USE OF SILCOCAN™ CANISTERS FOR STORING LOW-LEVEL (1ppb-20ppb) REACTIVE SULFURS IN AIR

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INTRODUCTION

Analysis of sulfur-containing volatile organic compounds (VOCs) such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), ethyl mercaptan (C_2H_3SH), and dimethyl disulfide (CH_3SSCH_3) has become important because of health concerns and complaints about odors near manufacturing sites and refineries. Collection and measurement of these compounds in the atmosphere is very difficult because of their low concentrations and high reactivity. These sulfur compounds can react not only with each other, but also with the vessels in which they are collected, resulting in low recoveries.

Tedlar® bags traditionally have been used for collecting sulfur VOCs; however, the stability of low-level (≤100ppbv) sulfur VOCs is poor, even within 24 hours of sampling.[1] Electropolished canisters (e.g., SUMMA® canisters) are excellent for storing VOCs in ambient air, but sulfur compounds react with the metal surface, making these canisters unsuitable for collecting and storing low-level sulfur VOCs.[2] SilcoCan™ air monitoring canisters, which feature a Silcosteel® treated surface, greatly increase the storage stability of low-level sulfur VOCs.

This study is twofold. The purpose of Experiment 1 was to demonstrate the suitability of SilcoCan™ canisters for storing very low levels (1-20ppbv) of reduced sulfurs. This was accomplished by quantifying several sulfur compounds daily during storage in SilcoCan™ canisters. Experiment 2 was designed to study the effects of various canister cleaning processes on subsequent suitability of the canisters for storing sulfur compounds.

ANALYTICAL SYSTEM

High resolution capillary gas chromatography (GC), in conjunction with a sensitive, selective detector such as a sulfur chemiluminescence detector (SCD) or a flame photometric detector (FPD), offers many advantages for trace analysis of sulfur VOCs. For this study, a 60m x 0.53mm ID x 7.0µm dimethyl polysiloxane (Rtx®-1) capillary column was used, along with a Sulfinert® treated six-port Valco® valve, a Sulfinert® treated 1mL sample loop and 1/16" sample pathway, and a Sievers SCD. Figure 1 is a block diagram of the analytical setup used for both experiments. Figure 2 is a chromatogram of the reduced sulfurs standard on the Rtx®-1 column.

Figure 1. Block diagram of analytical system.

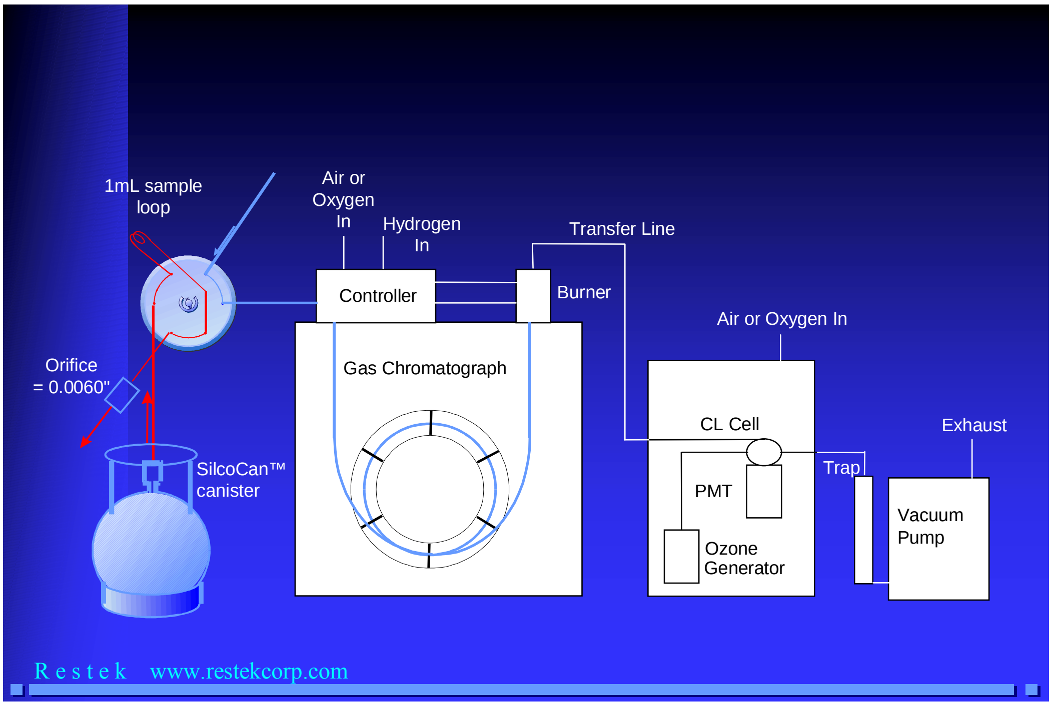
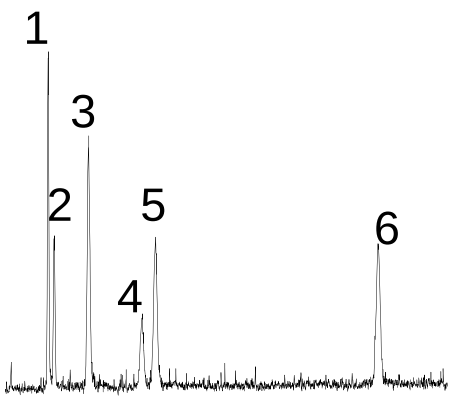


Figure 2. Reduced sulfurs on 60m x 0.53mm ID x 7.0µm Rtx®-1 column.



1. H_2S
2. COS
3. methyl mercaptan
4. ethyl mercaptan
5. dimethyl sulfide
6. dimethyl disulfide

EXPERIMENT 1: INITIAL STABILITY STUDY

Eighteen SilcoCan™ canisters and two electropolished canisters were used for this study. The sulfur standard consisted of the compounds listed in Table 1, at 100ppmv each, provided by DCG Partnership. Dimethyl sulfide was the internal standard. A 55ppbv calibration/reference standard made from the stock standard was analyzed three times each day for six days to ensure the system was in control. Subsequently, dry test standards were made by diluting the stock standard, using a 2mL Sulfinert® treated sample loop, aliquots were introduced into the evacuated canisters, and the canisters were pressurized to 30psig. The resulting concentration of the sulfurs was 11ppbv.

Table 1. Target sulfur compounds.

Compound	**Formula**	**Stock Conc. (ppmv)**	**Standard Conc. (ppbv)**	**Standard Conc. as S (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
dimethyl sulfide	CH_3SCH_3	99	10.85	6.81
dimethyl disulfide	CH_3SSCH_3	100	10.96	7.46

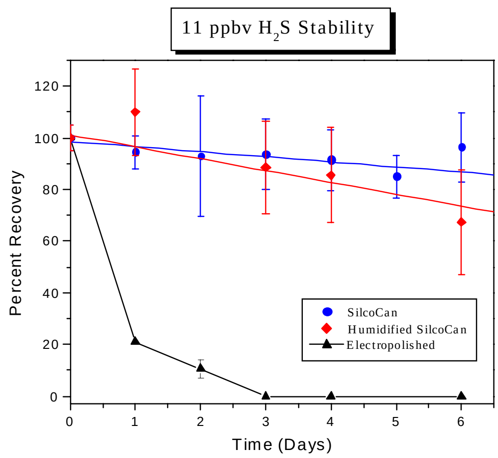
HUMIDITY EFFECTS

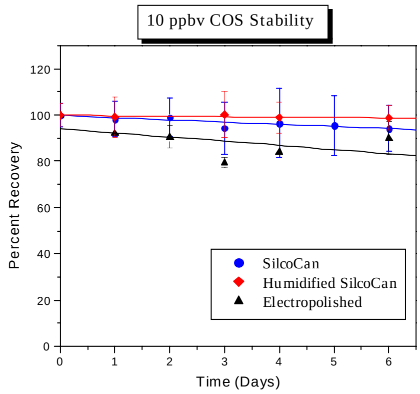
Five SilcoCan™ canisters that were used in the stability test were cleaned according to US Environmental Protection Agency (EPA) Compendium of Toxic Organics Method TO-14, then were used in a humidity study.[3] After 100µL of deionized water was added to each canister, the resulting relative humidity was 32%. 2mL of the stock sulfur standard was added to each canister, then was analyzed over six days. Data indicated the 32% RH was too low to affect stability values. Consequently, in Experiment 2, we increased the RH to 44% by adding 135µL of deionized water to each canister.

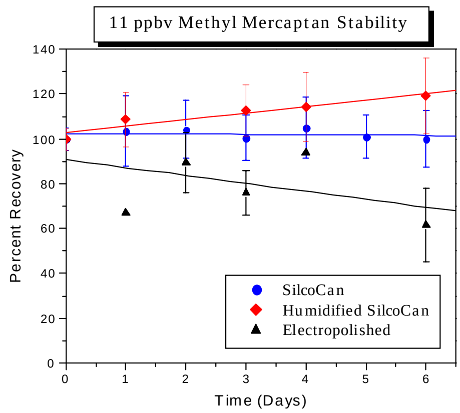
RESULTS AND DISCUSSION: EXPERIMENT 1

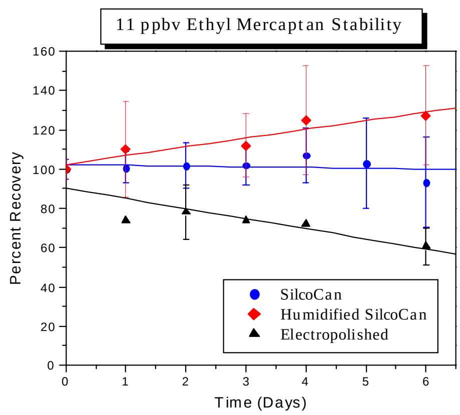
Figure 3 shows the results of the stability study, by compound. These results indicate that H_2S is the most reactive of the compounds used in this study. The results also indicate SilcoCan™ canisters are very suitable for storing low levels of these reactive sulfurs for several days, and that electropolished canisters (SUMMA® canisters) are not suitable for storing sulfur compounds such as H_2S.

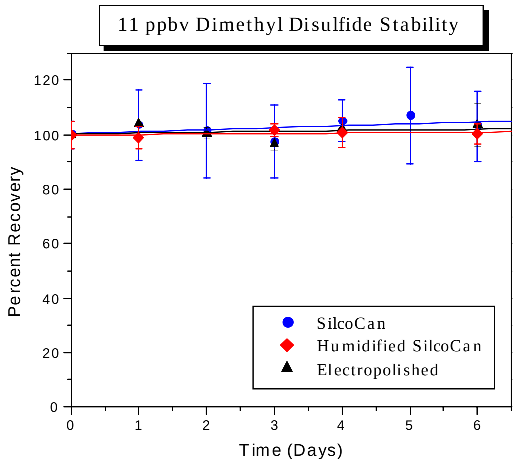
Figure 3. Stability of 11ppbv volatile sulfur compounds in SilcoCan™ canisters and electropolished canisters, under dry or humid conditions.




10 ppbv COS Stability
Percent Recovery
Time (Days)
SilcoCan
Humidified SilcoCan
Electropolished


11 ppbv Methyl Mercaptan Stability
Percent Recovery
Time (Days)
SilcoCan
Humidified SilcoCan
Electropolished


11 ppbv Ethyl Mercaptan Stability
Percent Recovery
Time (Days)
SilcoCan
Humidified SilcoCan
Electropolished



FURTHER DISCUSSION LEADING TO EXPERIMENT 2

Experiment 1 was designed to evaluate the stability of low-level sulfur VOCs (1-20ppbv) in SilcoCan™ and electropolished canisters, under both dry and humid conditions. At a concentration of 11ppbv, hydrogen disulfide, methyl mercaptan, and ethyl mercaptan degraded in electropolished canisters. In contrast, these compounds exhibited good stability in SilcoCan™ canisters, under both dry and humid conditions, after six days. There is concern, however, about canisters "aging" over time, and consequent effects on the ability to store sulfur compounds.[4]

Many factors might affect a canister's long-term performance, including handling of the canister prior to sampling, the matrix and composition of collected samples, and the cleaning procedure employed after the canister is used. In Experiment 2 we evaluated the effects of cleaning conditions. Some laboratories follow US EPA or other guidelines for cleaning canisters, many laboratories develop their own cleaning processes; some analysts use humidified nitrogen, others use humidified air; some heat the canisters, others do not. Experiment 2 was designed to compare the subsequent performance of canisters cleaned with humidified nitrogen or humidified air at various temperatures.

EXPERIMENT 2: EXPERIEMNTAL DESIGN

The purpose of Experiment 2 was to determine the effects of various cleaning processes on the suitability of a canister for storing low-level sulfurs. Ten new SilcoCan™ canisters were used, and 6 cleaning phases, described in Table 2, were designed. Phase 1 was used to qualify the canister, as in Experiment 1. Phase 2 was to reevaluate the humid standard, but at higher humidity (44% RH) than used in Experiment 1. Once the SilcoCan™ canisters were qualified, we began the various cleaning processes. In Phase 3, we baked the 10 canisters at 80ºC with humidified nitrogen for 2 hours, re-cleaned the canisters using our standard cleaning process (pressurize with humidified nitrogen, then evacuate; repeat cycle several times) which does not involve heat, then retested the canisters with the sulfurs standard. In Phase 4, we baked the canisters at 125ºC with humidified nitrogen for 2 hours, re-cleaned the canisters using our standard cleaning process, then retested the canisters with the sulfurs standard. In Phase 5 and Phase 6 we used humidified air and baked the canisters at 80ºC or 125ºC, respectively.

Table 2. Cleaning phases used in Experiment 2.

Phase 1: standardize canister – DRY
Phase 2: 44% RH (135µL H_2O added to canister) – HUMID
Phase 3: Bake 2 hrs at 80ºC – HUMIDIFIED N_2
Phase 4: Bake 2 hrs at 125ºC – HUMIDIFIED N_2
Phase 5: Bake 2 hrs at 80ºC – HUMIDIFIED AIR
Phase 6: Bake 2 hrs at 125ºC – HUMIDIFIED AIR

TEST CONDITIONS

For Experiment 2, we monitored the stability of a 3-component stock standard of H_2S, methyl mercaptan, and COS (internal standard), provided by DCG Partnership. The working concentration, again 10-11ppbv, was obtained by using a 2mL Sulfinert® treated sample loop. Samples were introduced onto the GC column using a 1mL Sulfinert® treated sample loop and were analyzed at 30ºC. The duration of each stability study was 3 days.

RESULTS AND DISCUSSION: EXPERIMENT 2

Table 3 shows the recovery values for H_2S and methyl mercaptan under dry conditions (Phase 1). All 10 SilcoCan™ canisters qualified for the study by exhibiting good stability for both H_2S and methyl mercaptan over the 3-day test period.

Table 3. Recovery values for H_2S and methyl mercaptan: dry canister (Phase 1).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100
H_2S Day 1	106	103	97	91	95	86	92	100	102	88
H_2S Day 2	123	96	104	94	100	93	93	100	97	103
H_2S Day 3	108	83	92	83	88	82	76	85	80	81
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	110	114	87	87	100	94	93	95	109	88
CH_3SH Day 2	105	112	99	91	91	104	90	107	102	90
CH_3SH Day 3	98	88	89	95	86	92	80	72	98	89

- indicates lower than 75% recovery

Table 4 shows the recovery values for humidified (44% RH) H_2S and methyl mercaptan (Phase 2). All 10 SilcoCan™ canisters exhibited poor stability for the humid standard within 24 hours. Based on the results of Phase 1, it appears that poor stability can be attributed to the reactivity of the sulfur compounds in a humid environment, not to the surface of the canisters.

Table 4. Recovery values for H_2S and methyl mercaptan: humidified canister, 44% RH (Phase 2).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100
H_2S Day 1	n/a	38	55	0	0	88	0	57	31	0
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	n/a	86	120	0	38	86	71	40	0	100

Table # 5 shows the recovery values for a dry H_2S and methyl mercaptan standard after the canisters were cleaned with humidified nitrogen at 80ºC for 2 hours (Phase 3). Only one canister exhibited lower than 75% percent recovery of H_2S over 3 days.

Table 5. Recovery values for H_2S and methyl mercaptan: 80ºC bakeout with humidified N_2 (Phase 3).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100
H_2S Day 1	74	105	95	123	81	95	90	93	78	93
H_2S Day 2	90	99	98	106	63	88	69	90	84	72
H_2S Day 3	96	92	83	90	54	86	78	91	79	75
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	94	119	106	105	121	120	103	104	91	108
CH_3SH Day 2	110	123	111	129	128	106	96	104	97	88
CH_3SH Day 3	111	134	100	129	130	103	102	105	87	86

Table # 6 shows the recovery values for a dry H_2S and methyl mercaptan standard after cleaning the canisters with humidified nitrogen at 125ºC for 2 hours (Phase 4). All 10 SilcoCan™ canisters exhibited good stability for the sulfur compounds over 3 days.

Table 6. Recovery values for H_2S and methyl mercaptan: 125ºC bakeout with humidified N_2 (Phase 4).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100

H_2S Day 1	105	114	109	100	96	122	102	130	104	84
H_2S Day 2	110	106	108	93	97	118	98	113	107	90
H_2S Day 3	99	110	88	86	86	122	96	114	103	84
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	150	114	106	132	95	96	95	120	109	95
CH_3SH Day 2	166	106	108	110	97	110	106	109	105	97
CH_3SH Day 3	133	104	109	117	99	133	102	65	102	118

Table 7 shows the recovery values for a dry H_2S and methyl mercaptan standard after cleaning the canisters with humidified air at 80ºC for 2 hours (Phase 5). Three of the 10 canisters exhibited lower than 75% percent recovery of H_2S over 3 days.

Table 7. Recovery values for H_2S and methyl mercaptan: 80ºC bakeout with humidified air (Phase 5).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100
H_2S Day 1	98	90	90	98	60	102	87	118	100	68
H_2S Day 2	83	86	79	90	57	82	74	72	81	66
H_2S Day 3	78	80	79	83	55	72	76	104	102	52
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	97	112	115	120	82	103	100	121	111	93
CH_3SH Day 2	83	92	83	121	88	97	80	73	84	105
CH_3SH Day 3	76	94	110	101	77	89	68	104	107	84

Table 8 shows the recovery values for a dry H_2S and methyl mercaptan standard after cleaning the canisters with humidified air at 125°C for 2 hours (Phase 6). Seven of the 10 canisters exhibited lower than 75% percent recovery of H_2S over 3 days.

Table 8. Recovery values for H_2S and methyl mercaptan: 125ºC bakeout with humidified air (Phase 6).

	SilcoCan™ Canister #									
	1000	1001	1002	1003	1004	2000	2001	2002	2003	2004
Compound / Day	**% Recovery**									
H_2S Day 0	100	100	100	100	100	100	100	100	100	100
H_2S Day 1	101	104	95	107	95	81	82	100	88	92
H_2S Day 2	88	80	74	84	53	60	56	70	56	54
H_2S Day 3	97	90	70	73	67	60	73	107	70	60
CH_3SH Day 0	100	100	100	100	100	100	100	100	100	100
CH_3SH Day 1	121	84	119	82	106	123	79	114	102	86
CH_3SH Day 2	83	71	102	80	64	79	53	87	67	60

CH_3SH Day 3	85	85	93	82	79	87	69	103	82	73

CONCLUSION

Experiment 1 demonstrated that SilcoCan™ canisters are suitable for storing reactive sulfur compounds at the low levels encountered in air. However, Experiment 2 showed various canister preparation processes, and high humidity, can adversely affect the canister's ability to store sulfur compounds. Based on these data, we recommend use of humidified nitrogen when cleaning canisters for sulfurs. It is important to ensure the canisters are properly dried after cleaning, to eliminate any negative effects associated with humidity.

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