Applications Note

Sulfur Compound Sampling, Storage, and Transfer Considerations

More accurate results and faster cycle times, using Sulfinert® treated components

Introduction

Accurate analyses for parts-per-million to parts-per-billion levels of sulfur-containing compounds in petrochemical streams are critical to meeting new regulations for lower levels of sulfur in diesel fuel and gasoline. Many organo-sulfur compounds—hydrogen sulfide, methyl mercaptan, and ethyl mercaptan among them—adsorb strongly to metal surfaces. Adsorption of sulfur compounds in sampling, storage, and/or transfer apparatus can cause prolonged analysis cycle times as well as inaccurate, falsely low values.

In the studies described here, active sulfur gases were sampled, stored, and transferred in control (untreated) and Sulfinert® treated static (storage) and flow-through system components, to determine quantitative losses of the sulfur gas species. Concentrations of the sulfur gases spanned the low parts-per-million to low parts-per-billion range.

Sulfur Compound Storage: Sulfinert® Treated vs. Untreated Sample Cylinders

Figure 1a depicts results from a comparison in which a gas containing 17ppbv of hydrogen sulfide was stored for 7 days in untreated or in Sulfinert® treated stainless steel sample cylinders. The response ratio for hydrogen sulfide, relative to a stable reference material, dimethyl sulfide, is steady at approximately 1:1 for at least seven days in Sulfinert® treated cylinders. The data show a Sulfinert® treated system will reliably store ppb levels of the active sulfur-containing compound during transport from the sampling site to the analytical laboratory. In contrast, hydrogen sulfide degraded rapidly in the untreated cylinder, and was lost totally within 24 hours.

In a similar study in which gas containing 18.8ppbv methyl mercaptan was stored for 60 hours in Sulfinert® treated sample cylinders, recovery of the active sulfur compound was equally high relative to the stable reference material, dimethyl mercaptan, as shown in Figure 1b.

Sample Transfer: Adsorption of Sulfur Compounds to Tubing Surfaces

Comparison of the transport properties of Sulfinert® treated electropolished stainless steel tubing (TrueTube™ EPS tubing, surface roughness average (RA): 5-10, O'Brien Corporation, St. Louis, MO), untreated electropolished stainless steel tubing (TrueTube™ EP tubing, RA 5-10, O'Brien Corporation), and raw commercial grade stainless steel tubing (RA 23-27) show only Sulfinert® treated electropolished stainless steel has the inertness necessary for quantitatively transferring sulfur compounds at low ppmv to low ppbv concentrations in sample streams. An experiment was designed to confirm whether a sulfur-containing stream passing through stainless steel tubing would passivate active sites on the steel surface, through adsorption of the active sulfur species. The amount of time elapsed before a representative sample, containing a stable and accurate sulfur content, exited the tubing was the measured indicator of surface activity in the tubing.

Avoid downtime, save money

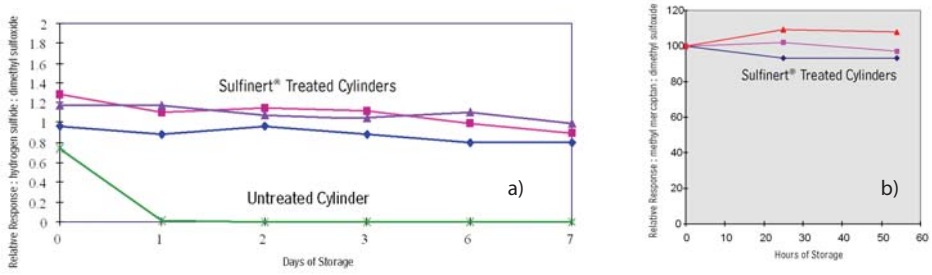
Sulfinert® treatment adds value to your process by ensuring:

- Accurate results
- Improved yields
- Faster cycle times

Avoid these losses!
A 1-hour delay can cost:[1]

- 800,000 tpy ethylene plant: $50,000
- 250,000 tpy LDPE unit: $36,000
- 250,000 tpy EBSM styrene plant: $33,000
- 200,000 tpy anti-freeze process: $3,600

Figure 1 Sulfur compounds are stable in Sulfinert® treated stainless steel systems
a) 17ppbv hydrogen sulfide in 500mL cylinders
b) 18.8ppbv methyl mercaptan in 300mL cylinders



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Figures 2 and 3 compare the transport properties of 100-foot (30.5-meter) lengths of the three types of seamless 316L stainless steel tubing, 1/8" OD x 0.020" wall, using a gas stream containing 0.500ppmv methyl mercaptan in helium as the test material. Tests were performed at room temperature, using a gas flow rate of 40cc/minute.

Figure 2 demonstrates uptake of the sulfur compound by the three surfaces. The performance of the Sulfinert® treated, electropolished surface is quite dramatic in comparison to that of untreated electropolished tubing. Sulfinert® treated electropolished tubing did not adsorb methyl mercaptan to any measurable extent, delivering a representative sample with no delay. The untreated electropolished tubing, in contrast, totally adsorbed methyl mercaptan for more than 75 minutes, and the sulfur gas level did not stabilize until approximately 130 minutes. Conventional 316L seamless tubing totally adsorbed methyl mercaptan for more than 90 minutes, and the sulfur gas level did not stabilize until approximately 140 minutes.

Closely correlated to the adsorption of sulfur compounds by system components is the subsequent release of the adsorbed compounds. When adsorption of sulfur-containing compounds is prolonged, desorption from the surface also is slow. This "memory" of adsorbed active compounds can cause long delays in equilibrating a sample stream. Figure 3 demonstrates the memory effects of the three types of tubing used to transfer streams containing sulfur compounds. The Sulfinert® treated tubing shows less retention of sulfur compounds by several orders of magnitude, indicating very high inertness.

Figure 2 Sulfinert® treated electropolished stainless steel tubing (red) does not adsorb methyl mercaptan (500ppbv). Blue—untreated electropolished tubing, violet—commercial grade tubing.

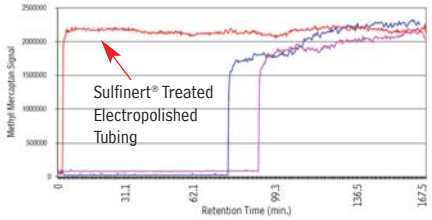
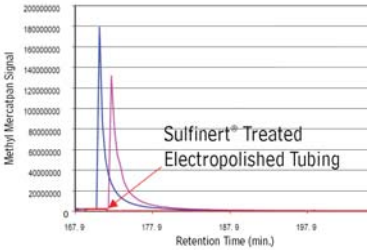


Figure 3 Sulfur memory is prolonged in raw commercial grade stainless steel tubing (violet). Red-Sulfinert® treated electropolished tubing; blue-untreated electropolished tubing (500ppbv methyl mercaptan in helium).



Sulfinert®-Treated Electropolished Tubing

ID	OD	cat.#	5-24 ft.	25-99 ft.	100-299 ft.	>300 ft.
0.085"	1/8"	22538				
0.180"	1/4"	22539				

Coiled Sulfinert®-Treated Seamless 316 Grade Stainless Steel Tubing

ID	OD	cat.#	5-24 ft.	25-199 ft.	200-399 ft.	>400 ft.
0.055" (1.40mm)	1/8" (3.18mm)**	22508				
0.180" (4.57mm)	1/4" (6.35mm)**	22509				

Sulfinert®-Treated Sample Cylinders

D.O.T. rated to 1800psi at room temperature.

Size	qty.	cat.#
75cc	ea.	24130
150cc	ea.	24131
300cc	ea.	24132
500cc	ea.	24133
1000cc	ea.	24134
2250cc	ea.	21394

Restek offers many **Sulfinert®-treated fittings, valves, sample loops.** For more information and ordering, call us or visit us online.

please note

An extra charge is applied for cutting Sulfinert® tubing, calculated from the total number of pieces produced for each line item:

of Pieces
5 to 15
16 to 30
31 to 75
76 to 99
100 to 200

free literature

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**0.035" wall thickness
1/8" OD: 5 ft. to 100 ft. in one continuous coil; 1/4" OD: 5 ft. to 300 ft. in one continuous coil. Longer lengths will be more than one coil.
Note: (required length in meters) x (3.2808) = length in feet.

Value of an Inert Pathway

The value of surface treated sampling and transfer equipment is twofold: more accurate results and faster cycle times. Improved accuracy and reliability of data for sulfur, achieved using Sulfinert® treated transfer and sampling equipment, mean downstream processes can be more precisely controlled, with associated cost savings. Shorter cycles translate directly into more samples collected and analyzed in a given period of time. Typical savings can be calculated by looking at the average per-hour cost of operating a process that relies on accurate quantification of sulfur compounds.[1] Example monetary values are reported on the front of this note.

In Summary

We obtained accurate data, with no delay between samples, by using Sulfinert® treated electropolished tubing in the sampling-storage-transport system. In contrast, we obtained significantly less accurate data, even with delays of more than two hours between samples, by using untreated tubing. Analysts charged with monitoring sulfur levels in process streams can significantly improve profitability by using Sulfinert® treated system components and Sulfinert® treated electropolished tubing transport lines.

Reference
1. *Application of TrueTube™ in Analytical Measurement* Cardinal UHP August 2004
Available at www.restekcoatings.com or by contacting us at 800-356-1688, ext. 4. Request lit. cat.# 59088.

Acknowledgement
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