

Breakthroughs in Material Compatibility of Inert Coatings for Sampling and Analytical Systems

Clay Smith, SilcoTek Corporation

Gulf Coast Conference 2023

Background

- Coatings have a long history of use in sampling and analytical systems to improve sensitivity and performance.
  - Electropolishing to smoothen tubing surfaces
  - PTFE (Teflon®)-lined sample cylinders, valves, fittings, and tubing

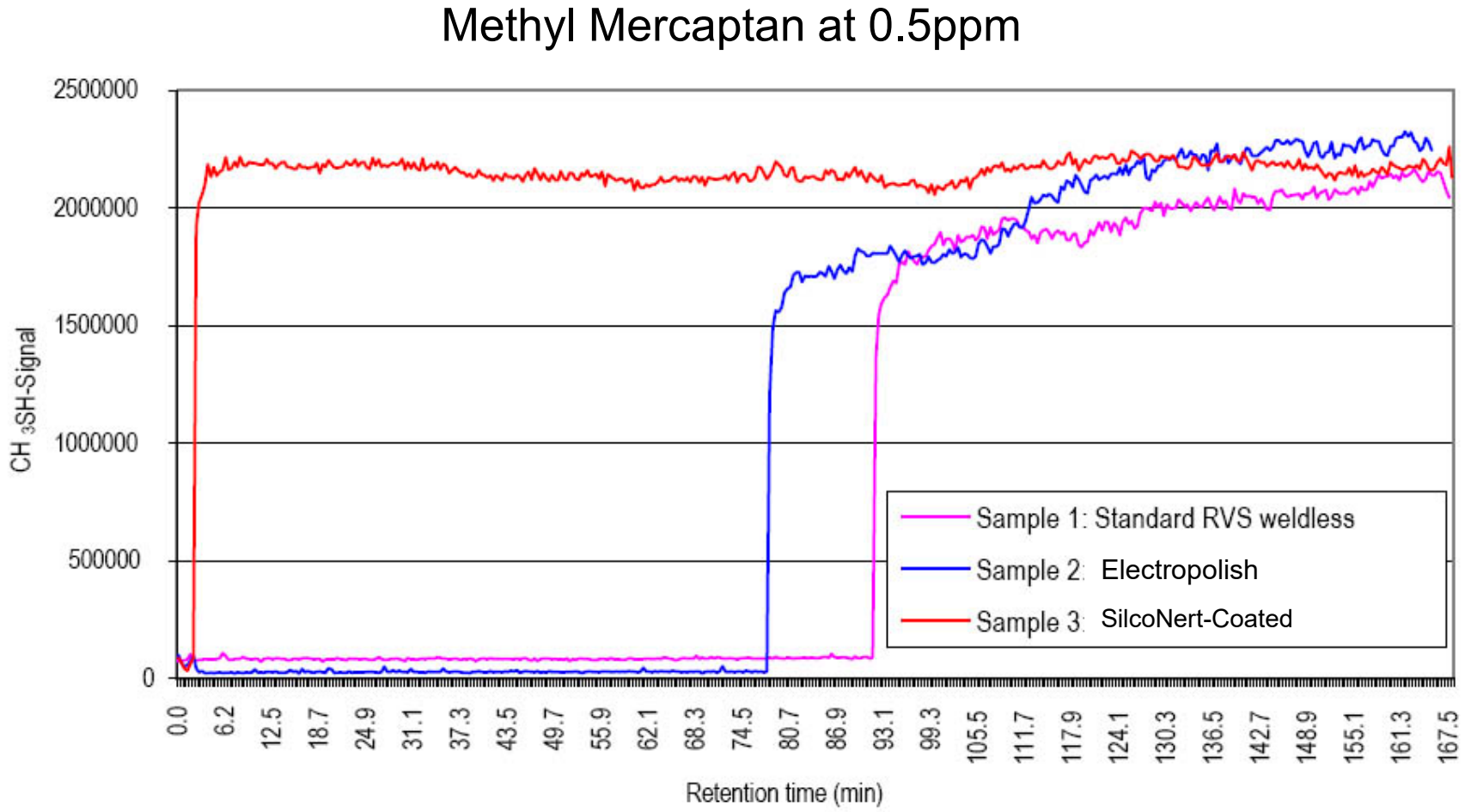
- Ultra-low-sulfur fuel (ULSD & ULSG) standards introduced in the 1990s lowered required analytical detection limits and increased demand for more inert sample transfer components.

- Industry needed better alternatives to PTFE capable of higher temperatures with greater adhesion, density, and durability.

Sulfurs and Steel

- Most chemical pathways consist of steel and stainless steel.
- Over time, in contact with sulfurs, these surfaces will self-passivate or equilibrate, a process referred to as “priming.”
- This process can take hours given concentration changes, and part-per-billion level analysis is not possible.
- Coatings are proven solutions for these materials to improve reliability, speed, and analytical results.
- Variety of work has shown that the smoother the better. Reduce surface area = lower chance of contact points and more efficient and effective coating.

Instant, Accurate Response with SilcoNert-Coated Electropolished Tubing



Today

- SilcoNert® (previously Silcosteel® and Sulfinert®) can make any stainless steel analytical system component chemically inert.

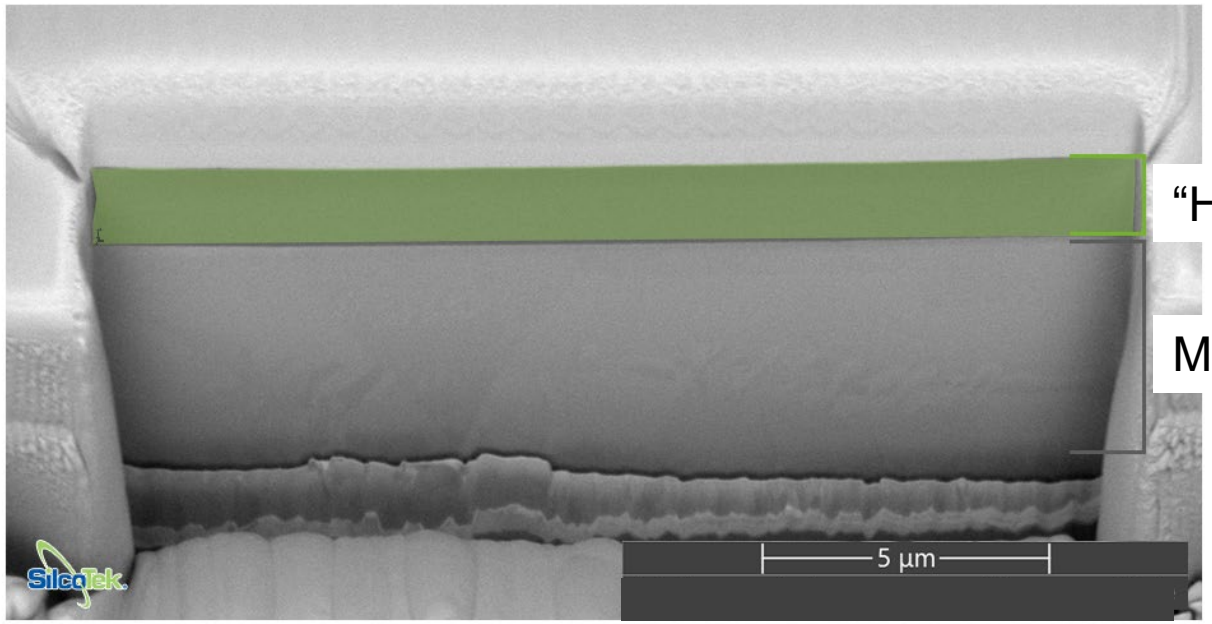
- However, other materials of construction are now desired in chemical processes that have historically been incompatible with these inert silicon-based CVD coatings:
  - Monel® to withstand harsh chemistries, such as in Philips HF alkylation units.
    - Still a need to measure sulfur compounds like H_2S that coatings are required for
  - Aluminum to reduce cost, weight, and variation in raw material quality

- Post-pandemic supply chain conditions have led refineries and system integrators to ask – do we *need* electropolished tubing?

Solution

- Since developing SilcoNert®, SilcoTek has commercialized several new silicon-based coatings that show greatly improved compatibility with aluminum and copper-based materials.

- New “hybrid” coating recipes combine a base layer of coating that is compatible with the metal substrate, followed by a top layer of SilcoNert® that completely adheres to and covers the base coating layer, leaving only SilcoNert® exposed to the process stream.



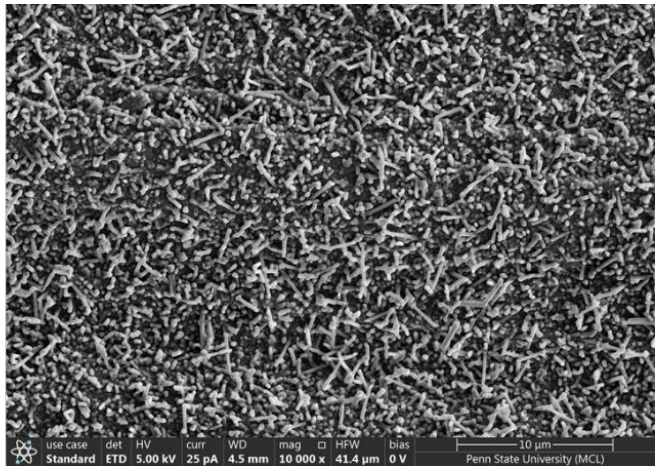
Sulfurs and Copper

- Brass substituted for stainless steel in cost-cutting efforts.
- No data from copper-containing sample systems can be trusted.
  - H_2S and sulfurs will be scrubbed from Monel® and brass sample systems
- Hashem, et. al. from Schlumberger Oilphae DBR demonstrates that 50 ppm H_2S samples are completely scavenged in Monel® tubing[1].
- With Monel® required for HF-containing streams, hybrid SilcoNert coating technique makes both corrosion resistance and inertness possible.

[1]Hashem, et. al, "Low-Level Hydrogen Sulphide Detection using Wireline Formation Tester", International Petroleum Technology Conference, IPTC 11582, (2007)

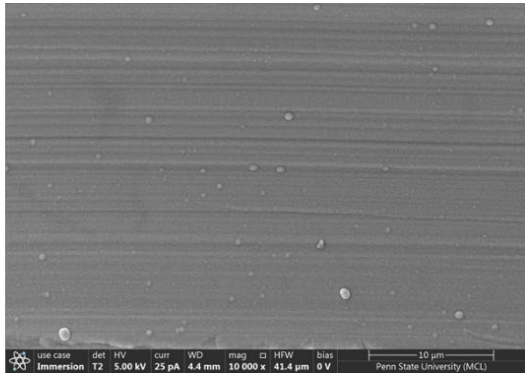
SilcoNert®-Coated Monel®

Original SilcoNert® process applied to Monel® 400 (top) showed poor appearance, adhesion, and surface quality under SEM (10k magnification). Reaction with substrate causes micro-crystallization of silicon.



H_2S inertness testing with SilcoNert-coated Monel sample cylinders currently in progress.

Hybrid SilcoNert® process with silicon oxynitride base layer applied to Monel® 400 (bottom) shows clean, complete coating film growth that passes standard quality checks.



Aluminum

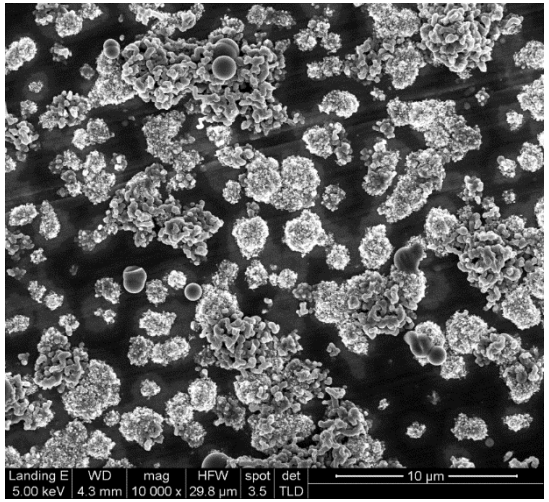
- Aluminum is the most common material of construction for gas cylinders and is a desirable alternative to steels for cost, weight, and material quality reasons.
- However, like Monel®, aluminum has historically been challenging for silicon CVD coatings like SilcoTek's.
  - Original coating process catalyzes silicon crystallization and promotes "nanowire" growth on the substrate
  - This leads to inconsistent and unpredictable coating output
  - Negative impact on cosmetics and performance (especially corrosion resistance)

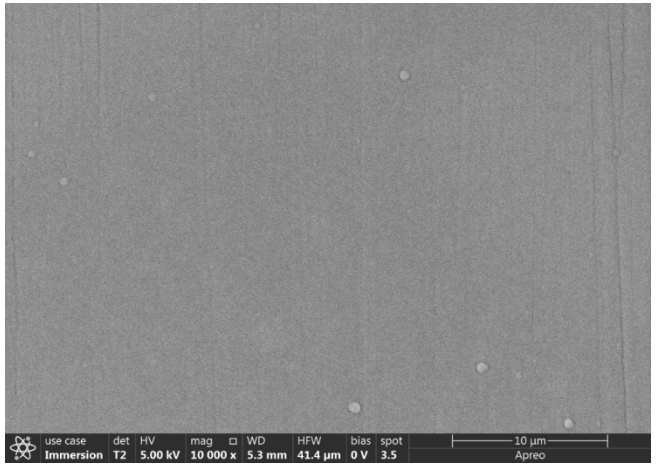
Original SilcoNert vs. Hybrid SilcoNert on Aluminum

Original SilcoNert on Al

Hybrid SilcoNert on Al

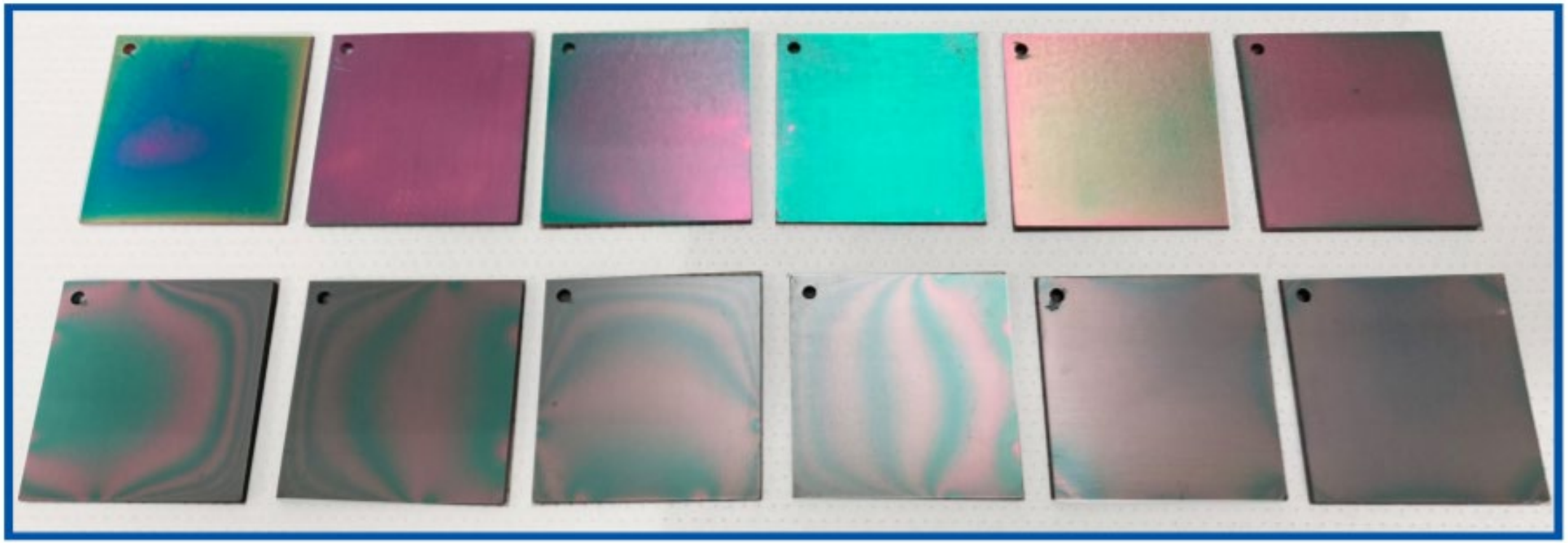
10K mag

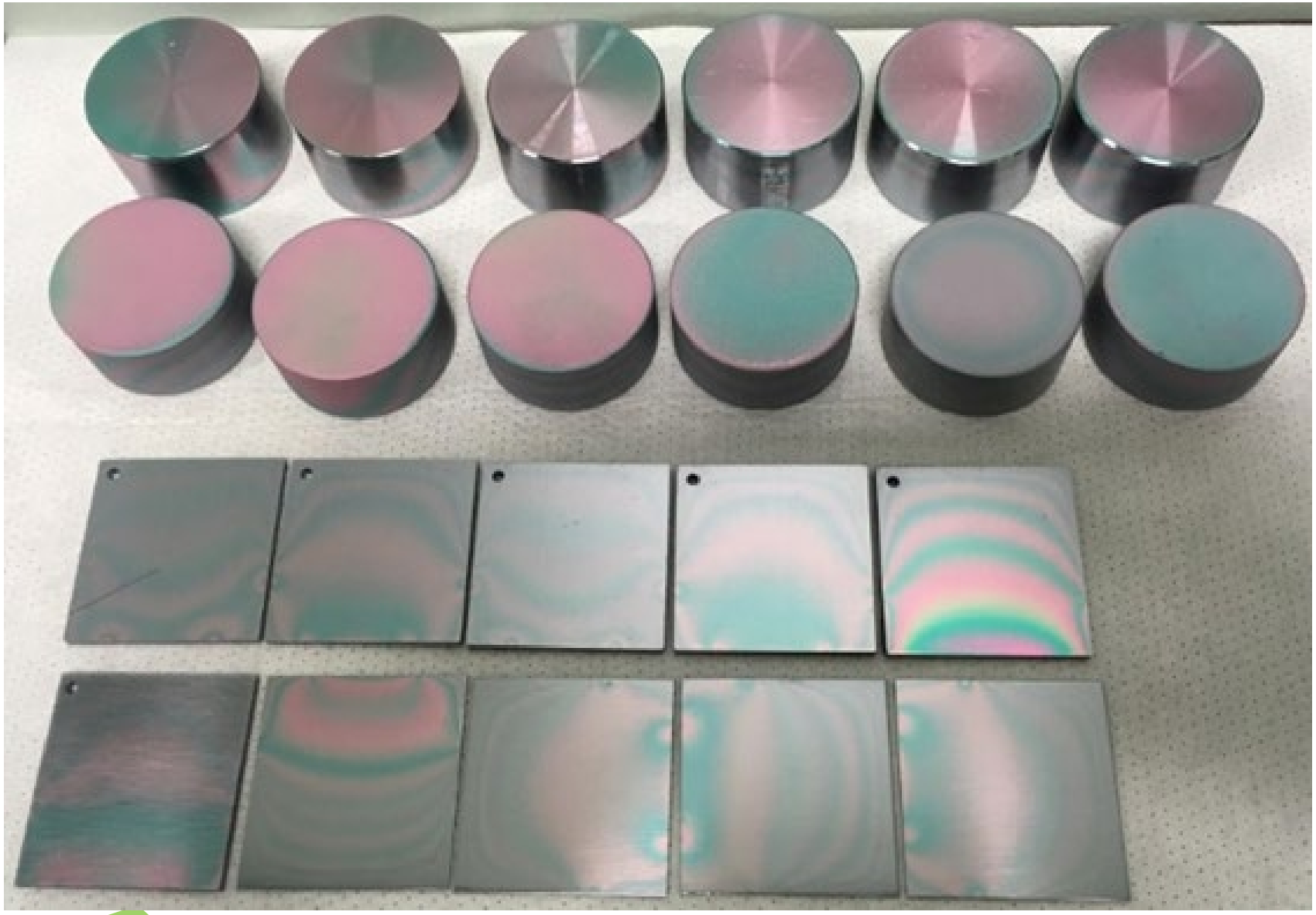




10K mag

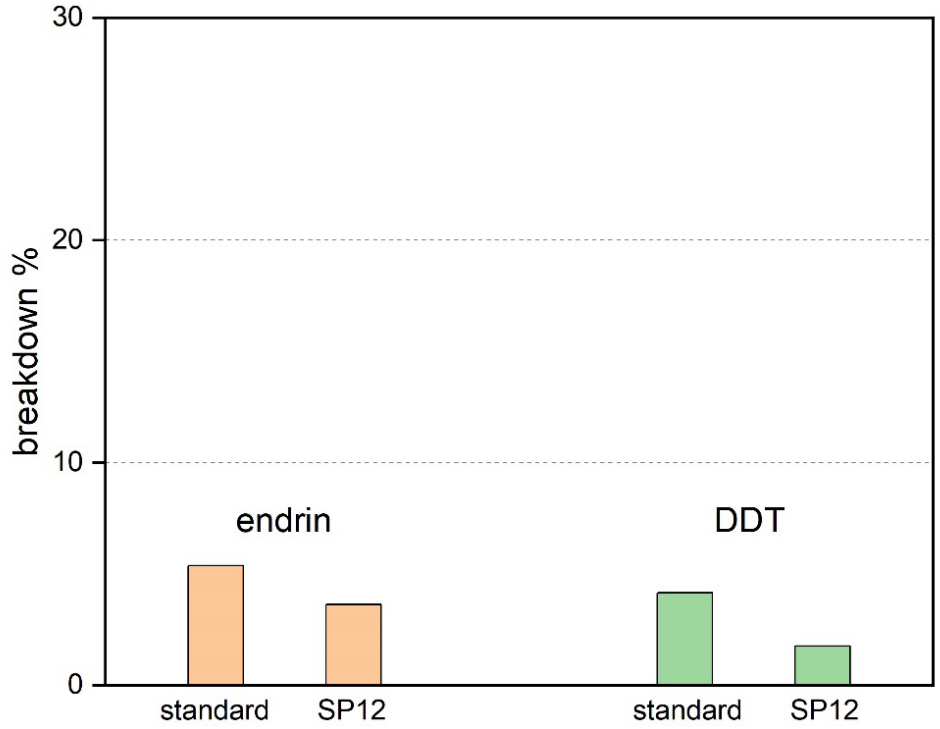
Coated aluminum using new optimized SilcoNert® process





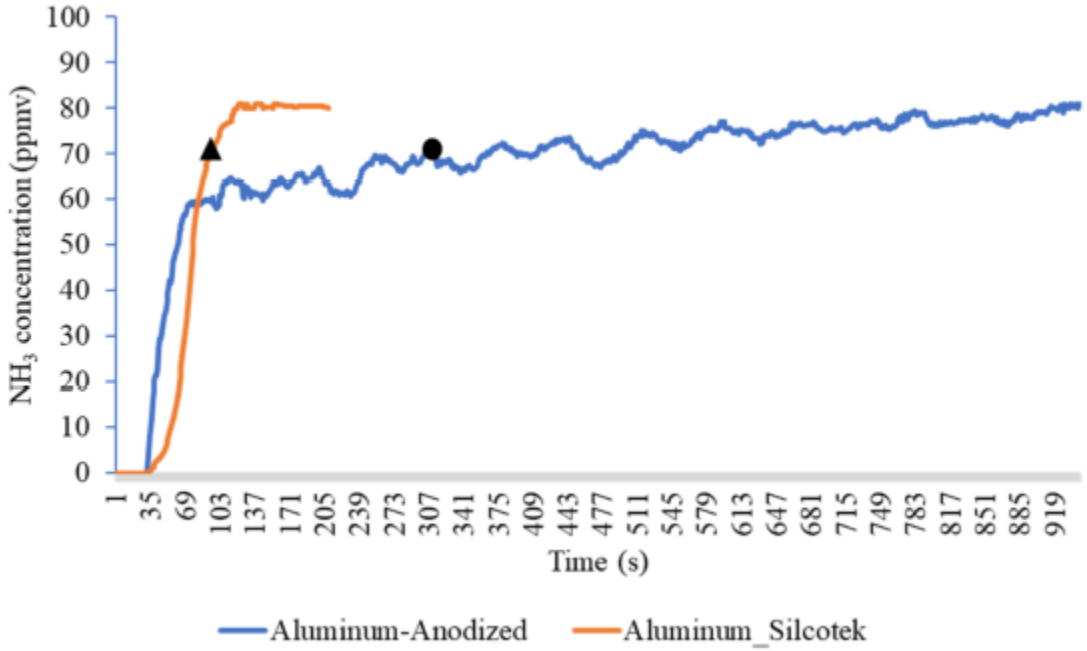
Inertness Testing - Pesticides

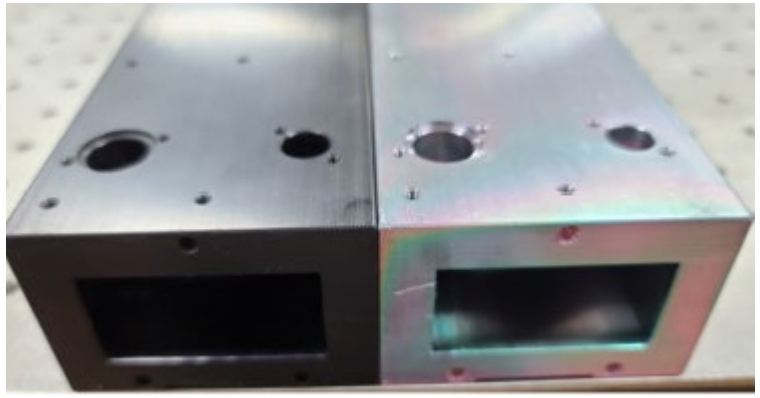
- GC inlet liner testing (courtesy of Restek) showed comparable performance of new hybrid SilcoNert coating to standard SilcoNert-coated borosilicate liners in trace level pesticide analysis
- Test conditions: Endrin at 50 pg/µL and DDT at 100 pg/µL
- Typical pass/fail criteria are below 10% breakdown rates, which are met by both coatings



Inertness Testing - Ammonia

- NH_3 analysis performed by Konkuk University (South Korea) to measure emissions from an urban household solid waste incinerator[1]
- 80 ppmv of NH_3 using non-dispersive infrared (NDIR) analyzer with two aluminum sample chambers; one anodized, one SilcoNert 2000-coated with new hybrid process
- Analyzer coupled with the SilcoNert 2000-coated aluminum chamber showed sensitive and reproducible results while the anodized chamber showed high variability and total sample loss





Anodized Aluminum

SilcoNert 2000 Coated Aluminum

[1]Dinh, T.-V.; Choi, I.-Y.; Park, B.-G.; Lee, J.-H.; Kim, I.-Y.; Gil, H.-N.; Lee, S.-W.; Kim, J.-C. Development of a Negligible Zero-Drift NDIR Analyzer for Measuring NH3 Emitted from an Urban Household Solid Waste Incinerator. Atmosphere 2021, 12, 858. https://doi.org/10.3390/atmos12070858

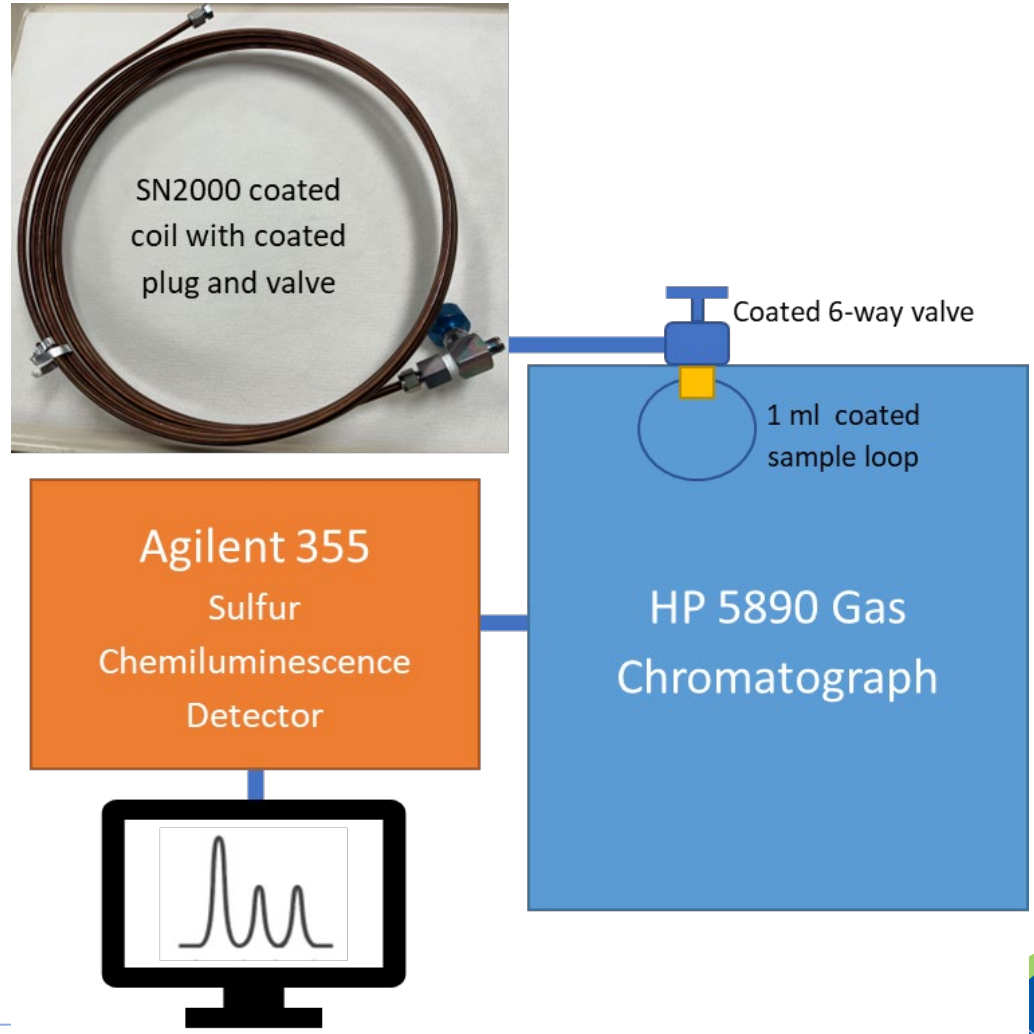
Is Electropolishing (EP) Required?

- Never required for the silicon coating process.
- However, prior work has proven that a smoother surface reduces active sites and can make notable improvements especially at ppb-levels of analysis[2].
- How does SilcoNert-coated stainless steel tubing ***without*** EP compare to non-coated tubing ***with*** EP?

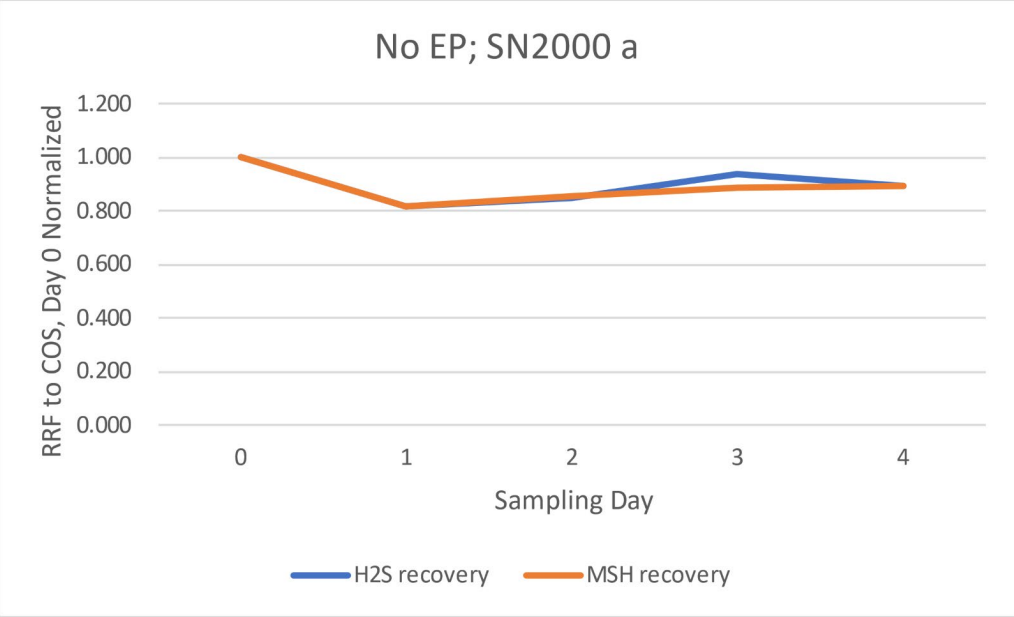
[2]Harris, P. Pelligrini, M. Mass transport in sample transport lines adsorption desorption effects and their influence on process analytical measurements. https://www.silcotek.com/hs-fs/hub/22765/file-13441094.pdf?

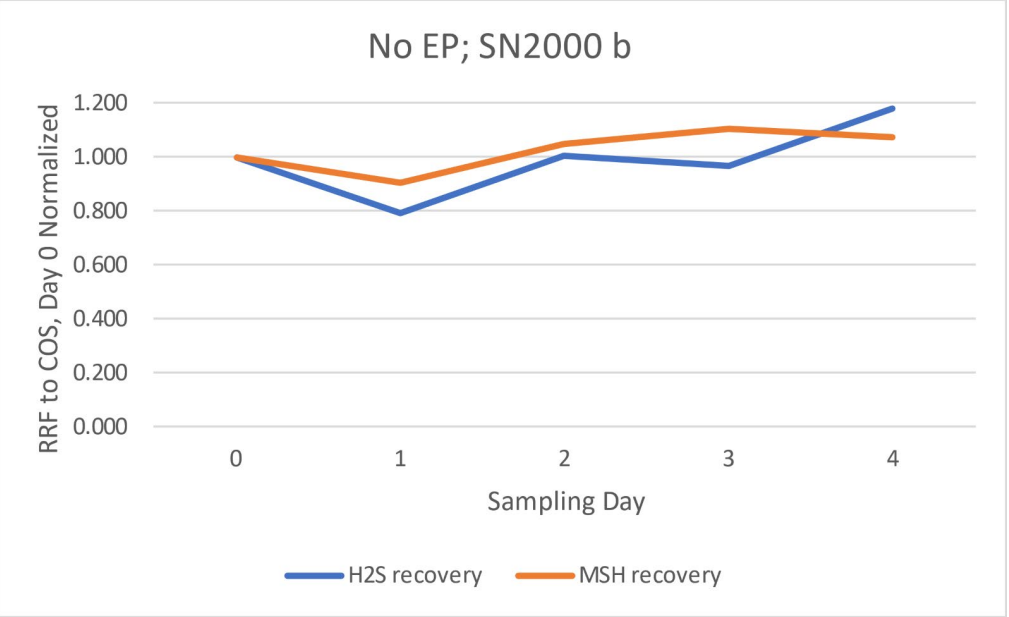
Non-EP SilcoNert® vs. Non-SilcoNert® EP

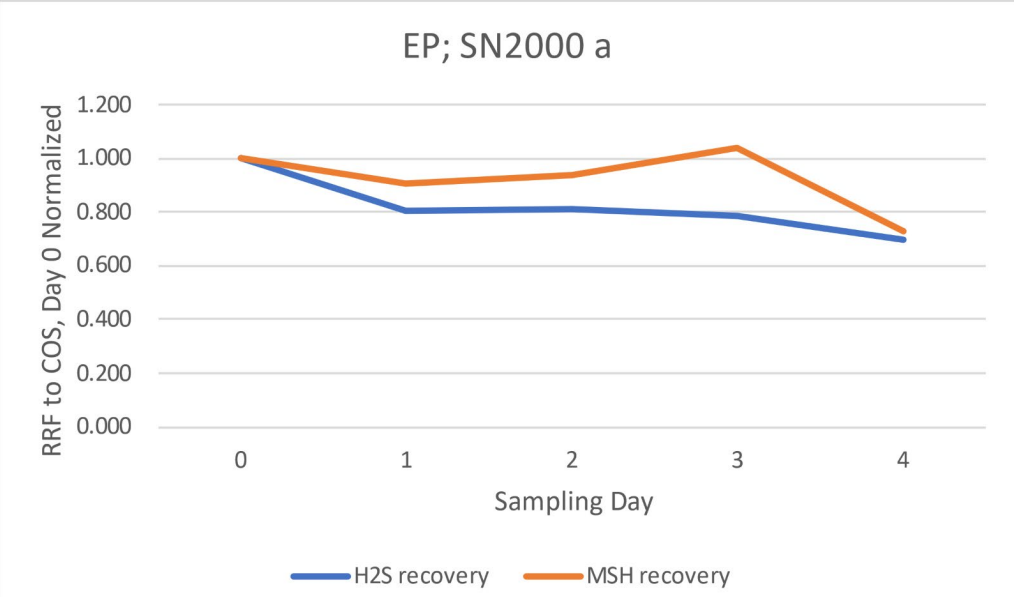
- 20’ lengths of ¼” OD stainless steel tubing. (1) only coated with SilcoNert® 2000; (1) electropolished but not coated.
- Connected to HP 5890 GC with Agilent 355 SCD
- Test mix containing hydrogen sulfide (H_2S), carbonyl sulfide (COS), and methyl mercaptan (MeSH) at 20ppbv

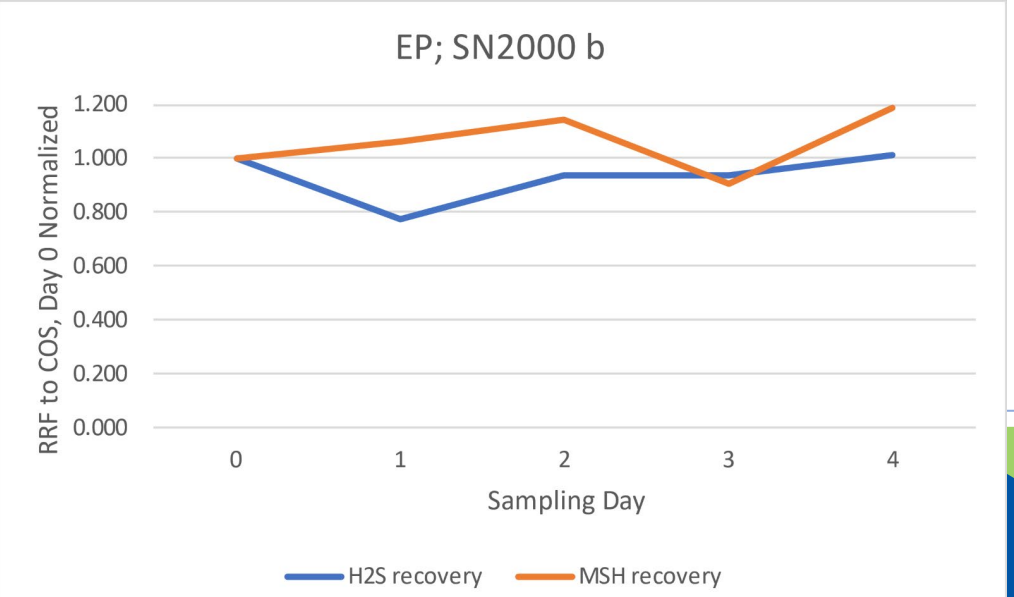


Results: EP showed no significant impact on the inertness of the analytical system for measuring 20ppb sulfurs mix. Coating without EP performed best.









Takeaways on Electropolishing

- A good-quality electropolish (EP) will always result in smoother surfaces and thus fewer potential sites for chemical activity.
- This smooth surface can be important for extremely sensitive analyses such as ppb- or ppt-level moisture.
- However, in most analytical applications, EP did not show a statistically significant advantage in testing so far.
  - In fact, strangely, EP + coating was less inert in the previous test. There is potential for high variation in EP quality.
- **This insight may help the industry overcome rising costs and material lead times.**

Conclusion

- Samples are becoming more complex while detection limits must continue to be lowered to meet evolving technical and regulatory needs.
- Inert coatings within sampling and analytical flow paths are required to enjoy the many benefits of metallic sample system construction.
- As a solutions provider to the chemical analysis industry, SilcoTek continues to invest in its capabilities to meet the industry's requirements.
- SilcoNert® coating is now available on materials that have historically been impossible to coat like Monel®, aluminum, and more.

Thank you!

clay.smith@silcotek.com

www.SilcoTek.com