Inertness comparison of electropolished and non-electropolished 316 surfaces with coated and non-coated variants.

Technical Insight

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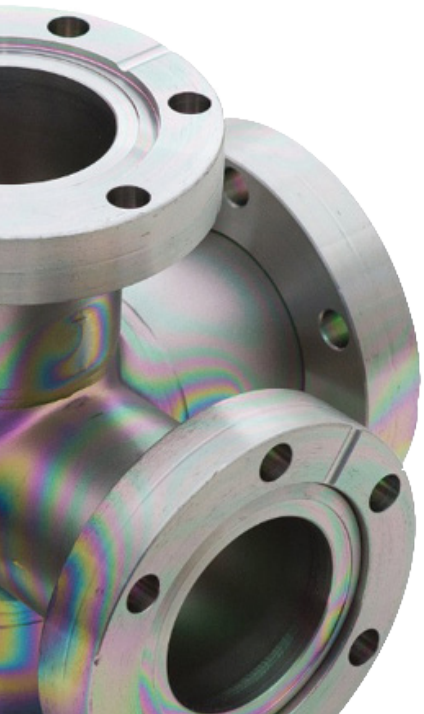
Synopsis

There is a need to measure the chemical inertness of a SilcoNert 2000 coated, non-electropolished (EP), tube compared to a non-coated EP tube. The following coils of 20' x ¼" OD tubes were prepared: 1 non-EP, non-coated; 2 non-EP, SN2000 coated; 1 EP, non-coated; and 2 EP, SN2000 coated. Each coil was charged with a gas-phase test mix of hydrogen sulfide (H2S), carbonyl sulfide (COS), and methyl mercaptan (MeSH) at 20ppbv. Over a period of 4 days, each coil was tested repeatedly to determine the recovery of active components (H2S and MeSH) vs. the inactive component (COS). If the internal surface in the tube is chemically inert, the active components should be easily extracted and measured throughout the testing period. If the active components are adsorbed to the tubing ID over time, then the interior surface is measurably active and less inert. This experiment proved that the SN2000 coating on an inferior non-electropolished surface is significantly more inert than either uncoated EP and non-EP surfaces, and equally inert as a SN2000-coated EP surface.

Background



The use of electropolished (EP) tubing and electropolished components has become standard throughout many industries, including those in Semiconductor, Analytical, and Life Sciences. The EP process removes free iron from the surface of stainless steel substrates (thereby passivating the surface), removes surface roughness, often to a mirror appearance, and results in a surface enriched with chrome and nickel oxides. From a performance perspective, EP surfaces are less likely to be adsorptive to compounds in contact with it (moisture and active chemicals) and offer some improvements in corrosion resistance when compared to non-EP surfaces. Electropolished components, however, can vary wildly in quality, can be expensive for a high-quality process, and can be very difficult to source, particularly for EP tubing. There is an opportunity for SilcoTek to market non-EP tubing and components coated with inert SilcoNert 2000. Non-EP tubing is more readily available, and if the coated version is more chemically inert than an uncoated EP tube, there may be significant interest within the aforementioned market areas for customers to purchase tubing and parts in a non-EP, SilcoNert 2000 coated configuration.

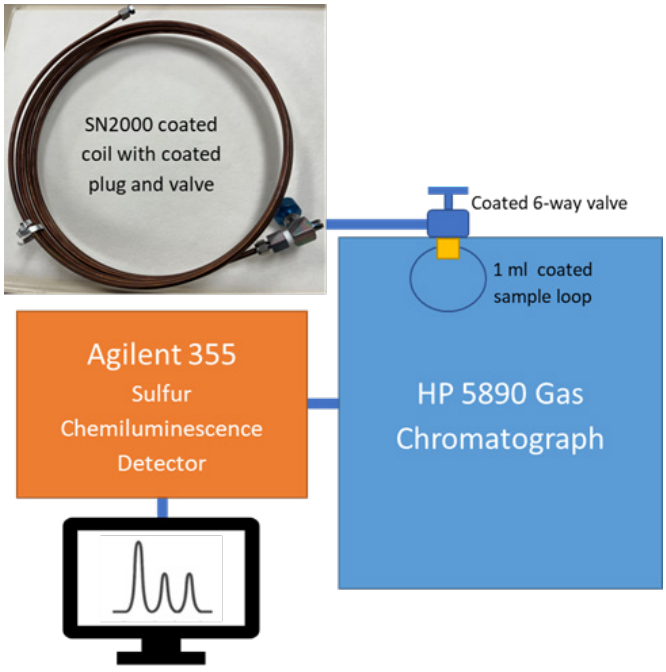
Experimental (Schematic 1)

6 sticks of 20' x 0.25"OD x 0.18"ID tubing (100ml internal volume) were coiled to 18" diameter:

1 – non-EP, non-coated
2 – non-EP, SOP coated with SN2000
1 – EP, non-coated
2 – EP, SOP coated with SN2000

Each coil was sealed on one end with a SN2000 coated compression fitting and end plug. The other end was fitted with a SN2000 coated valve. Each was then evacuated to <50 mTorr and charged to 100 psig with a standard mixture containing hydrogen sulfide (H2S), carbonyl sulfide (COS), and methyl mercaptan (MeSH) at 20ppbv (each) in nitrogen. An additional 300ml, SN2000 coated sample cylinder that is confirmed as stable and inert was prepared with the same standard for use as a daily system check prior to performing coil measurements.

Directly after charging each coil with the standard, it was connected to a GC analytical system equipped with a sulfur chemiluminescence detector (SCD – see appendix for GC parameters). The contents of a coil would flow into the GC sampling system and analyzed for recovery of the 3 sulfur components, thereby providing the Day 0 measurement. This process is repeated for each coil, every day over the next 4 days, to obtain recovery data of the active H2S and MSH components vs. the inactive internal COS standard.



Schematic 1: Coil and GC analytical setup

Data and Discussion

The inertness of tubing surfaces was measured over a period of 5 days (Day 0-4) whereas each coil was a static vessel containing a pressurized mixture of two active and one inactive component(s). If the internal diameter surfaces are chemically inert, there will be zero adsorption of the active components over the storage period. Therefore, when a sample of gas is removed from an inert coil, the same amount of active component will be sampled each time over the 4-day exposure period as compared to the day 0 test. If the internal surface of the coil is active and adsorptive, response from active components will decrease over time.

Figure 1 shows Day 0 (black) chromatogram with excellent response for H2S and MeSH compared to the inactive COS peak on the Electropolished, uncoated coil. Day 0 typically shows good response since there is little time (< 1-2 minutes) for active compounds react with or adsorb to the coil ID. By Day 1 (blue), however, there is complete adsorption of MeSH and significant loss of the H2S. The internal standard of COS, however, is unchanged. By Day 4 (red), H2S has been almost completely adsorbed by the electropolished, uncoated inner surface of the test coil.

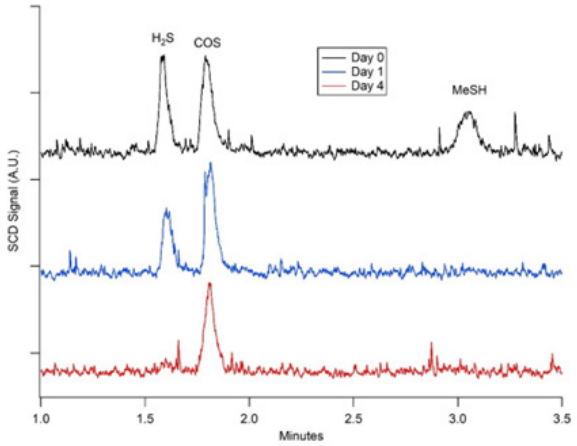


Figure 1. Progressive loss (Day 0-4) of active components in the Electropolished, uncoated coil.

Figure 2 Illustrates the same 4-day time period but for a non-electropolished, SilcoNert 2000 coated tubing coil. Note very little difference in chromatographic response from Day 0 (black) to Day 4 (red), indicating a highly inert internal surface (despite the lack of electropolished treatment) and excellent recovery of the active compounds after 4 days of static storage.

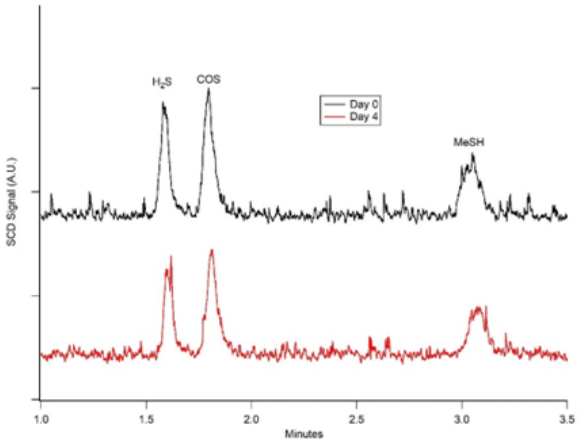


Figure 2. Excellent recovery of active components in the Non-Electropolished, SN2000-coated coil.

Figures 3-8 show the recovery trends for both active compounds (H2S in blue, MeSH in orange) over the 5-day test period for each test coil. The results are grouped according to the base material finish as non- electropolished 316 tubing (Figures 3-5) or electropolished 316 tubing (Figures 6-8). Within those classifications, there were two coils each coated with SilcoNert 2000, giving an “a” coil and a “b” coil.

Each figure data point was generated by dividing the peak area of the active component (H2S or MeSH) by the peak area of COS. This is called the Relative Response Factor, or RRF. Since Day 0 is theoretically the optimal RRF that can be obtained, each day RRF after Day 0 was then normalized to Day 0 (i.e., divided by the corresponding Day 0 RRF) to show the degree of change from Day 0 onward. A perfectly inert coil would therefore maintain a value of 1.0 from Day 1 through Day 4. An active surface will show a decline of normalized RRF’s over time.

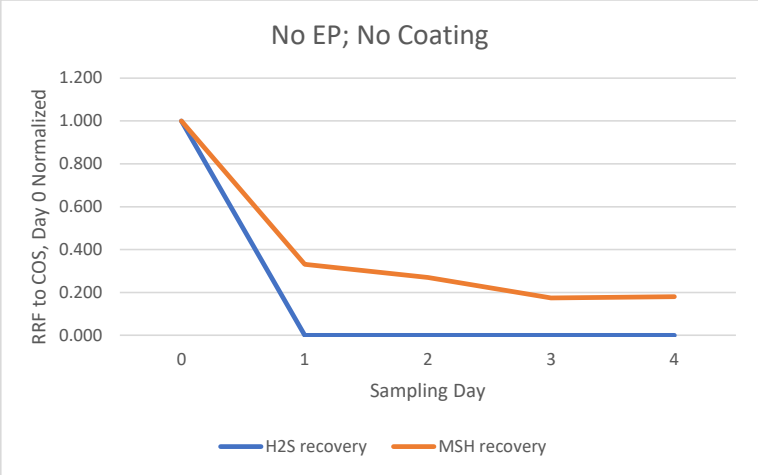


Figure 3. RRF ratios to Day 0; No EP, No Coating

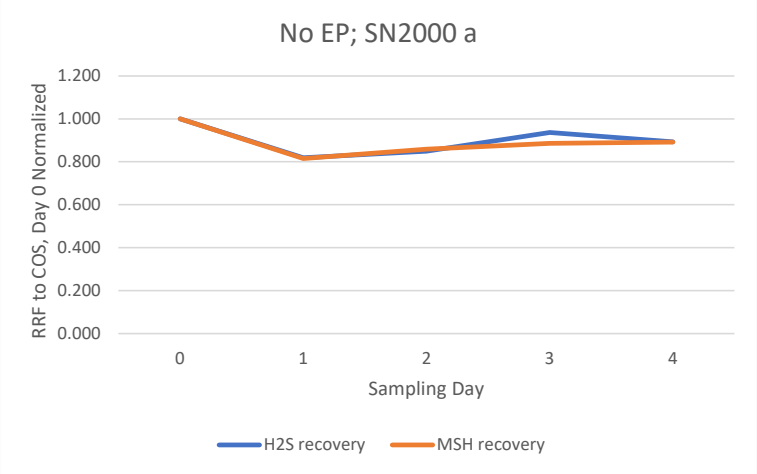


Figure 4. RRF ratios to Day 0; No EP, SN2000 a

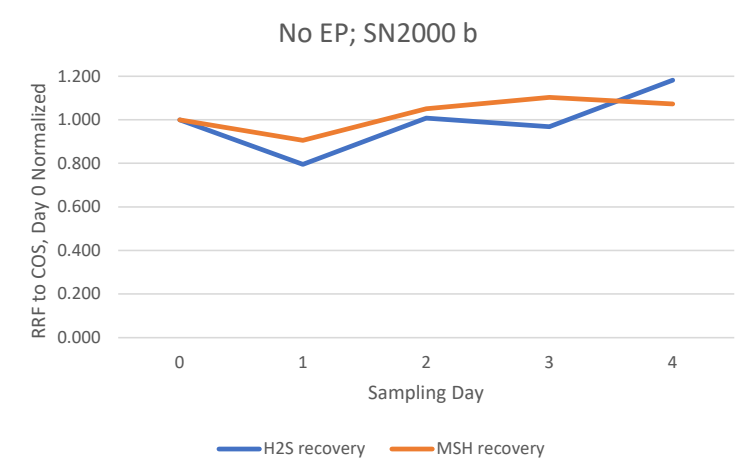


Figure 5. RRF ratios to Day 0; No EP, SN2000 b

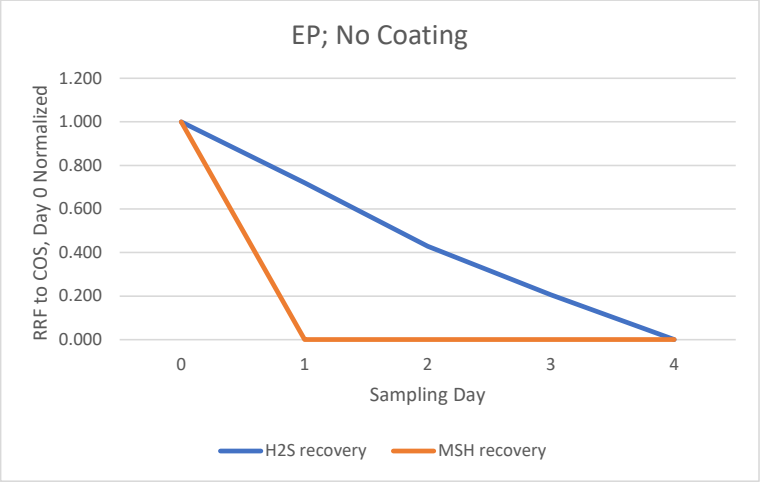


Figure 6. RRF ratios to Day 0; EP, No Coating

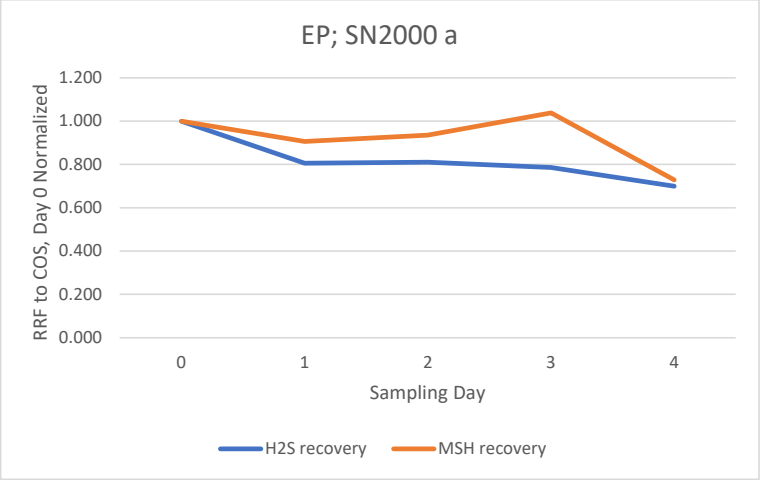


Figure 7. RRF ratios to Day 0; EP, SN2000 a

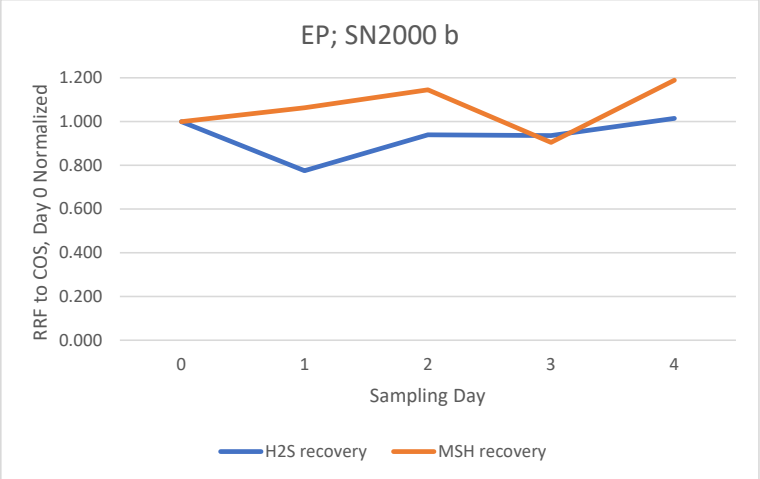


Figure 8. RRF ratios to Day 0; EP, SN2000 b

The uncoated, non-electropolished coil (Figure 3) revealed significant surface activity and adsorption over the initial 24 hours of a 4 day test with complete adsorption (0% recovery) of H2S and only 33% recovery of MeSH. By Day 4, only 18% of MeSH was recoverable. The two non-electropolished coils coated with SN2000 (Figures 4 and 5) showed excellent recovery of both test probes over the 4 day exposure period.

The uncoated, electropolished coil (Figure 6) had a curious adsorptivity result in comparison to the non-electropolished coil. For the electropolished coil, within 24 hours the MeSH test probe completely adsorbed to the substrate surface while 72% of H2S was recovered within the same time frame. Then, over the following 3 days, H2S had a nearly linear recovery loss rate, but eventually showed complete adsorption (0% recovery) by Day 4. It is interesting that the electropolished (uncoated) surface was highly adsorptive to MeSH and less so to H2S, whereas the non-electropolished (uncoated) surface was highly adsorptive to H2S and less so to MeSH. Further studies of the surface chemistry relative to the test probes would need to be conducted in order to fully understand this phenomena.

The electropolished SN2000 coated coils (Figures 7 and 8) correspondingly exhibited excellent inertness to the test probes. It is interesting that the non-electropolished, coated surface coils slightly outperformed the coated electropolished coils. Testing of additional samples to establish a better statistical data set would be necessary to determine whether the difference is significant.

Conclusion

Using highly adsorptive test probes (hydrogen sulfide and methyl mercaptan) at low concentrations, the inertness of electropolished, non-electropolished, SN2000-coated electropolished, and SN2000-coated non-electropolished surfaces were compared. Using a gas chromatograph with a sulfur chemiluminescence detector, coiled tubes of the test surfaces were charged with a known-concentration standard, then sampled 5 times over a 4-day period to measure recovery of the reactive test probes. Based on the recovery results, it was shown that SN2000 coating applied to a raw, non-electropolished surface was highly inert with effectively zero adsorption over the testing period, whereas the electropolished, uncoated tube was highly adsorptive to the test probes within a short period of time.

Appendix - GC Instrumentation and Conditions:

Sample: Hydrogen sulfide, carbonyl sulfide, methyl mercaptan at 20ppbv each in nitrogen
Test Vessel: 20’ x 0.18”ID x 0.25”OD coil of tubing, each with ends connected to a SN2000-coated endcap and a SN2000-coated needle valve.
Analytical Column: Restek Rtx-1, 60m, 0.53mm ID, 7.0um
Injection System: 1ml sample loop (SN2000 coated), connected to Valco 6-way valve (SN2000 coated)
Hewlitt Packard 5890 Gas Chromatograph equipped with Agilent 355 Sulfur Chemiluminescence Detector
Carrier Gas: Helium at 10psi constant pressure
Oven Temp: 30°C (3 min hold), 30°C/min ramp to 100°C (hold 10 min)
Detector Temp: 800°C

Note: Due to operating near the SCD detector limit of detection, high signal-to-noise chromatograms precipitated slight variations in peak integration reproducibility from run to run.

