

Instrument and Sampling
Equipment Passivation
Requirements to Meet Current
Demands for Low-Level Sulfur
Analysis

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Project Objective

- To create passivation processes for stainless steel and glass surfaces which will allow the analysis of low-ppbv sulfur gases
 - Chromatographic sampling system
 - Containment vessels (high pressure vessels and air sampling canisters)

Testing System for Sulfur Gas Storage & Transfer

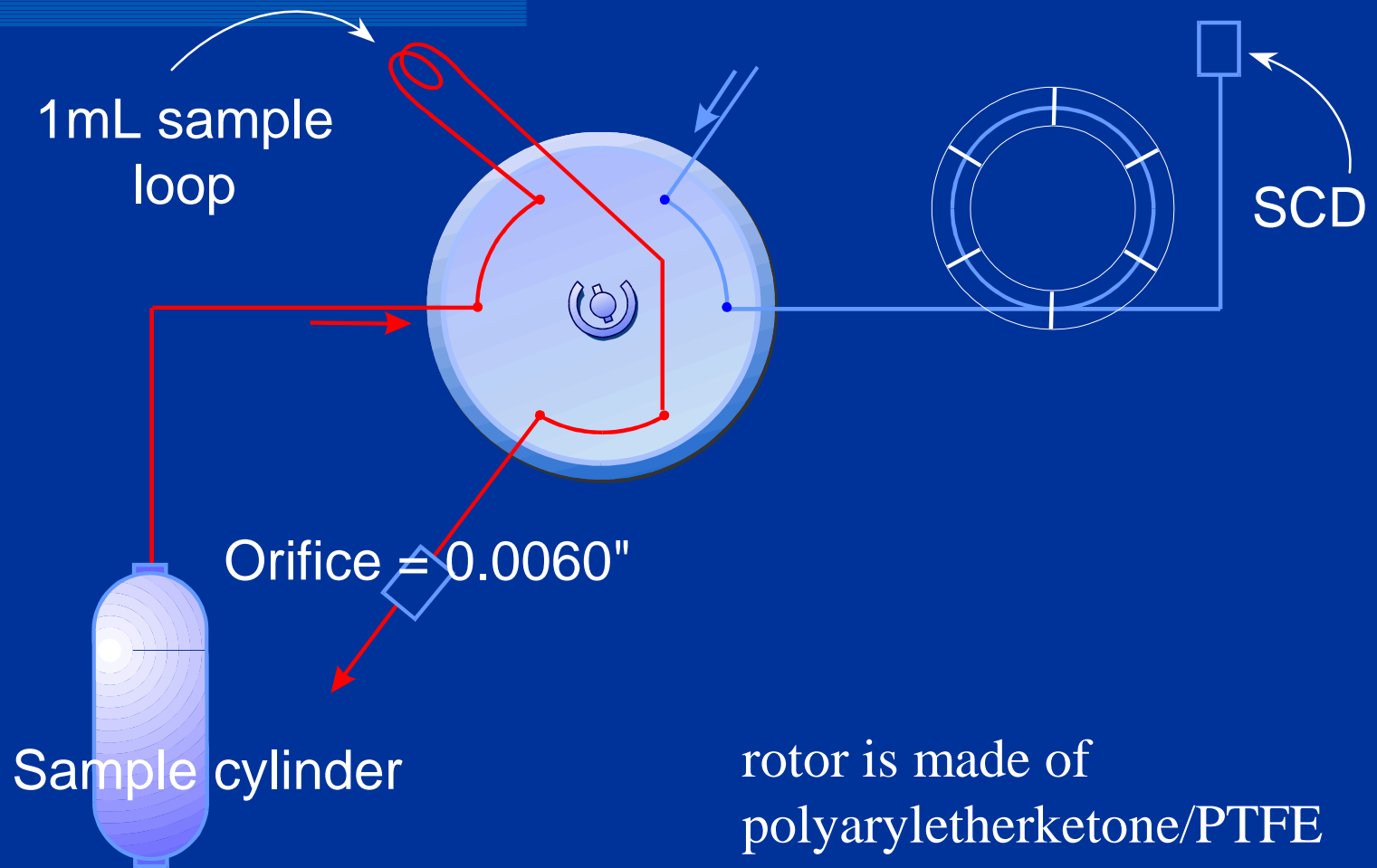
- Sulfinert™-deactivated sample cylinders with Sulfinert™ sample valves
- Sulfinert™-deactivated sampling system (transfer line, sampling valve, 1ml sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard



What is Sulfinert™?

Unique passivation treatment (patent pending) that provides a durable, thermally-stable and highly inert surface on steel.

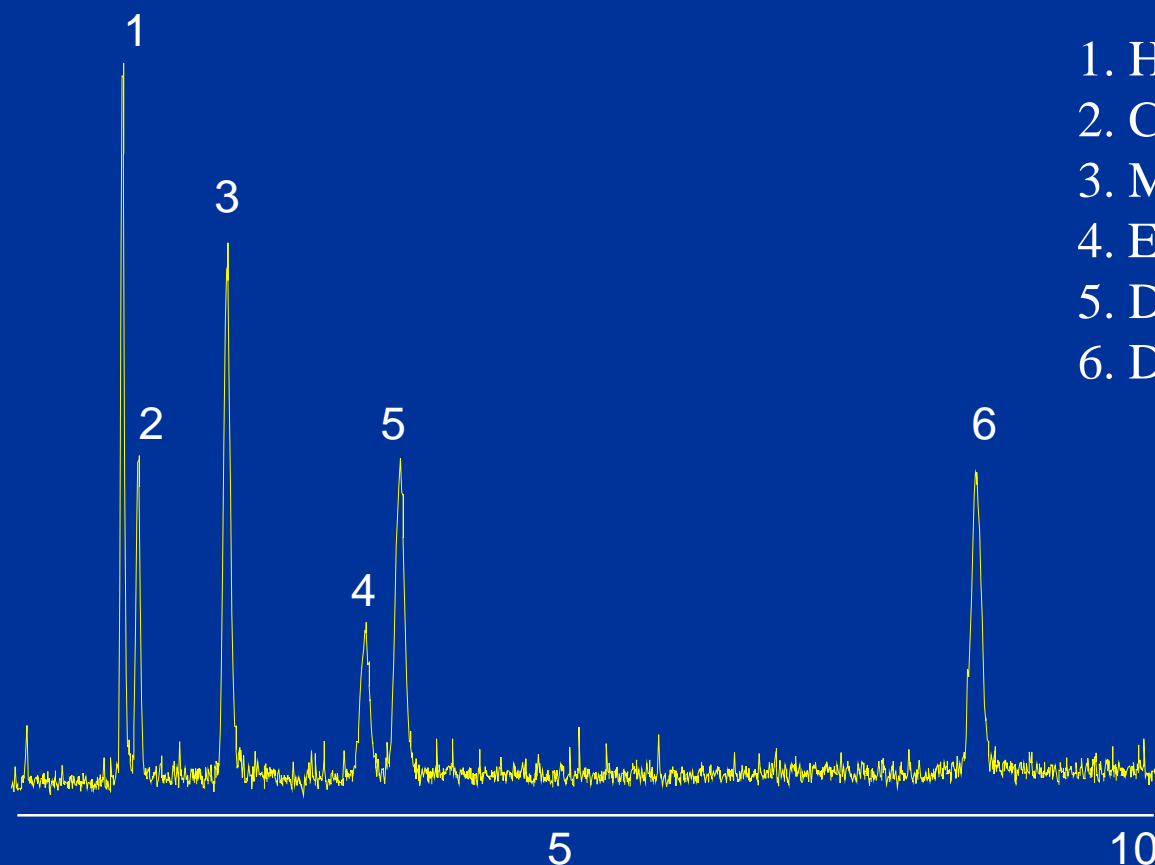
Sulfinert™-Treated Inlet System



Run Conditions

- Rtx-1 60m x 0.53mm, 7.0 μ m film
- 10mL/min. helium
- 30°C (1min) to 180°C @ 10°C/min
- GC/SCD (Sievers)

11ppbv Sulfur Standard



1. H₂S
2. COS
3. Methyl Mercaptan
4. Ethyl Mercaptan
5. Dimethyl Sulfide
6. Dimethyl Disulfide

Rtx-1 60m x 0.53mm, 7.0μm

List of Sulfur Compounds

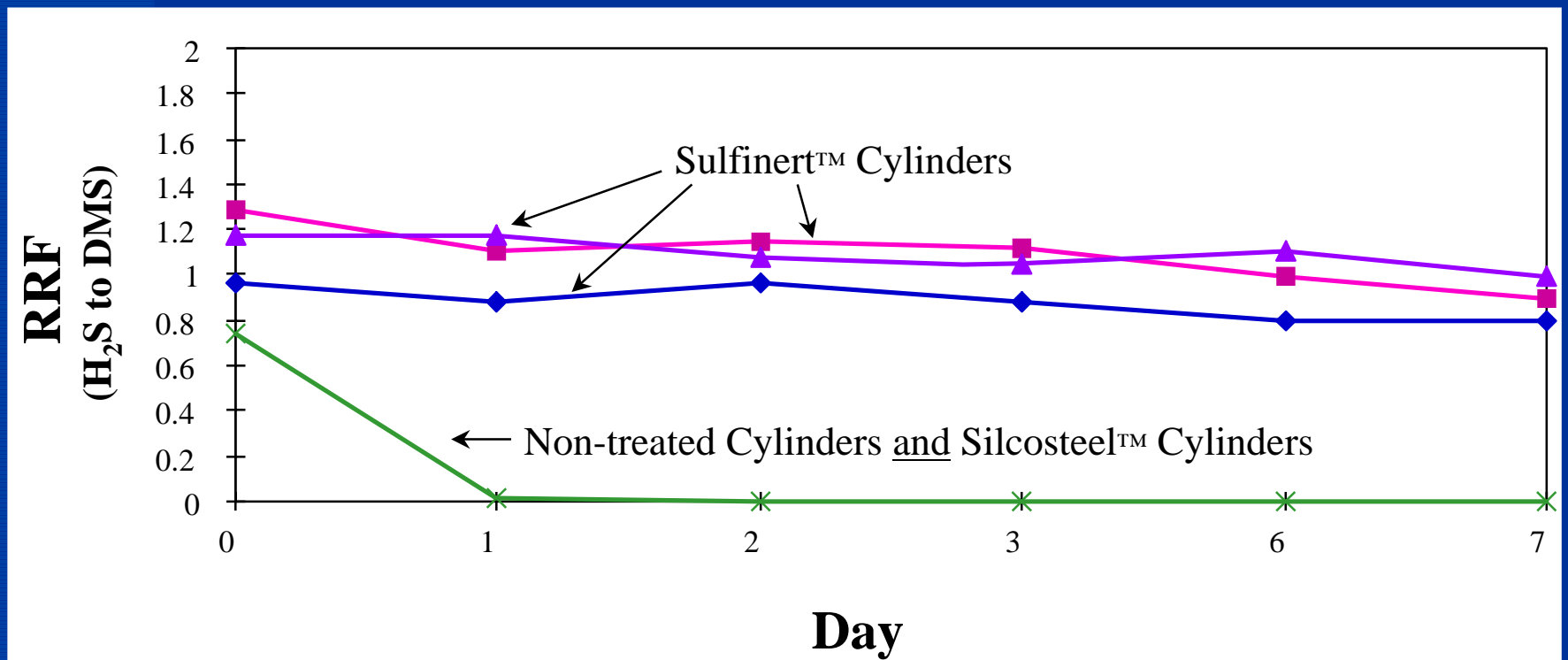
Compound Name	Formula	Conc (ppmv)	Conc (ppbv)	Conc as S (ppbv)
hydrogen sulfide	H ₂ S	105	11.51	10.83
carbonyl sulfide	COS	98	10.74	5.73
methyl mercaptan	CH ₃ SH	101	11.07	7.38
ethyl mercaptan	CH ₃ CH ₂ SH	101	11.07	5.71
dimethylsulfide	CH ₃ SCH ₃	99	10.85	6.81
dimethyl disulfide	CH ₃ SSCH ₃	100	10.96	7.46

System Repeatability

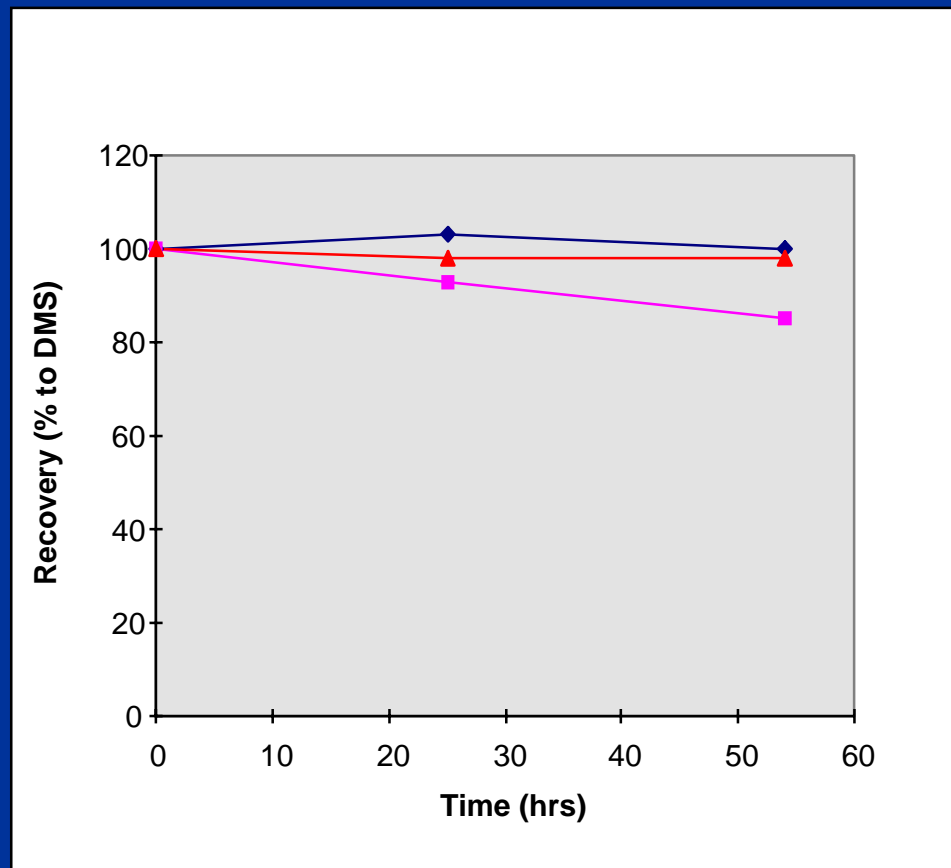
Compound Name	%RSD
hydrogen sulfide	2.2
carbonyl sulfide	4.2
methyl mercaptan	2.0
ethyl mercaptan	8.7
dimethylsulfide	3.3
dimethyl disulfide	9.2

n=7

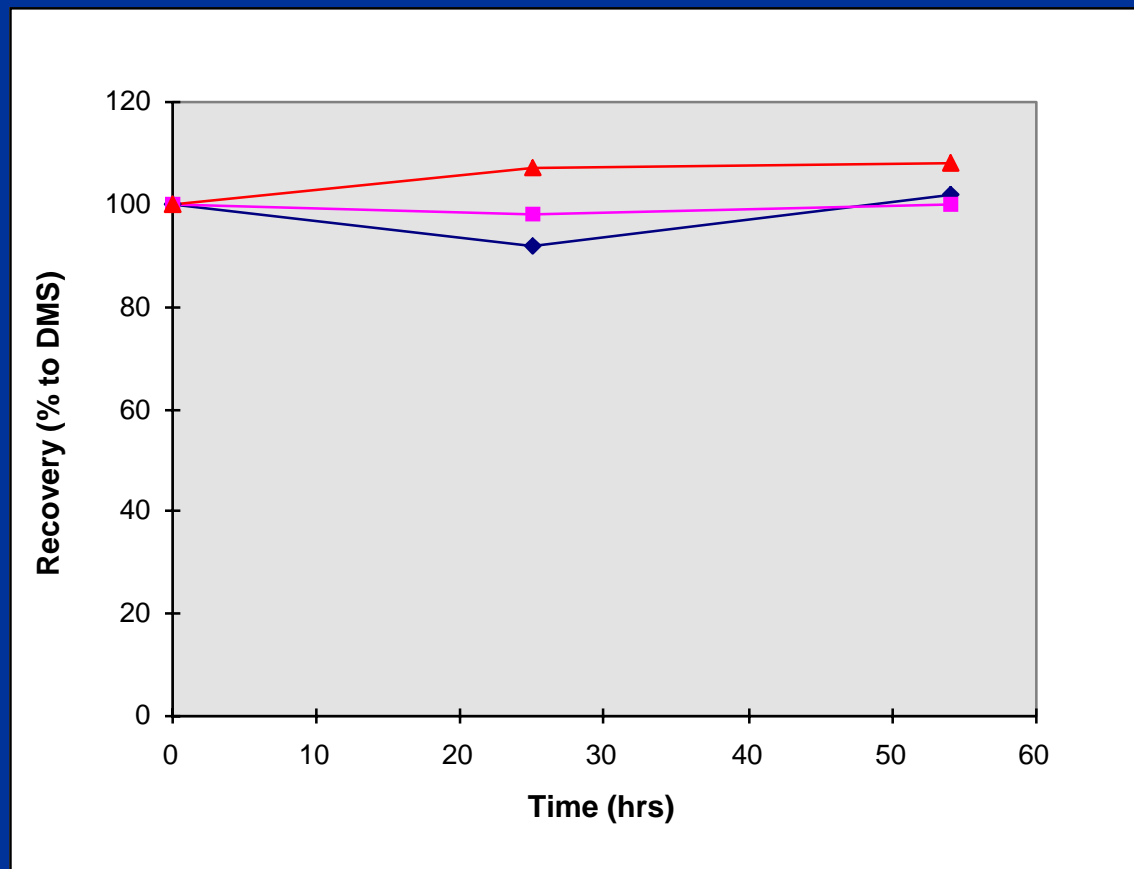
17ppbv H₂S Containment in 500ml Cylinders



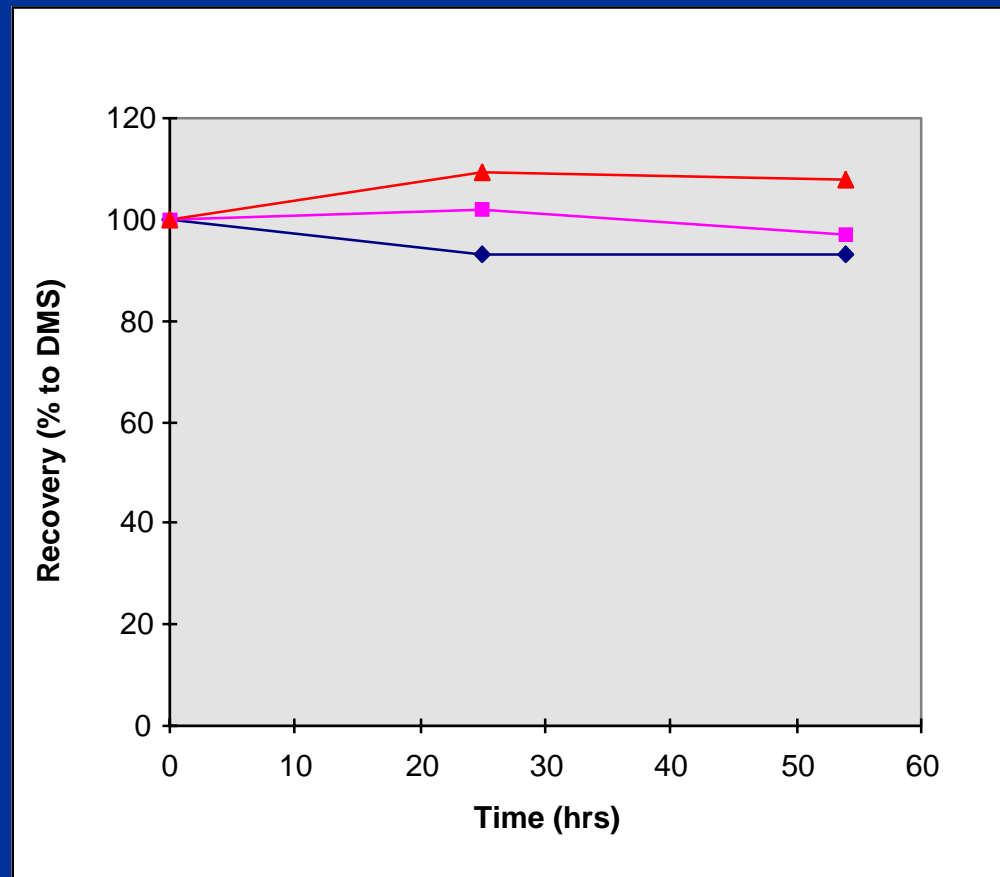
H₂S at 27.57ppbv in 300ml Sulfinert™ Cylinders



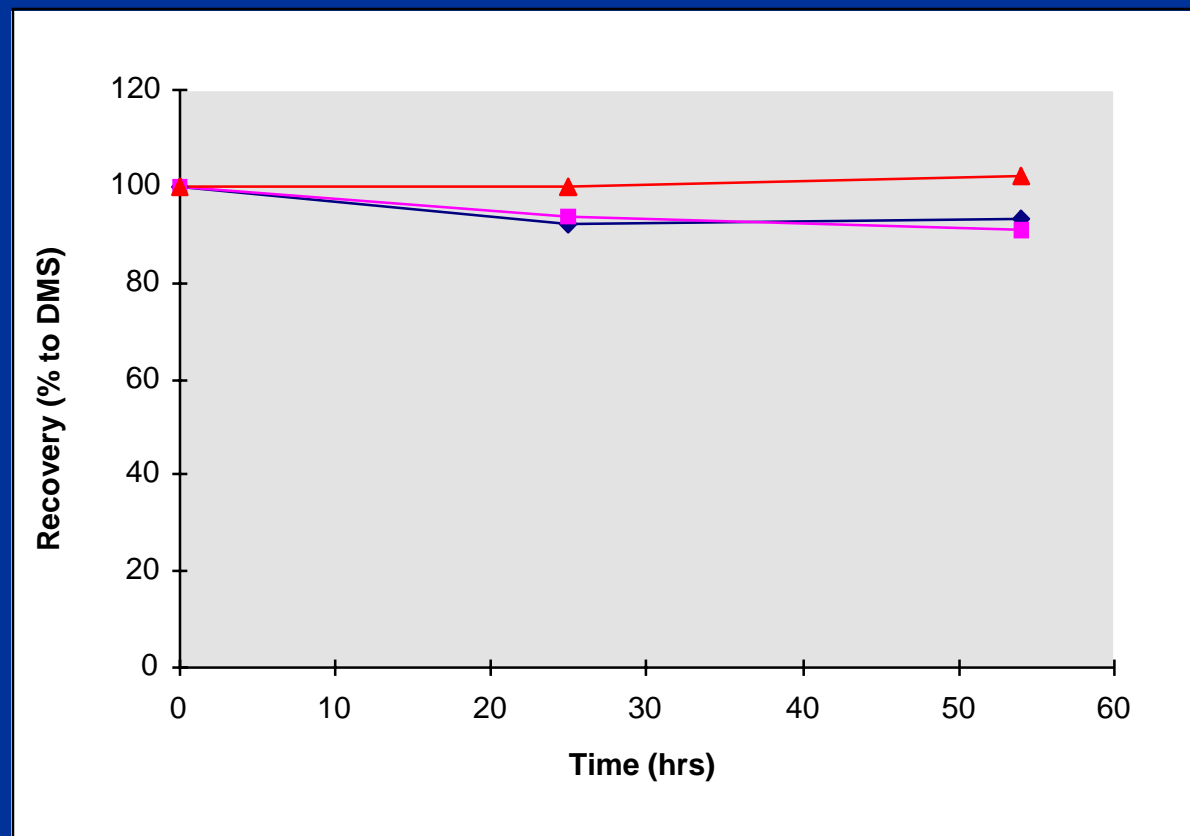
COS at 14.59ppbv in 300ml Sulfinert™ Cylinders



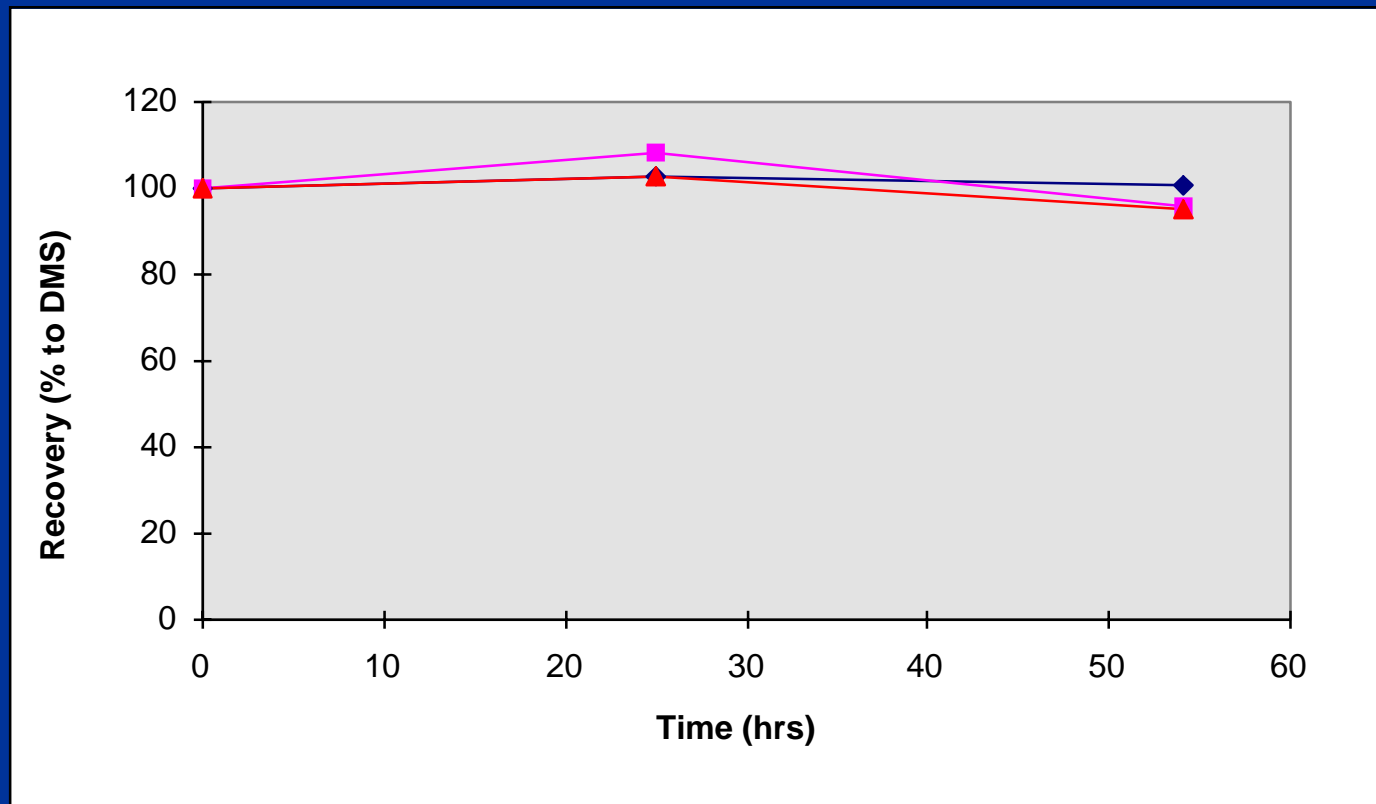
Methyl Mercaptan at 18.8ppbv in 300ml Sulfinert™ Cylinders



Ethyl Mercaptan at 14.53ppbv in 300ml Sulfinert™ Cylinders



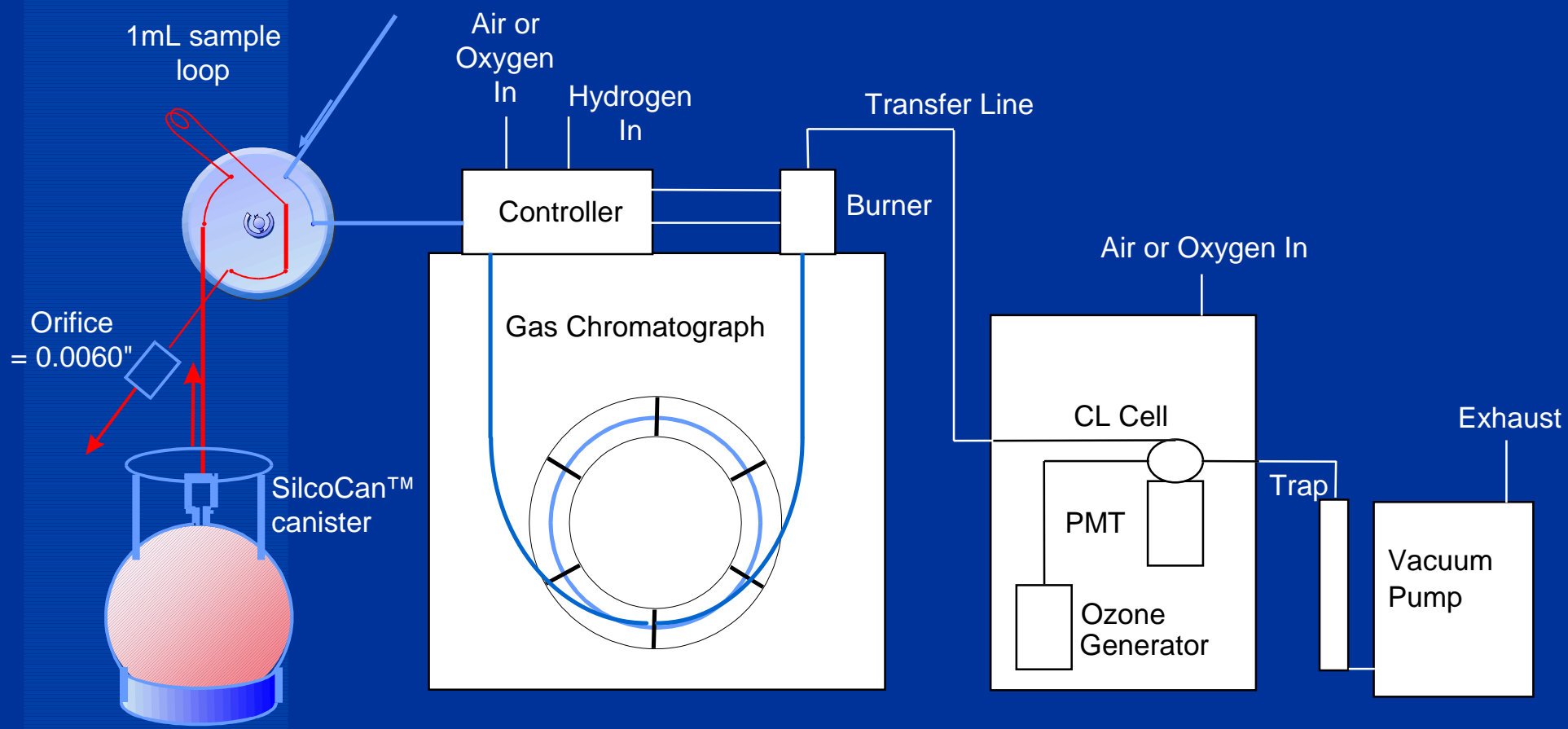
Dimethyl Disulfide at 18.99ppbv in 300ml Sulfinert™ Cylinders



Ambient Air Sampling Canisters Objective

- Demonstrate suitability for storage of low level (1-20ppbv) sulfurs in SilcoCan™ canisters.

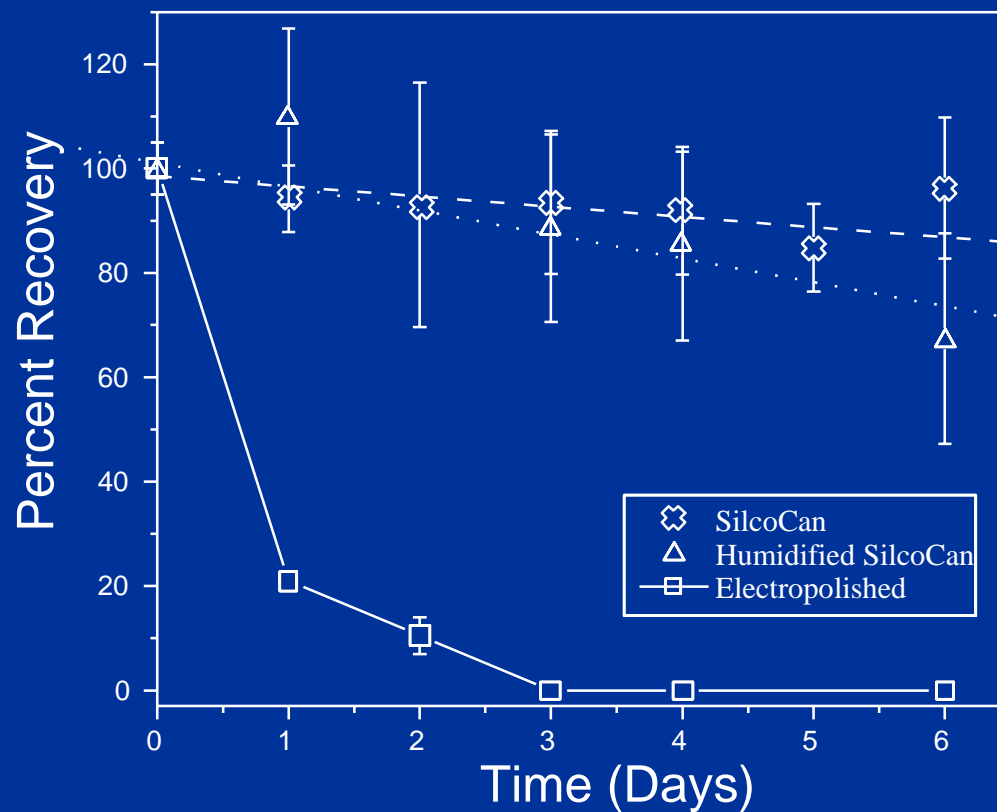
Block diagram of Analytical System



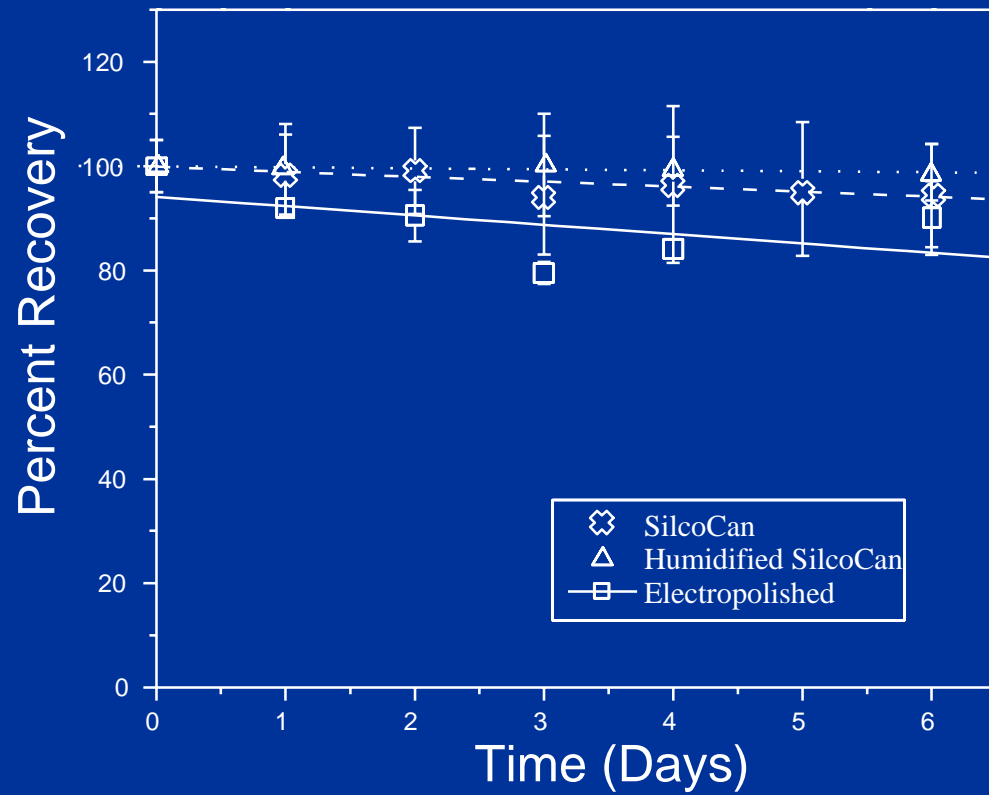
Stability Study Test

- 11ppbv
- 6 days stability study
- Reference std is at 55ppbv
- Dimethyl sulfide as internal standard
- SilcoCans (n=18)
- Humidified (rh=50%) SilcoCans (n=5)
- Electropolished Cans (n=2)

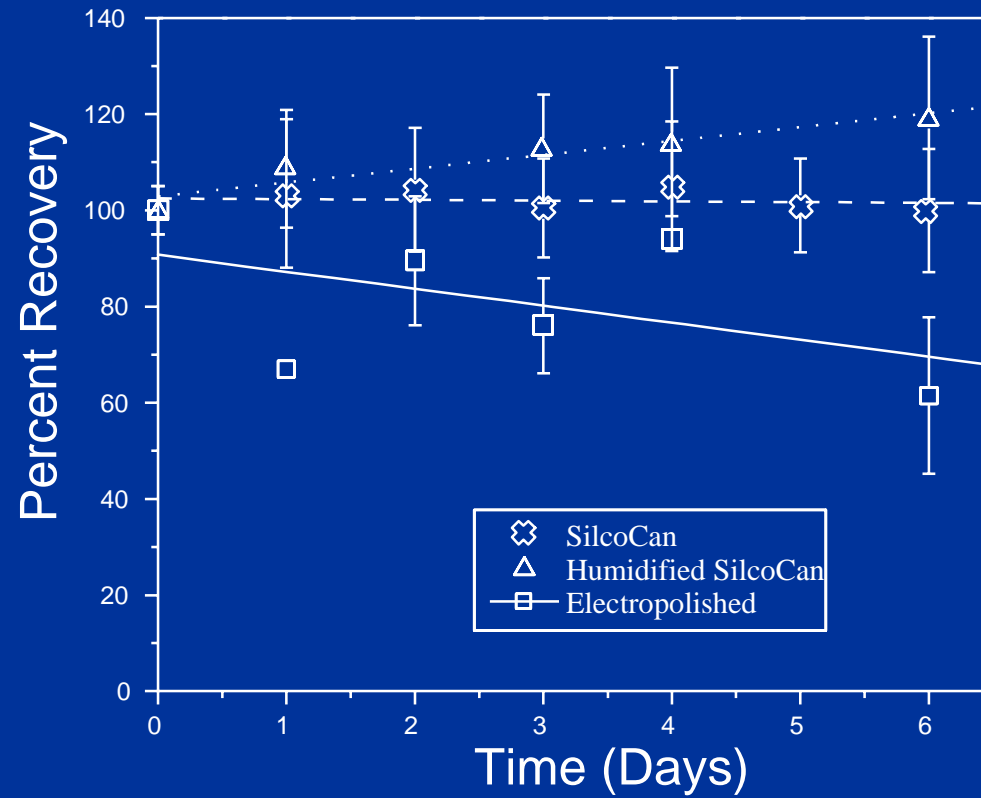
H₂S at 11ppbv in 6l Air Sampling Cans



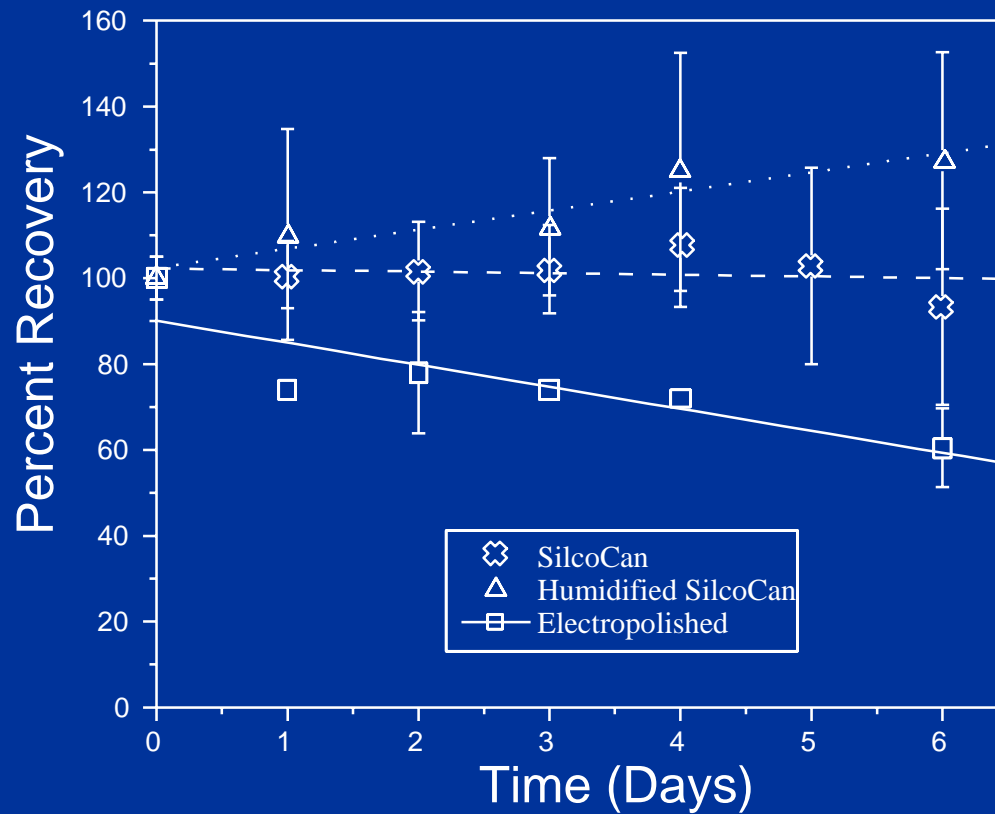
COS at 10ppbv in 6l Air Sampling Cans



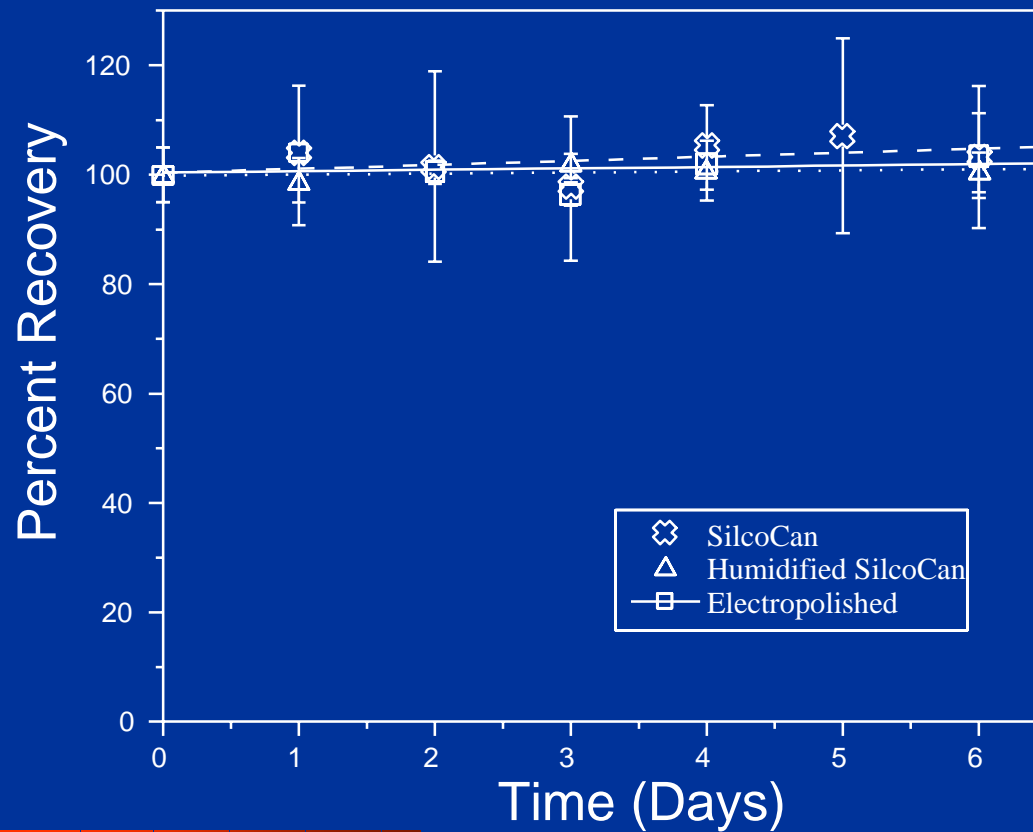
Methyl Mercaptan at 11 ppbv in 6l Air Sampling Cans



Ethyl Mercaptan at 11ppbv in 6l Air Sampling Cans



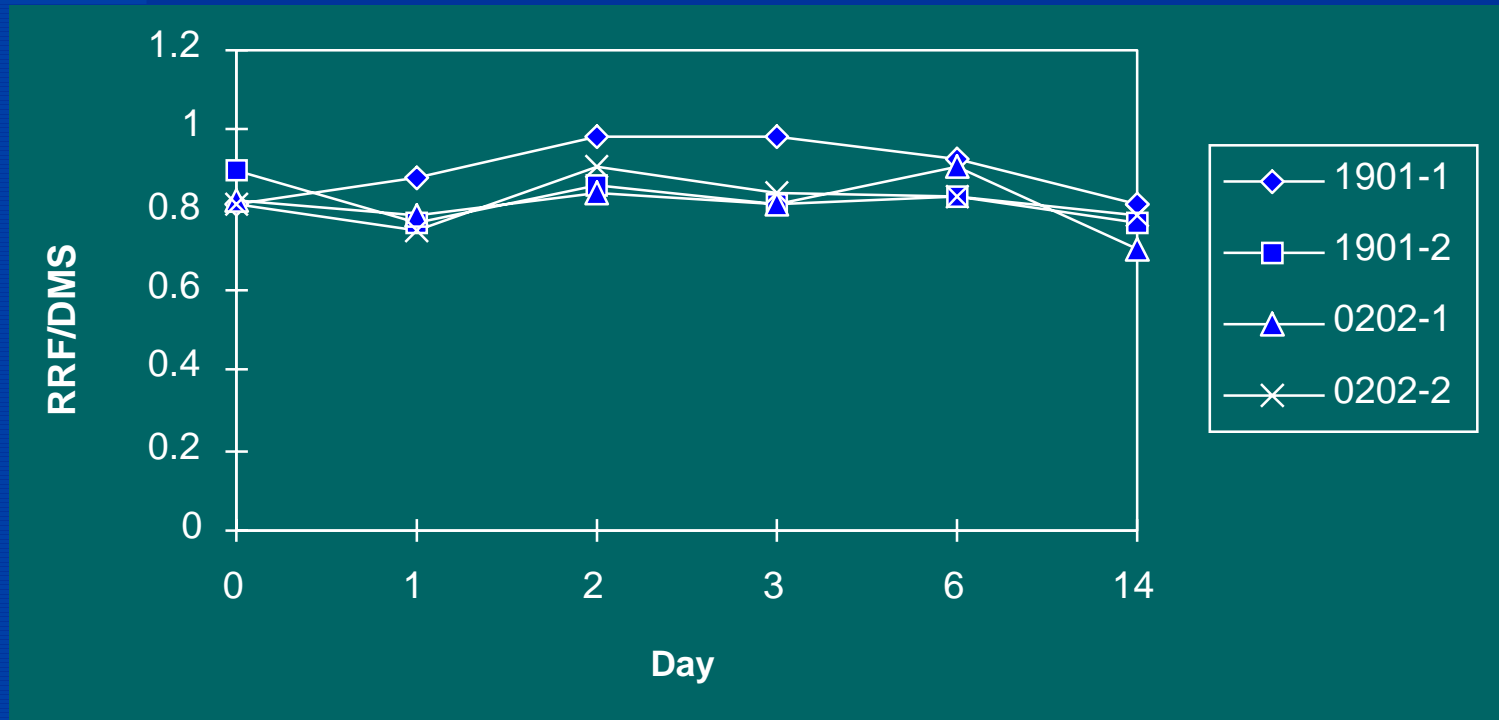
Dimethyl Disulfide at 11ppbv in 6l Air Sampling Cans



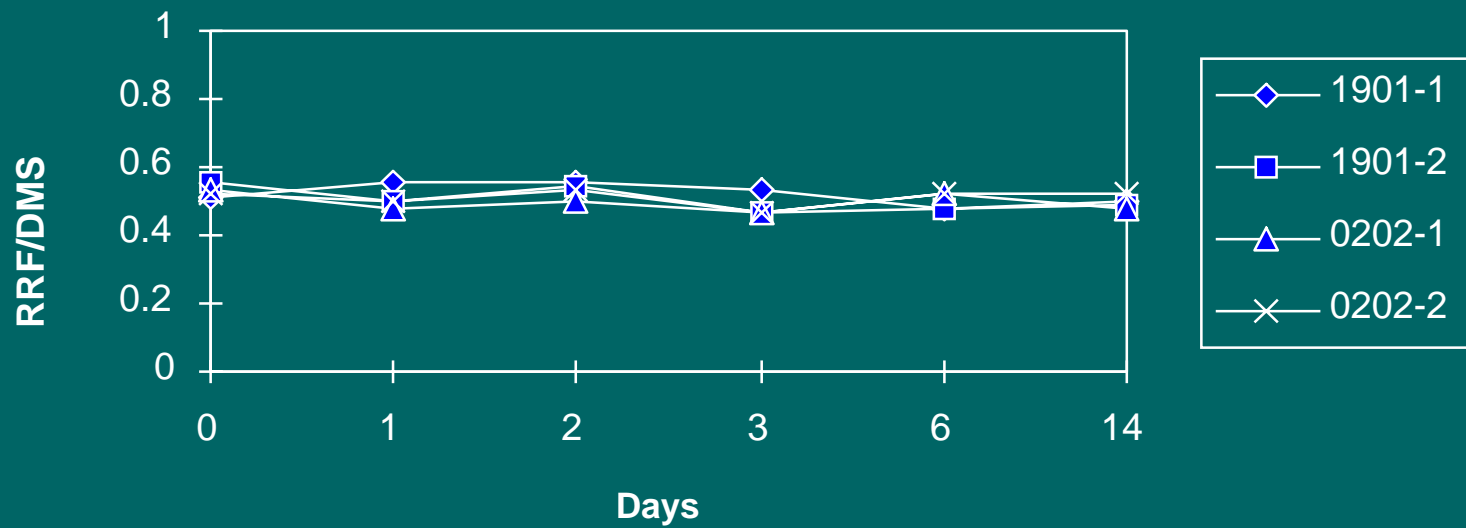
Extended Stability Study

- Is the SilcoCan capable of storing 11ppbv sulfurs longer than 6 days?
- Tested 4 SilcoCans on Day 14

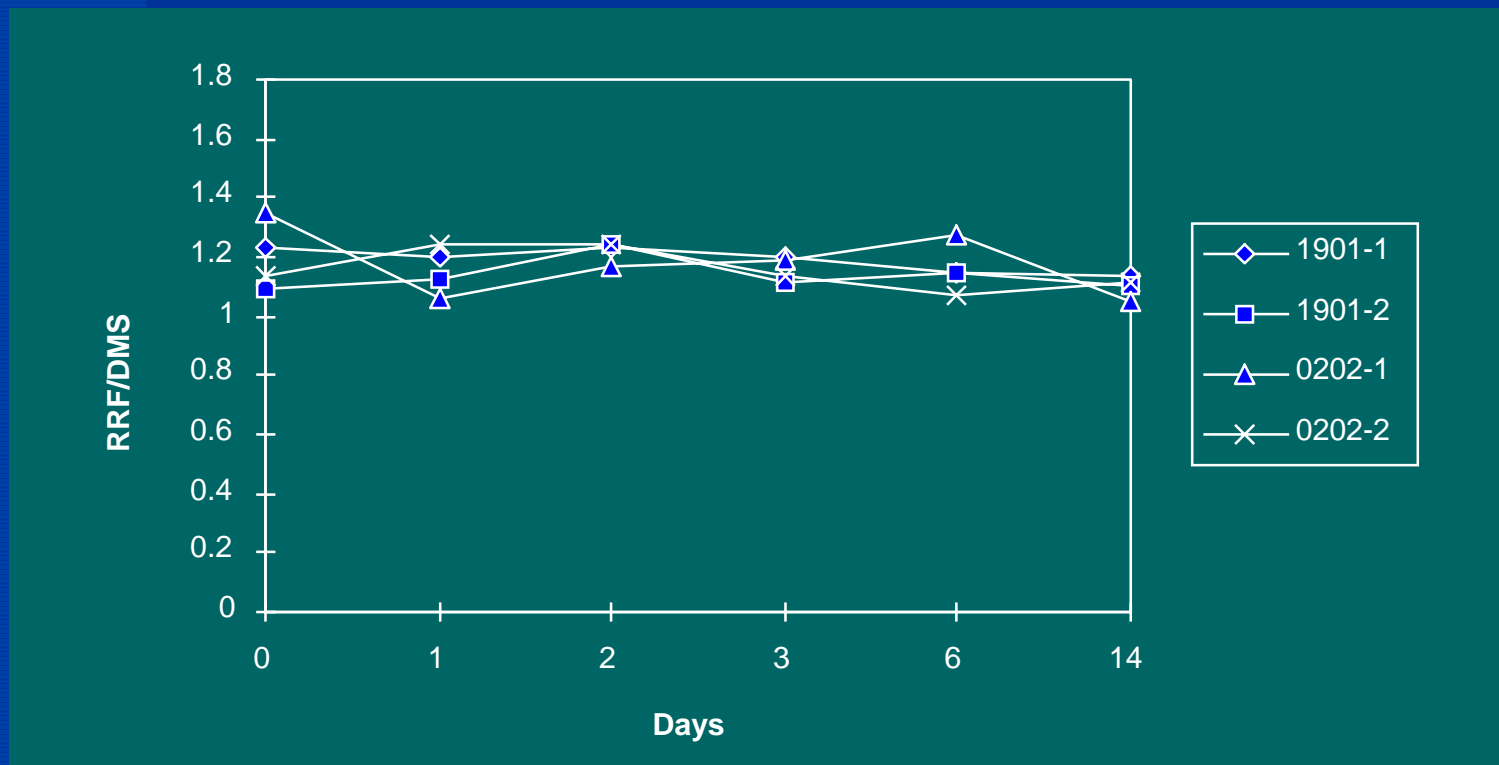
H₂S at 11ppbv for 14 days



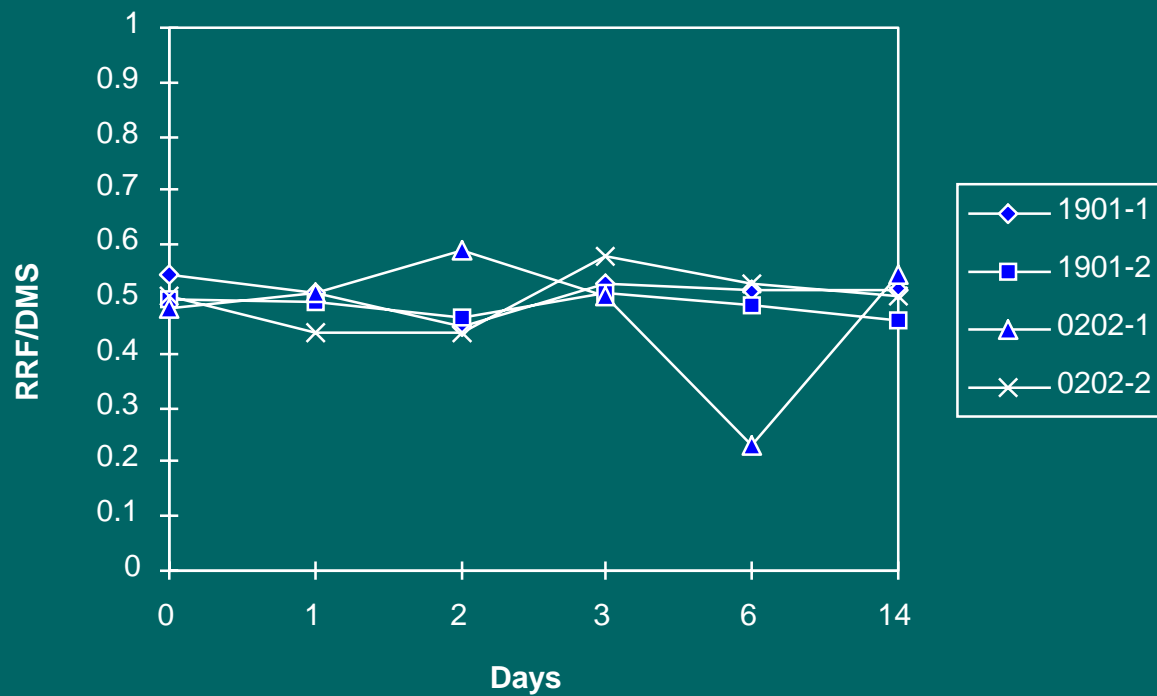
COS at 10ppbv for 14 Days



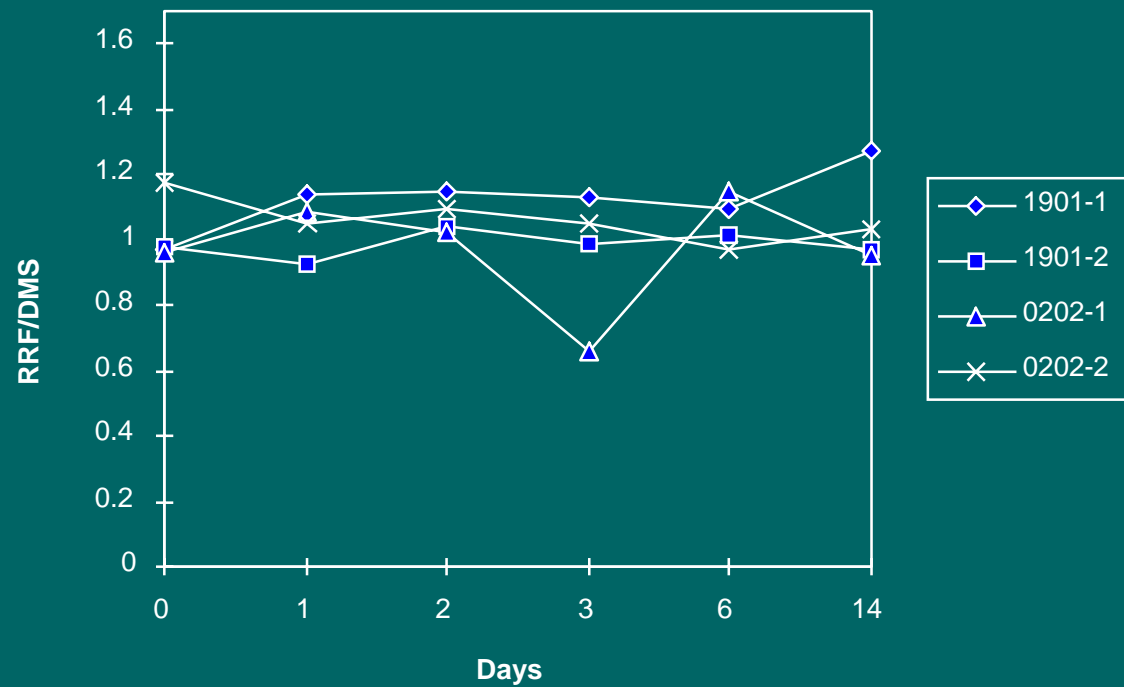
Methyl Mercaptan 11 ppbv for 14 Days



Ethyl Mercaptan at 11ppbv for 14 Days



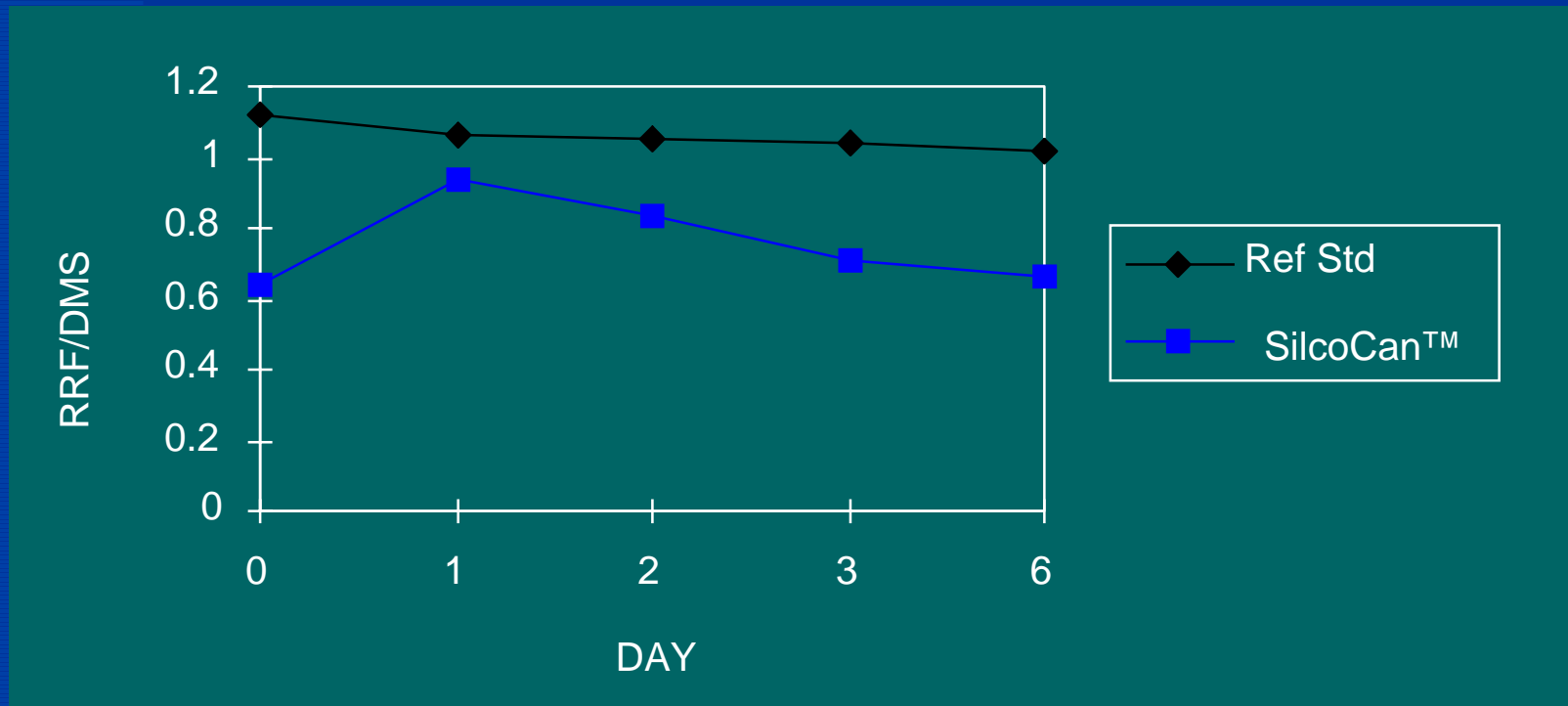
Dimethyl Disulfide at 10ppbv for 14 Days



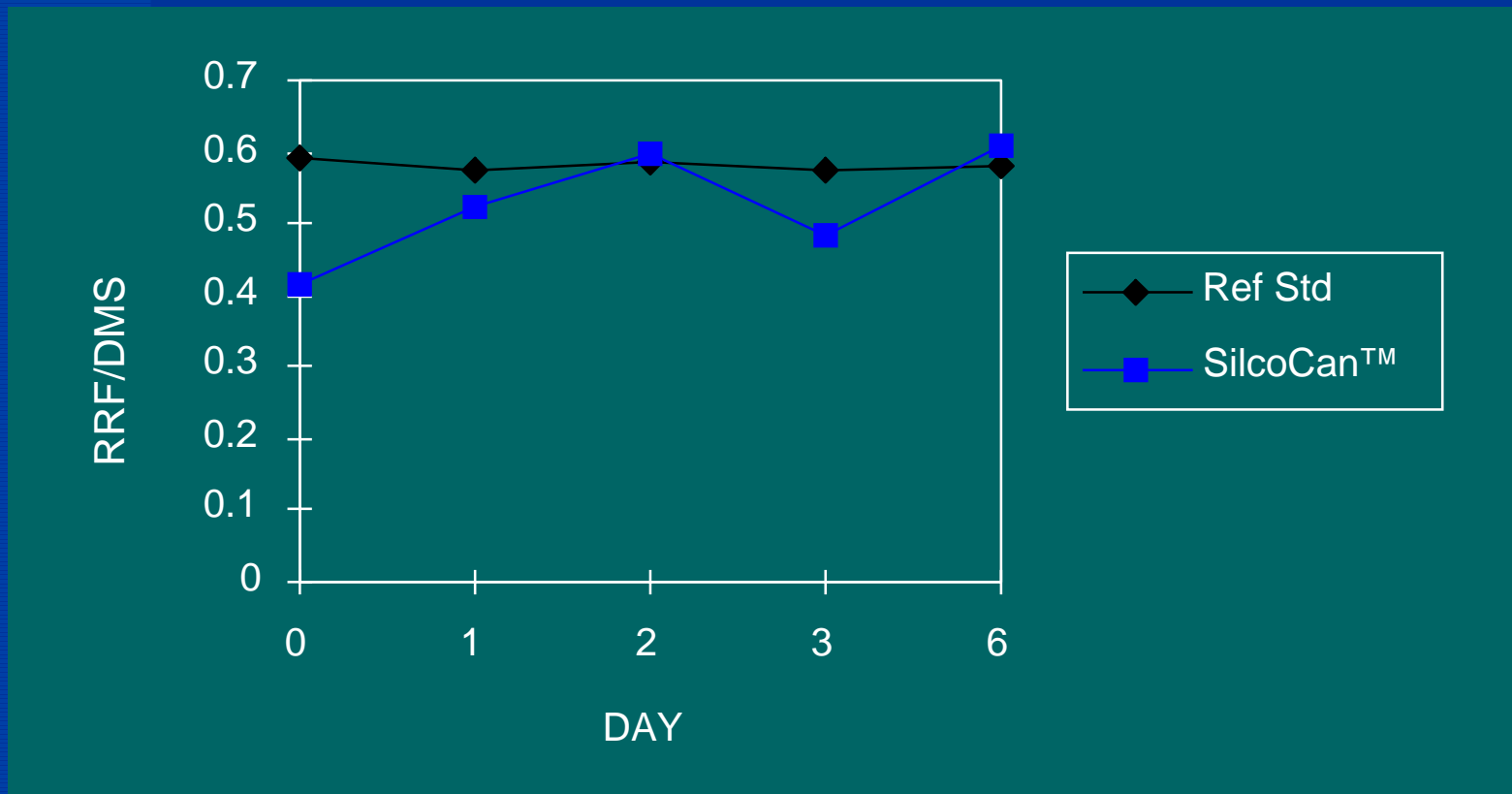
Can the SilcoCan go to lower levels?

- Is the SilcoCan surface treatment stable for sulfurs at 1.5ppbv?

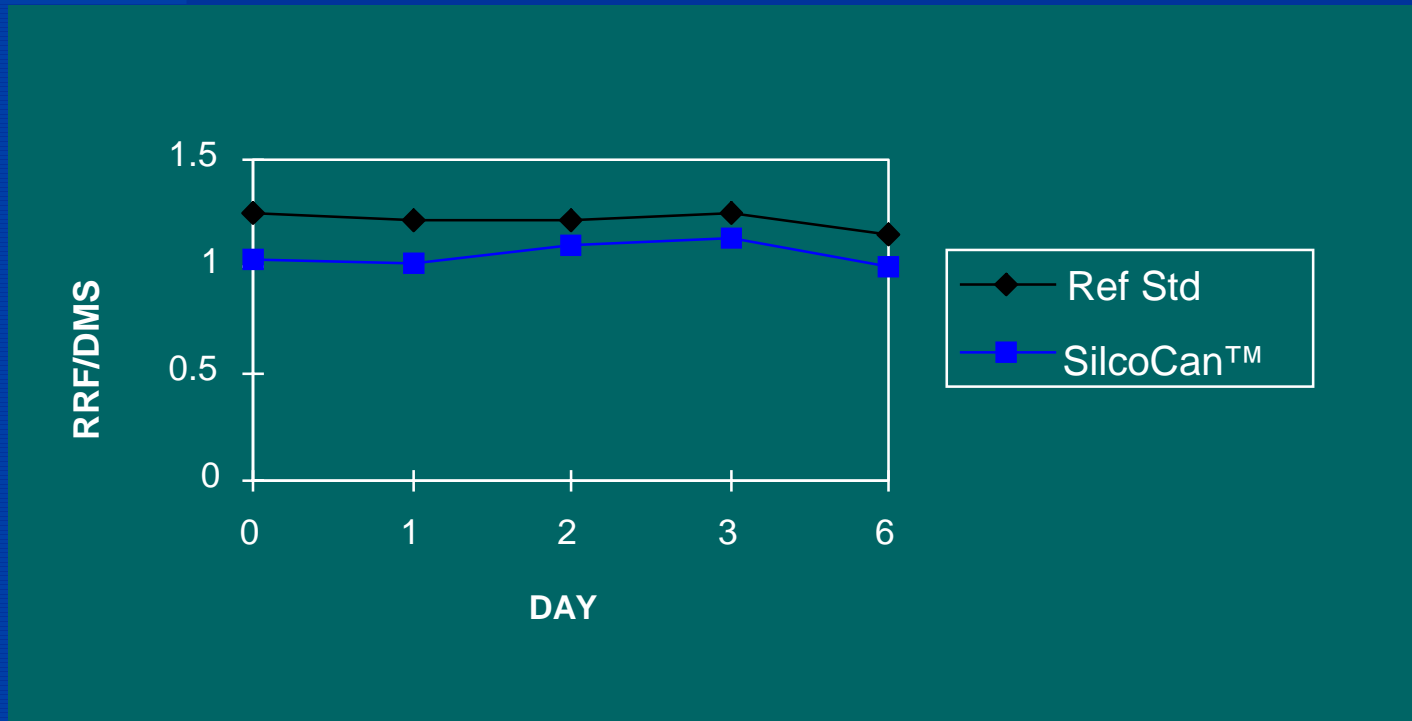
H₂S at 1.5ppbv



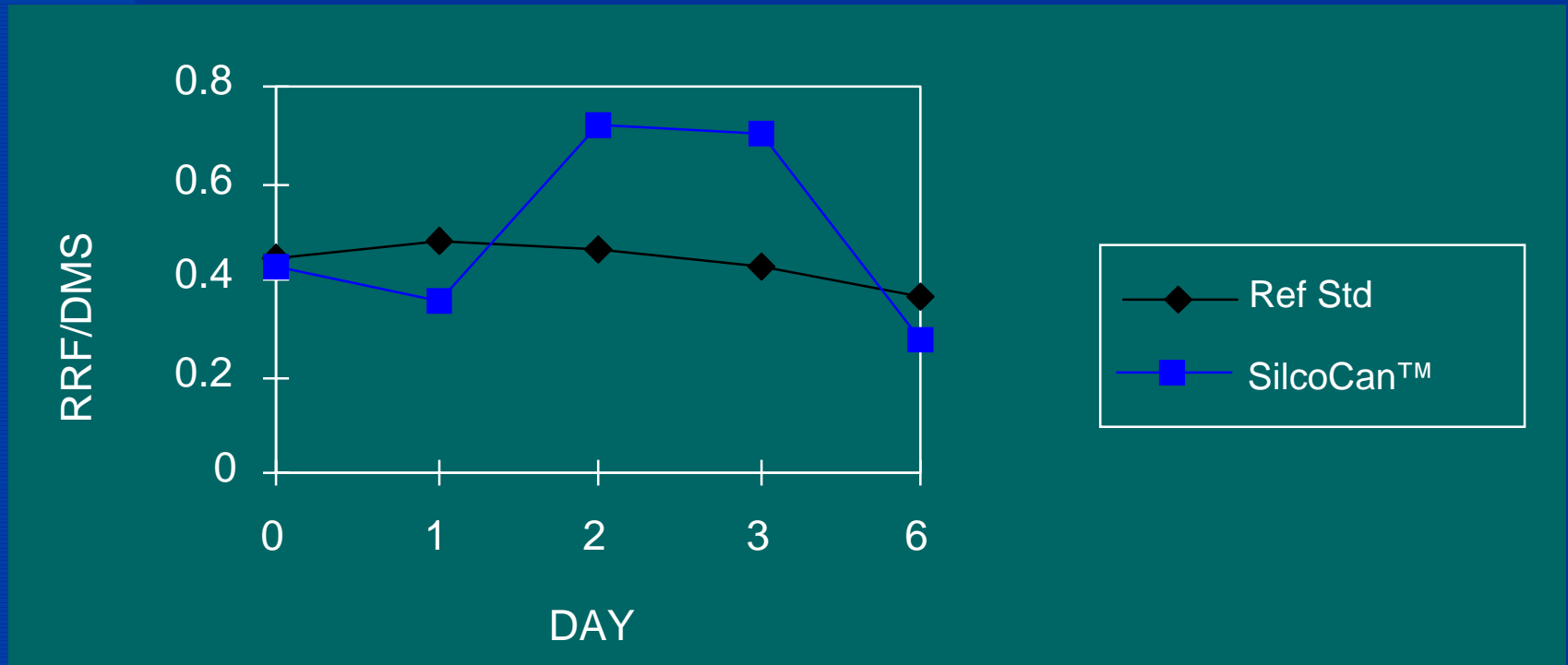
COS at 1.5ppbv



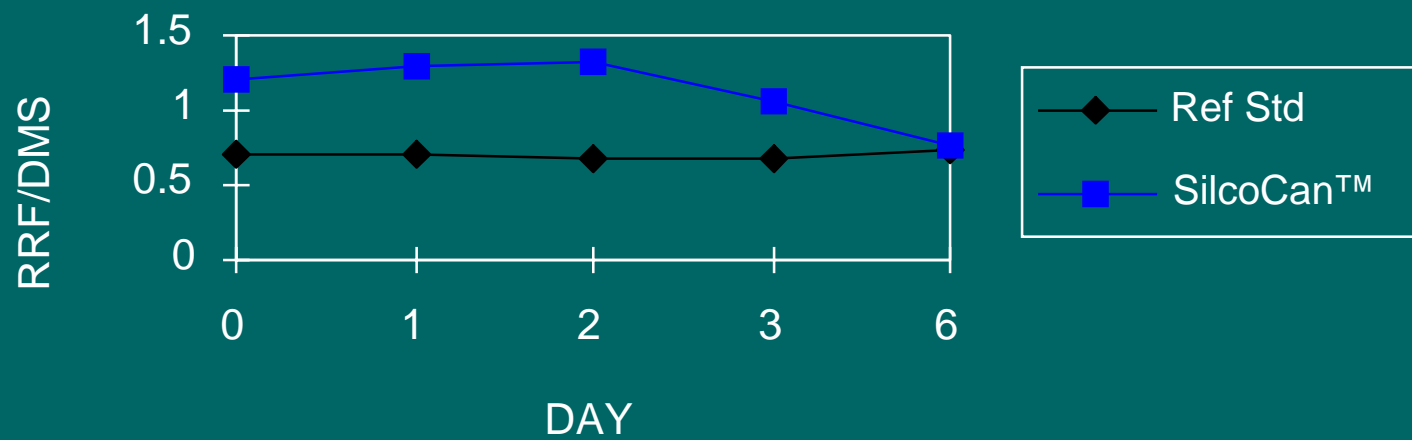
Methyl Mercaptan at 1.5ppbv



Ethyl Mercaptan at 1.5ppbv



Dimethyl Disulfide at 1.5ppbv



Conclusions

- Surface treatments for steel surface allow low-ppbv containment, transfer and subsequent analysis of sulfur gases
 - Sulfinert™ (for raw steel surfaces)
 - Silcocan™ (for electropolished, smooth surfaces)
- Future directions include applying Sulfinert™ to GC column materials (glass and/or steel tubing, packings)

Acknowledgements

- Sievers Instrument Inc. for their cooperation.
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