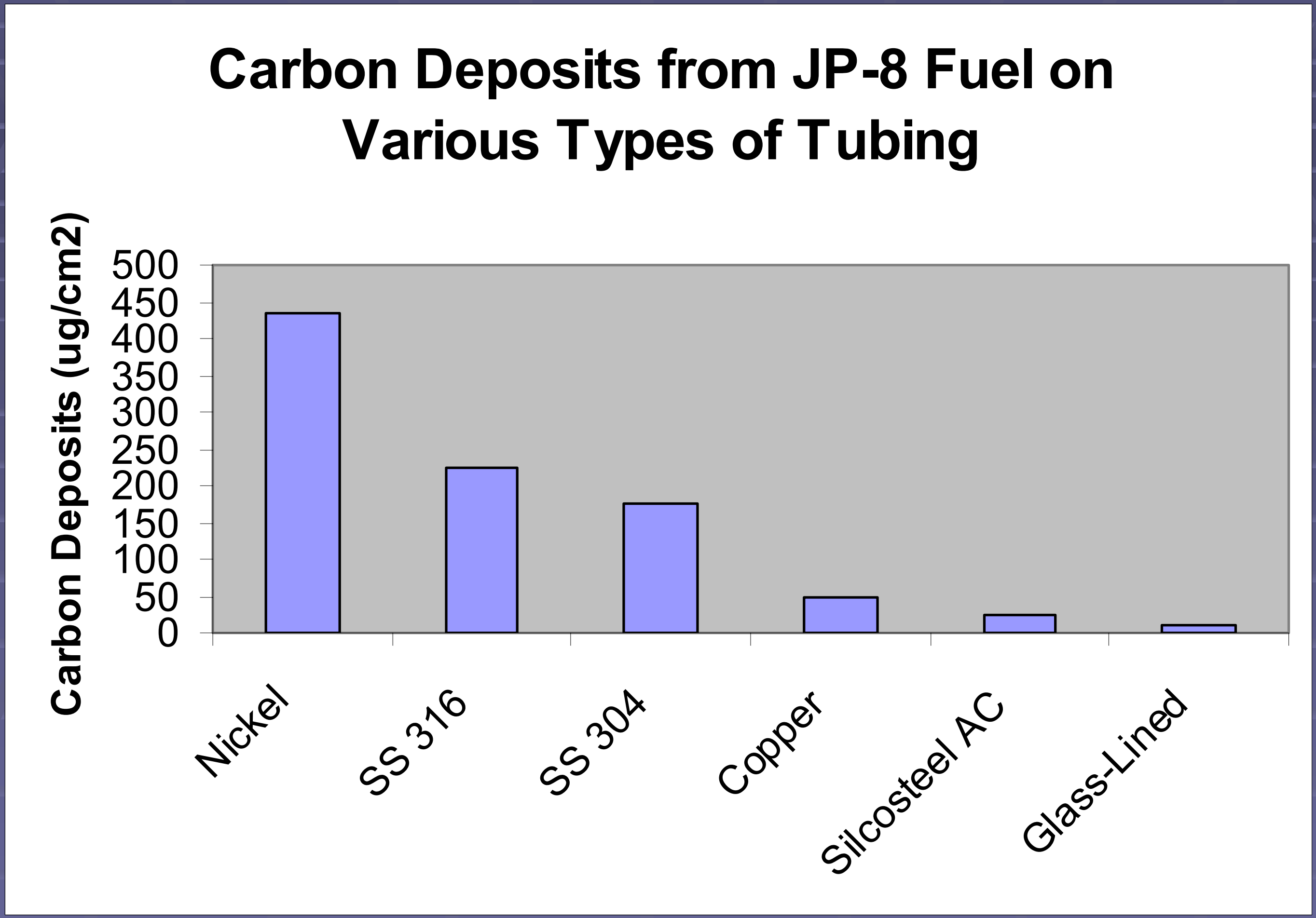
# Examples of applications

- Purge and Trap systems manufactured to test water quality use Restek treated tubing to insure transfer
- Varian Ion trap mass spectrometer elements are coated to eliminate adsorption of ions
- Sulfur sampling and transfer equipment is coated to eliminate loss of active compounds
  - Testing of Ethylene and Propylene
  - Testing of Beverage grade $CO_2$ for sulfur
  - Testing of Sulfur compounds in beer
  - Natural Gas; LPG; Gasoline; Diesel

# Anti-Coking

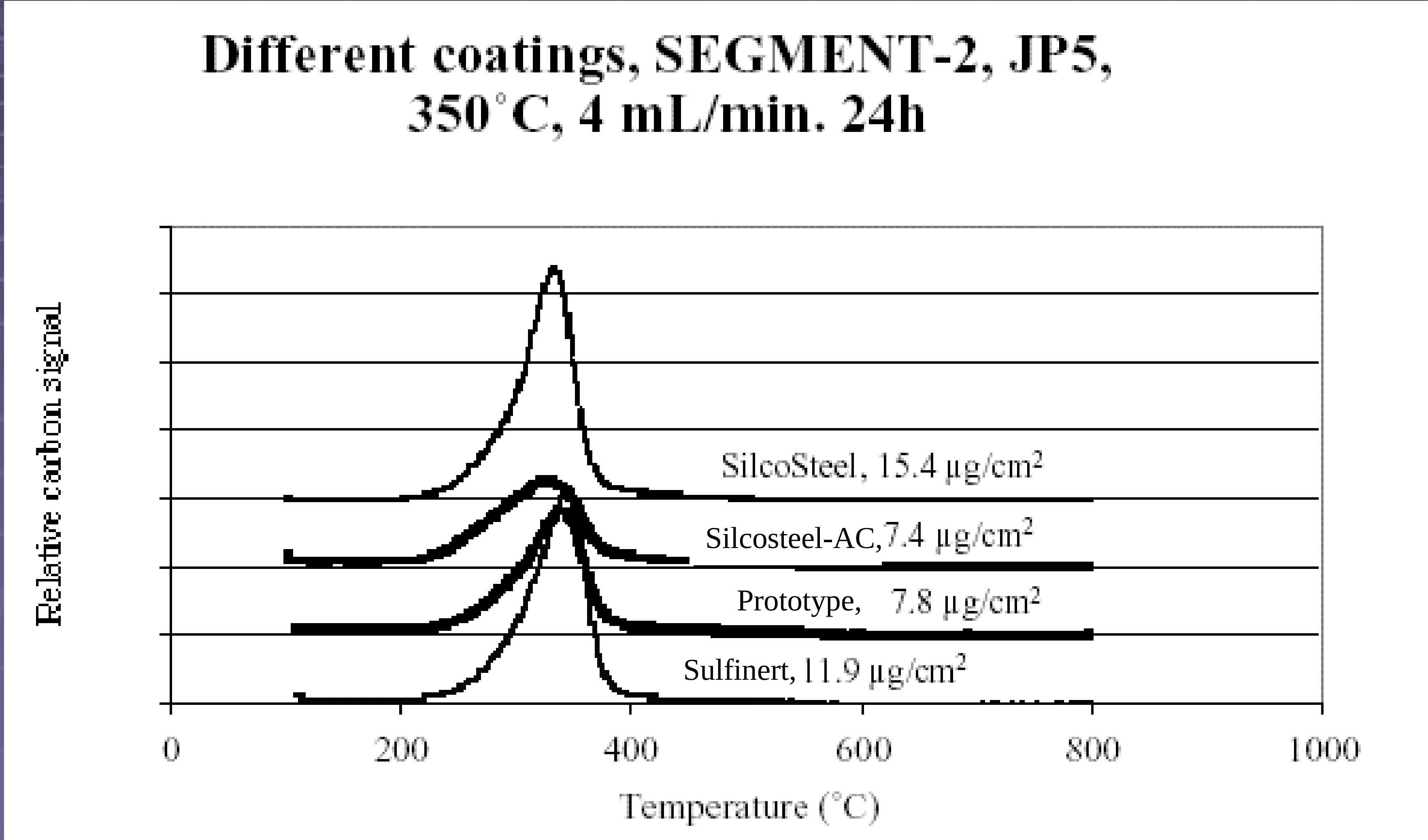
- In applications of heated hydrocarbon transfer, carbon deposits can form
- Carbon deposits are catalyzed by nickel, sulfur and carbon in steel lattice
- The Silcosteel-AC coating produces a barrier that eliminates catalytic carbon buildup

# Anti-Coking Data




- Semih Eser; PSU Prof. Fuel Sciences
- 8x improvement over raw 316L

# Anti-Coking Data (cont.)



# Example Applications

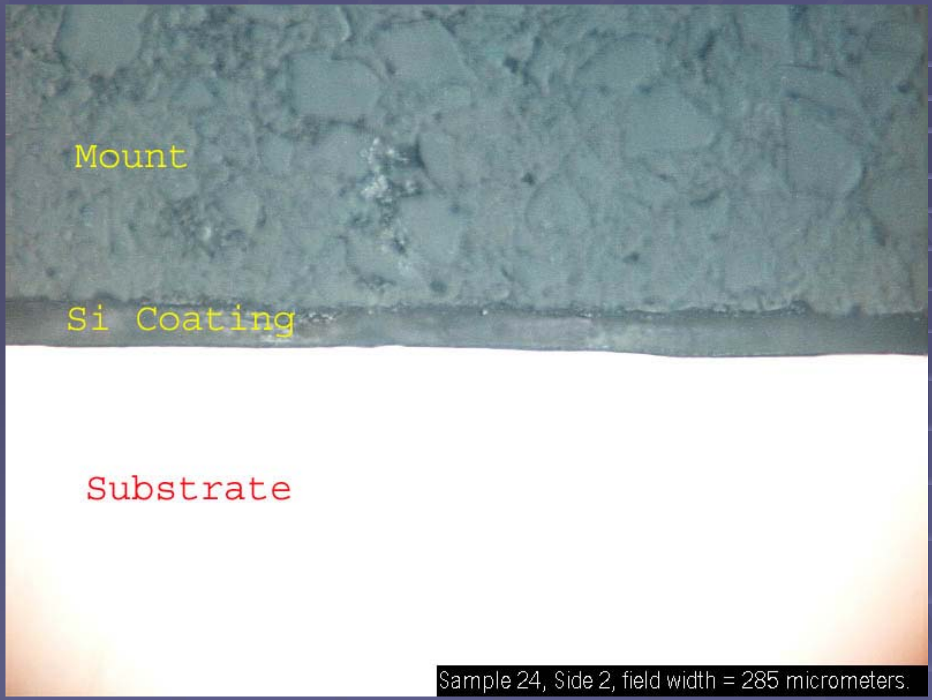
- Coating fuel injector nozzles to decrease buildup
- Increasing lifetimes of Ethylene and Propylene Plug Flow reactors
- Increasing reliability of valves used in internal combustion engines
- Reduces fouling in heat exchangers

# Corrosion Resistance

- Stainless steel surfaces susceptible to attack from hydrochloric acid, sulfuric acid and nitric acid
- Silcosteel-CR treatment produces a layer of amorphous silicon
- Amorphous silicon is insoluble in hydrochloric acid, sulfuric acid and nitric acid

# Corrosion Data (cont.)

- Evaluation
  - Certified corrosion engineers
  - Spectroscopic analysis
  - Mechanical testing
  - Electrochemical
    Cyclic Polarization in neutral, acidic, alkaline
  - Atmospheric corrosion
    - ASTM moisture condensation
    - Salt spray ASTM B117
  - Stress corrosion cracking (MgCl; ASTM G36)



# ASTM G45 B Data

- ASTM G45 method B; Pitting and Crevice Corrosion
  - 6% Ferric Chloride solution
  - 72hrs, 20ºC
  - Gasket wrap

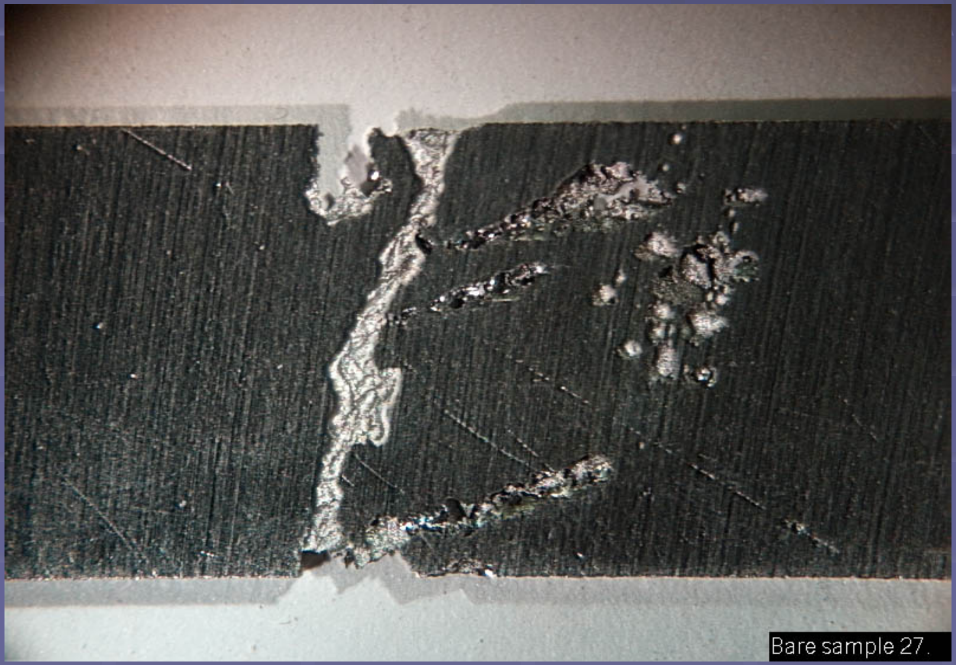
| Sample | Initial Weight (g) | Final Weight (g) | Weight Loss (g) | Weight Loss ($g/m^2$) |
|---|---|---|---|---|
| Silco-CR Sample 17 | 10.4105 | 10.3710 | 0.0395 | 19 |
| Silco-CR Sample 28 | 10.1256 | 10.0743 | 0.0513 | 25 |
| Silco-CR Sample 47 | 10.1263 | 10.0742 | 0.0521 | 25 |
| Bare Sample 27 | 10.0444 | 9.5655 | 0.4789 | 231 |
| Bare Sample 34 | 10.1265 | 9.6923 | 0.4342 | 209 |
| Bare Sample 37 | 10.1007 | 9.6276 | 0.4731 | 228 |

# ASTM G45 B (cont.)

- Silcosteel®-CR treated sample showing no crevice corrosion only slight pitting corrosion

# ASTM G45 B (cont.)

- Bare 316L Stainless Steel coupon showing severe crevice corrosion



# ASTM G-61Data

- ASTM G-61; Cyclic Polarization Electrochemical Corrosion Testing
  - Acid, neutral, basic aqueous solutions with varying $Cl^-$ ion concentrations (100, 3000, 5000ppm)
  - EG&G VersaStat System, 23ºC
  - 316L vs. Silcosteel®-CR on 316L, 304L

Neutral solution;
3000ppm $Cl^-$

-CR vs 316L Raw: 50x improvement

| Sample | Ec, mV | Ic, uA/cm^2 | Eb, mV | CR, mpy |
|---|---|---|---|---|
| 316 L | -418 | 0.096 | 370 | 0.04 |
| Silcosteel-CR 316 L | -533 | 0.002 | 1460 | 0.0009 |
| 304 L | -435 | 0.145 | 361 | 0.06 |

Ec = corrosion potential
Ic = current density at Ec
Eb = pitting potential
CR = corrosion rate

# ASTM-G61 (cont.)

Acidic Solution; 1N H2SO4; 3000ppm $Cl^-$

-CR vs 316L Raw: 10x improvement

| Sample | Ec, mV | Ic, uA/cm^2 | Eb, mV | CR, mpy |
|---|---|---|---|---|
| 316 L | -662 | 1.920 | 370 | 0.83 |
| Silcosteel-CR 316 L | -843 | 0.123 | 927 | 0.05 |
| 304 L | -639 | 2.650 | 587 | 1.14 |

Basic Solution; 1N NaOH; 3000ppm $Cl^-$

-CR vs 316L Raw: 4x improvement*

| Sample | Ec, mV | Ic, uA/cm^2 | Eb, mV | CR, mpy |
|---|---|---|---|---|
| 316 L | -419 | 0.193 | 265 | 0.08 |
| Silcosteel-CR 316 L | -816 | 0.036 | 618 | 0.02 |
| 304 L | -388 | 1.120 | 668 | 0.48 |

# ASTM B117 Data

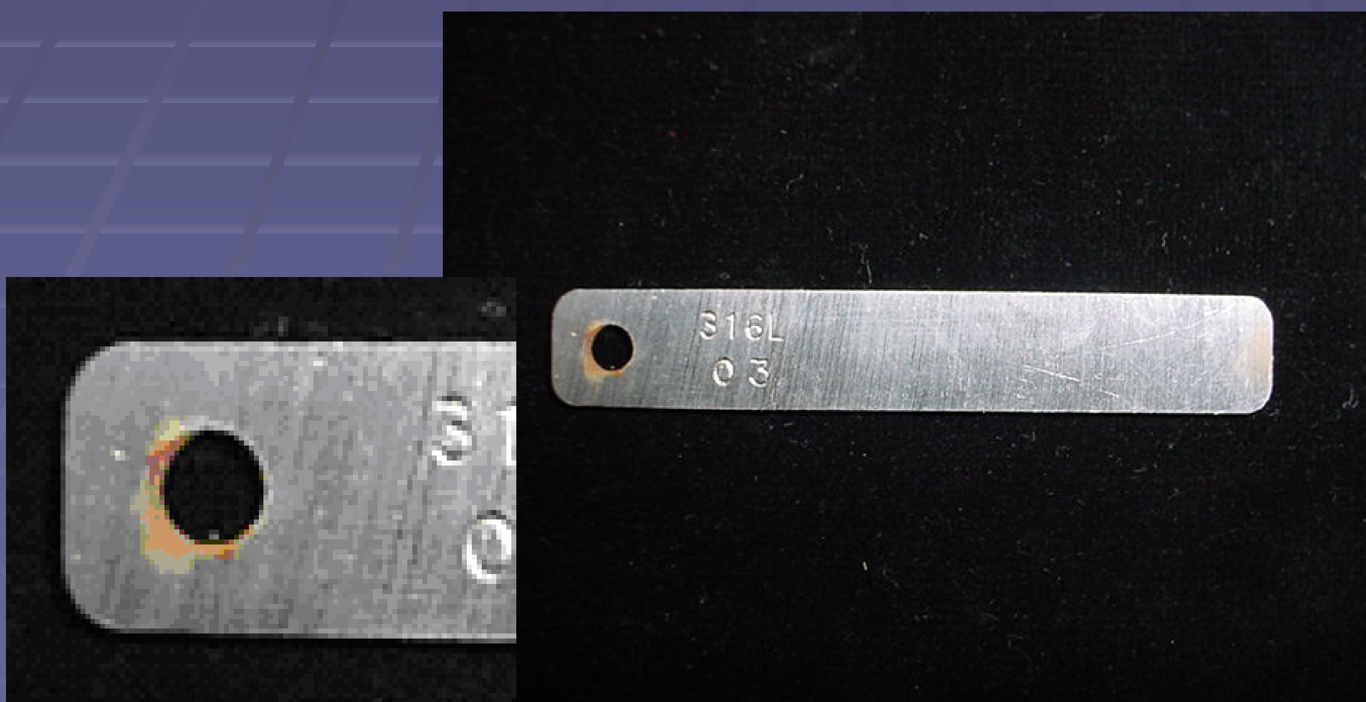
- ASTM B 117 – “Practice for Operating Salt Spray (Fog) Apparatus.”
  - 1000 hour exposure
  - 100 degree Fahrenheit
  - 3.5% by weight sodium chloride
- Reproduces exposure to marine environments.

# ASTM B117 Data (cont.)

- Silcosteel®-CR treated samples showed no signs of bleeding, rusting, or pitting corrosion

# ASTM B117 Data (cont.)

- The non-treated samples showed some light surface rusting, but no signs of pitting corrosion.



# ASTM D4585 Data

- ASTM D 4585, "Practice for Testing the Water Resistance of Coatings Using Controlled Condensation."
  - 1000 hour study
  - 100 degrees Fahrenheit
  - Distilled water
- Reproduces exposure to atmospheric conditions

# ASTM D4585 (cont.)

- Silcosteel®-CR treated samples showed no signs of bleeding, rusting, or pitting corrosion

# ASTM D4585 (cont.)

- Only a very light surface oxide film was seen on the bare samples.

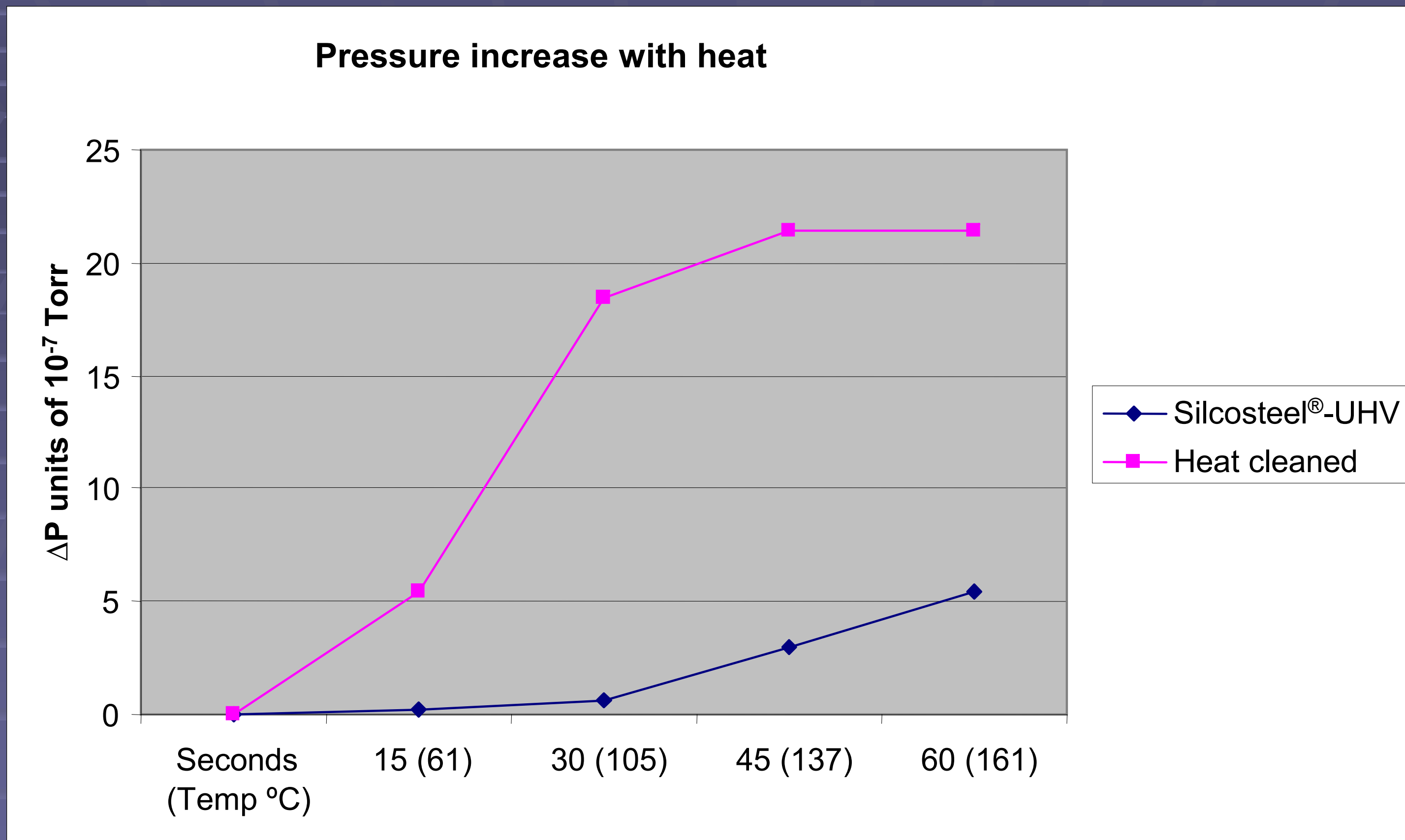
# Examples Applications

- Using Silcosteel-CR treated 316L stainless steel instead of items made from Hastelloy or Inconel in corrosive environments
- Protecting the value and extending the life of expensive existing equipment in corrosive environments by use of protective coating
- Increase cycle lifetime of equipment

# Ultra-High-Vacuum (UHV)

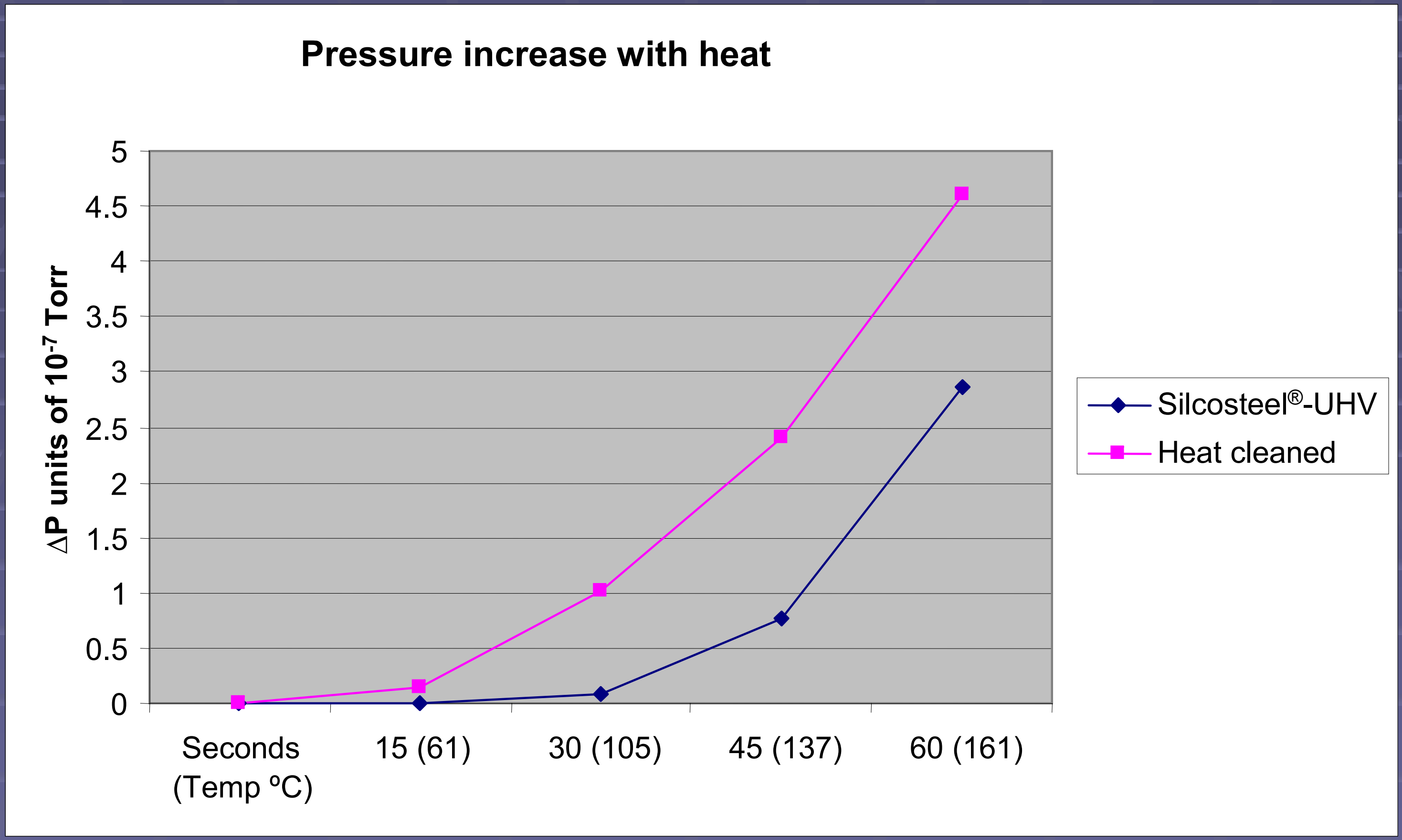
- UHV environments are characterized as having a vacuum of $1x10^{-7}$ Torr or better
- In these conditions, materials trapped to the surface of and inside the steel outgas into the vacuum environment
- The outgassing of material increases pressure in the environment
- Large pumps and long “pump down” times are required to achieve UHV environments
- Silcosteel-UHV treatment produces a barrier that blocks materials from outgassing into the vacuum environment.

# Ultra-High Vacuum Data




- Bruce Kendall: Elvac Labs, PSU Physics prof. (ret.)
- Turbopump, 4.6 x $10^{-7}$ Torr base pressure
- 1hr under vacuum (ΔP1)
- 27x improvement at 61ºC

# Ultra-High Vacuum Data (cont.)




- Turbopump, 7.5 x $10^{-8}$ Torr base pressure
- 10hr under vacuum (ΔP2)
- 14x improvement at 61ºC

# Example Applications

- Coating of accelerator chambers to create higher vacuum environment
- Use in coating of semi-conductor manufacturing equipment to decrease defect rate
- Reducing time needed to achieve high vacuum environments in analytical equipment (SEM, XPS, etc.,.)

# Future

- Currently renovating for expansion
- New process oven (31” ID x 24” deep)
- Continual process improvement and new product development
  - Hardness
  - Improved corrosion resistance
  - Customized surfaces