air monitoring

#59347

Applicationsnote

Stability Study of Low-Level (1ppb-20ppb) Reactive Sulfurs in SilcoCan™ Canisters

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. These sulfur compounds not only can react with each other but also with the vessels in which they are collected. This results in low recoveries of compounds such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), ethyl mercaptan (C_2H_3SH), and dimethyl disulfide (CH_3SSCH_3).

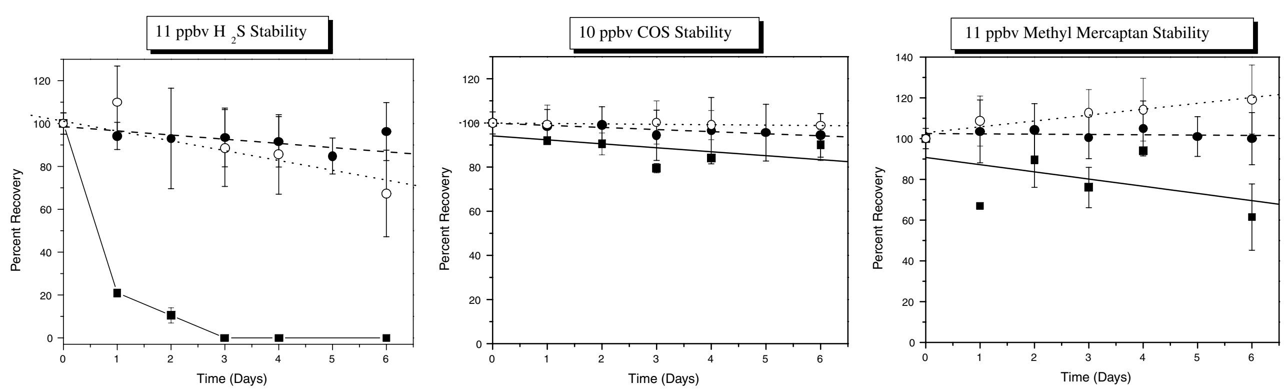
Tedlar bags traditionally have been used for collecting sulfur VOCs; however, the stability of low-level (100ppbv) sulfur VOCs is poor within 24 hours of sampling.[1] It is well documented that electropolished canisters (e.g., SUMMA® canisters) are excellent for storing VOCs in ambient air, however the sulfur compounds react with the metal surface so these canisters are unsuitable for collecting and storing low-level sulfur VOCs.[2] SilcoCan™ air monitoring canisters, which feature a Silcosteel®-treated surface, increase the storage stability of low-level sulfur VOCs. This study evaluated the stability of sulfur VOCs within SilcoCan™-canisters at very low levels (1–20ppbv) for six days. A comparison study of dry vs. humidified standards demonstrates the ability of SilcoCan™ canisters to store low-level sulfur VOCs in real-world conditions (Figure 1).

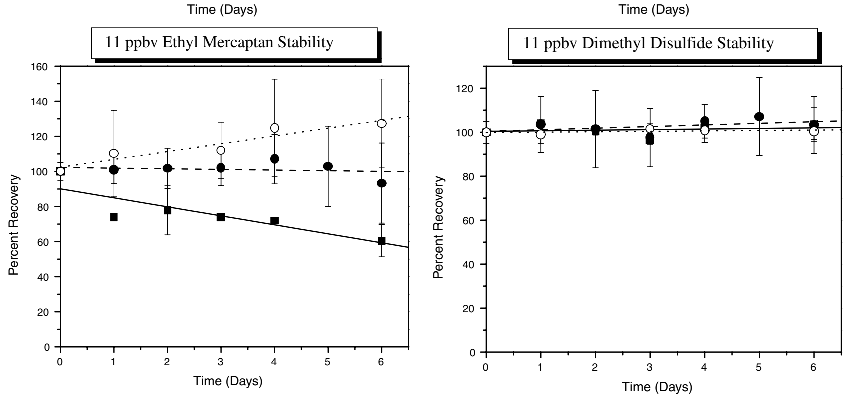
Analytical System

High resolution capillary gas chromatography (GC) offers many advantages for performing trace analysis of sulfur VOCs in conjunction with sensitive, selective detectors such as a sulfur chemiluminescence detector (SCD) or a flame photometric detector (FPD). For this study, an Rtx®-1 capillary column was used along with a Silcosteel™ treated six-port Valco® valve, and a Silcosteel® 1mL sample loop and 1/16" sample pathway (Figure 2).

Figure 1

Stability data demonstrates ability of SilcoCan™ canisters to store low-level organic sulfur compounds in real-world conditions.





Conditions

GC:	HP 5890GC
Column:	Rtx-1, 60m, 0.53mm ID, 7.0µm, (cat.# 10193)
Det.:	Sievers Model 355 SCD
Temp.:	30°C (hold 1.0 min.) to 180°C @ 10°C/min. (hold 5 min.)
Flow rate:	8.5mL/min.
Sample:	1mL sample loop of 11ppbv

● Dry SilcoCan™ (n=18)
○ Humidified SilcoCan™ (n=5)
■ Electropolished (n=2)

Standards:
Dry standards were made by taking 2mL of a 100ppm stock sulfur standard and adding it to each precleaned and evacuated canister, then pressurizing to 30psig with ultra-pure nitrogen. The resultant concentrations are listed in Table I. Humidified standards were made by injecting the evacuated canisters with 100µL of deionized water prior to adding the 2mL aliquot of stock standard. This resulted in 50% RH.

air monitoring

Stability Test

A reference standard was made at 55ppbv and analyzed three times each day for six days. The concentration of the sulfurs was 11ppbv. Dimethyl sulfide was used as the internal standard. Eighteen SilcoCan™ canisters and two electropolished canisters were used for this study. The results showed excellent stability of each of the low-level sulfur VOCs in the dry standard for the SilcoCan™ canisters. The electropolished canisters exhibit rapid degradation of hydrogen sulfide, methyl mercaptan, and ethyl mercaptan (Figure 1).

Humidity Effects

Five SilcoCan™ canisters that were used in the stability test were cleaned according to US Environmental Protection Agency (EPA) Compendium of Toxic Organic Method TO-14 and resubmitted for the humidity study.[3] After adding 100µL of deionized H_2O to each canister, the resultant relative humidity was 50%. Two mL of the stock sulfur standard was added to each canister and analyzed over six days (Figure 1). The results show no difference in the performance the SilcoCan™ canisters for storing humidified sulfur VOCs as compared to dry standards.

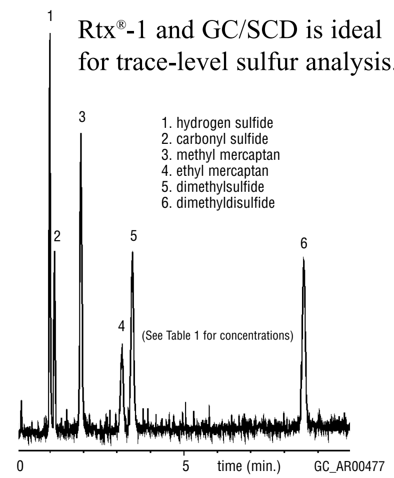
Conclusion

This study investigated the stability of very low-level sulfur VOCs (1-20ppbv) in SilcoCan™ and electropolished canisters, using both dry nitrogen and humid conditions. The electropolished canisters exhibit degradation of reactive sulfur VOCs such as hydrogen disulfide, methyl mercaptan, and ethyl mercaptan. Both dry and humidified 11ppbv sulfur exhibited virtually no breakdown or reactivity in SilcoCan™ canisters after six days.

Table 1

Compound	Stock Conc. (ppmv)	Standard Conc. (ppbv)	Standard Conc. as Sulfur (ppbv)
hydrogen sulfide (H_2S)	105	11.51	10.83
carbonyl sulfide (COS)	98	10.74	5.73
methyl mercaptan (CH_3SH)	101	11.07	7.38
ethyl mercaptan (CH_3CH_2SH)	101	11.07	5.71
dimethylsulfide (CH_3SCH_3)	99	10.85	6.81
dimethyldisulfide (CH_3SSCH_3)	100	10.96	7.46

Figure 2



Rtx-1, 60m x 0.53mm ID x 7.0µm (cat.# 10193)
Oven temp.: 30°C (hold 1 min.) to 180°C @ 10°C/min. (hold 5 min.); **Carrier gas:** helium; **Flow rate:** 8.5mL/min.

Product Listing

SilcoCan™ Canisters

Sizes (L)	cat.#
1.0	24112
3.0	24113
6.0	24114
15.0	24115

Rtx®-1 GC Column (Fused Silica)

ID	0.53
df (µm)	7.00
temp. limits	-60 to 240/260°C
length	60-meter
cat.#	10193

Restek offers SilcoCan™ accessories and other Rtx®-1 column dimensions. To see the complete product listing, please request our Annual Chromatography catalog.

References

1. Quang Tran, You-Zhi Tang; Stability of Reduced Sulfur Compounds in Whole Air Samplers, 1994 AWMA/EPA International Symposium of Measurement of Toxic and Related Air Pollutants.

2. Hoyt, Steven; Longacre, Vivian; and Stroupe, Michale; Measurement of Oxygenated Hydrocarbons and Reduced Sulfur Gases by Full Scan GC/MS: EPA TO-14; Sampling and Analysis of Airborne Pollutants, Eric Winegar, Lawrence Keith.

3. Method TO-14A, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography; Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Jan 1997.

References not available from Restek.

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