

Analysis of Low-Level 1ppb to 20ppb Reactive Sulfurs in Air Samples

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Introduction

The analysis of low-level sulfur volatile organic compounds (VOCs) has become important because of odor complaints near manufacturing sites and refineries.

Collection and measurement of these compounds in the atmosphere is very difficult because of their low concentration and high reactivity.

Reactivity of Sulfur Compounds

Active sulfur compounds not only react with each other but with the vessels in which they are collected.

Reactions can be caused by adsorption (hydrogen sulfide) or the combining of two mercaptan molecules to form one disulfide.

(2) methyl mercaptan \rightarrow (1) dimethyl disulfide

Collection vessels

Tedlar bags traditionally have been used for collecting sulfur VOCs; however, the stability of low-level (<100ppb) sulfur VOCs is poor.

It is well documented that electropolished steel canisters and sample cylinders are reactive and adsorptive with sulfur compounds and are unsuitable for collecting and storing low-level sulfur VOCs.

SilcoCan

Restek has developed a steel cylinder that is specially coated with a coating that is completely non-reactive or adsorptive to sulfur VOCs.

The coating of this canister is Sulfinert™



What is Sulfinert?

Sulfinert™

- The Sulfinert coating is applied to all exposed surface areas of an item
- The Sulfinert layer acts as an inert barrier between the active steel surface and the sulfur VOCs
- Resteks SilcoCan is a stainless steel ambient air sampling vessel that has been coated internally with Sulfinert

Experimental

Sample

10-11ppbv mixture of:
hydrogen sulfide
carbonyl sulfide
methyl mercaptan
ethyl mercaptan
dimethyl disulfide

Experimental

Canisters

18 SilcoCan canisters filled with “dry” standard

5 SilcoCan canisters filled with “humidified” standard

2 Electropolished, non-coated canisters

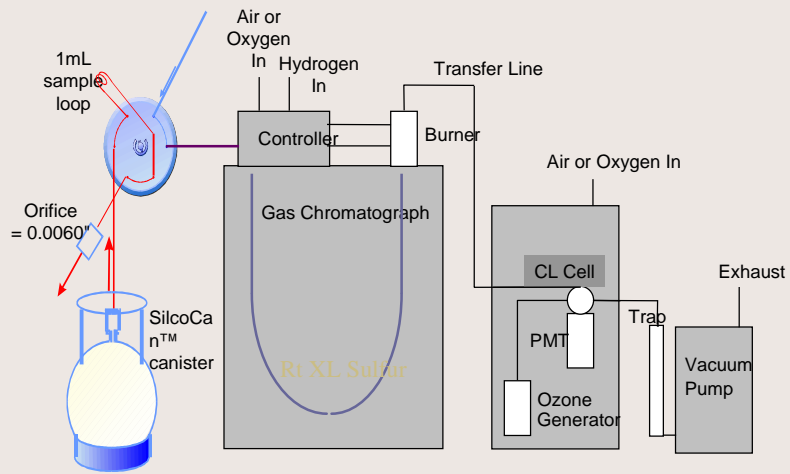
Analytical System

Samples from the canisters were delivered to a Gas Chromatograph (GC) using a gas sampling valve, a 1cc sample loop and 1/16” Sulfinert treated tubing.

The gas sample was separated into the individual sulfur compounds within the GC using an Rtx-1 capillary column.

Detection of the sulfur compounds was achieved using a Sievers sulfur chemiluminescence detector (SCD)

Analytical System



Stability Test

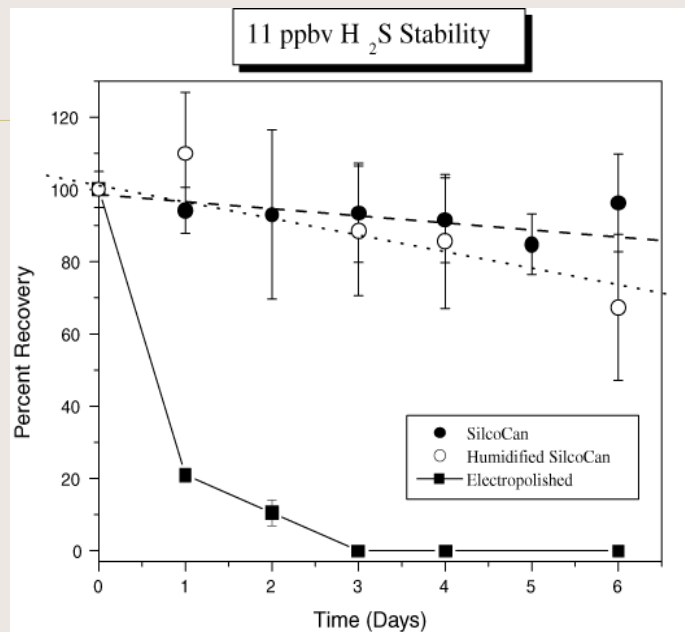
- Standards were introduced into the canisters at the following concentrations

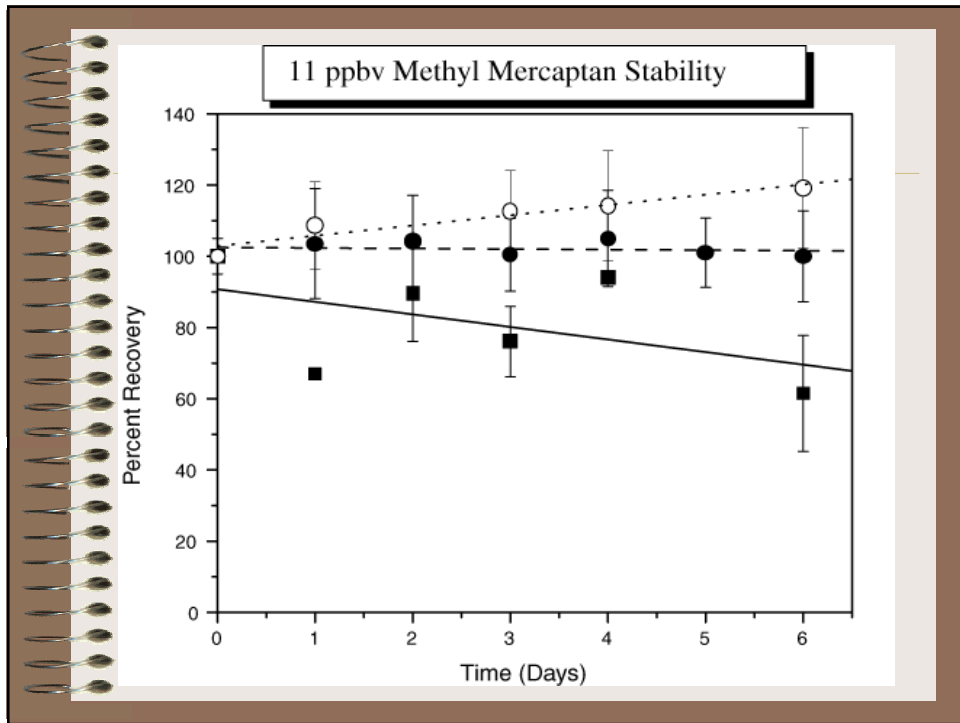
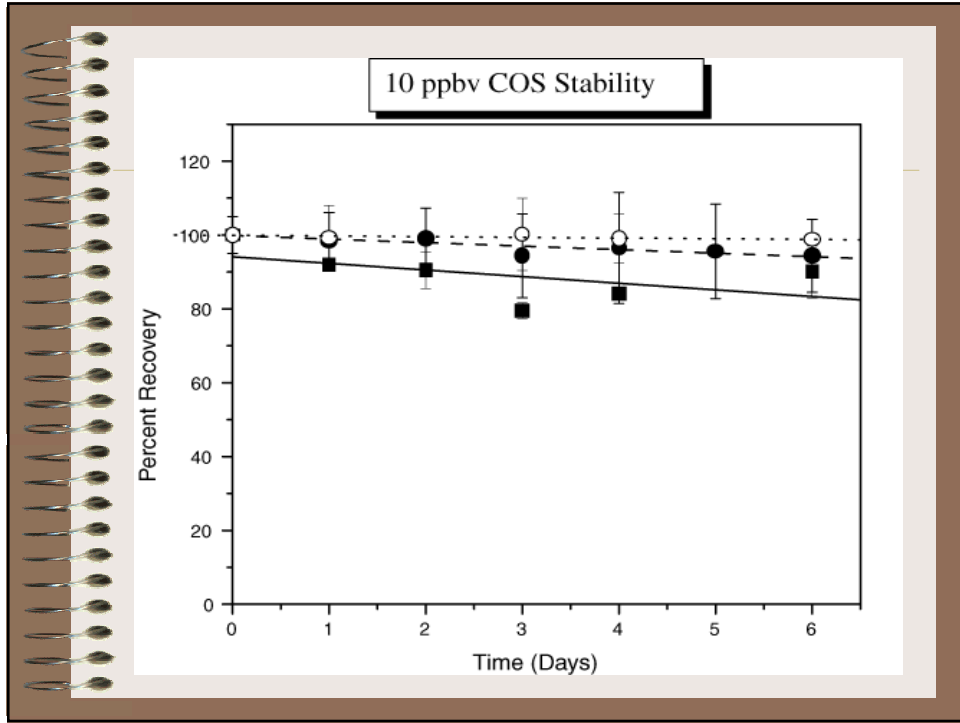
Table 1

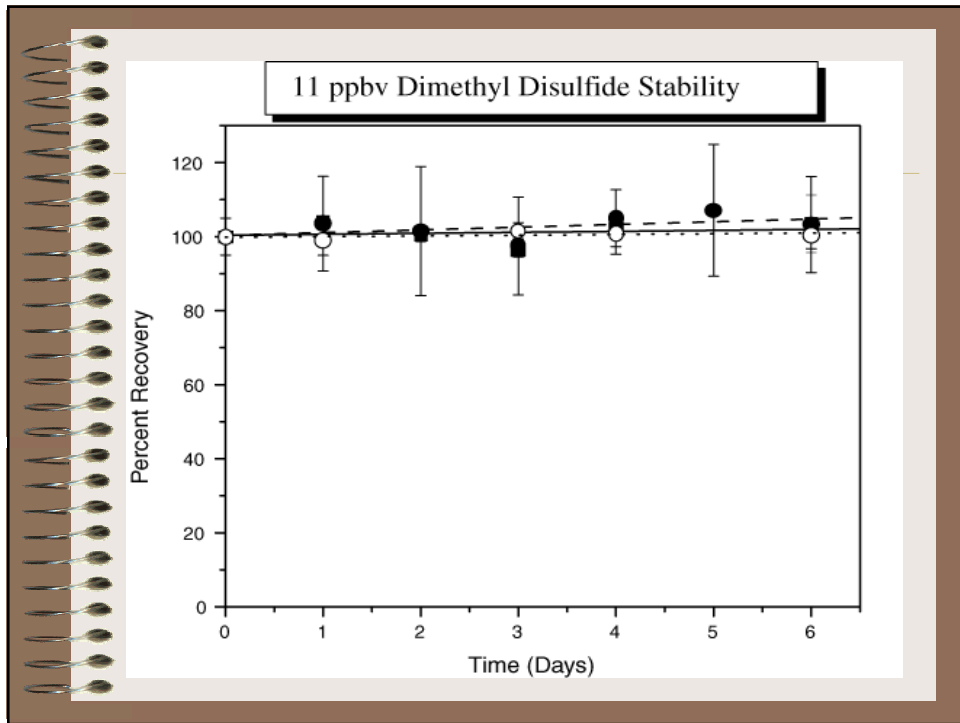
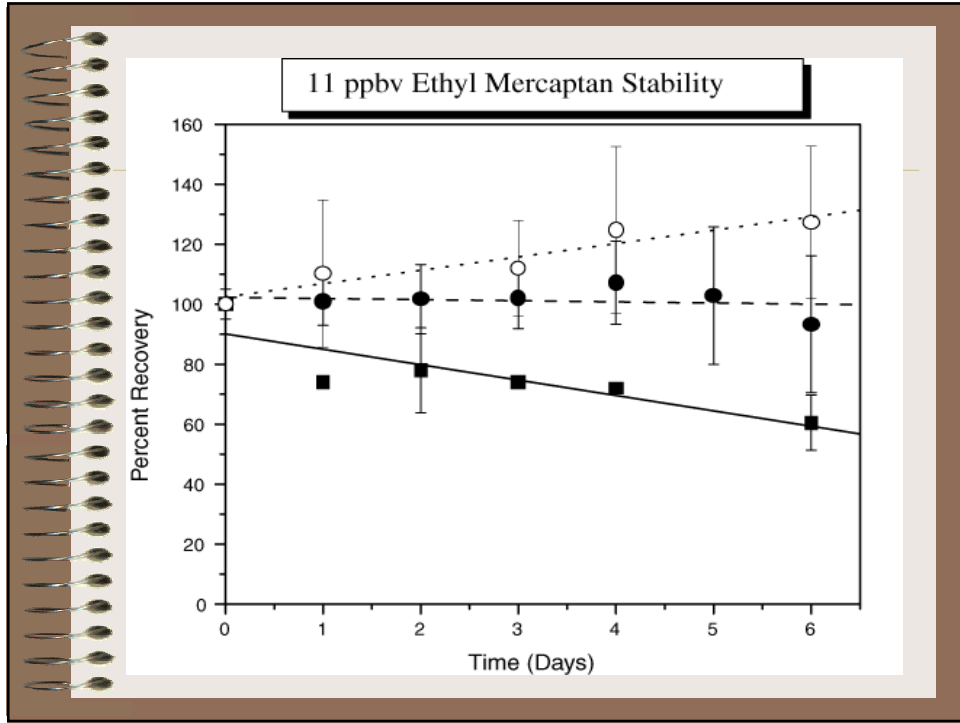
Compound	Stock Conc. (ppmv)	Standard Conc. (ppbv)
hydrogen sulfide (H ₂ S)	105	11.51
carbonyl sulfide (COS)	98	10.74
methyl mercaptan (CH ₃ SH)	101	11.07
ethyl mercaptan (CH ₃ CH ₂ SH)	101	11.07
dimethylsulfide (CH ₃ SCH ₃)	99	10.85
dimethyldisulfide (CH ₃ SSCH ₃)	100	10.96

Stability Test

- Each day the contents of the canisters were analyzed.
- The period of the stability study lasted 6 days
- The 5 humidified canisters contained the sulfur standard at a relative humidity inside the canister of 50%







Results

- Sulfinert coated vessels inhibited reactivity or adsorption of sulfur compounds
- Non-Coated, Electropolished canisters exhibit degradation of reactive Sulfur VOCs
- Humidified sulfur samples, as would be found in the environment, are stable in Sulfinert coated canisters

Conclusion

This Study investigated the stability of very low-level sulfur VOCs (1-20ppbv).
The Stability of these compounds is very dependent on the composition of containers and transport equipment used
Surfaces such as stainless steel will exhibit adsorption or reactivity with sulfur VOCs
Sulfinert coated stainless steel vessels are ideal for the collection and storage of low-level sulfur VOCs