Stability of Reduced Sulfur Compounds In Inert Glass Canisters

Application Note:

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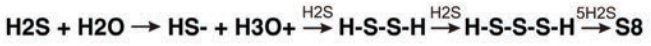
Abstract

Collection, storage, and analysis of reduced sulfur compounds can be complicated by their high volatility, reactivity, light sensitivity, and absorptive/adsorptive properties. Collecting whole air samples has previously been shown to be the method of choice for monitoring reduced sulfur compounds, as the reactive interactions between sample and strong solid adsorbent media is avoided. Tedlar bags have demonstrated only modest success for H2S and mercaptans due to their absorptive nature, resulting in acceptable storage times for H2S and CH3SH to be as little as 1 day or less. Traditionally, the cost of purchasing and transporting silica lined canisters has been a drawback for routine sampling of sulfur compounds in a number of applications, and silica lined canisters have also been shown to have stability issues at relative humidity levels above 25-30% RH.

A more economical deactivated glass container is presented that performs sampling using an internal vacuum, just like silica lined canisters. Two different approached for handling sample moisture to improve sulfur compound stability during storage were investigated to see their relative effects on sulfur compound recovery after a 3 day holding time.

Introduction

Reduced sulfur compound analysis at low and sub-PPB levels has presented many challenges to analytical chemists. Both alkyl mercaptans and hydrogen sulfide have demonstrated poor recoveries, poor precision, and overall low confidence in analytical results when sampled in tubes and Tedlar bags. Silica lined canisters have also shown variable recoveries which are highly dependent on the relative humidity of the sample. As humidity increases, the recovery from silica lined canisters decreases. It is believed that water adhering to the surface when relative humidities climb above about 20% RH causes loss of sulfur compounds via the following mechanism:



$$H_2S + H_2O \rightarrow HS^- + H_3O^+ \xrightarrow{H_2S} H\text{-}S\text{-}S\text{-}H \xrightarrow{H_2S} H\text{-}S\text{-}S\text{-}S\text{-}H \xrightarrow{5H_2S} S_8$$

When Mercaptans are involved in the same mechanism, the result can be a series of di-, tri-, or larger sulfide chains depending on whether the reaction occurs between 2 mercaptans, or a mercaptan and H2S, leaving an acidic proton to be eliminated in another chain lengthening condensation reaction. The presence of both water and reactive Si-OH groups on the surface of glass or silica seem to catalyze this reaction. Other loses of sulfur compounds can occur due to reaction with metals which are common in untreated glass, and of course on untreated stainless steel surfaces.

A sampling container called a Bottle-Vac has provided an economical means of collecting Volatile compounds for subsequent GCMS analysis in the laboratory. Bottle-Vac samplers use a “Micro QT Valve” that allows these bottles to be treated like stainless steel canisters. Cleaning is performed through a series of fill/evacuation cycling, with a final vacuum left in the canister to allow easy sampling in the field by just opening the valve. Bottle-Vac samplers have been shown to be very effective in collecting and storing VOCs and Microbial VOCs. Research to validate their use for sulfur compounds was the next logical step. Bottle-Vac samplers are available with amber glass or with Silonite coated clear glass. Various deactivation steps have been studied for covering up the impurities when using amber glass, whereas the Silonite coated bottles already have a pure layer of silica that is applied to cover the reactive glass surface. Two approaches were studied to reduce the loss of sulfur compounds due to reaction with surface bound water.

For this study, 500mL amber Bottle-Vacs and Silonite coated clear glass Bottle-Vacs were used. In one set of Bottle-Vacs, 0.1g of Silica Gel was added to act as a dessicant to prevent the formation of surface bound water when collecting samples ranging from 10-100% Relative Humidity. In a second approach, Bottle-vacs were filled to 0.75 atmospheres with dry nitrogen, resulting in a 4:1 dilution upon sampling. A sample initially at 80% RH would then be effectively 20% RH in the bottle. The original concentration can be determined by multiplying the analytical data by 4x to obtain the original concentration.

Experimental

Standards were prepared by diluting a stock 2-5 PPM cylinder standard (HP Gas, Houston, TX) to 5 PPB using a 4600A Dynamic Diluter (Entech Instruments, Simi Valley, CA). A cylinder standard containing H_2S, CH_3SH, COS, CS_2, and Dimethylsulfide was blended with UHP nitrogen into a Tedlar bag which was spiked with additional water to bring the humidity to about 70%. Immediately, Bottle-Vac samplers that had been prep'd on a 3100A canister cleaning system (Entech Instruments) were connected to the bag to quickly draw in the sample to fill the bottles to atmospheric pressure. Two types of bottles were used, amber and Silonite coated, and 3 conditions were studied;

1. Bottle-Vac filled to atmospheric pressure with 70% RH Sulfur standard to test recovery after 3 days.
2. Bottle-Vac with 0.1 g drying agent, filled to atmospheric pressure with 70% Sulfur std to test after 3 days.
3. Bottle-Vac filled initially to 0.75 atm absolute with dry N_2, then filled to 1 atm with 70% RH Sulfur Std, providing a 4x dilution.

The mixture was allowed to sit for 3 days prior to analysis on a 7100A Preconcentrator (Entech Instruments) with a 6890/5973 GCMS (Agilent, Palo Alto, CA). An aliquot of 200cc was drawn into the 7100A and preconcentrated using Extended Cold Trap Dehydration which is capable of eliminating water vapor without loss of the sulfur compounds. Final focusing of the sample down to a few microliters permitted split-less injection of the original sample, with ultimate detection limits reaching 0.2 PPB or less. Samples were introduced directly into the 7100A through one of the 4 direct sample inlets, or by using the 7500 robotic autosampler to provide multi-sample automation.

Discussion

Figure 1 and **2** show the analytical system used to perform the analysis. Water elimination was performed using Cold Trap Dehydration in the Entech 7100A, which effectively eliminates water without loss of sulfur compounds by preventing interaction of the sample with liquid water during the dehydration step. **Figure 3** gives a close-up view of the 500mL Bottle-Vac samplers with the vacuum tight microvalve inlets. Both amber and Silonite coated bottles are shown on the left and right, respectively. **Figure 4** is a typical chromatogram obtained with the analytical system, showing extremely good signal to noise at 5 PPB. Detection limits with this system is roughly 25-50 times lower.

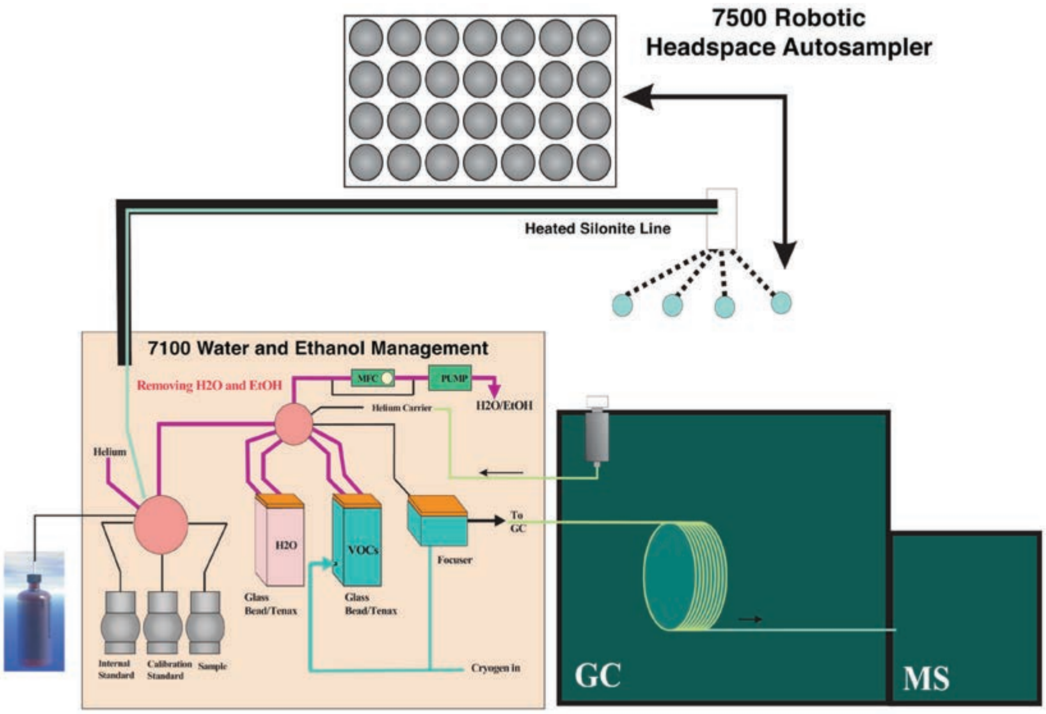


Figure 1

Figure 2 - 7500/7100A/6890/5973 Sulfur Analyzer with Bottle-Vac Glass Canisters

Figure 3 - Amber and Silonite Coated Bottle-Vac Glass Canisters used for Sulfur Stability Study

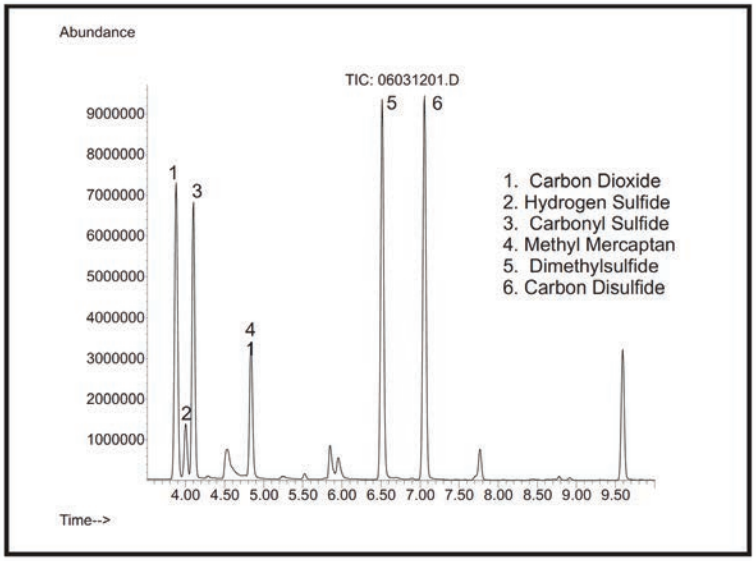
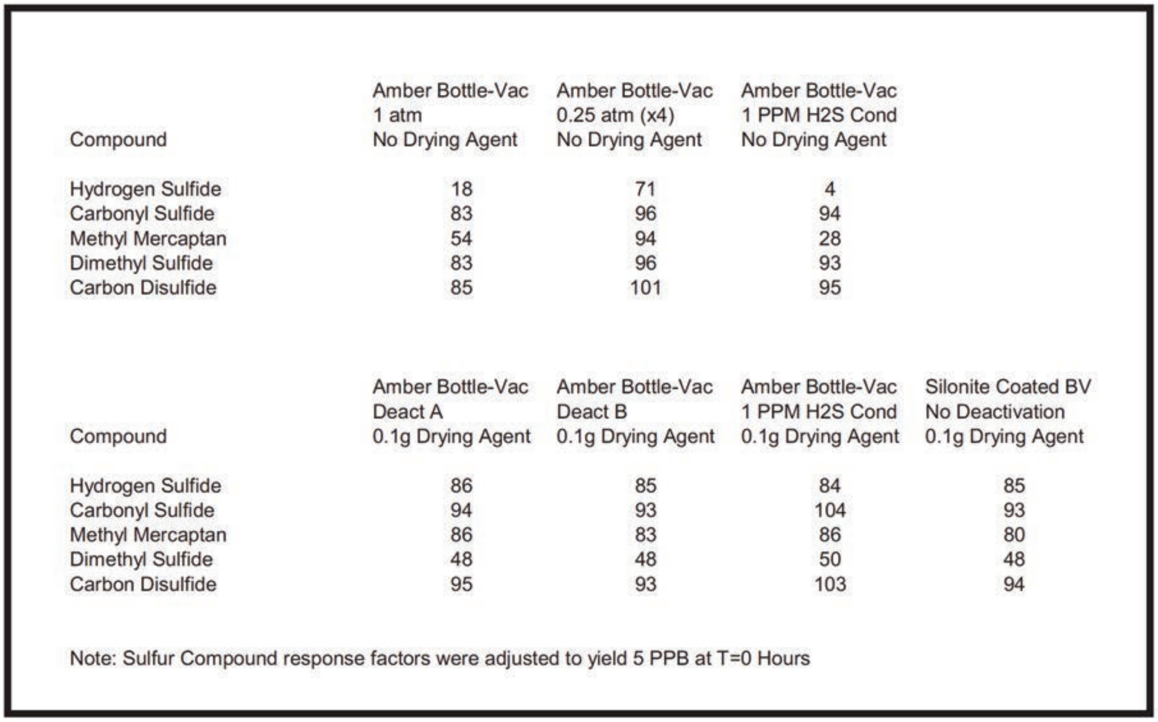


Figure 4 - Sulfur standard at 5 PPB

Figure 5 shows the results obtained for a 3-day stability test for Bottle-Vacs with not water management, with the drying agent added, and with the 4:1 dilution in dry UHP Nitrogen. Due to the interaction of water on the surface of the bottles at 70% RH, H2S recovery was severely affected (18% recovery). By diluting the sample by a factor of 4 with dry Nitrogen and then multiplying the results by 4, the H2S recovery was much higher at 71%, as was the methyl mercaptan at 94%. Interestingly, attempting to deactivate the Bottle-Vac by pre-exposing the bottle to 1 PPM H2S for 1 hour prior to filling with the 5 PPB standard offered no improvement in increasing stability, with H2S dropping off to just 4% at 70% RH in 3 days.

Adding drying agent to the bottles showed major improvement in the H2S and methyl mercaptan stability. Recoveries of H2S and methyl mercaptan were very acceptable at about 85%. However, the dimethylsulfide fell off to around 50% in all cases, probably due to absorption into the drying agent. Therefore, the use of a Silica Gel drying agent should only be considered for the analysis of light sulfur compounds, including H2S, CH3SH, CS2, and COS.



Compound	Amber Bottle-Vac 1 atm No Drying Agent	Amber Bottle-Vac 0.25 atm (x4) No Drying Agent	Amber Bottle-Vac 1 PPM H2S Cond No Drying Agent
Hydrogen Sulfide	18	71	4
Carbonyl Sulfide	83	96	94
Methyl Mercaptan	54	94	28
Dimethyl Sulfide	83	96	93
Carbon Disulfide	85	101	95

Compound	Amber Bottle-Vac Deact A 0.1g Drying Agent	Amber Bottle-Vac Deact B 0.1g Drying Agent	Amber Bottle-Vac 1 PPM H2S Cond 0.1g Drying Agent	Silonite Coated BV No Deactivation 0.1g Drying Agent
Hydrogen Sulfide	86	85	84	85
Carbonyl Sulfide	94	93	104	93
Methyl Mercaptan	86	83	86	80
Dimethyl Sulfide	48	48	50	48
Carbon Disulfide	95	93	103	94

Note: Sulfur Compound response factors were adjusted to yield 5 PPB at T=0 Hours

Figure 5 - Sulfur stability data in Bottle-Vac samplers. A 5 PPB standard was prepared in a Tedlar bag at 70% RH and immediately transferred into Bottle-Vac Sampler with andand without drying agent

Conclusion

The Bottle-Vac samplers were shown to be effective for the sampling, 3-day storage, and subsequent analysis of several reduced sulfur compounds, including H2S. Results clearly indicated the importance of keeping sulfur compounds away from water during storage, using either dilution or the utilization of a drying agent showing dramatic increases in the recovery of H2S and methyl mercaptan. Dilution into dry nitrogen did not increase recovery of H2S as much as adding the drying agent, but it did show a better recovery of both the methyl mecaptan and the dimethylsulfide. When having to recover a wide range of VOCs, including H2S and Methyl Mercaptan, the dilution method should be strongly considered if everything must be analyzed in a single analysis. The determination of Freon 12 that is in most places globally at 0.45 PPBv can be used to confirm the dilution factor. In addition, stack gas collection into a bottle that is initially at 80 or even 90% filled with dry nitrogen can prevent the condensation of water in the bottle, thereby improving the analysis of polar compounds Weighing the bottle under vacuum, when at 80-90% filled with N2, and finally after sampling can provide an extremely accurate determination of the dilution factor, considering that 1 liter of air at atmospheric pressure weighs about 1200 mg per liter.

This data was generated previously on an Entech 7500A/7100A instrument, which has now been replaced by a superior solution (Entech 7650-M/7200-01). With the new solution, volume measurement accuracy and flow path inertness have both been improved, allowing the analysis of sulfur compounds on a more routine basis, as long as water has been managed directly inside of the Bottle-Vac or Silonite Canister.

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