Analysis of Low-Level (1–20ppb) Reactive Sulfurs In Air Samples

David M. Shelow, Gary Stidsen
Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823

Abstract

Storage of volatile sulfur compounds is a challenge for analysts. Tedlar bags traditionally have been the media for collecting volatile organic compounds (VOCs). Several researchers have investigated canister-based methods for the collection of sulfur VOCs but have found them unsuitable due to the canisters' reactive nature. In SilcoCan™ canisters a surface treatment process called Silcosteel® has been developed which bonds a layer of silica-like material to the inner surface of the electropolished stainless steel ambient air canisters. This surface treatment creates a protective barrier between the sulfur compounds and the reactive metal surface of canister. Stability studies up to 6 days were performed to demonstrate the ability of the SilcoCan™ canister to store sulfur VOCs at very low ppbv levels in dry and humid conditions.

Introduction

The analysis of low-level sulfur volatile organic compounds (VOCs) has become more important due to odor complaints near manufacturing sites and refineries. Collection and measurement of volatile sulfur compounds in the atmosphere is very difficult because of their low concentration and high reactivity. These compounds not only react with themselves but can also react with the vessels they are collected in. This results in low recoveries. These compounds include hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), ethyl mercaptan (C_2H_5SH), and dimethyl disulfide (CH_3SSCH_3). Tedlar bags traditionally have been used for the collection of sulfur VOCs. However the stability of low level sulfur VOCs at 100ppbv is poor within 24 hours[1]. It is well documented that electropolished canisters (e.g., SUMMA canisters), are excellent for storage of VOCs in ambient air, however the samples react with the canister's metal surface. This makes electropolished canisters unsuitable for the collection and storage of low-level sulfur VOCs[2]. Silcosteel® treatment is a process in which a silica-like layer is deposited on the surface of stainless steel. Electropolished canisters have been treated with the Silcosteel® process to create a barrier between the reactive compounds and the metal surface. Silcosteel® treatment increases the storage capability of the sulfur VOCs in canisters. Parmar et al studied the capability of SilcoCan canisters for the storage of sulfurs at concentrations of 200-1000ppbv[3]. The purpose of this study was to evaluate the stability of sulfur VOCs within SilcoCan™ canisters at very low levels (1-20ppbv) for 6 days. A comparison study of dry vs. humidified standards was also performed to demonstrate the ability of SilcoCan™ canisters for storage of low-level sulfur VOCs in real-world conditions.

Experimental Design

Analytical System

High resolution capillary gas chromatography offers many advantages for performing trace analysis of these sulfur VOCs in conjunction with sensitive selective detectors such as sulfur chemiluminescences detectors (SCD) or flame photometric detectors (FPD). For this study a 60m, 0.53mm ID, 7.0µm Rtx®-1 capillary column was selected. A 6-port Valco® valve was used with Silcosteel® 1mL sample loop and 1/16" sample pathway lines. The GC was a HP5890GC with Sievers Model 355 SCD. The temperature profile was 30°C (1.0 min.) 10°C/min to 180°C (5 min.). The flow rate was 8.5mL /min. measured with an electronic flow meter (Figure 1).

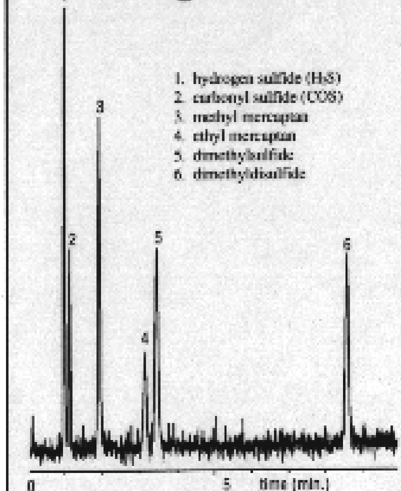
Canisters

For this study 18 SilcoCan™ caniters and 2 electropolished TO-Can™ canisters were used (Restek Corporation).

Standards

The 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. The humidified standards were made by injecting the evacuated canisters with 100µL of DIH_2O prior to adding the 2mL aliquot of stock standard. The resultant %RH was 50%.

Figure 1



Rtx-1, 60m x 0.53mm ID x 7.0µm
30°C (hold 1 min.) to 180°C @ 10°C/min. (hold 5 min.)
Carrier gas: helium @ 8.5mL/min.

Table # 1

Compound Name	Formula	Stock Conc (ppmv)	Standard Conc (ppbv)	Standard Conc as S (ppbv)
hydrogen sulfide	H2S	105	11.51	10.83
carbonyl sulfide	COS	98	10.74	5.73
methyl mercaptan	CH3SH	101	11.07	7.38
ethyl mercaptan	CH3CH2SH	101	11.07	5.71
dimethylsulfide	CH3SCH3	99	10.85	6.81
dimethyl disulfide	CH3SSCH3	100	10.96	7.46

Results and Discussion

Section # 1 Analytical system repeatability. To ensure the analytical system was repeatable, the reference standard canister was run at 55 ppbv final concentration for 7 replicate runs. Raw area counts were plotted and %RSD was calculated (Table II). All values are below 10%, indicating the system is in control.

Table # 2

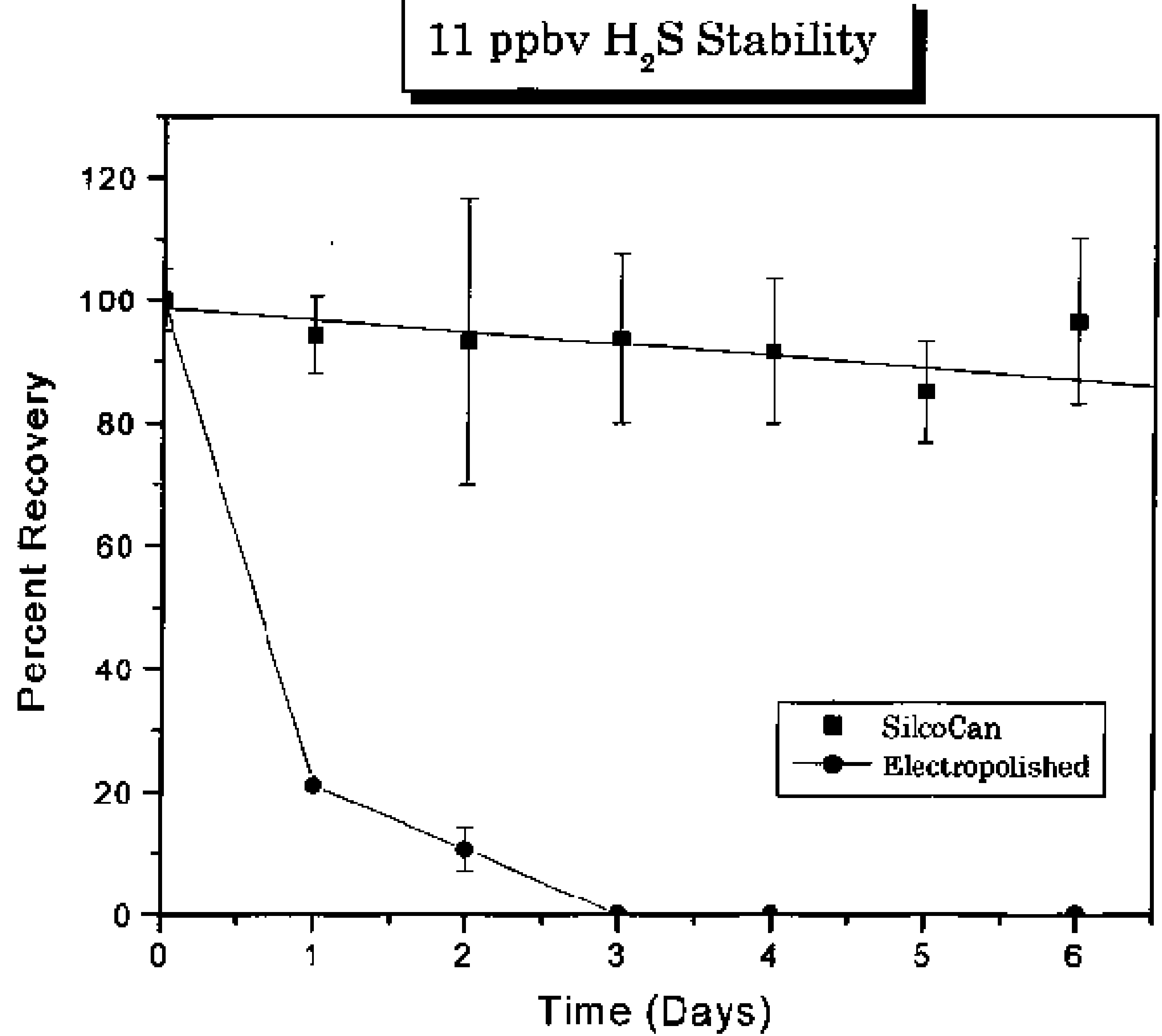
Compound Name	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	%RSD
hydrogen sulfide	341976	338133	334164	321637	327805	332097	325412	2.2
carbonyl sulfide	202037	206494	192443	183263	192524	188622	189439	4.2
methyl mercaptan	403861	390882	404358	390528	401388	407396	388261	2.0
ethyl mercaptan	154550	132887	157266	122290	140219	150073	145671	8.7
dimethylsulfide	342990	353464	344496	326731	338573	345838	321469	3.3
dimethyl disulfide	255783	249647	256716	198271	257623	267076	240651	9.2

Section # 2 Standards preparation reproducibility. This was evaluated to ensure the process for making the standards was consistent. This was achieved by analyzing the diluted standards by GC/SCD immediately after their preparation. Table III shows the raw area counts for 7 SilcoCan™ canisters and %RSD for each compound. All the values are below 10% except methyl mercaptan at 17%. This may be due to instability of the compounds immediately after the standard are made. There was no equilibration time allowed.

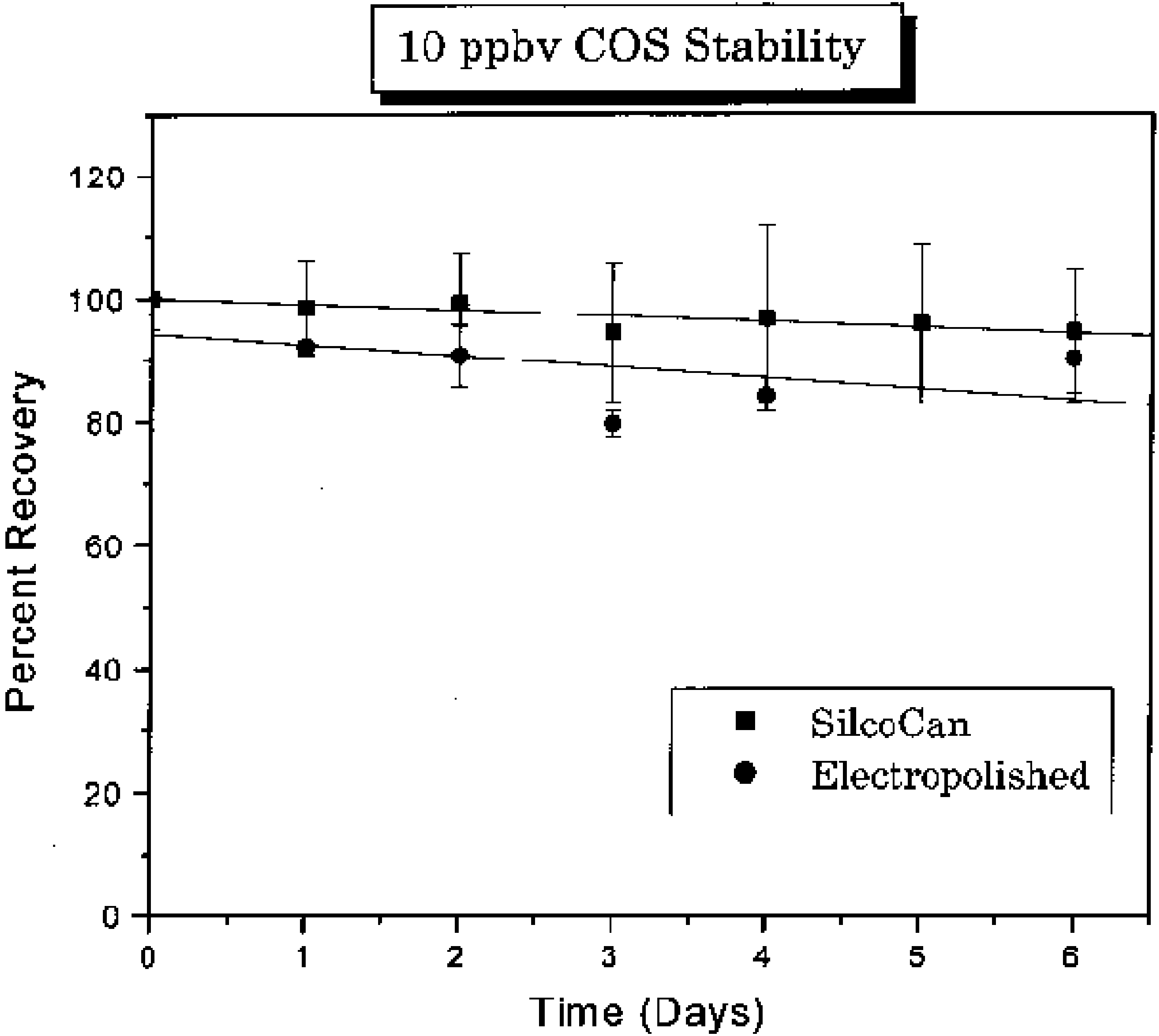
Table # 3

Compound Name	6874	6872	6602	1901-1	1901-2	0202-1	0202-2	%RSD
hydrogen sulfide	151135	145070	149589	157606	165487	151564	155534	4.3
carbonyl sulfide	89946	79774	96010	99457	101822	97249	100290	8.1
methyl mercaptan	140662	219308	194347	238200	199373	247989	216972	17.0
ethyl mercaptan	83856	90000	80927	105565	92097	88750	96807	9.0
dimethylsulfide	184539	201190	196821	193154	183285	183227	191405	3.7
dimethyl disulfide	200742	215654	209997	187717	180067	176338	224980	9.3

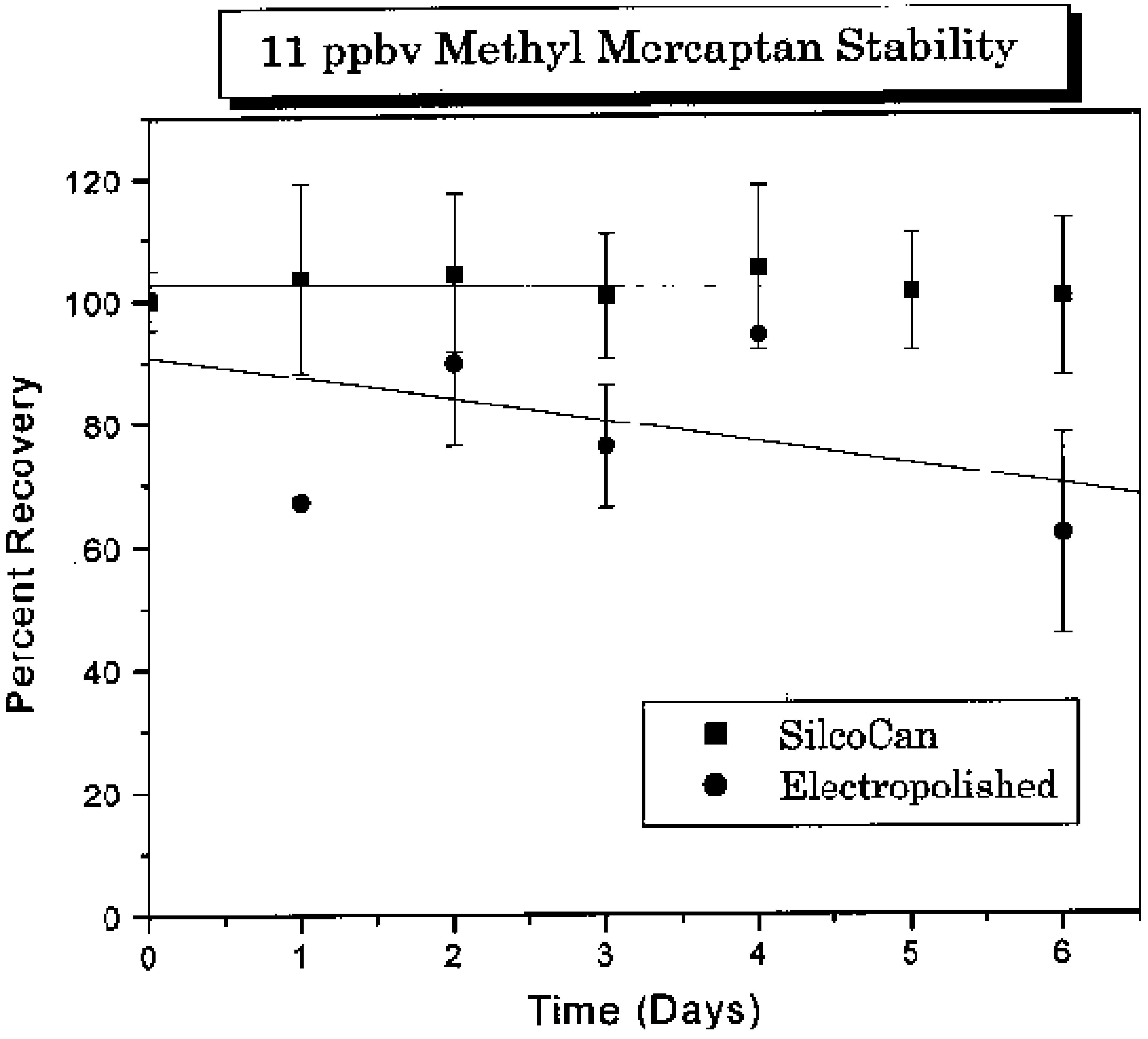
Section # 3 the stability test within the canisters. The duration of the stability study was 6 days. A reference standard was made at 55ppbv and run 3 times each day. The concentration of the sulfurs was 11ppbv. Dimethyl sulfide was used as the internal standard. The results showed excellent stability of each of the low level sulfur VOCs in the dry standards of all 18 SilcoCan™ canisters. The electropolished canisters exhibit rapid degradation of the H_2S, methyl mercaptan and ethyl mercaptan (Figures 2-6).



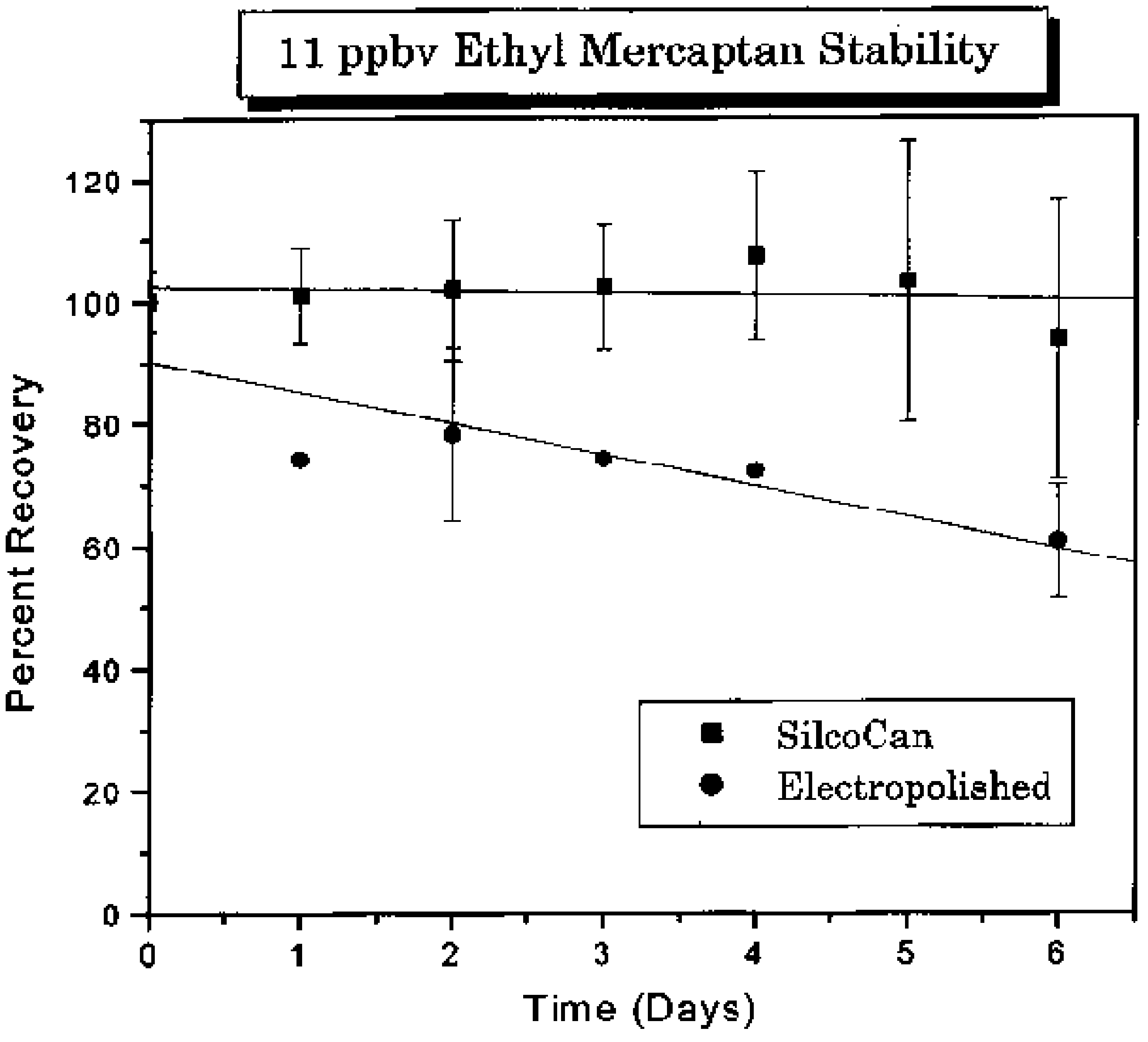
11 ppbv H_2S Stability
Percent Recovery
Time (Days)
SilcoCan
Electropolished
0
20
40
60
80
100
120
0
1
2
3
4
5
6



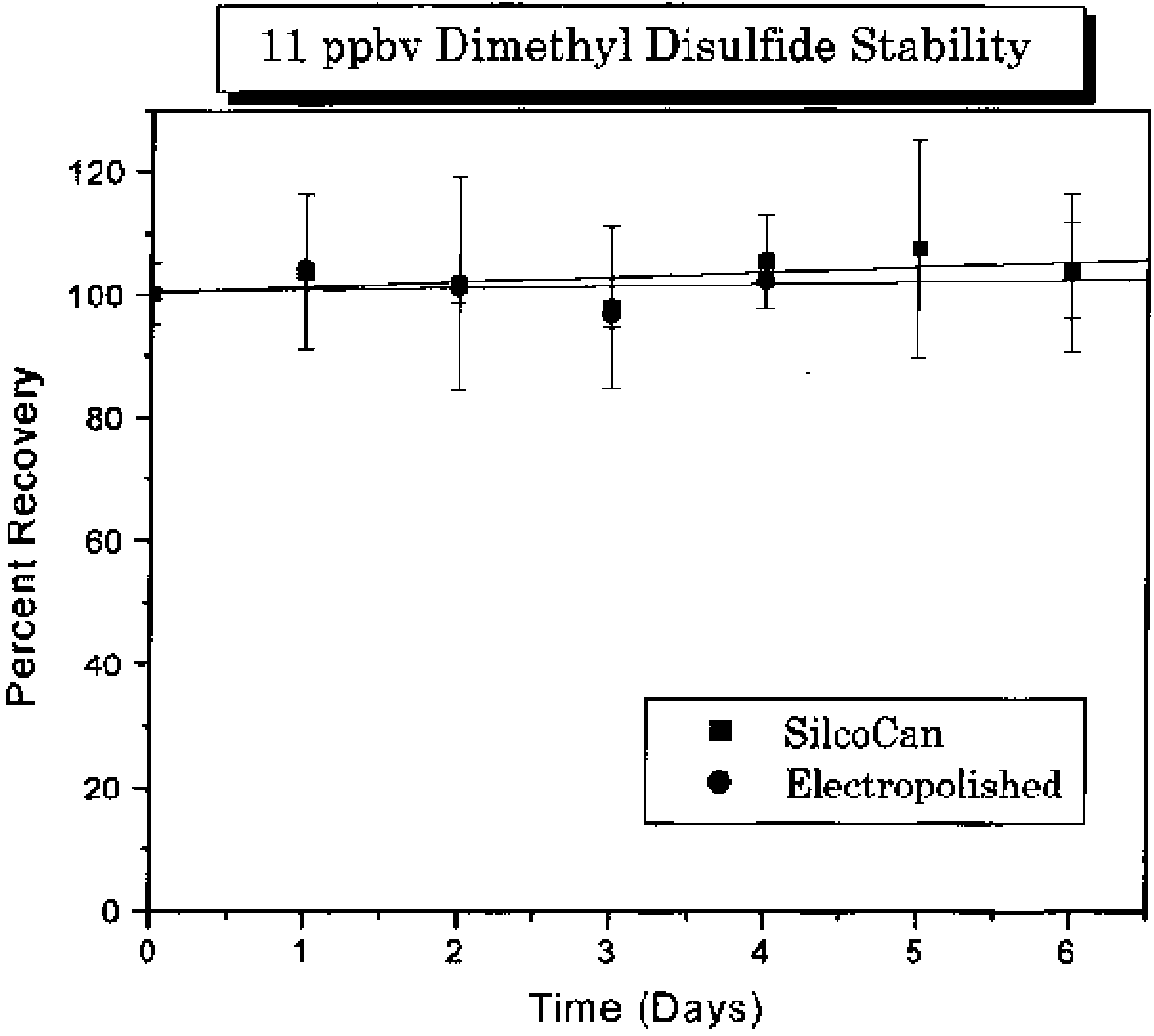
10 ppbv COS Stability
Percent Recovery
120
100
80
60
40
20
0
0
1
2
3
4
5
6
Time (Days)
SilcoCan
Electropolished



11 ppbv Methyl Mercaptan Stability
Percent Recovery
120
100
80
60
40
20
0
0
1
2
3
4
5
6
Time (Days)
SilcoCan
Electropolished

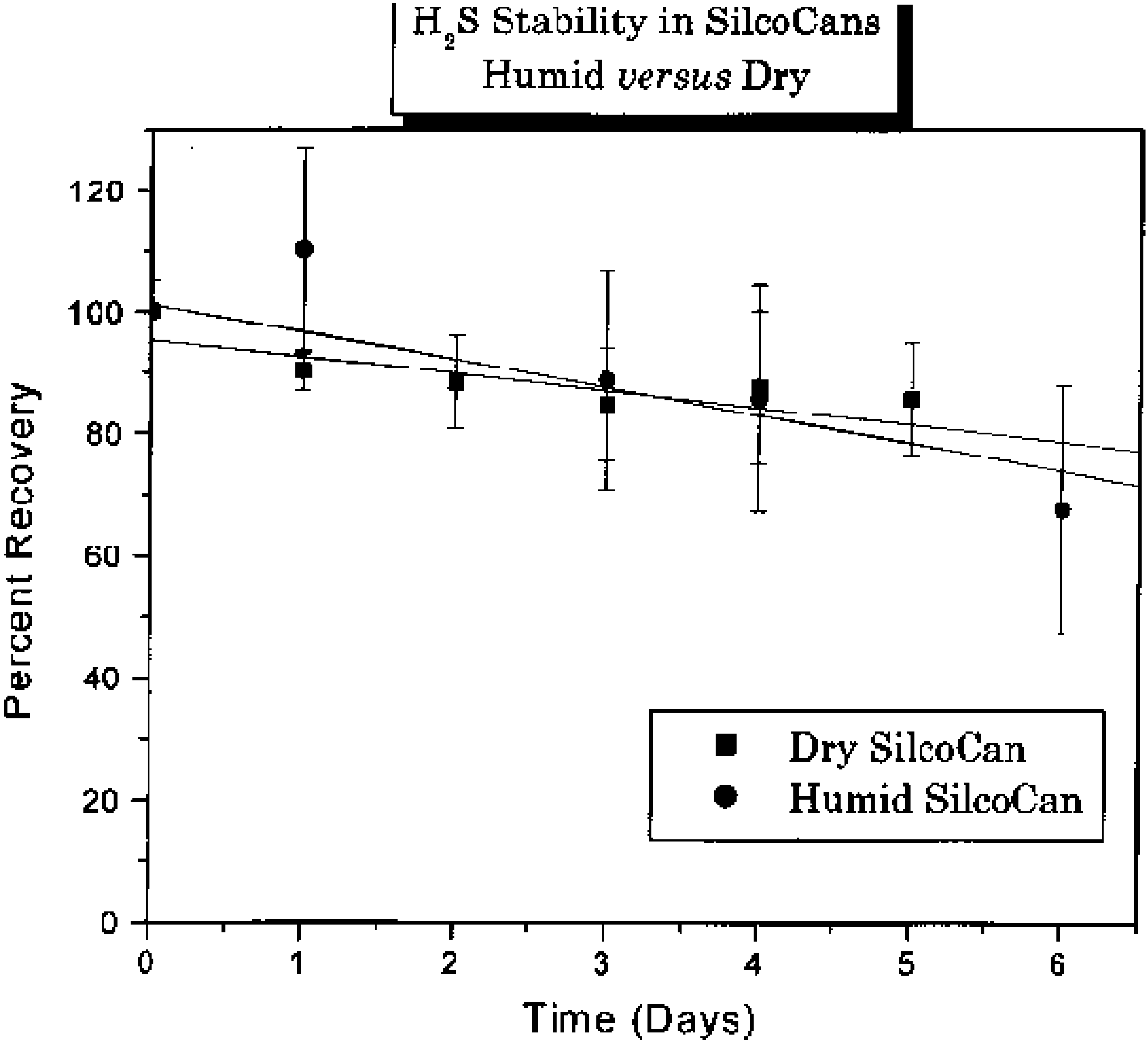


11 ppbv Ethyl Mercaptan Stability
Percent Recovery
Time (Days)
SilcoCan
Electropolished
0
20
40
60
80
100
120
0
1
2
3
4
5
6

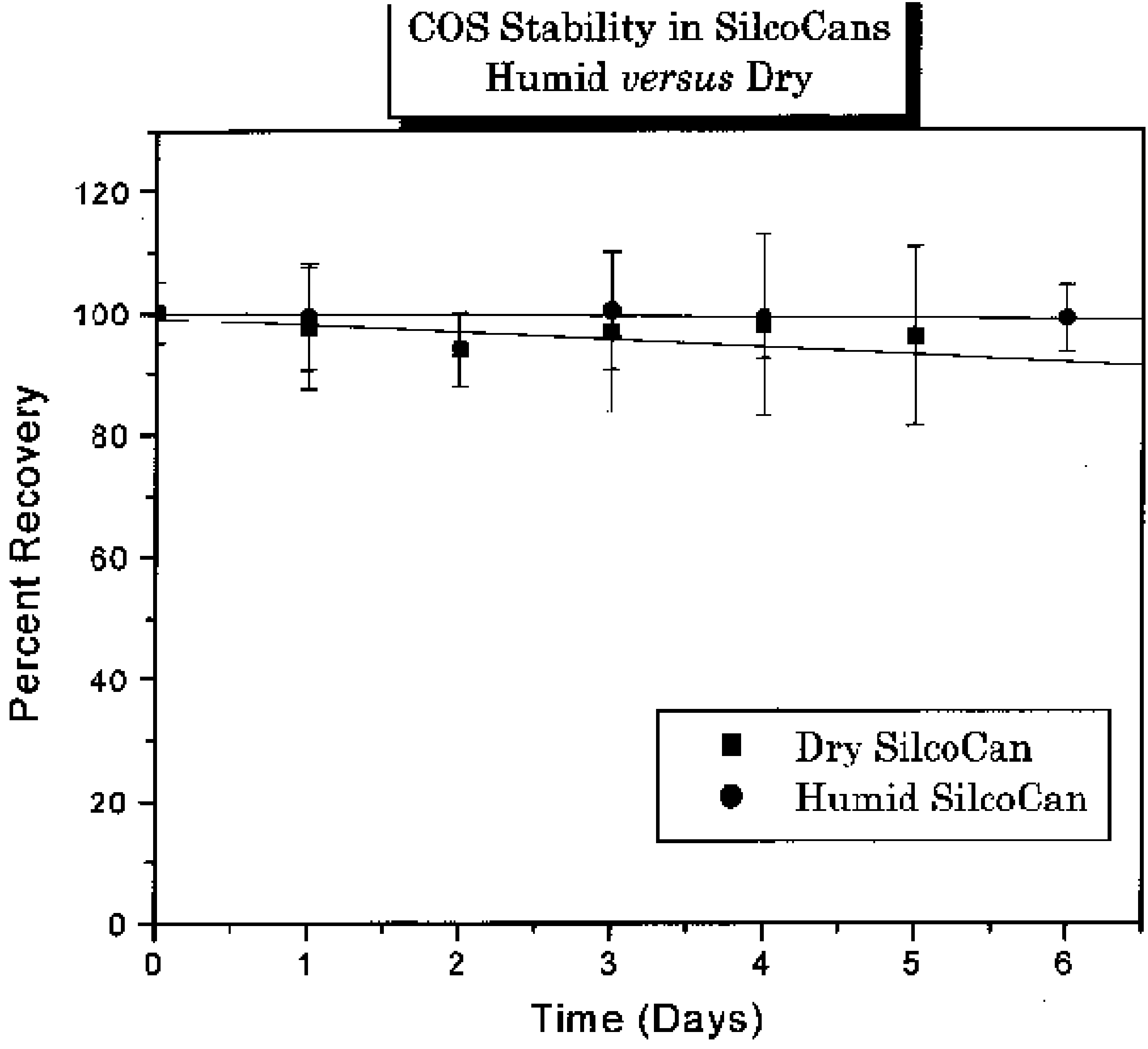


11 ppbv Dimethyl Disulfide Stability
Percent Recovery
120
100
80
60
40
20
0
0
1
2
3
4
5
6
Time (Days)
SilcoCan
Electropolished

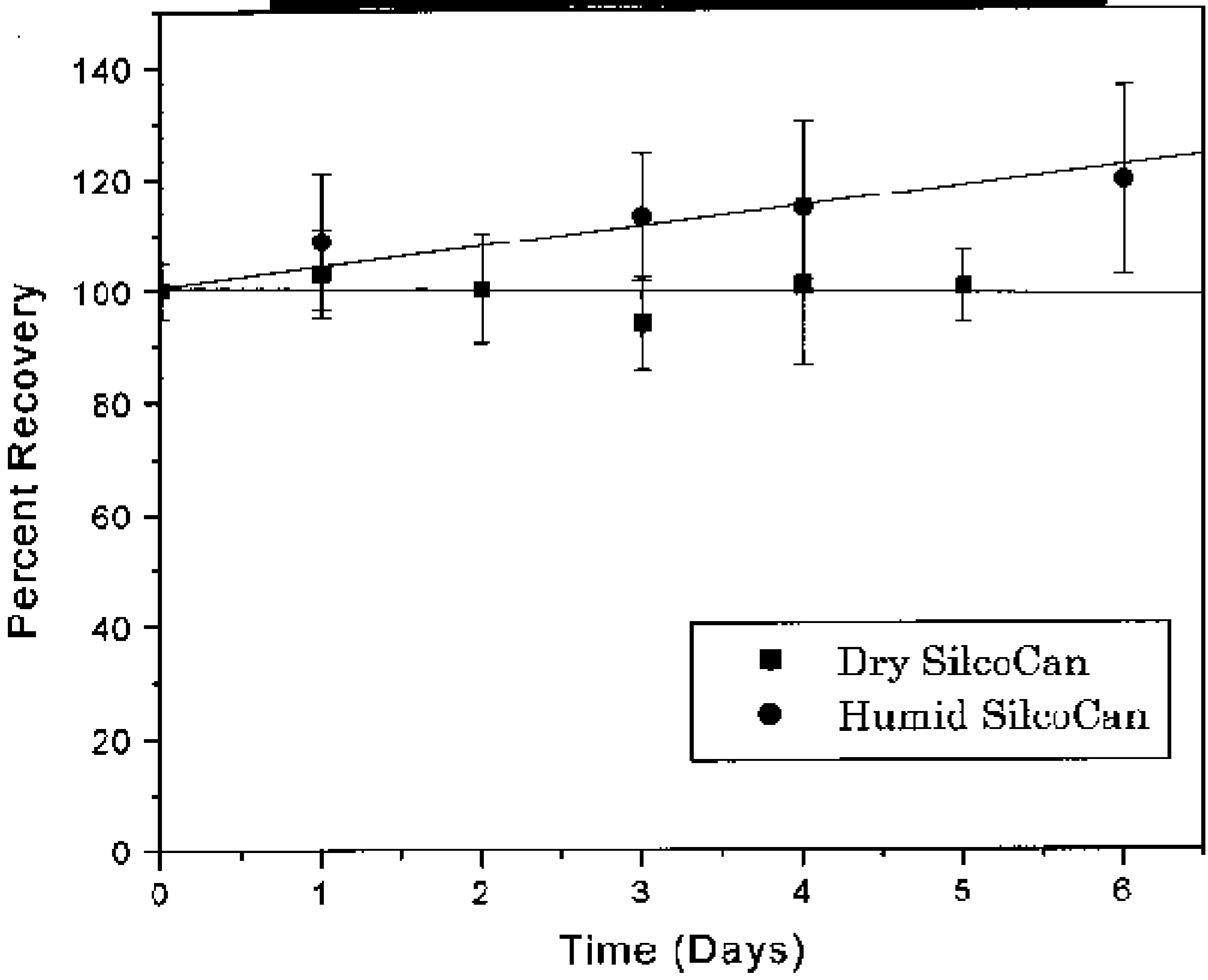
Section # 4 Humidity Effects. Fivee SilcoCan™ canisters used in the first part of the study were cleaned according to the US EPA Compendium of Toxic Organic Methods TO-14 and resubmitted for the humidity study[4]. After adding 100µL of DIH_2O to each canister, the resultant relative humidity was 50%RH. 2mL of the stock sulfur standard was added to each canister and analyzed for 6 days. Figures 7-11 show the stability of each sulfur VOC for the 5 canisters compared to the results of the dry standards. The results show the SilcoCan™ canisters are suitable for storing humidified sulfur VOCs as they show no difference to the performance of the SilcoCan™ canister in the dry standard study.



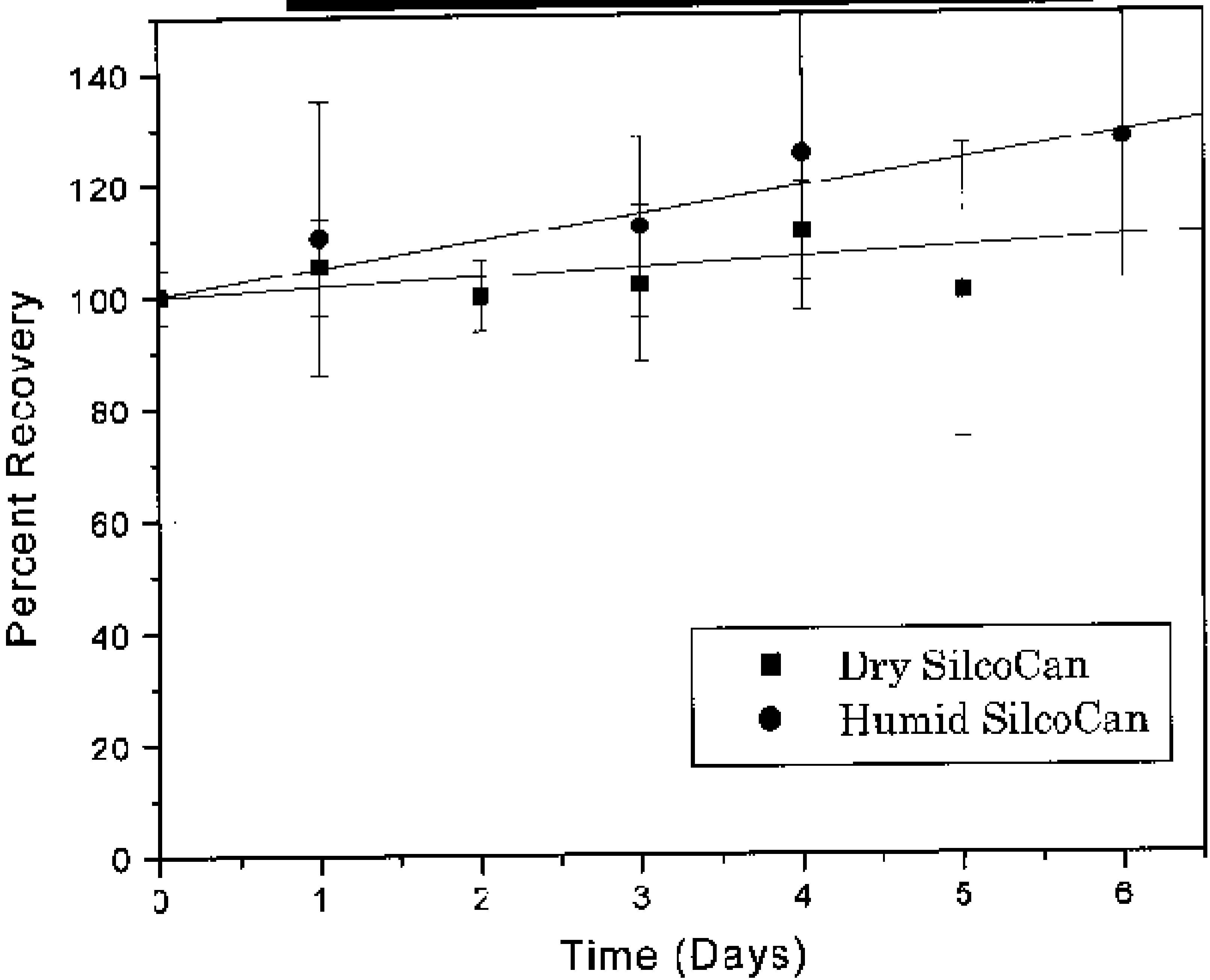
H_2S Stability in SilcoCans
Humid *versus* Dry
Percent Recovery
0
20
40
60
80
100
120
0
1
2
3
4
5
6
Time (Days)
Dry SilcoCan
Humid SilcoCan

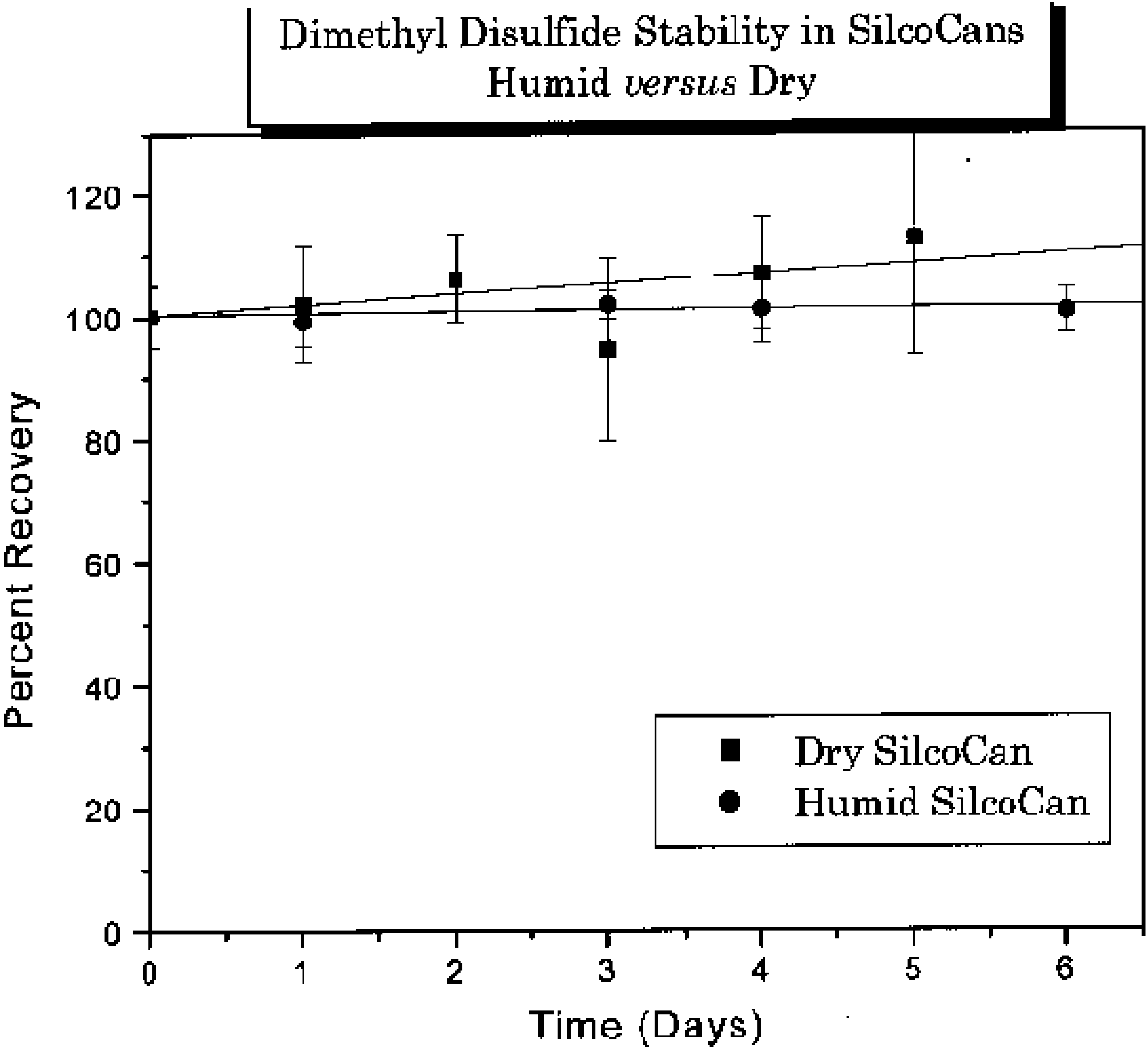

COS Stability in SilcoCans
Humid versus Dry
Percent Recovery
120
100
80
60
40
20
0
0
1
2
3
4
5
6
Time (Days)
Dry SilcoCan
Humid SilcoCan

Methyl Mercaptan Stability in SilcoCans
Humid *versus* Dry



Ethyl Mercaptan Stability in SilcoCans
Humid *versus* Dry




Dimethyl Disulfide Stability in SilcoCans
Humid *versus* Dry
Percent Recovery
0
20
40
60
80
100
120
Time (Days)
0
1
2
3
4
5
6
Dry SilcoCan
Humid SilcoCan

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 sulfurs VOCs such as H_2S and methyl mercaptan and ethyl mercaptan. Both dry and humidified 11ppbv sulfur VOCs exhibited virtually no breakdown or reactivity in SilcoCan™ canisters after 6 days of storage.

References

1. Quang Tran, You-Zhi Tang; Stability of Reduced Sulphur 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, Michael; 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. Parmar, Sucha; Kitto, Andrew; Ugarova, Luda: A Study of “Holding Times” for Sulfur Compounds in Restek SilcoCan Canister, 1996 AWMA/EPA International Symposium of Measurement of Toxic and Related Air Pollutants.
4. 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