Stability of Sulfur Compounds in Whole Air Sampling

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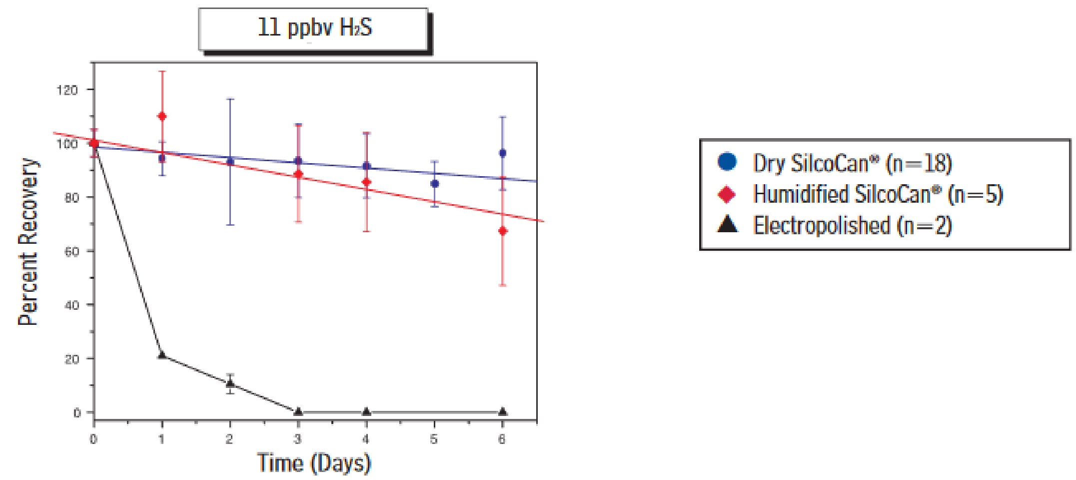
Outline

- Historical sulfur evaluations using nitrogen
- Comparison of dry and humid air stability (Restek and competitors)
- Evaluation of Restek TO and SilcoCans with varying humidity
- Potential for reducing humidity during sampling
- Conclusions

Stability Under Nitrogen

- Use of fused silica-lined canisters recommended for sulfur analysis
- Nitrogen commonly used as a fill gas in testing
- However, nitrogen is inert and doesn't represent real world conditions
- Recent emphasis on using humidified air as a fill gas for standards and blanks

SilcoCan® canisters effectively store very low levels of sulfur compounds.



28% RH in nitrogen

Stability Under Nitrogen

- Both humidity and oxygen content affect the stability of sulfurs in canisters.

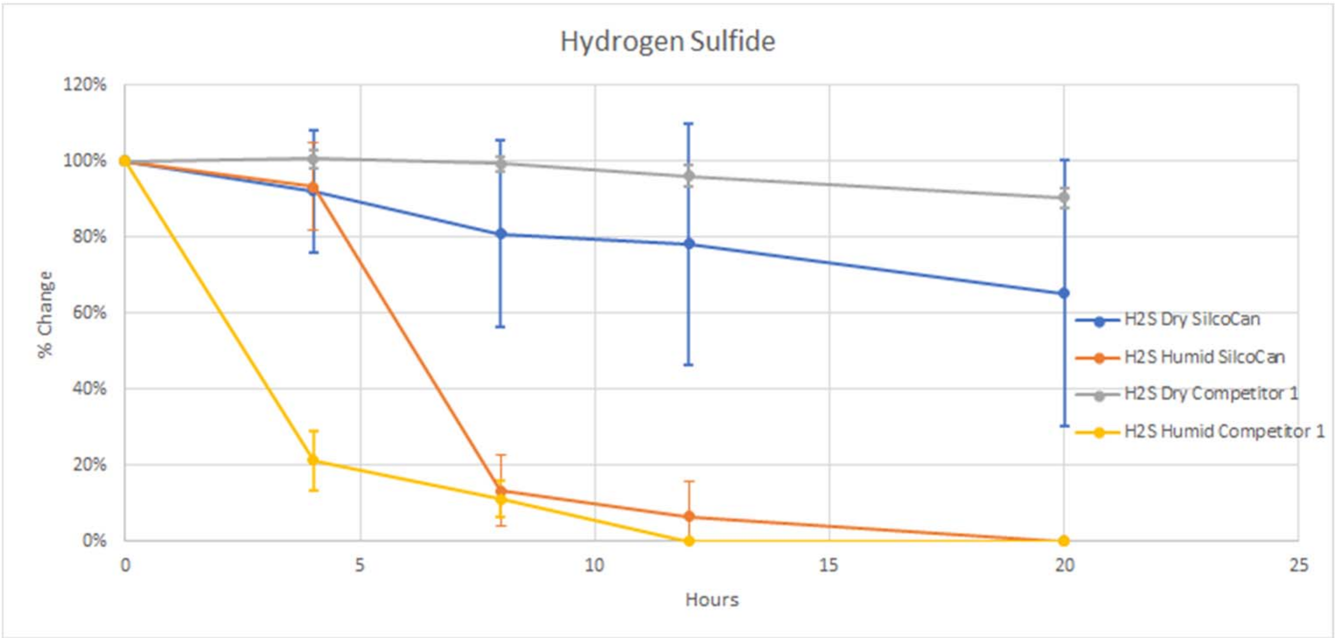
"However, the introduction of water into canisters resulted in both hydrogen sulfide and ethanethiol rapid degradation with less than 60% recovered after 4 h. It should be pointed out that the stability of hydrogen sulfide and methanethiol was somewhat related to the oxygen content of the air matrix …"

S. Trabue, et al, 2008. Field sampling method for quantifying volatile sulfur compounds from animal feeding operations. Atmospheric Environment 42, 3332-3341

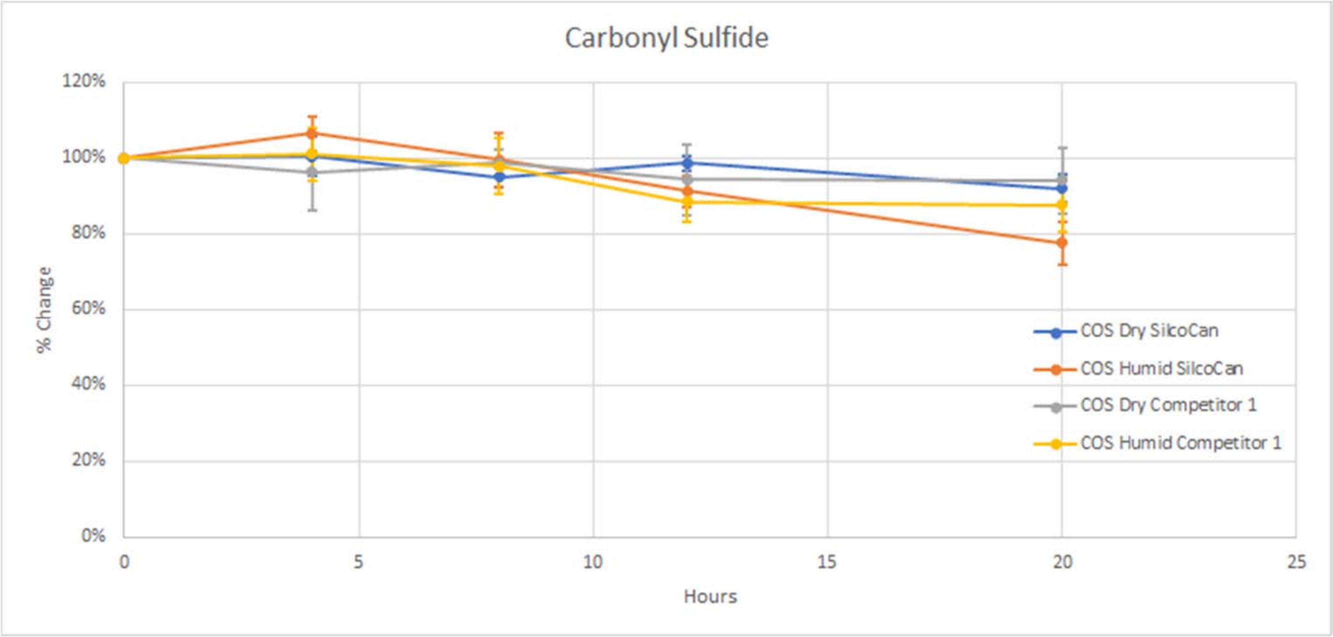
Dry and 50 % RH Air

- True evaluation of compound stability should be done under humid air conditions
- 3 Restek SilcoCan and 3 competitor canisters used
- Canisters filled to 30psig and spiked at 50ppb
- Testing done by GC/MS using a preconcentrator
- Testing done using both dry zero air and 50%RH zero air

Dry and 50% RH Air



Dry and 50% RH Air



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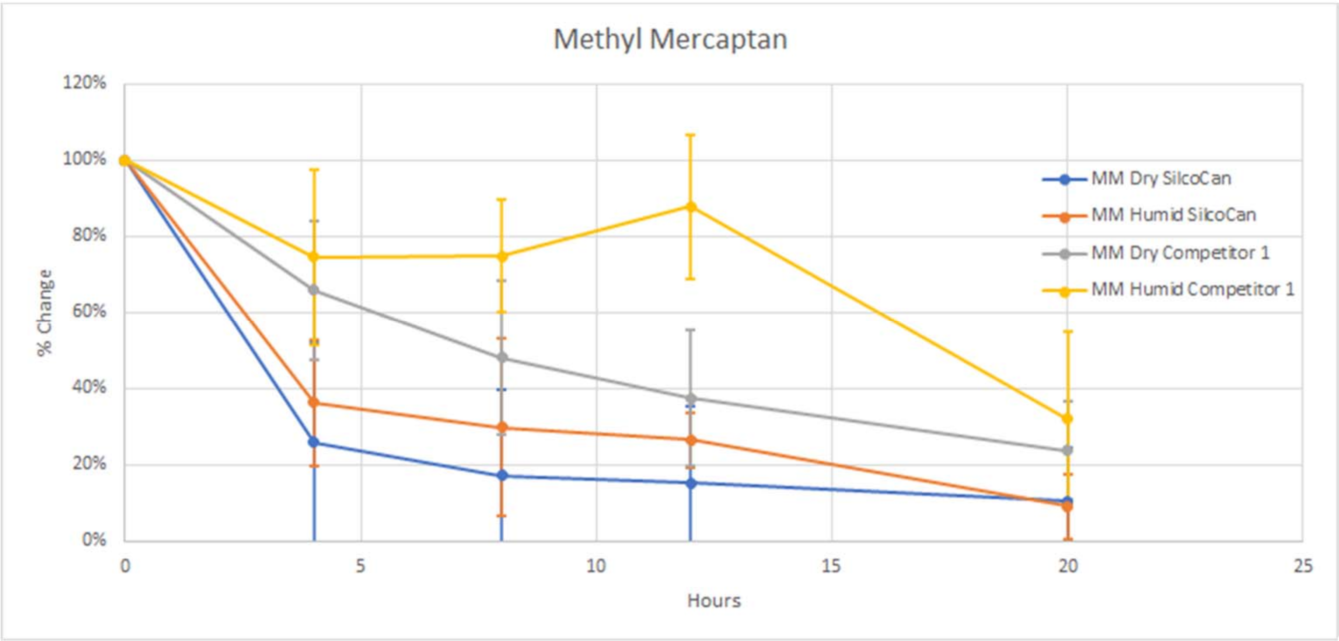

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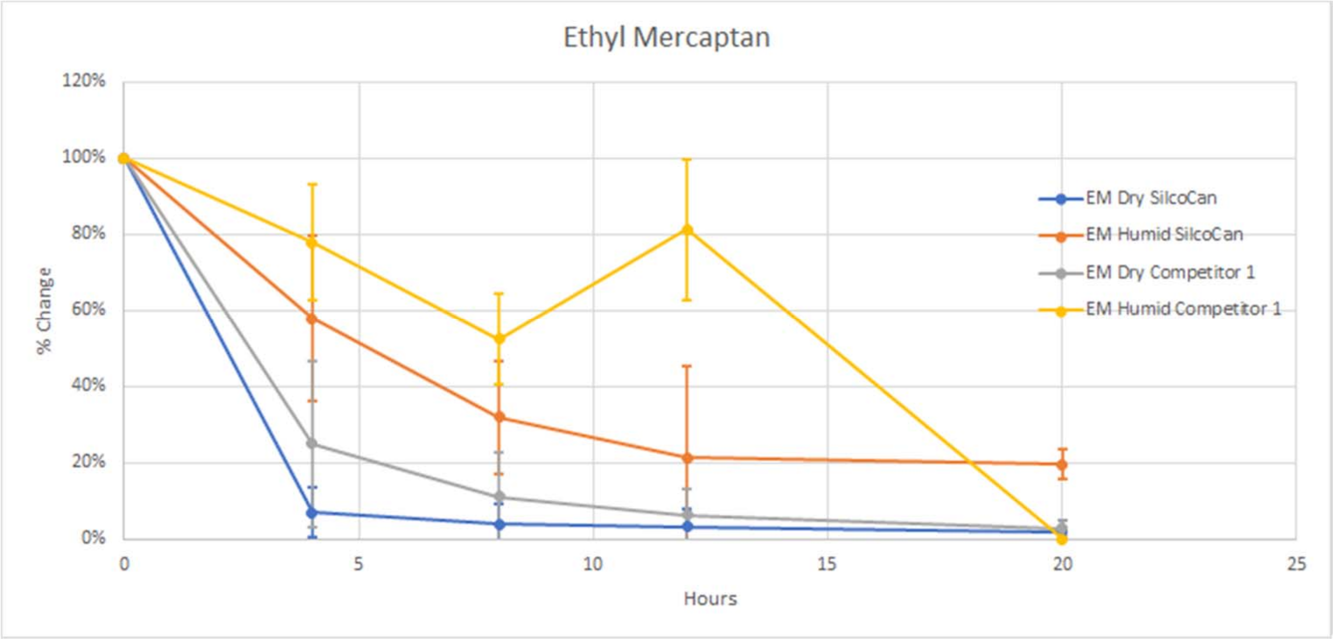

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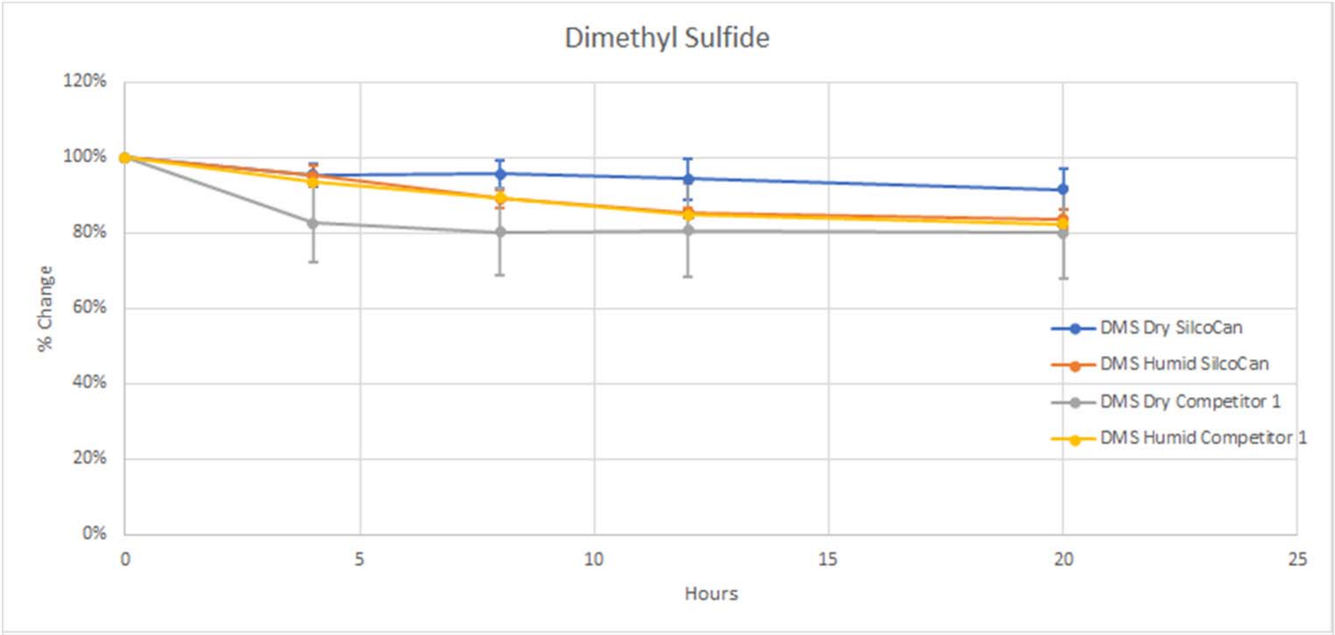

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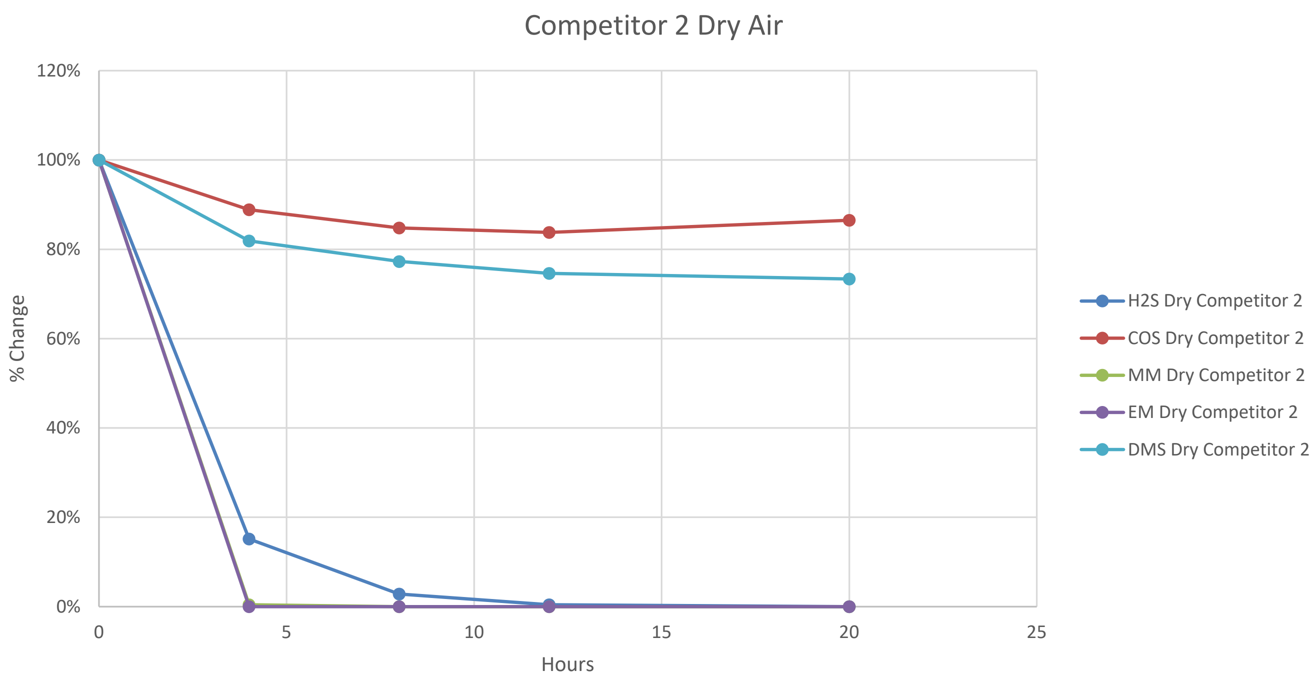
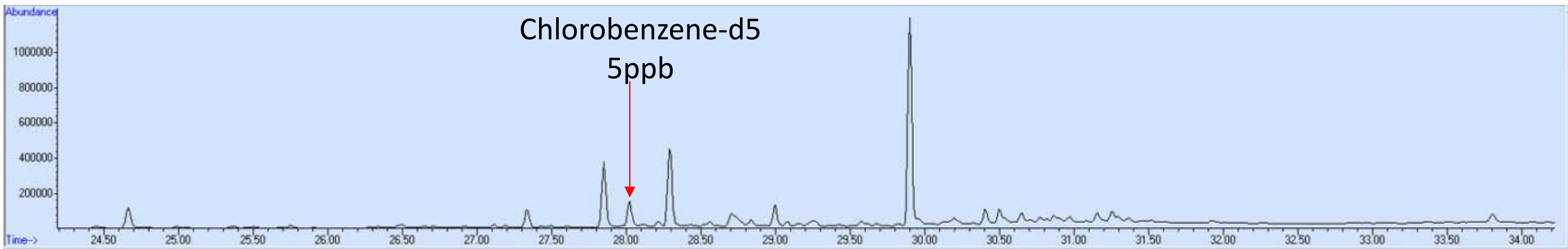


Dry and 50% RH Air

- Examination of TIC in competitor 2 showed many unidentified peaks
- Response change in standards made in inert fill (He) after running competitor 2 cans
- Potential effect of other compounds on sulfur stability
- Cleanliness and % RH effects similar to ethylene oxide

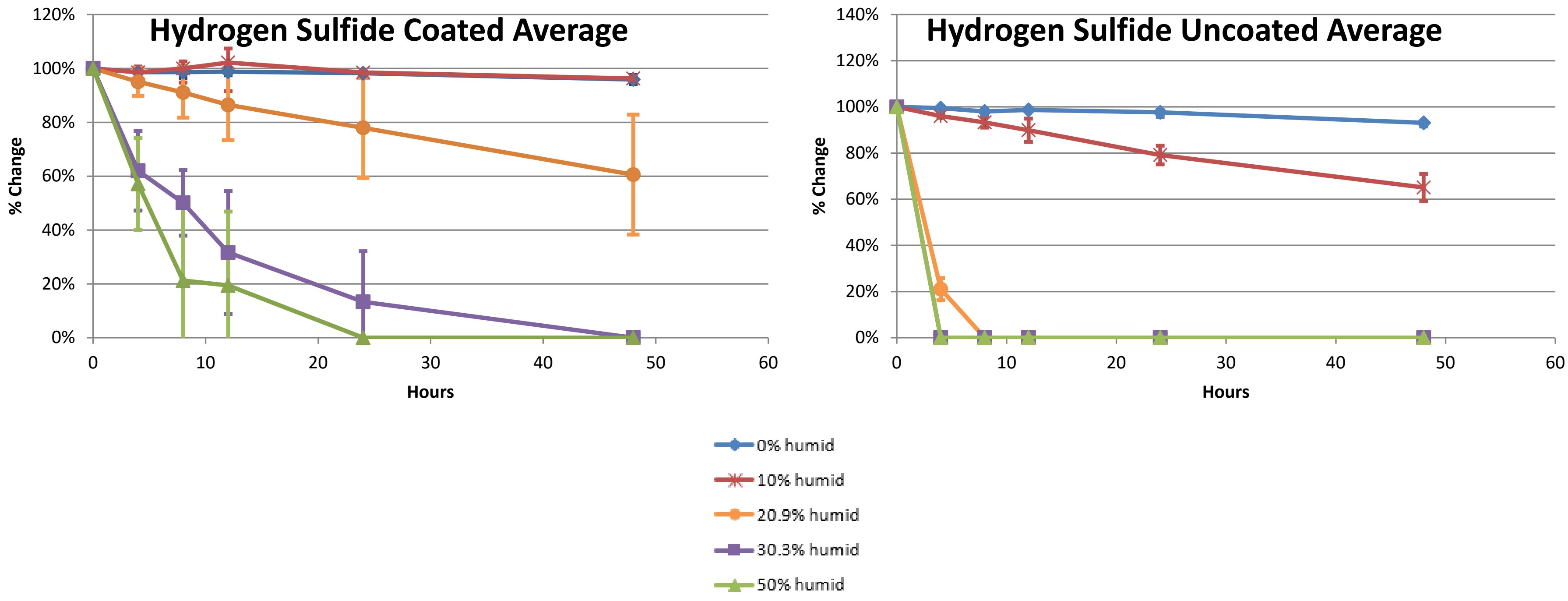


Name	% Recovery in He Standard (+3hr)	% Recovery in He standard after Competitor 2 analysis (+2hr)
Hydrogen Sulfide	95%	91%
Carbonyl Sulfide	94%	98%
Methyl Mercaptan	102%	55%
Ethyl Mercaptan	101%	44%
Dimethyl Sulfide	100%	96%

Effect of RH on Sulfur Stability

- 3 new TO and SilcoCans used to minimize potential interferences
- Samples tested at 0, 20, 30, and 50% RH
- Samples were analyzed by FPD using a 5 mL sample loop
    - Simpler flow path and no cryo trap
- Canisters filled to 30 psig and spiked at 50 ppb

Effect of RH on Sulfur Stability



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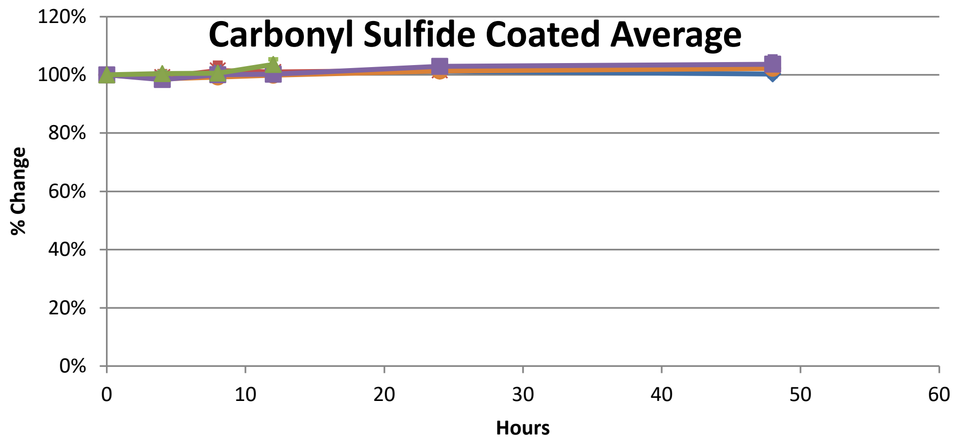
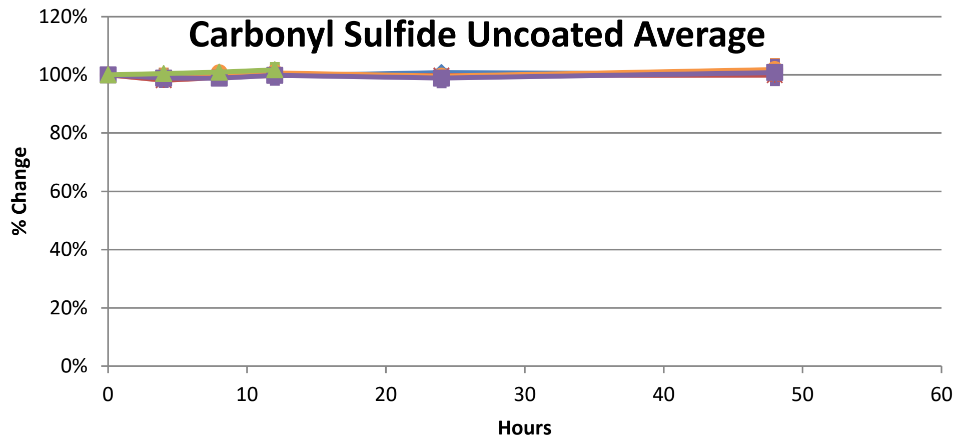
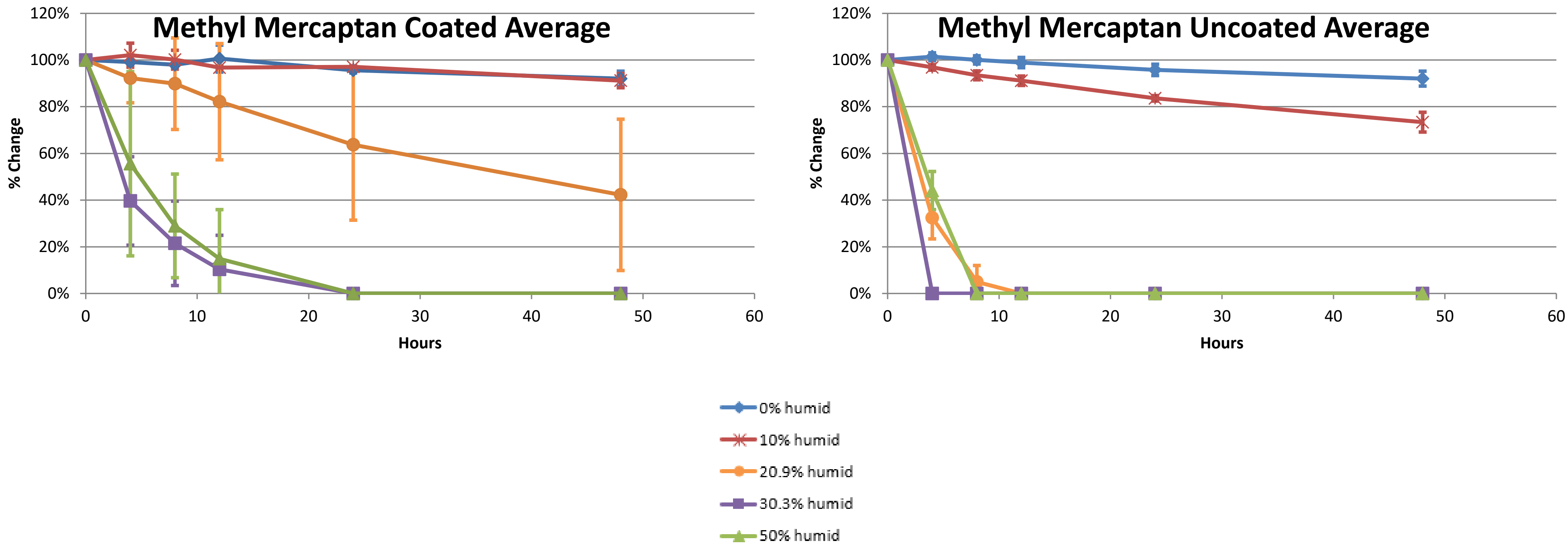




0% humid
10% humid
20.9% humid
30.3% humid
50% humid

Effect of RH on Sulfur Stability



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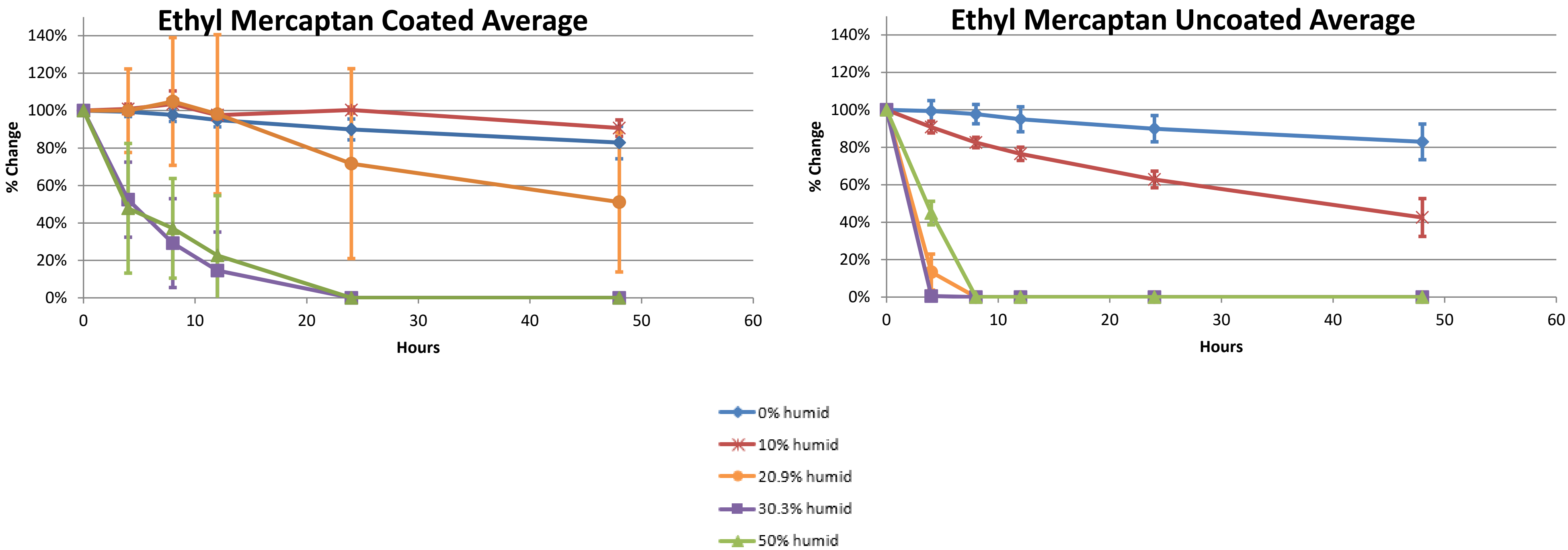

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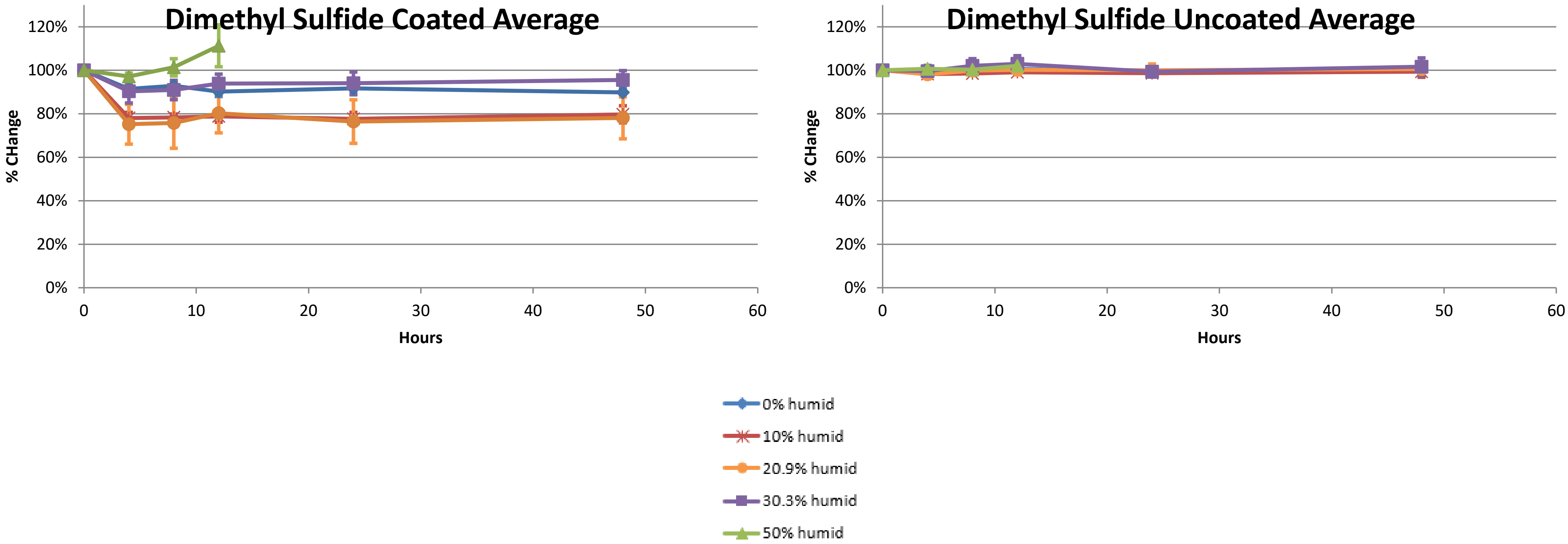

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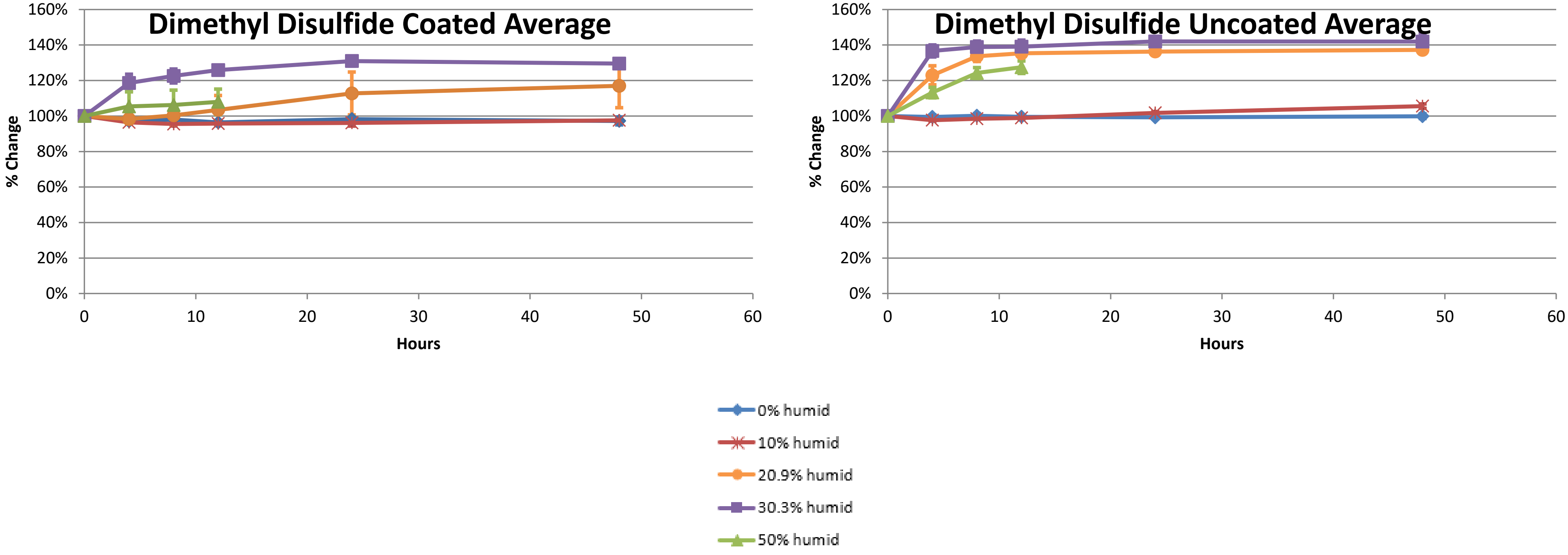
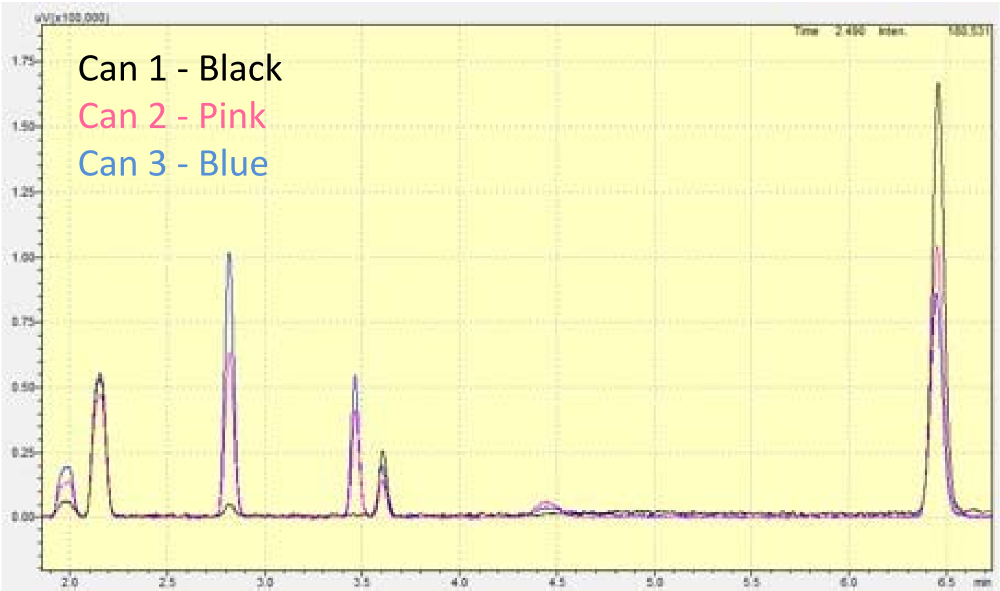


Effect of RH on Sulfur Stability

SilcoCans, 20.9% RH, 24 hours

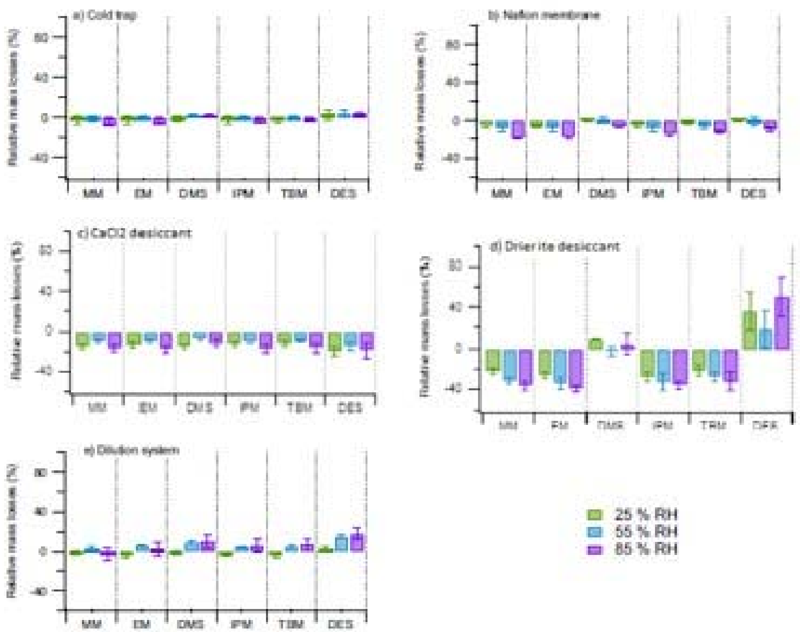


Compound	Can 1 Area	Can 2 Area	Can 3 Area	%RSD
H2S	32,651	76,850	100,339	40%
COS	246,016	222,242	244,822	5%
MM	16,273	211,579	334,367	70%
EM	0	117,738	158,982	73%
DMS	74,293	44,389	61,103	20%
DMDS	730,397	478,102	389,227	27%

Effect of RH on sulfur stability

- Silco and TO-Cans show similar performance at 0% RH, except for dimethyl sulfide
- High variability and low recoveries for mercaptans/hydrogen sulfide above 10% RH in SilcoCans, above 0% for TO-Cans
- SilcoCans show similar recoveries at 10% and 0% RH
- Silco and TO-Cans are stable for COS
- Dimethyl disulfide increases as other sulfurs decrease
  - Polymerization of mercaptans known to create larger sulfur compounds
- TO-Cans show consistent recoveries for dimethyl sulfide, SilcoCans show initial drop then stability for <50% RH

Dehumidification Methods



C. Merlen, et al, 2018. A preconcentration method based on a new sorbent for the measurement of selected reduced sulfur compounds at ppb level in ambient air. Microchemical Journal 143, 47-54

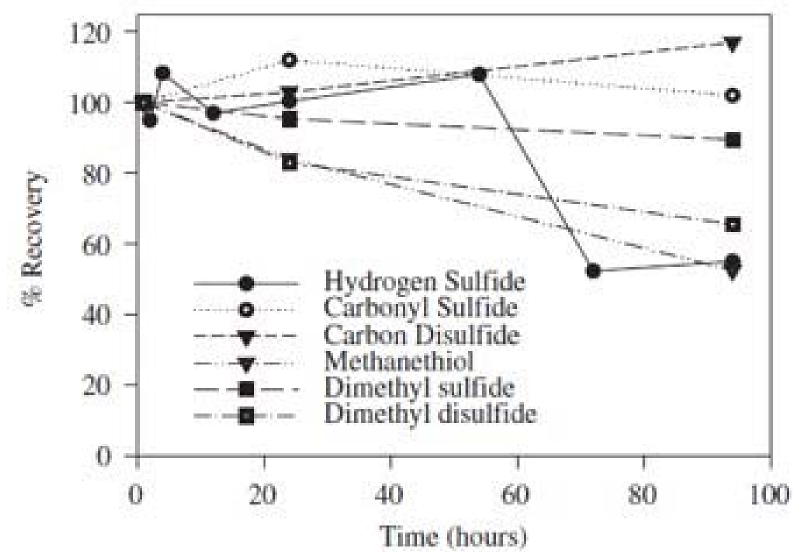


Fig. 4. Storage stability of reduced sulfur compounds in field samples after passing through calcium chloride drying tube.

S. Trabue, et al, 2008. Field sampling method for quantifying volatile sulfur compounds from animal feeding operations. Atmospheric Environment 42, 3332-3341

Dehumidification Methods

- Cold trap, nafion dryer, and dilution with dry air or nitrogen not practical for field sampling
- Replicate $CaCl_2$ dryer with refillable hydrocarbon trap/steel tubing

Dehumidification Methods

	% H2S	% COS	% MM	% EM	% DMS	% DMDS	Initial RH	Final RH
Hydrocarbon trap w/$CaCl_2$	65%	89%	44%	16%	13%	3%	50%	0%
10cm x ¼” SS w/$CaCl_2$	13%	109%	65%	46%	103%	54%	50%	0%
5cm x ¼” SS w/$CaCl_2$	112%	98%	118%	94%	100%	73%	50%	0%
2.5cm x ¼” SS w/$CaCl_2$	124%	100%	137%	121%	99%	79%	50%	0%

- Canister filled to 45 psig with 50% RH air and spiked with 50 ppb sulfur mix
- After initial analysis sample was passed through the drying column to a second canister and analyzed
- % RH of second canister was tested after GC analysis
- 2.5 cm tube held 0.3244 g CaCl2 and dried 9.6L of 89.5% RH to 0% RH (0.17 g H2O capacity)

Conclusions

- Sulfur stability in fused silica-lined cans under humid air conditions above 20% RH is very limited
- High variability between canisters at higher humidities
- Use of humid air for standards and blanks is recommended to match real samples
- Hydrogen sulfide and mercaptans convert into larger sulfurs (dimethyl sulfide, dimethyl disulfide, others) leading to both low and high biases
- Proper use of drying agents can reduce humidity and potentially extend sulfur lifetime
- Other compounds present in air samples may have unexpected effects on sulfur lifetime
- Minimizing time between collection and analysis is recommended

Other Sampling Methods

- Thermal desorption tubes are also affected by relative humidity
- ALTEF and foil bags suitable for some sulfurs only up to 24-48 hours per manufacturers recommendations
- Glass samplers are fragile and still prone to effects from humid air