Setting the Standard for Automation™

STUDY OF CHEMICAL AND PHYSICAL ADSORPTION PROPERTIES OF MOISTURE, SULFUR, AND MERCURY STREAMS THROUGH A VARIETY OF TUBING SUBSTRATES

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Outline

- Functionalized silicon coating process and characteristics
- Characterization of sulfur adsorption in sample holding and transfer
- Effect of moisture uptake and release
- Mercury adsorption by stainless steel
- Conclusion

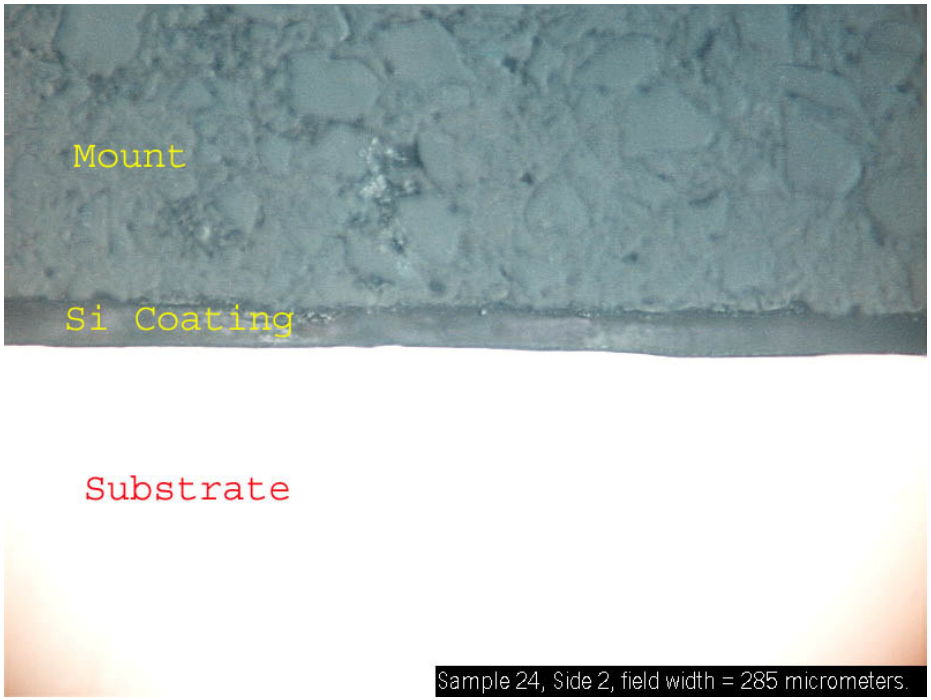
Functionalized Amorphous Silicon

- Study focused on functionalized amorphous silicon because:
- Durable coating for a variety of surfaces
- High temperature capability
- Addresses physisorption and chemisorption issues
  - Highly inert
  - Reduce activity of substrate (i.e., stainless steel) to minimize adsorption of compounds
  - Coated system products deliver better reproducibility and accuracy by reducing hold-up of active compounds

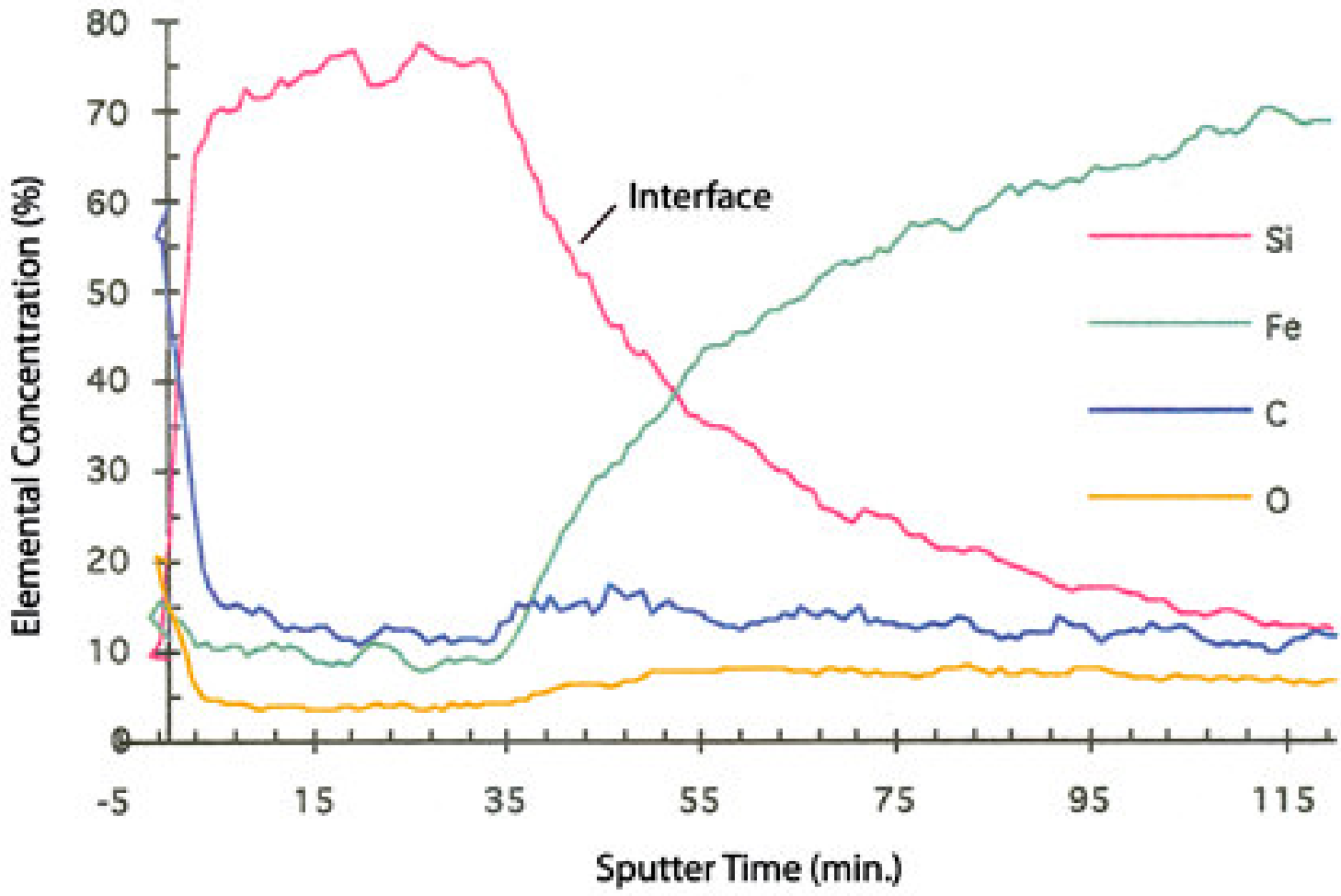
Chemical Vapor Deposition Process

- Thermal decomposition of silanes
- Amorphous silicon deposition
- Functionalization of surface if desired
- Process
  - Clean (caustic surfactant; ultrasonic)
  - Vacuum
  - 400ºC
  - Applied in vessel or oven chamber
- Total 3D coverage, not line-of-sight
- High volume (size dependent)

Coating Cross Section



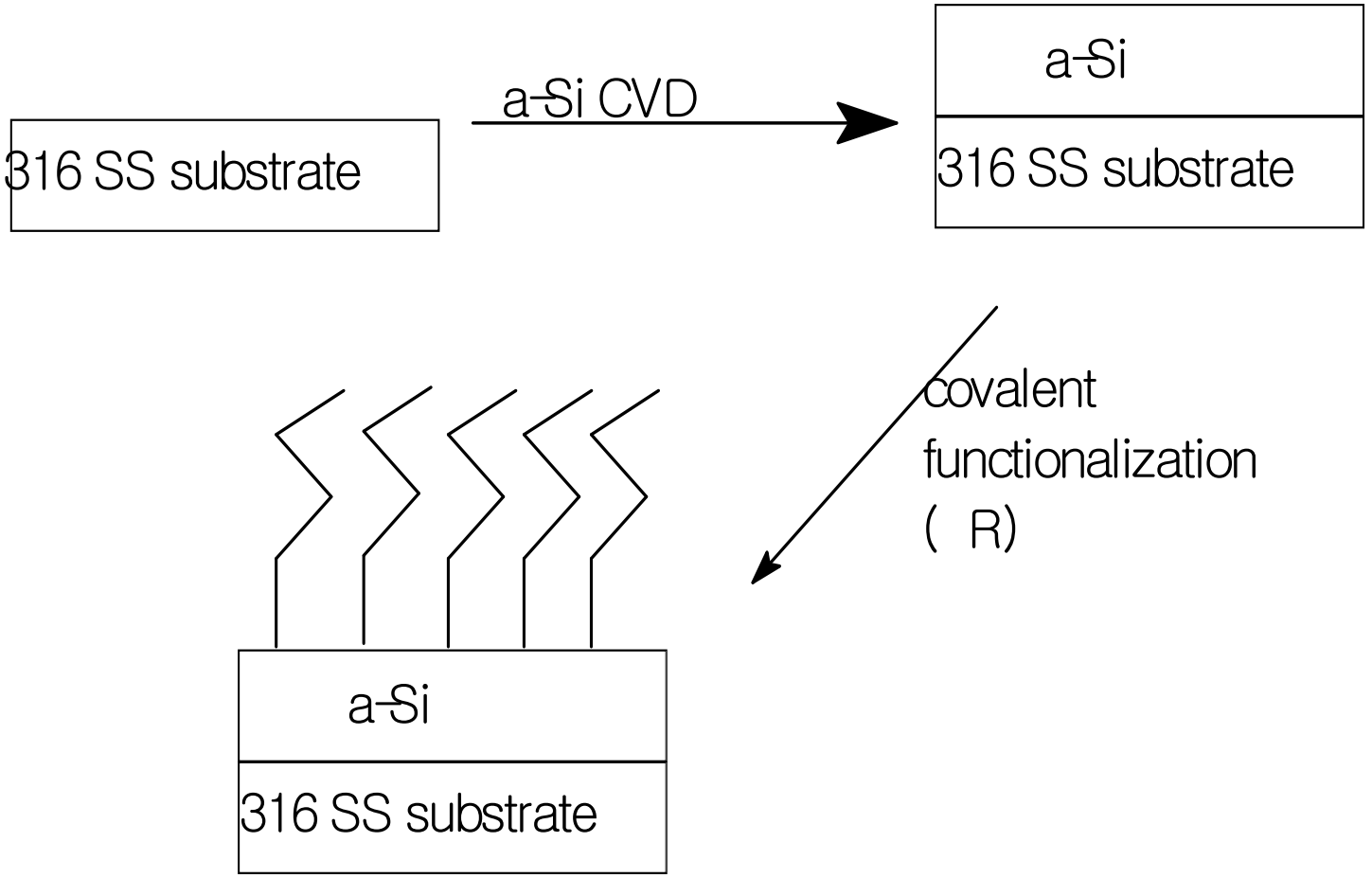
Auger Depth Profile



Secondary Enhancements

- Amorphous silicon deposition
  - Up to 20um in depth
  - Multiple layers to eliminate pin-holes
  - Enhances corrosion resistance
- Additional organic functionalization
  - Decrease of pin-holes
  - Improving surface inertness

Patented Functionalization



Coating Appearance

Common Coated Components

Sampling Systems
Transfer Tubing
Valves
Particle Filters
Tube Fittings and Adaptors
Sample Cylinders; Outage Tubes
Analyzer components
Continuous Emission Monitoring (CEM) equipment

Effect of sulfur• Sulfur Issues

- Unwanted reactivity
- Corrosion – contributes to sulfuric acid formation
- Adsorbs to stainless steel surfaces
  - Analytical reliability issues
    - Delayed response
    - Memory effects

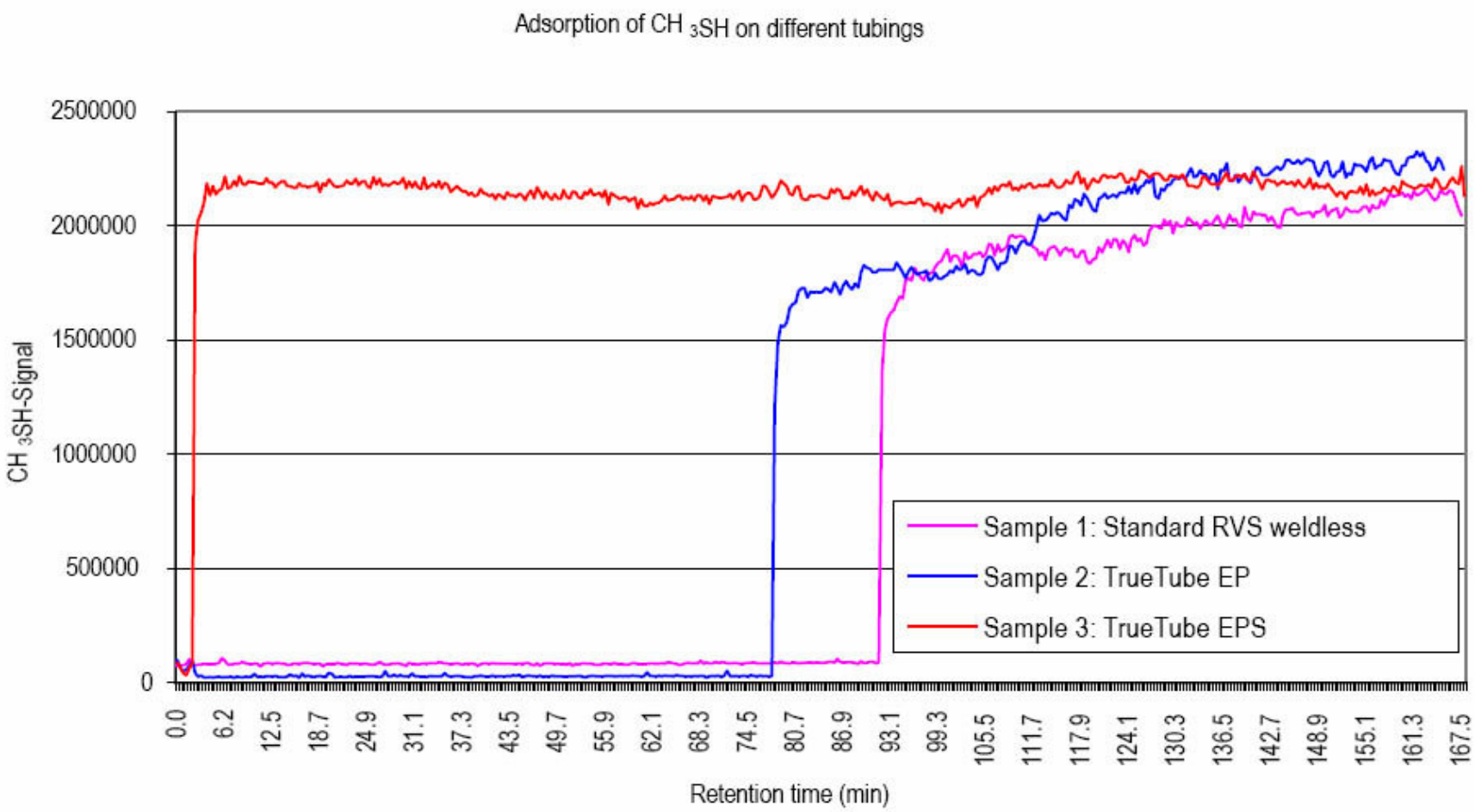
Effect of sulfur

- Functionalized silicon coating improves response
  - Reduces adsorption effects
  - Improves analytical reliability
  - Faster cycle times and increased accuracy

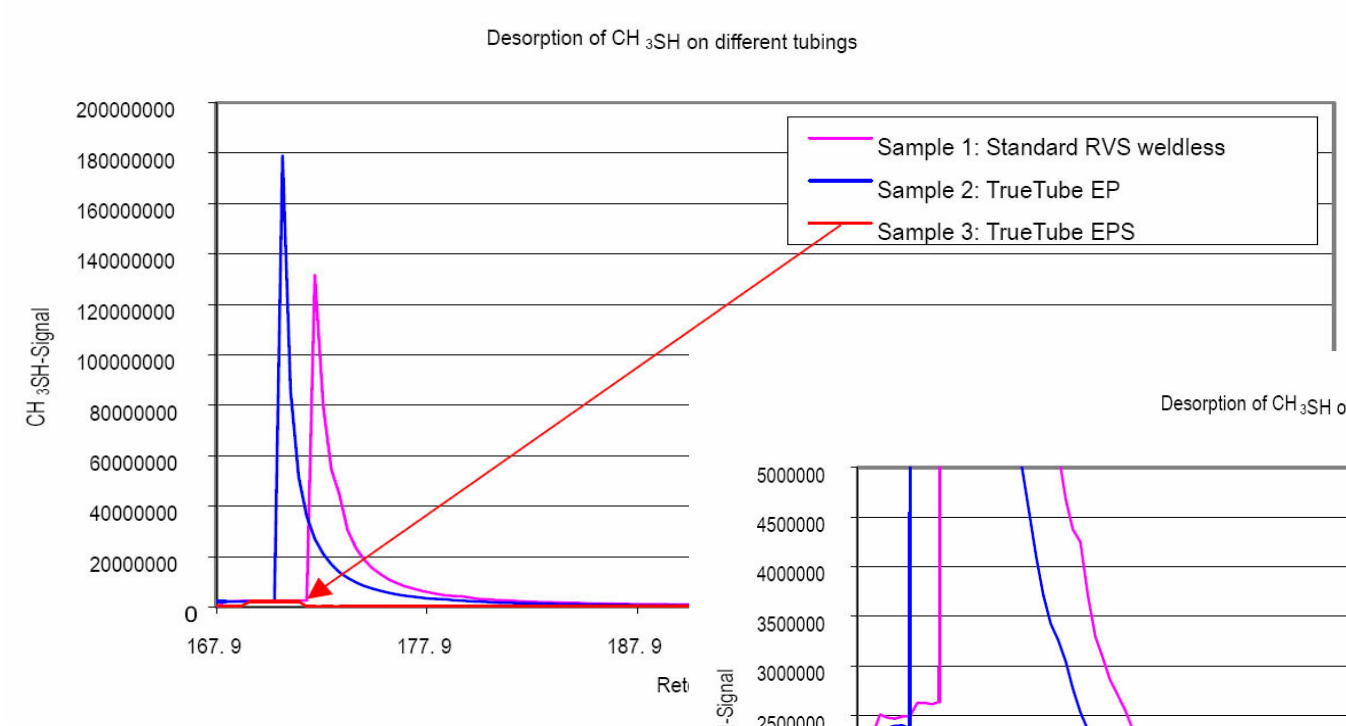
Sulfur Flow-through data

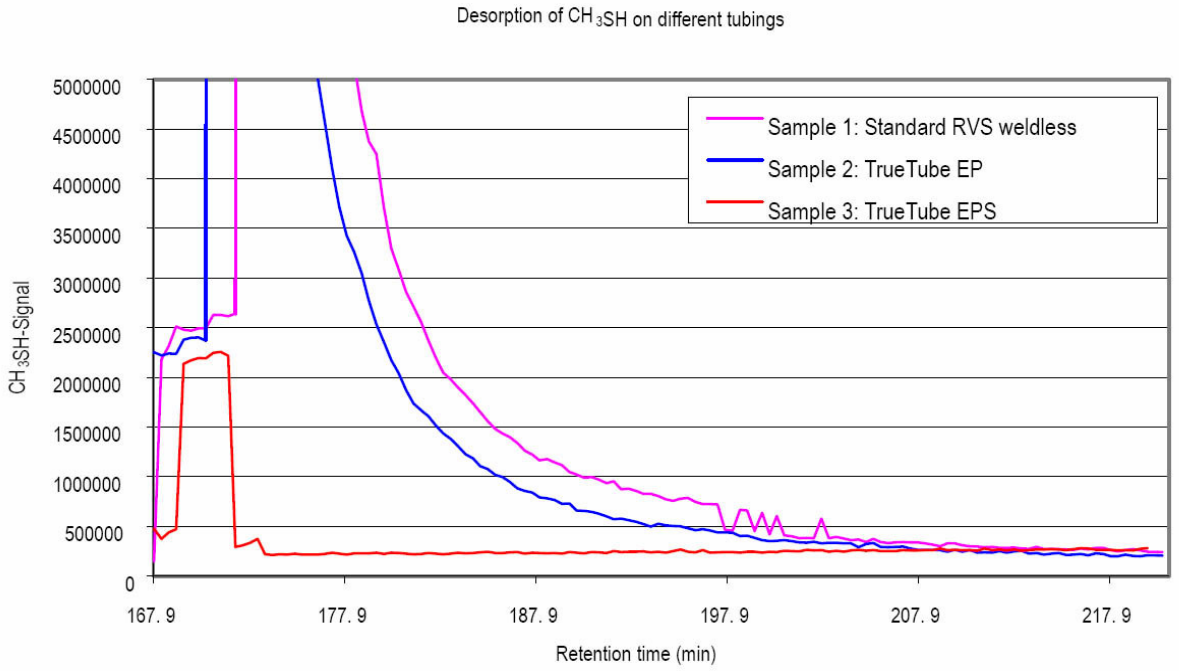
- 100’ 1/8” x .020” tubing
  - Standard seamless 316L
  - Electropolished 316L
  - a-silicon coated EP 316L
- 0.5ppmv methylmercaptan in He
- SCD detection
- Data courtesy of Shell Research Technology Centre, Amsterdam

Example of tubing characteristics: Chemisorption major contributor



Inert surface minimizes "memory" effect





Effect of moisture

- Moisture Issues
  - Sample hold-up
  - Unwanted reactivity- Polar water molecules on surface increase activity of surface
  - Corrosion – contributes to acidic/basic formation during sampling
    - Example: SO_2 to HSO_3 and H_2SO_4
    - NH_3 to NH_4OH

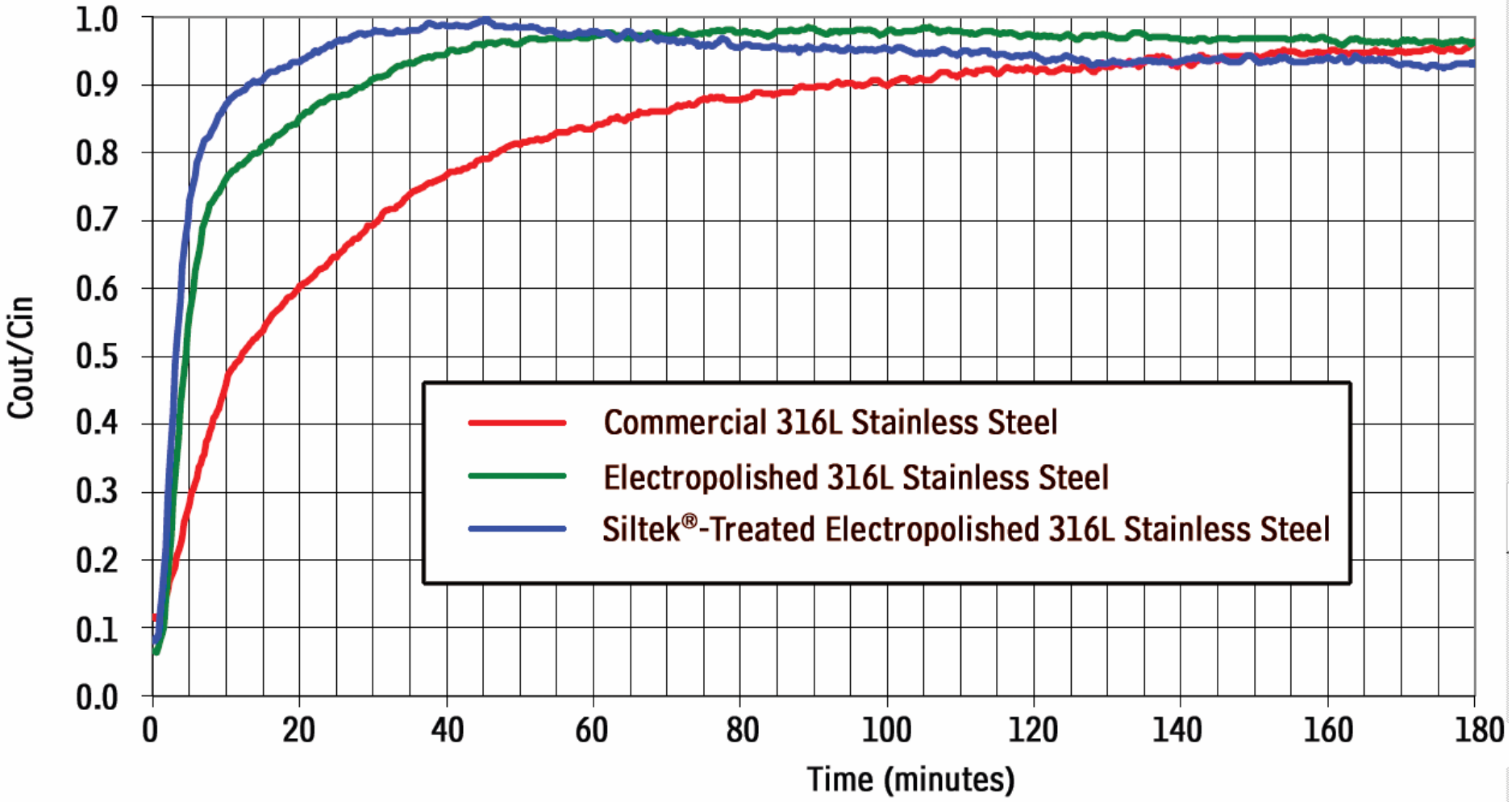
Effect of moisture

- Hydrophobic coating decreases adsorption of water
  - Quicker removal of moisture through sampling lines
  - Components less susceptible to corrosion
  - Faster cycle times and increased accuracy with less moisture hold-up in tubing

Moisture Data

- 1ppm moisture, 0.35slpm
- Amount of time to equilibrate a 1ppm moisture sample through 100 feet of dry tubing:
  - Commercial Seamless 316L tubing:
    - 180 minutes (96% equilibrated)
  - Electropolished Seamless 316L tubing:
    - 60 minutes (98% equilibrated)
  - Functionalized a-silicon coated e-polished seamless 316L tubing
    - 30 minutes (98% equilibrated)

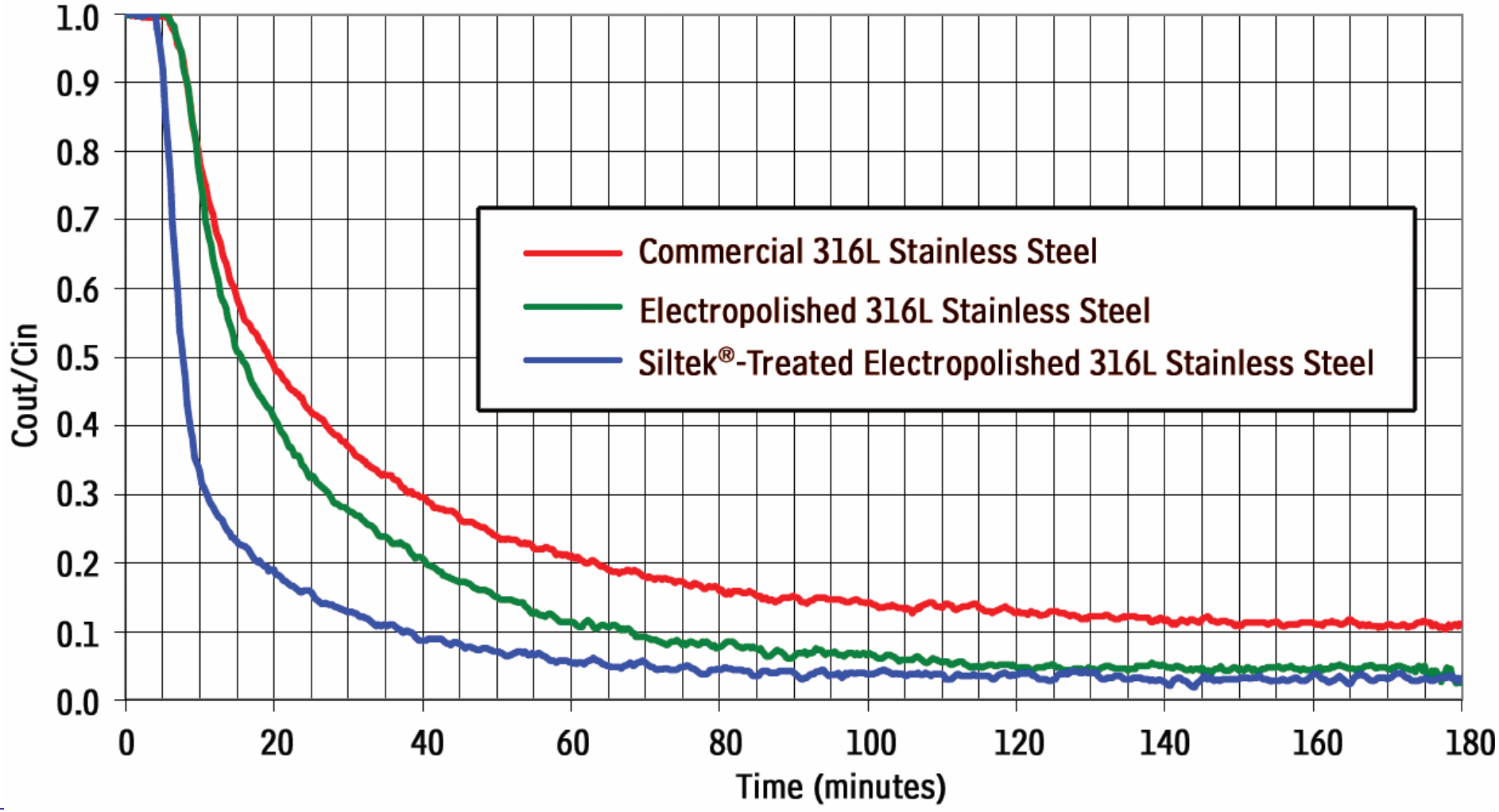
Wet-Up 50% faster response



Moisture Data (cont)

- Time to dry 100’ tubing wetted with 1ppm of moisture when connected to a dry purge
  - Commercial Seamless 316L tubing:
    - 175 minutes
  - Electropolished Seamless 316L tubing:
    - 65 minutes
  - Functionalized a-silicon coated e-polished seamless 316L tubing
    - 35 minutes

Dry-Down 50% faster response



Effect of Mercury

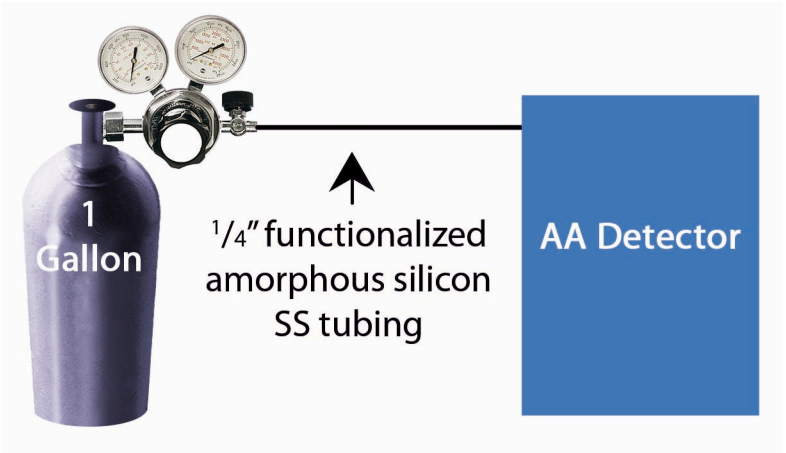
- Stack mercury emissions exist in 3 forms
  - Elemental mercury (Hg)
  - 2^+ Oxidation state (Hg^{++})
  - Attached to particulate matter
- Hg^{++} reacts with stack compounds and stainless steel surfaces making analysis unreliable
- Tube Wall Adsorption
    - Physical Adsorption (Physisorption)
    - Chemical Adsorption (Chemisorption)

Effect of Mercury

- Problem: Mercury is oxidized by steel surfaces resulting in loss during holding and transfer
- Functionalized amorphous silicon
- Improved by sound analytical design
  - Heat trace tube
  - Short tube runs
  - Eliminate dips/pockets
  - Maintain target flow
- Electropolished Surfaces (Physisorption)
- Teflon

Mercury Adsorption by Stainless Steel

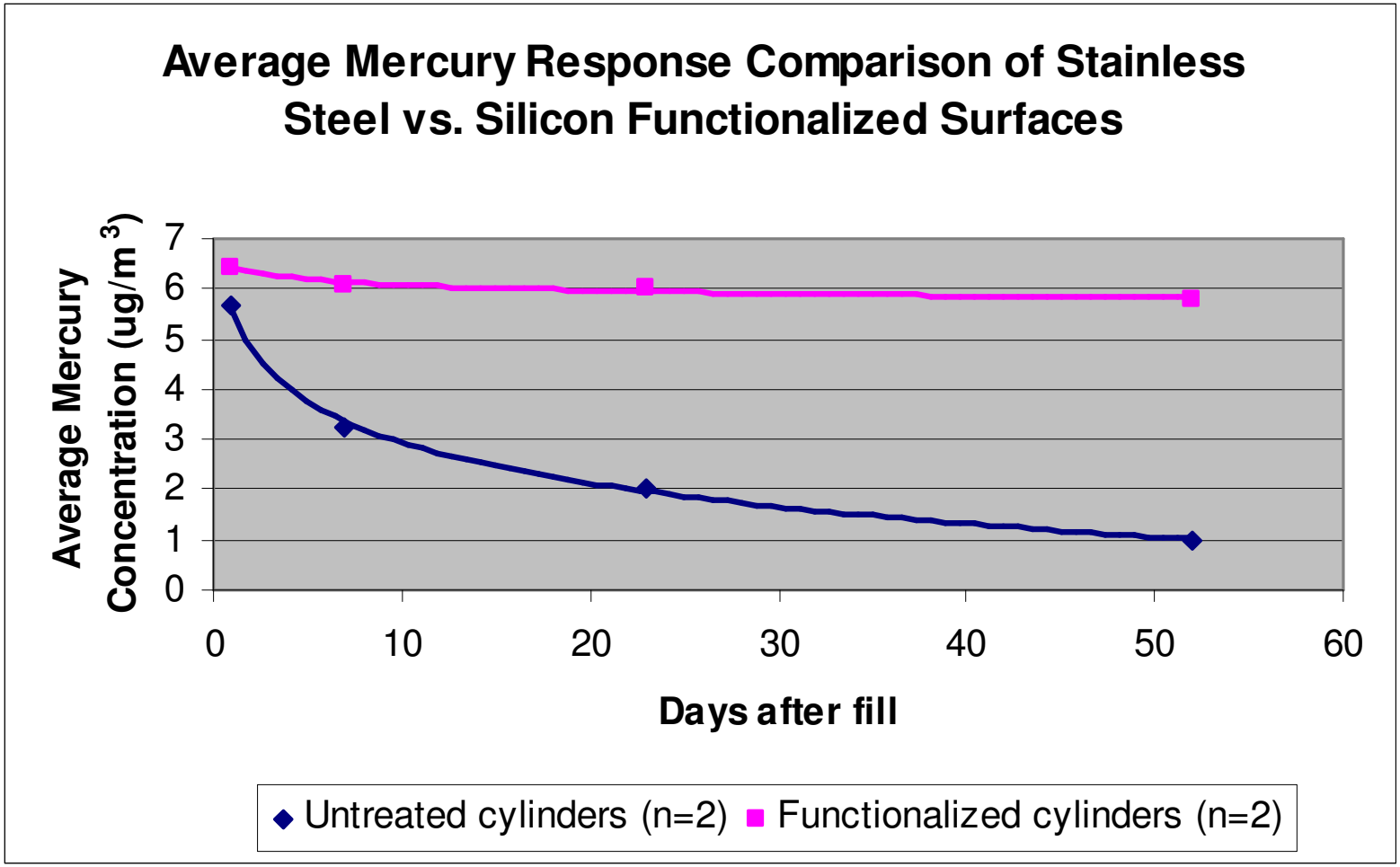
- 5 ug/m^3 Hg Standard
  - Spectra Gasses Inc.
- 1 Gallon Sample Cylinder 1800psi DOT rated
  - Swagelok Corp
- NIST Traceable
- Nominal Temp. 70°F
- Test Cycle Day 0,7,19,50
- Direct Interface Gas Sampling
- Atomic Adsorption Detector
- Functionalized Silicon Coated Regulator and Tube



Comparison of Hg Stability in 304SS vs. Functionalized Silicon Coated Cylinders

Test Day	Avg response 304 SS cylinders ug/m3	Loss vs. Day 0	Avg response Functionalized Silicon ug/m3	Loss vs. Day 0
0	5.65	-	6.45	-
7	3.25	42%	6.1	5%
19	2.05	64%	6	7%
50	1	82%	5.8	10%

Mercury 50 Day Stability Chemisorption major contributor



Current Applications

- Sulfurs, Moisture and Mercury: Application areas
  - Coal Fired Power Plants
  - Natural Gas; LPG
  - Ethylene; Propylene
  - Fuel Cells
  - Petrochemical Process Streams
  - Beverage Grade CO_2 (Soda/Beer)
  - Flavor (Wine/Beer)
  - Moisture Monitors
  - Sample Transfer

Conclusion

- Functionalized silicon surfaces can improve mercury, moisture and sulfur analytical response
- Improve sulfur & sulfur species response in transfer systems by 97%
- Low level sulfur species stable for 7 days in static containment systems
- Moisture dry down performance improved by 50%

Conclusion

- Reduce mercury adsorption by 70% in static containment systems
- Sulfur compound transfer heavily dependent on surface chemistry vs. surface roughness
- Moisture hold-up and transfer a function of both surface chemistry and surface roughness