



Accurate Monitoring of Sulfur Compounds in Silonite™ Fused Silica Lined Canisters Utilizing a New Approach for Water Removal During Field Sampling

Application Note: Sulfur Compound Monitoring

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Abstract

Glass and Silonite™ ceramic treated stainless steel canisters offer higher recoveries of TO-15 Compounds than many other sampling devices, including electropolished canisters, Tedlar® bags and thermal desorption tubes. Recovery of H₂S and light Mercaptans are still problematic however, primarily due to a surfaced induced condensation reaction that occurs when enough water exists on the surface to allow dissociation of the acidic proton found in these light, reduced sulfur compounds. Even at relative humidities as low as 30%, a water layer can exist on the surface to catalyze these reactions. Independent laboratories have attempted canister use for routine reduced sulfur compound monitoring and found less than optimal recoveries, even with holding times as short as 1 to 2 days.

It is well known that dropping the water content to below 10% RH in glass bottles and Silonite™ treated stainless steel canisters allows for excellent long term

storage of these light sulfur compounds. Unfortunately, the practical application of water management in the field has been limited. A new approach is presented here utilizing a Cold Trap Dehydration (CTD) technique to eliminate most water content in a sample prior to introduction into a glass or Silonite™ canister.

Introduction

Current techniques for Hydrogen Sulfide (H₂S) monitoring involve the use of field instruments, adsorbent tubes, Tedlar® bags, or fused silica treated canisters for sampling. All of these techniques present various challenges; field instruments can have false positives for H₂S and are only good for ppm levels. Adsorbent tubes can degrade H₂S, making sample recoveries questionable. Tedlar® bags are limited to a 24 hour holding time and recovery is variable, even given this short time frame. Fused silica lined canisters can provide excellent recoveries relative to other techniques, but often show poor recovery after 1-2 days when relative humidity is above 30%.

Sampling into glass and Silonite™ treated canisters does present several advantages which make canister use for sulfur monitoring very attractive. This includes the ability to recover all TO-15 compounds. Canisters are very rugged, inert, and have an increased holding time if the relative humidity can be kept below 30%. Different dehydration techniques have been evaluated, including Nafion® dryers (*not TO-15 friendly*) and sample dilution with dry nitrogen after collection (*Sample dilution has an adverse affect upon detection limits*). Using Cold Trap Dehydration (CTD) to remove water during sample introduction into the canister has shown to be the most effective technique for sulfur compound collection and analysis.

The Cold Trap Dehydration (CTD) sampling method solves the canister storage challenge by dehydrating the sample in the field during sample collection. CTD is used to drop the water content down to a -30°C to -40°C dew point during the sampling process. Grab sampling is accomplished using a small container of liquid CO_2 that is vented around a section of the inlet line just prior to sampling in order to achieve the required dehydration temperatures. At temperatures between -30°C to -40°C , all TO-15 compounds are recovered quantitatively, allowing for complete monitoring analysis including any present light sulfur compounds. This sampling approach will be presented in the following pages, including data showing stability of low humidity H_2S and sulfur compounds within a 2-4 week range.

Experimental

Various dehydrating techniques have been employed and evaluated. Techniques include: Nafion[®] dryer, dilution with dry nitrogen, the inclusion of silica gel within Bottle-Vac[™] samplers, and field sampling into canisters using CTD. The focus for this paper is the evaluation of Cold Trap Dehydration (CTD) during field sampling. Several canisters, including MiniCan[™] and Bottle-Vac[™] samplers, were used to collect samples of H_2S and other sulfur compounds. The collection process is shown in **Figure 1**. A small liquid carbon dioxide (LCO_2) cylinder is filled in the laboratory, providing 3.5 ounce of liquid CO_2 to cool down a flow path section to about -30°C . This is cold enough to condense out water while still allowing H_2S and the full range of TO-15 compounds to pass through. The canister is then connected to the outlet of this flow path to collect a grab sample.

The sample was prepared in a 10L Tedlar[®] bag. A 40 ppbv mixture of sulfur compounds was diluted using a 4600A Dynamic Diluter (Entech Instruments, Inc., Simi Valley, CA). The humidifier was bypassed so that a known amount of water could be added to create a known % Relative Humidity in the bag. 150 μL of water was added to the 10L tedlar bag with the 40ppbv mixture yielding 70% relative humidity. This standard was used within 1 hour of preparation to avoid any significant losses of H_2S . Dry standards were collected into canisters to create a calibration standard for comparison with humidified samples. Analysis was performed using a 6890/5973 GCMS (Agilent Technologies, Inc., Palo Alto, CA), operated in full scan mode. A 7100A Volatiles Preconcentrator (Entech Instruments, Inc., Simi Valley, CA) was utilized to concentrate 100cc of sample in order to gain required sensitivity to accurately detect ppbv levels of sulfur components.



Figure 1 - A CO_2 Cylinder is attached to the cooling tee during sample collection into a 1.4L MiniCan[™].

Alternative Dehydration Techniques – % Recovery

Compounds of Interest	Bottle 1 Atm No Drying Agent	Bottle 0.25 Atm 4x Dilution w/ Dry N ₂	Bottle A 0.1g Silica Gel	Bottle B 0.1g Silica Gel
H ₂ S	18	71	86	85
COS	83	96	94	93
CH ₃ S	54	94	86	83
DMS	83	96	48	48
CS ₂	85	101	95	93

Table 1 - Other techniques of dehydration also show good recovery of H₂S, but with some limitations, such as diluted sample volume and low recovery of heavier compounds (as seen with addition of silica gel).

Discussion

The data reveals substantial H₂S stability improvement when water is removed during the sampling process. Results in **Table 2** show unacceptable H₂S recovery after only three days when samples are contained at 70% relative humidity. Techniques displayed in **Table 1** are effective, but with some limitations. Drying the sample by only collecting 1/4 of the sample and then filling the canister with dry nitrogen does keep H₂S stable, but requires having a source of dry nitrogen in the field and dilutes the sample by a factor of 4. The use of silica gel to dehydrate the sample only works with disposable glass Bottle-Vac™ samplers and will affect the accurate recovery of heavier compounds, therefore a full list of VOCs cannot be sampled at the same time. **Table 3** displays the effectiveness of CTD in the field for water removal and the resultant stability of H₂S. This process creates a reliable canister environment for H₂S vapor sampling and has many important applications, particularly in the petroleum industry. A laboratory with the most reliable analytical instrumentation to detect H₂S must still depend upon trustworthy sample collection in the field and storage before analysis – If H₂S degrades before an analysis can be performed, the resulting analytical data is meaningless. Using a Cold Trap Dehydration technique during sample collection into MiniCan™ or Bottle-Vac™ containers ensures trustworthy sample storage and optimal analytical accuracy for H₂S, other sulfur components, and quantitative VOC collection when monitoring vapor matrices.

Non-Dehydrated Canisters

% of H₂S Recovery (3 Day Holding Time)

MiniCan™/Bottle-Vac™	% H ₂ S Recovery (40 ppbv)
1.4L MiniCan™ – 1	63
1.4L MiniCan™ – 2	49
1.4L MiniCan™ – 3	55
1L MiniCan™ – 1	37
1L MiniCan™ – 2	39
1L MiniCan™ – 3	43

Table 2 - Non-dehydrated canisters – Only 3 days after sample collection, analysis reveals low recovery of H₂S.

Dehydrated Canisters

% of H₂S Recovery (17 Day Holding Time)

MiniCan™/Bottle-Vac™	% H ₂ S Recovery (40 ppbv)
1.4L MiniCan™ – Dry Std.	97
1.4L MiniCan™ – 1	102
1.4L MiniCan™ – 2	91
1.4L MiniCan™ – 3	93
1L MiniCan™ – 1	83
1L MiniCan™ – 2	83
1L MiniCan™ – 3	95

Table 3 - After 17 days of sample storage H₂S is proven to be very stable as long as the sample is kept dry.

Chromatogram – Sulfur Standard

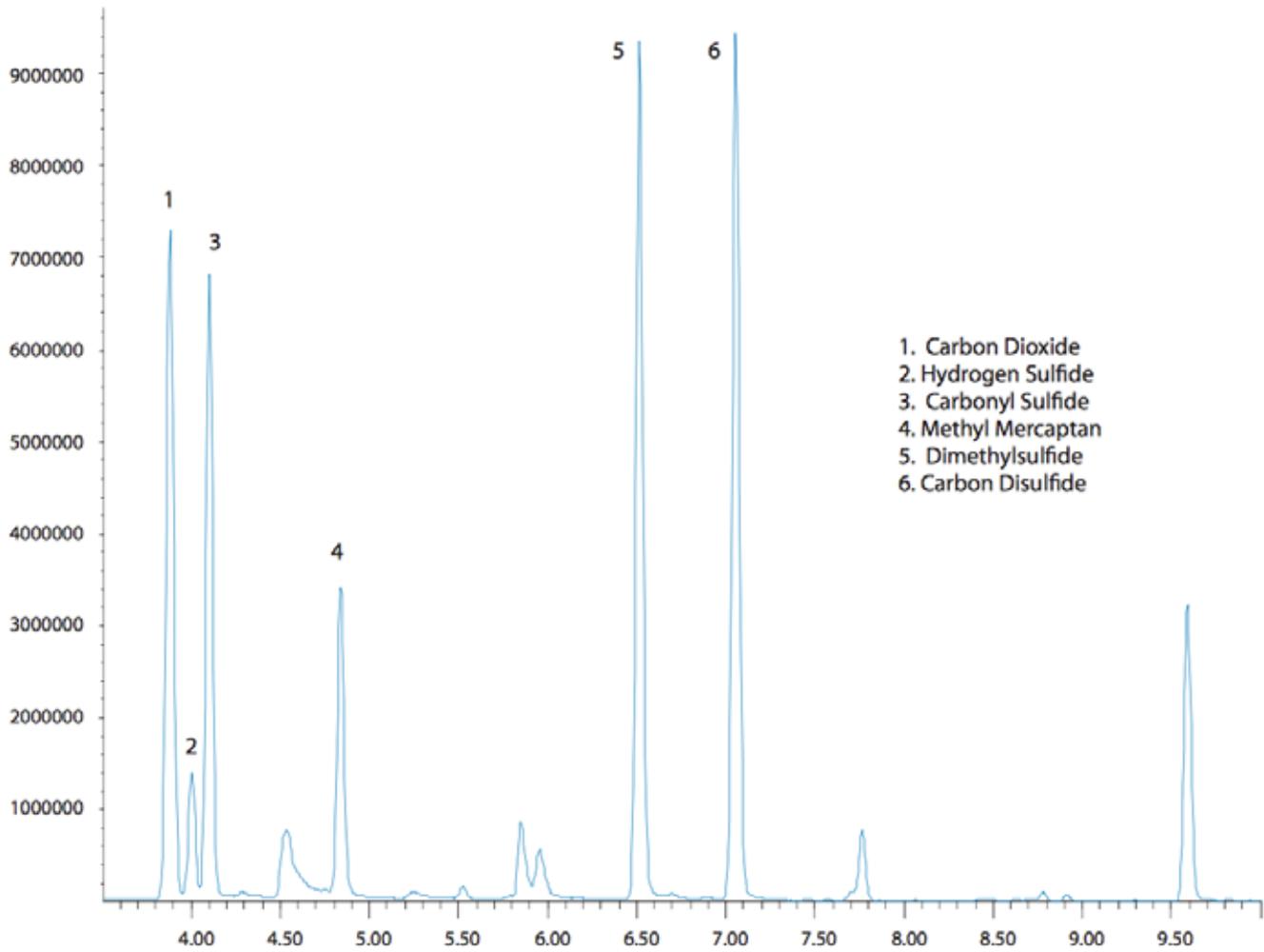


Figure 2 - 40ppbv Sulfur Standard (after 17 day holding time).

Conclusion

We have shown results of H₂S recovery when water vapor is present and it is clear that this data can lead to inaccurate reporting of H₂S concentrations in vapor monitoring. **Table 2** data at 70% RH shows some improvement from past reports that show even lower recoveries. Continued improvements in Silonite™ ceramic surface inertness for sampling canisters has helped in creating a much more stable atmosphere, but there is still more work to do before canisters can demonstrate reliable recoveries from a wet matrix. For now, we have a proven solution that effectively removes water as the vapor sample is pulled into the canister by lowering the temperature of the flow path and condensing out the water. Not only is this technique useful for sulfur components, but also for all components routinely monitored by EPA method TO-15. Compounds can now be quantitatively analyzed from the same canister sample, simplifying sample collection strategies – which in turn can significantly lower the cost of air and vapor monitoring for chemical pollutants in environmental and industrial applications.

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