The Use of Coatings to Improve the Physical and Analytical Reliability of Process Monitors Used for Ammonia, Mercury and Hydrogen Sulfide Service

Gary Barone, Marty Higgins, David Smith
SilcoTek Corporation

Overview

- Sampling & Test Reliability
- Coating Materials
- Corrosion Testing
- Hydrophobicity comparison
- Chemical Inertness
- Conclusion

Why Customers Need Reliability

- Reduce cost:
  - Lost time from re-testing
  - Improve product yields
  - Improve accuracy in grading feedstock
  - Emissions compliance
- Avoid false negatives and improve sample transfer
  - Sample stable from field to lab.
- Immediate response during process changes creates savings

Factors Contributing to Poor Sampling Reliability

- Durability/Wear
- Corrosion
- Moisture
- Design
  - Installation
  - Chemical & Material Compatibility/Inertness
  - Instrument Compatibility
- Inertness / Adsorption

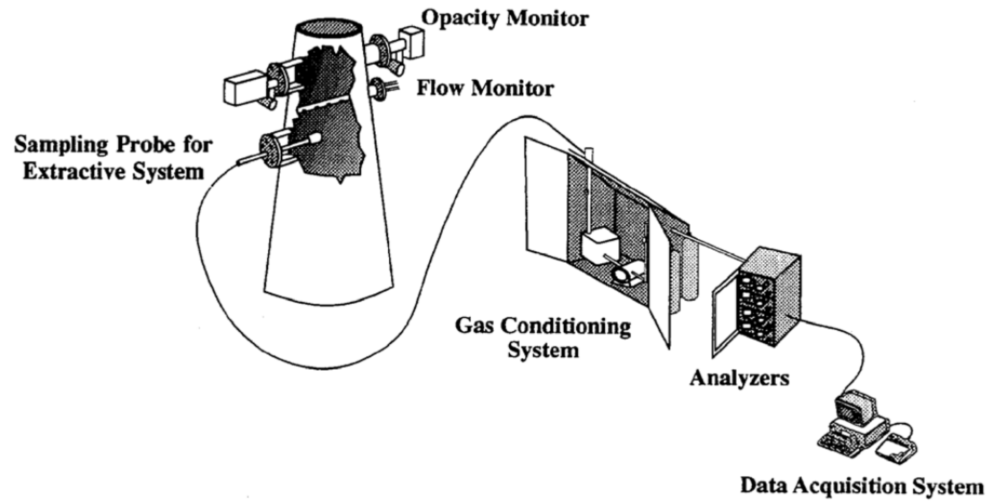


Figure 1: A typical continuous emission monitoring system (CEMS) (U.S. EPA Image)[4]

Using Coatings

- Most analytical pathways are stainless steel
  - Great structurally
  - Good corrosion resistance
  - Poor chemical properties for analytical chemists
- Coatings are now commonly used to improve the chemical properties.
- Need also to address corrosion and wear in harsh environments

Selecting Coatings

- Fluoropolymers
  - Very inert
  - Very corrosion resistant
  - Broad pH applicability
  - Poor adhesion
  - Poor wear resistance
  - Good to 260°C

- Silicon based (Sulfinert®; SilcoNert™)
  - Very inert
  - Great adhesion
  - No carryover
  - Good corrosion resistance
  - Limited pH range
  - Susceptible to steam cleaning
  - Poor wear resistance
  - Good to 450°C

New Coating

- Carboxysilane (Dursan™)
  - Good inertness
  - Great adhesion
  - No carryover
  - Good corrosion resistance
  - Broad pH applicability
  - Steam cleaning, no problem
  - Good wear resistance
  - Tested to 450°C so far
  - Still accumulating application data

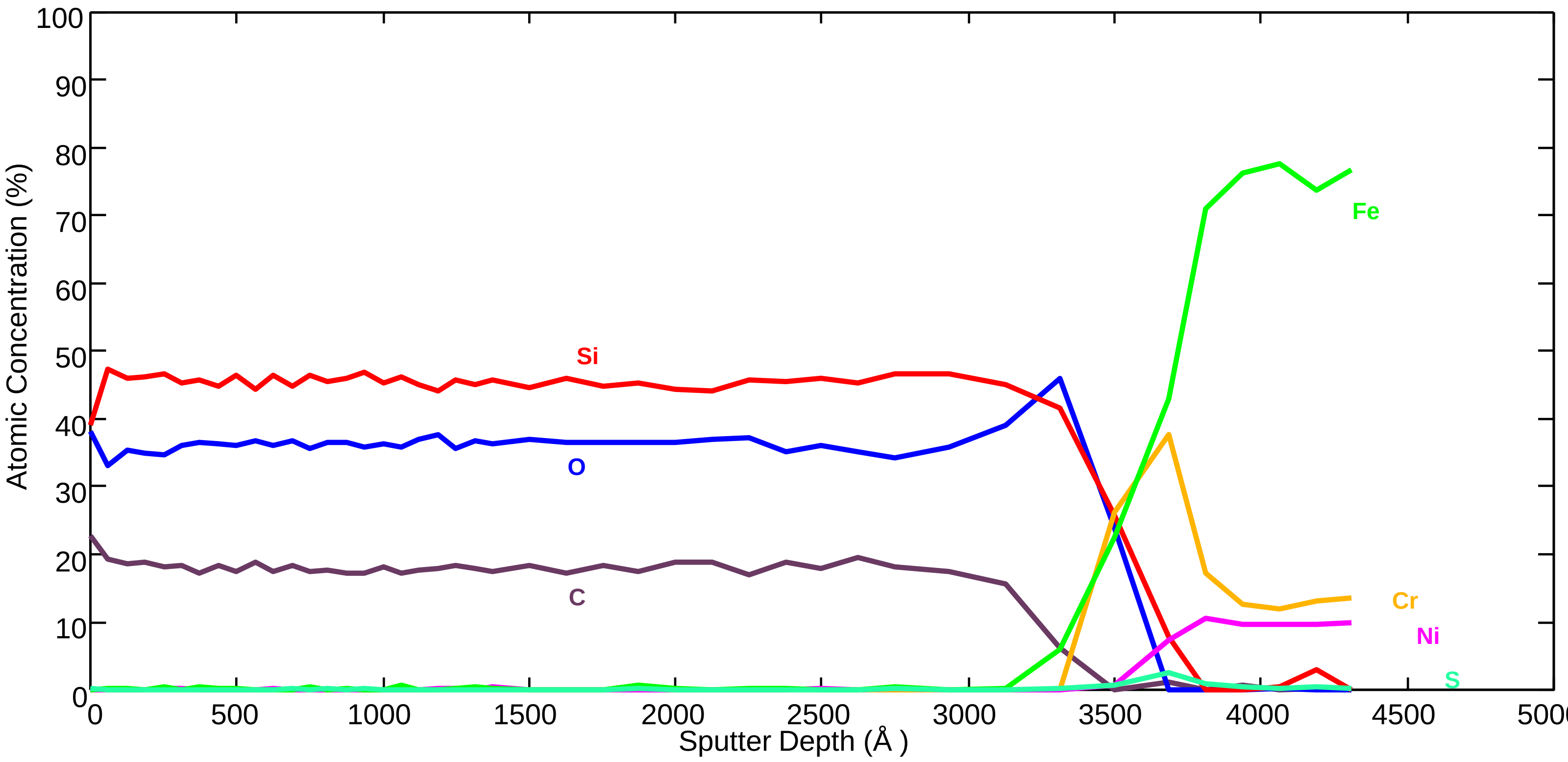
SilcoTek™ Driving Innovation

Coating/Material Properties

Property	SilcoNert 2000	Dursan	PTFE, PFA
Max Temperature	450ºC	450ºC	260ºC
Min Temperature	-196ºC	-100ºC	-240ºC
Low pH limit	0	0	0
High pH limit	7	14	14
Thickness	0.12um to 0.5um	0.5um to 1.5um	25um
Adhesion	Very Good	Very Good	Poor
Wear resistance	90% of Stainless	2 times 316 Stainless	10% of SS (est.)
Moisture contact	87°	104-140°	125°
Inertness vs. SS	Very Good	Very Good	Very Good

SilcoTek™ Driving Innovation

Composition of Dursan™



SilcoTek™
Driving Innovation

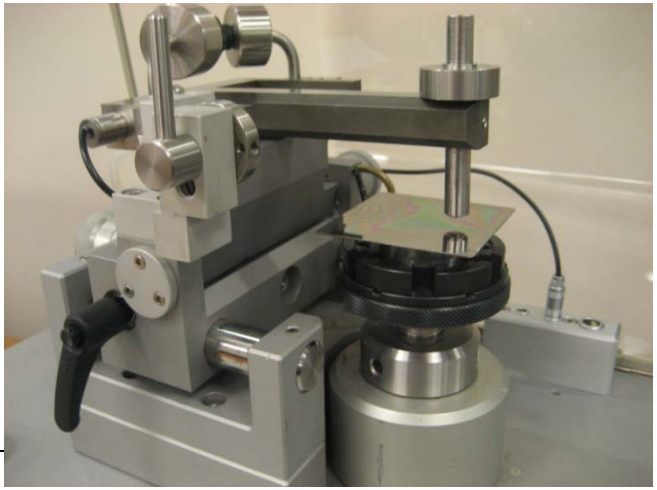
Improving wear resistance

- Equipment and sample conditions can present physical challenges
  - Valve cycling
  - Particulate in sample streams
  - Cleaning needs
- Existing coatings that are applied to improve chemical inertness and control corrosion can be removed easily in challenging environments

Wear Resistance Comparison

Pin on Disc; 2.0N	**316 SS**	**Silco**	**Dursan**
Wear rate (x10^{-5}mm^3/N m)	13.810	15.344	6.129
Improvement Factor over Stainless Steel	---	0.9 X	2 X

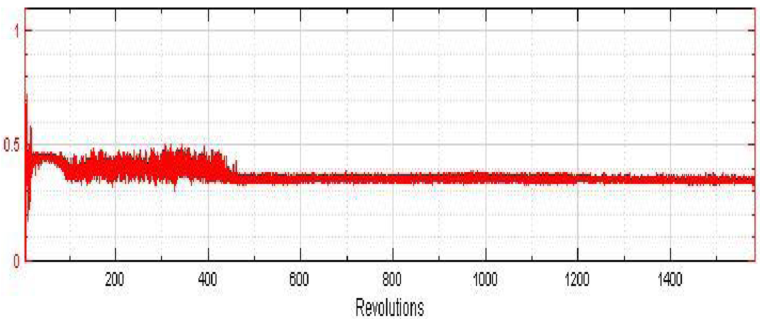
CSM Instruments Tribometer 18-343 used to measure surface wear resistance



Wear and Friction Data

- **Pin on Disc in accordance with ASTM G133**

	Avg. Coeff. Friction	Wear Rate ($x10^{-5}mm^3/Nm$)
Uncoated SS	0.589	13.810
Carboxysilane on SS	0.378	6.129



Load	2.0 N
Duration	20 min
Speed	80 rpm
Radius	3mm
Revolutions	1,554
Ball Diameter	6mm
Ball Material	SS 440

SilcoTek Driving Innovation

Courtesy of Nanovea Inc.

Challenge of Corrosion

- Samples can contain corrosives that quickly attack stainless
  - Hydrochloric acid (HCl)
  - Sulfuric acid (H_2SO_4)
  - Saltwater
- Physical loss of equipment due to corrosion
  - Maintenance
  - Replacement cycles
- Chemical inertness suffers with corrosion
- Silicon coatings susceptible to caustics

Comparative Corrosion Resistance

- ***3M HCl; 24hr; 22ºC***

ASTM G31	**316L SS**	**Silco**	**Dursan**
MPY	67.93	14.85	5.14
Improvement Factor over 316L stainless	---	4.6	13.2

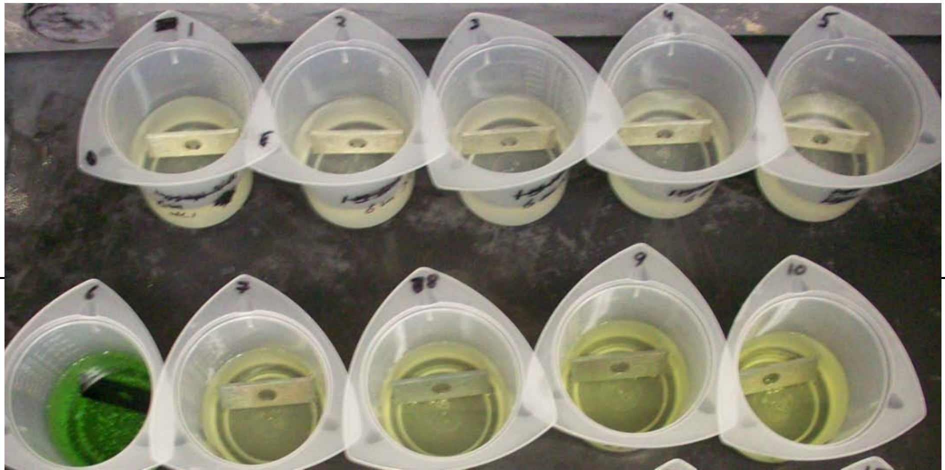


Acid Corrosion Resistance

- ***ASTM G31 Guidelines: <u>6M HCl</u>; 24hr; 23ºC***

	316L SS	a-Silicon	Carboxysilane
MPY	**181.98**	**4.32**	**0.44**
Improvement Factor over 316L stainless	**---**	**42**	**411**

Photo after 19hr exposure



SiCO coated

Control / a-Si coated

SilcoTek Driving Innovation

Comparative Corrosion Resistance

- *10% H_2SO_4; 24hr; 22ºC*

ASTM G31	316L SS	Silco	Dursan
MPY	22.35	2.52	2.42
Improvement Factor over 316L stainless	---	8.9	9.9

Exposure to Caustics

- ***1M KOH; 24hr; 22ºC***

ASTM G31	316L SS	Silco	Dursan
MPY	0	3.40	0.01
Improvement Factor Over Silicon	Infinite	--	261

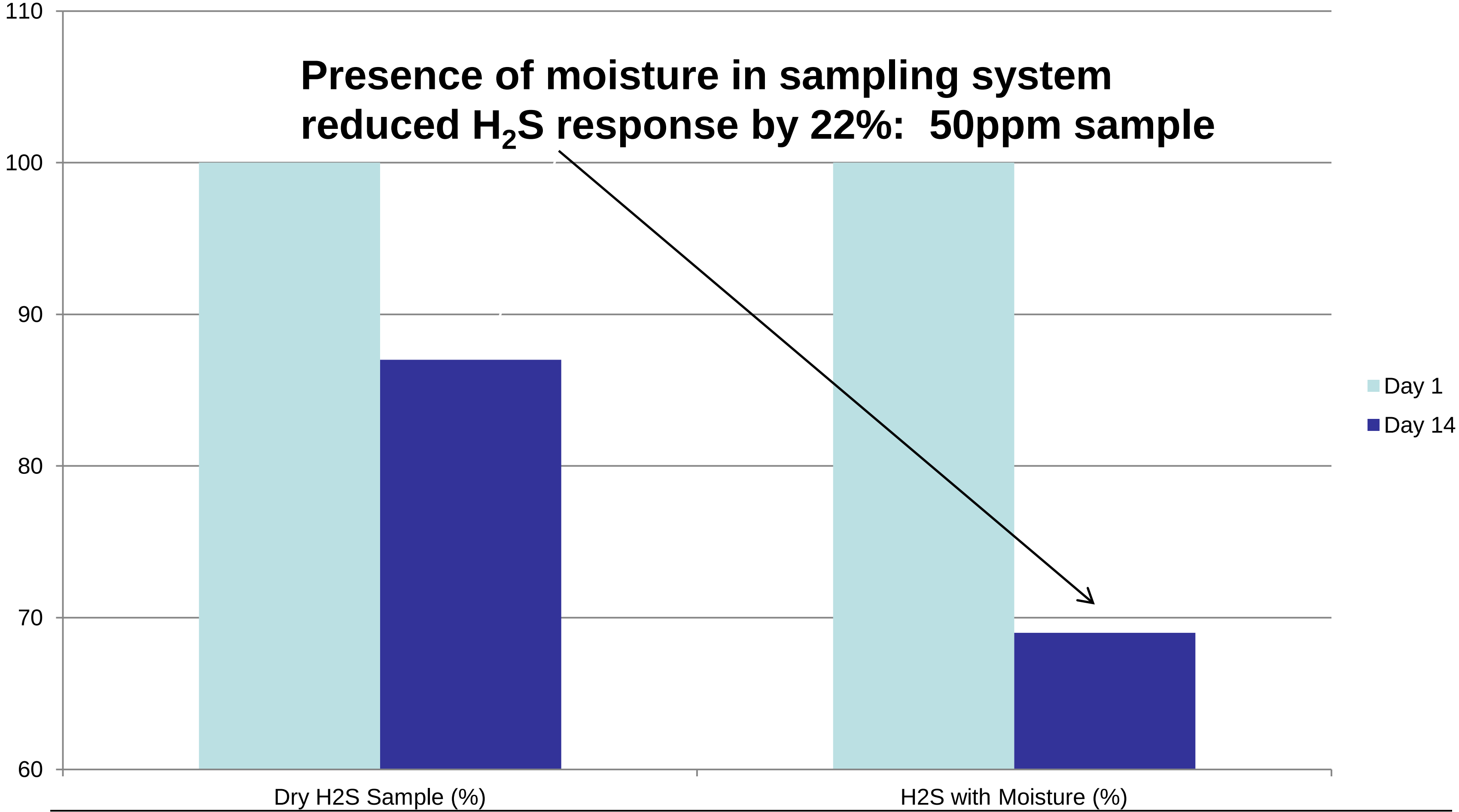
Challenges of Moisture

- Adsorption of active compounds into entrained water
- Formation of acids within the sample system
- Formation of adsorptive rust particles in the sample system.
- Sticks to steel need parts to shed water

Challenges of Moisture

- Benefits of coating that help release water faster
  - Components less susceptible to corrosion
  - Faster cycle times
  - Increased accuracy
  - Eliminate moisture/sample interaction

Impact of Moisture



SilcoTek
Driving Innovation

Measuring Hydrophobicity

Kruss K100 Tensiometer Testing on 304 SS ¼" OD tubing

DI Water	304 SS	Silicon	Sulfinert	Dursan	PTFE
Advancing	36.0	53.6	87.3	105.5	125.4
Receding	5.3	19.6	51.5	85.3	84

DI Water Contact Angle Illustrations (advancing) on flat surfaces

304 SS Silicon Sulfinert Dursan

Chemical Inertness

- Stainless Steel:
  - Adsorbs sulfur compounds
  - Causes loss of mercury
  - Demonstrates poor transportability (tailing) of polar organics such as alcohols
- Passivation when sulfur sampling shown effective at low temperatures, smooth surfaces[1]
  - Not effective with H_2S in heated sample lines[1]
    - [1] Biela, B., Moore, R., Benesch, R., Talbert, B., Jacksier., "The Do's and Don'ts in the Analysis of sulfur for Polyolefin Producers", presented as paper 081 at the Gulf Coast Conference, (2003)

Chemical Inertness

- SilcoNert™ and Fluoropolymers: Great inertness for sulfurs, mercury & ammonia, down to single digit ppb

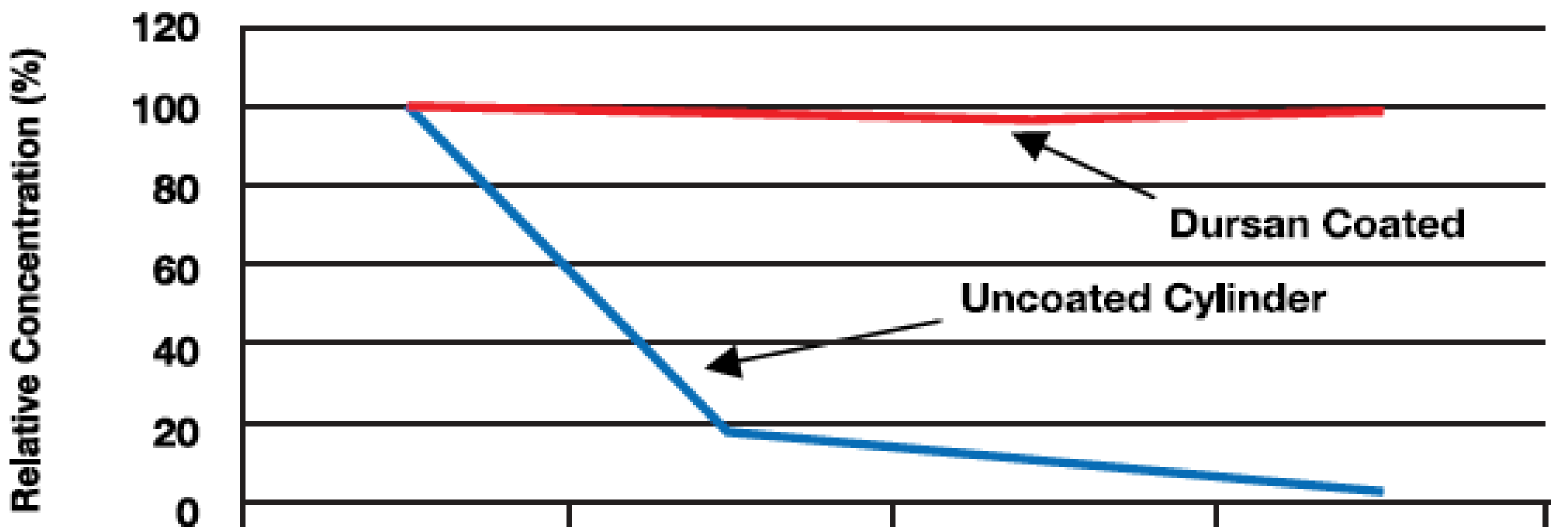
- Dursan™: Good for H_2S (10ppm) and OK for Ammonia.
  - Improvements to target replacing Silco coatings for inertness and corrosive applications!

SilcoTek™ Driving Innovation

Hydrogen Sulfide

H_2S Stability: Dursan vs. Stainless Steel

50ppmv, 300cc cylinder

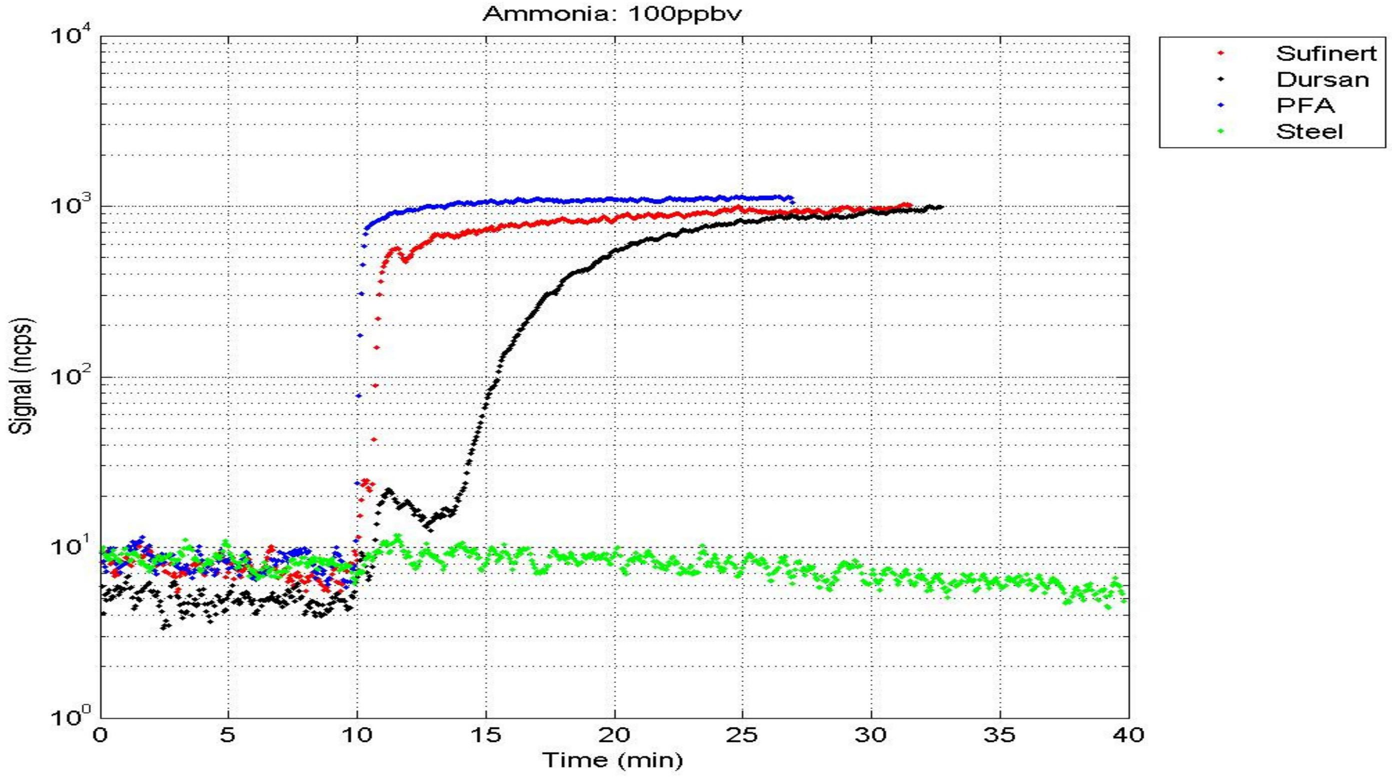


	0:00	25 hours	50 hours	75 hours
Stainless Steel	100	19	10	4
Dursan	100	98	96.6	98.3

SilcoTek™ Driving Innovation

Ammonia Adsorption

100PPV, 500sccm, 1.8m tubing, min



- *Measured PTR-MS signals of ammonia (m17). At t=10min the gas stream was switched in a way*
- *that it passed additionally the different 1.8m long lines. The PFA line seems to be best for Ammonia, while*
- *the steel line completely adsorbs the 100ppbv of Ammonia in the sample gas for hours. All lines were 1.8 m,*
- *not heated (30°C), sample gas flow was 500 sccm (std. ml/min) of 100 ppb of ammonia in N2.*

Conclusion

- Consider multiple design factors to maximize system performance and reliability
  – Surface Energy (moisture resistance)
  – Surface Roughness
  – Corrosion resistance
  – Wear resistance and other physical related factors
  – Surface interaction/inertness
- Review system design, balance target system performance and environment with material capability