Advantages to Using Inert, Coated Components for Sampling, Storage and Transfer of Organo-Sulfur Compounds

Gary A. Barone, David Shelow,
David Smith

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Introduction

- What to consider in sample flowpaths
- How to shield metal surfaces
- Examples of flowpath components
  - Sampling
  - Holding
  - Transfer
- Advantages to using coatings

In this presentation we will discuss the need for inert sample flowpaths for analysis of reactive chemical species.

In particular the reduction of activity of metal surfaces by application of an inert thin-film coating. This presentation will focus on the use of the Sulfinert™ coating, a proprietary thin-film coating developed by Restek Corporation.

This presentation will show the importance of passivated system components when transfer of sulfur compounds is required. We will demonstrate the need for activity-reduction in these components and show specific examples of the effectiveness of the layer.

Flowpath Considerations

- Transfer and holding of adsorptive or reactive species such as sulfurs, alcohols or pharmaceuticals
- Low-level analysis
- All Components:
  - Tubing
  - Valves
  - Cylinders
- All Wetted Flowpath Components

For the analysis of reactive or adsorptive species, the metal components of sampling and storage hardware often interfere in proper quantitation. For example, hydrogen sulfide will adsorb strongly to stainless steel components in instruments. When adsorption occurs proper quantitation of concentration is impossible.

When trying to quantitate trace levels of any chemical species all flowpaths must be considered active. During any transfer there is always an equilibrium that can occur between metal surfaces and chemical species. A non-adsorptive layer can be used to ensure chemical species are transferred without loss.

Sulfinert™ Coating Characteristics

- Capable of storing and transferring single digit part-per-billion levels of active sulfurs, such as H_2S, methyl mercaptan
- Will not delaminate
- Incorporated into lattice of substrate to insure no pin-holes

The Sulfinert™ layer is the leading passivation coating available for the storage and transfer of extremely low levels of organo-sulfur compounds.

Examples will be shown of 1.5ppbv holding of hydrogen sulfide and methyl mercaptan. Even lower levels are being tested!

These low levels are not possible on even inert Fused Silica based coatings.

Also, Fused Silica based coatings can hydrolyze when amines are present, creating reactive Si-OH groups that can adsorb organo-sulfur species.

The Sulfinert™ coating is strong, durable and flexible. Unlike polymeric coatings, the Sulfinert™ layer cannot delaminate. Sulfinert™ is the result of years of experience on surface coating developed by Restek.

The Sulfinert™ coating is uniform and dense enough that analytes transferred or stored in coated components cannot reach the active steel surface.

Physical Properties of Sulfinert™ Coating

- Durable and flexible
- Strong adhesion to substrate
- Non-porous surface
- Non-permeable surface
- Stable to high temperatures

The Sulfinert™ layer has several key properties which make it ideal for sample transfer and holding hardware.

The Sulfinert™ layer is bound to the surface and no problems such as delamination or fracturing can occur.

The Sulfinert™ layer is non-polymeric and will not suffer from any of the disadvantages associated with these coatings. These include porosity and gas permeability. This layer has no gaps or ribbons as such a polymer would, thus eliminating porous paths to the surface. Because the layer is non-polymeric it will have no ability to “dissolve” or permeate gases.

The Sulfinert™ coating has been used in application ranges up to 450°C.

Chemical Inertness Properties of Sulfinert™ Coating

- Has no interactions with organo-sulfurs, or polar organics
- Useful in a wide range of pH. Acidic to Caustic.

The Sulfinert™ coating is ideal for transfer and storage of organo-sulfur compounds because it cannot react or adsorb. No mechanism exists for adsorption or reaction to occur.

Sulfinert™ coatings have been tested under acidic and caustic conditions. The Sulfinert™ coating has demonstrated a useful pH range that makes it ideal for environmental or petrochemical applications.

Fused Silica coatings *cannot* be used when amines are present in the sample. The basic amines will open up the Si-O bonds, creating high levels of activity toward all polar organic compounds.

The Sulfinert™ coating, however, solves this problem, making the Sulfinert™ coating an ideal passivation technique or sampling and transfer hardware.

Components That Benefit from Inert Coatings

- Sample-holding vessels
- Valves and regulators
- Transfer tubing
- Vaporizing or flash chambers
- Reactors
- Tubing connectors and fittings
- All stainless internal components of GC
- Sample loops

A wide variety of parts can benefit from Sulfinert™ coating.

In general, if there are any species in your streams which are reactive or corrosive, all metal components in the sample stream should be shielded.

When sampling, storing, or transferring organo-sulfur compounds, always classify wetted hardware. Plan to use non-adsorptive hardware or else plan to passivate all stainless hardware. This will save possible troubleshooting efforts later on in your work.

Advantages of Inert, Coated Instrument Components

- Sulfur-containing compounds
- Coated storage vessels vs. non-coated storage vessels
- Analytical systems
- Results

Following are examples of storage of sulfur-containing species.

These tests are performed under static conditions. All samples are enclosed in vacuum/pressure chambers, either sampling canisters or sample cylinder.

The static condition is the most rigorous test for low-level organo-sulfur compounds. Under static conditions if any active, uncoated site exists, analysis will show a decrease in sample recovered.

Organo-Sulfur Compounds

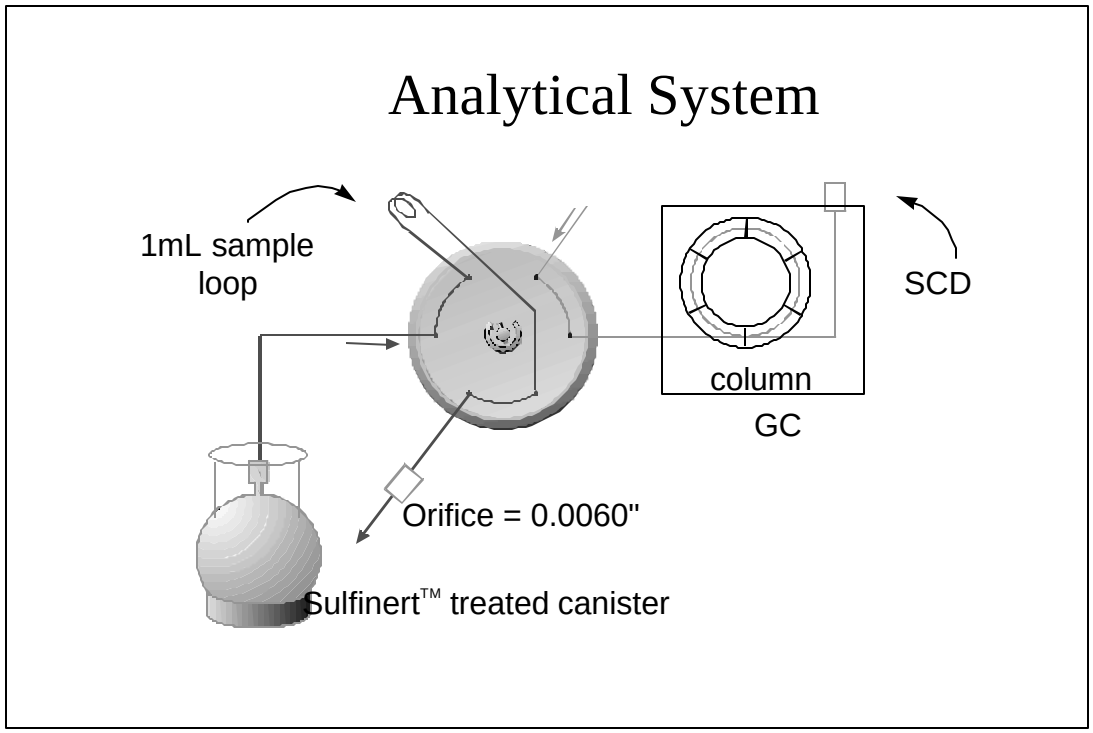
- Certain species adsorb to steel surfaces (e.g., hydrogen sulfide)
- Reactions can occur on a non-coated stainless steel surface (e.g., methyl mercaptan and ethyl mercaptan)
- Importance of accurate quantitation (e.g., odorants)

Organo-sulfur compounds are notorious for adsorption or reaction on non-coated stainless steel. For example, hydrogen sulfide will adsorb to non-coated steel and mercaptans will actually react on the surface to form disulfides.

It is quite important that any sampling, holding, or transfer equipment and the analytical system designed to measure low-level sulfur species use passivated components. This becomes apparent in the natural gas industry in which the odorants are often mercaptans and hydrogen sulfide. It is quite possible that the level of these can be wrongly reported due to activity associated with non-coated steel components in an analytical system.

Another example are sulfur impurities in ethylene and propylene. These sulfur compounds can poison catalysts used to make polyethylene and polypropylene.

The Sulfinert™ coating is the most advanced and reliable passivation technique available.



This is a diagram of the system used to test the sample vessels. A sample valve and loop were used to grab and transfer the sample from the sample vessel and deliver it to a chromatographic column. The column was optimized to separate all of the species contained in the sample. The detection system used was a sulfur chemiluminesence detector provided for this work by Sievers Instruments.

The chromatographic column was required because all data is generated on *mixtures* of organo-sulfur compounds, not just single standards.

Note that all metal flowpaths of this system were passivated using the Sulfinert™ coating process.

This method was used with both low-pressure sampling cans and high pressure sample cylinder.

Results of Stability Test

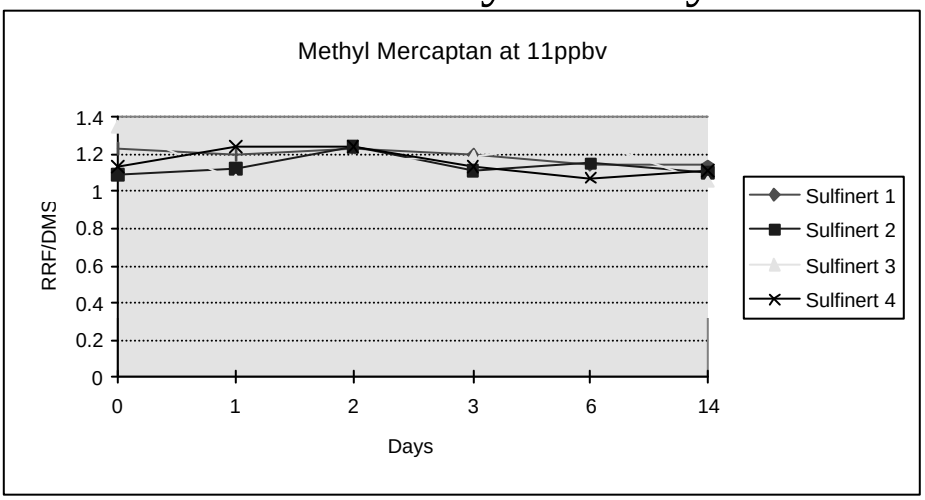
- Tests performed over several concentration levels and holding times
- Sulfinert™-treated canisters showed excellent stability of all levels of all sulfur compounds
- Loss of hydrogen sulfide, ethyl mercaptan, and methyl mercaptan will occur in non-coated canister

The following data demonstrate the performance of the Sulfinert™ coating for storage of low-level organo-sulfur compounds.

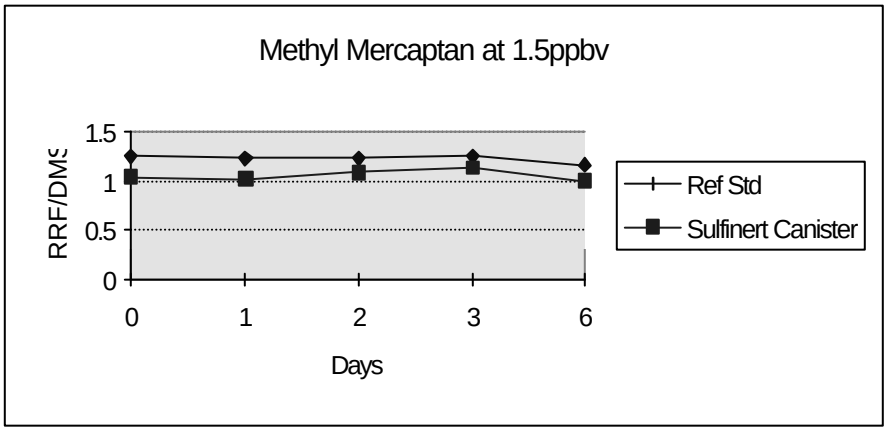
Without the use of a passive coating, rapid loss or active sulfur compounds — hydrogen sulfide and the mercaptans — will occur.

The Sulfinert™ coating is opening new doors to low-level organo-sulfur testing by offering a reliable and repeatable substrate for single digit part-per-billion samples, and even lower.

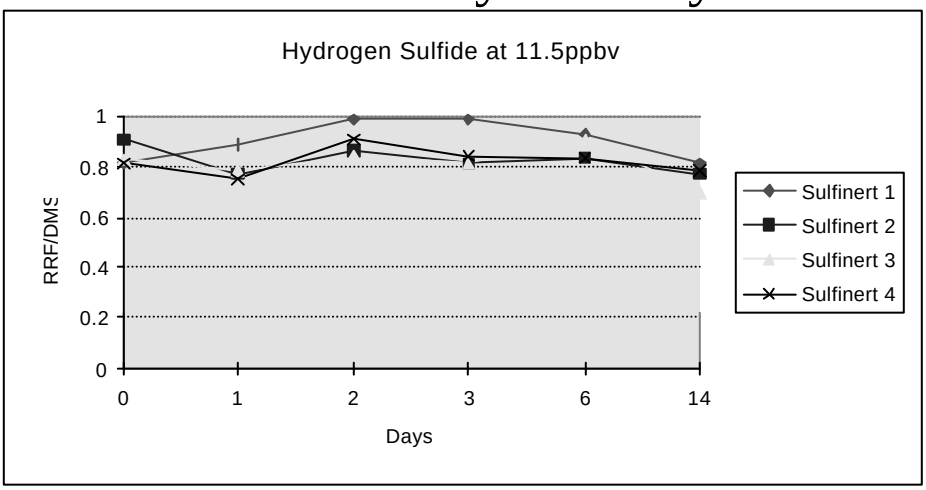
Methyl Mercaptan
11ppbv
Excellent 14 Day stability



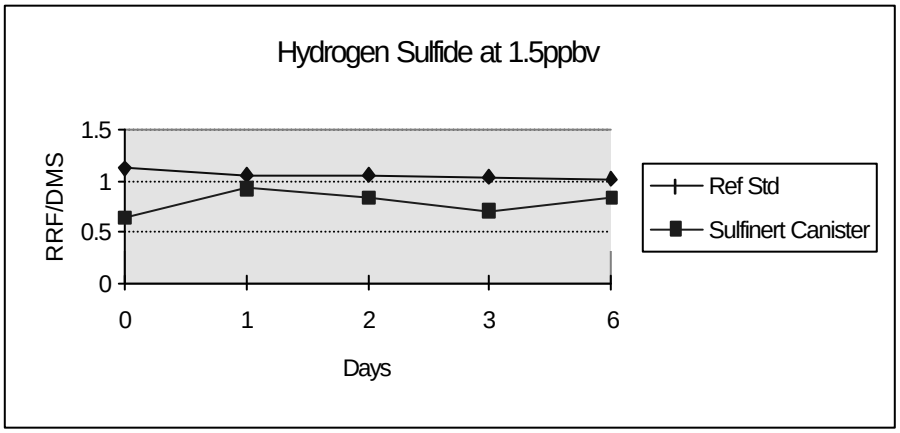
Methyl Mercaptan
1.5 ppbv
Excellent 6 Day Stability



Hydrogen Sulfide
11.5ppbv
Excellent 14 Day Stability



Hydrogen Sulfide
1.5ppbv
Excellent 6 Day Stability



Conclusion

- Consideration in sample flowpath construction
- Importance of shielding exposed metal surfaces
- Usefulness and advantages of using inert, coated components in the development of analytical instrumentation

This presentation has highlighted the importance of the passivation of metal surfaces when developing flowpaths for organo-sulfur sampling and analysis.

Applications such as organo-sulfur or polar organic quantitation require the use of inert components in sample flowpaths to reduce adsorption and breakdown.

The Sulfinert™ coating, when applied to metal surfaces that may be part of a sample flowpath, provides the most inert surface for low-level analysis of organo-sulfur species!