Storage Stability of 66 Volatile Organic Compounds (VOCs) in Silicon-Lined Air Canisters for 30 Days

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Abstract

The recoveries of 66 volatile organic compounds (VOCs) typically analyzed as part of the United States (U.S.) Environmental Protection Agency's (EPA's) Compendium Method TO-15, were evaluated for two commercially available silicon-lined (SL) air canisters. The VOC recoveries were determined both in dry (0% relative humidity [RH]) and humid (93% RH) conditions over a 30 day storage period, thereby evaluating stabilities. Six Restek® SilcoCan® canisters were compared to six of Vendor A's silicon-lined canisters. For the dry experiment, the mean SilcoCan® and Vendor A recoveries on Day 30 were 97 and 102%, respectively; and the mean SilcoCan® and Vendor A percent change from Day 0 to Day 30 were 17 and 17%, respectively. For the humid experiment, the mean SilcoCan® and Vendor A recoveries on Day 30 were 85 and 88%, respectively; and the mean SilcoCan® and Vendor A percent change from Day 0 to Day 30 were 13 and 9%, respectively. There were no statistically significant ($p < 0.01$) differences in the Day 30 recoveries for the two silicon-lined air canister types under dry conditions. However, acrolein was found to be significantly ($p = 0.006$) different between air canister types in the humid condition. Acrolein, dibromochloromethane, and bromoform were the only three compounds which appear to be unstable in both SL canister types; however, only under the humid (93% RH) condition. These results indicate that for the majority of the 66 VOCs, there were no appreciable differences in recoveries and stabilities between the silicon-lined air canisters for both dry and humid conditions over 30 days of storage. The detailed experimental design, analytical techniques, and results will be discussed in this manuscript.

Introduction

Volatile organic compounds (VOCs) are of great interest due to their ubiquitous presence in indoor, outdoor, and personal air, and also because VOCs and their atmospheric reaction products have well known adverse environmental impacts and detrimental human health effects. Therefore, the collection and measurement of VOCs has been the subject of countless studies. In particular, the United States (U.S.) Environmental Protection Agency's (EPA's) Compendium Methods TO-14A [1] and TO-15 [2] have received considerable attention over the past three decades. Both toxic organic (TO) methods are for the "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters"; however, TO-14A is for "Subsequent Analysis by Gas Chromatography" and TO-15 is "Analyzed by Gas Chromatography/Mass Spectrometry (GC-MS)" [2].

In application note EVAN1725A-UNV [3], Method TO-15's "performance-based" criteria were discussed. More importantly, it was determined that pairing Restek® (PA, USA) air sampling products with a Nutech™ 8900DS preconcentrator (EST Analytical, Ohio, USA) is a successful means for meeting all of Method TO-15 performance criteria. Optimized column dimensions and GC conditions reduced analysis times by ~50%. Such studies are vital to the continued advancement of analytical VOC methods. However, the handling of samples pre- and post-collection and prior to analysis is often overlooked. This may result in positive and/or negative errors being wrongly associated with the analytical method, rather than the sample handling procedures. In particular, storage stability of VOCs in air canisters, the subject of this manuscript, may result in said biases.

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Electropolished and SUMMA passivated, stainless steel canisters have been utilized for over three decades to collect VOC samples. Their use is recommended in Methods TO-14A [1] and TO-15 [2]; and numerous studies have evaluated the storage stability of several VOCs in air canisters under various conditions. Westberg et al. [4], Holdren et al. [5], Oliver et al. [6], Gholson et al. [7], Jayanty [8], Holdren et al. [9], Parmar [10], Merrill and Zapkin [11], Oliver [12], Kelly et al. [13], Holdren et al. [14], Brymer et al. [15], and Sin et al. [16] evaluated stabilities in SUMMA canisters. In addition, Pate et al. [17] evaluated stainless steel canisters with and without SUMMA passivation; and Gholson et al. [18] evaluated aluminum canisters. Kelly and Holdren provide a comprehensive review of the majority of these studies [19]; however, the following general conclusions may be deduced from this body of peer-reviewed literature:

1. The majority of VOCs targeted in Methods TO-14A and TO-15 are stable in electropolished and SUMMA passivated, stainless steel canisters under routine ambient air conditions after storage of up to 30 days [2].

2. A minimum amount of water vapor is required in electropolished and SUMMA passivated stainless steel canisters in order for particular VOCs (e.g., polar VOCs) to be stable. It is theorized that water occupies active sites on air canister walls, thereby increasing the inertness of the canister.

Over the past decade, silicon-lined (often improperly referred to as fused-silica-lined [FSL]) canisters have been growing in popularity. However, despite their increasing popularity only a few studies have evaluated the effectiveness of silicon-lined (SL) air canisters [14, 20-22]. Holdren et al. [14] evaluated the 7 day stabilities of 9 VOCs at 20 ppbv with 21 and 52% relative humidity (RH) and at 2 ppbv with 21% RH. They concluded that there were no significant differences between SUMMA passivated and SL stainless steel canisters. Hsieh et al. [22] evaluated the 7 day stabilities of 56 VOCs at 5 to 30 ppbv with 30 and 90% RH and at 24 and 35 °C. They observed that the average half-life of the 56 VOCs was 37±4, 45±6, and 52±6 days for Tedlar® bags, SUMMA canisters, and SilcoCan® canisters, respectively. Although the observed differences in loss rates between SUMMA canisters and SilcoCan® canisters were not statistically significant, they concluded that SilcoCan® canisters had fewer active sites and thus adsorbed less; therefore, VOCs were relatively more stable in silicon-lined air canisters. Ochiai et al. [21] evaluated the 28 day stabilities of 58 VOCs at 1.7 to 2.5 ppbv with 1.6, 8.0, 27, 39, 53, and >99% RH. They concluded that SL canisters had increased inertness when compared to SUMMA canisters, as evidenced by the recoveries of all analytes (>95%) under dry conditions (1.6% RH). Like Hsieh et al. [22], Ochiai et al. [21] concluded that this was the direct result of competitive adsorption of water vapor and VOCs on actives sites in the air canister interior surfaces.

Regardless of air canister type, the loss mechanisms for VOCs in canisters are as follows:

1. Physical adsorption, which is from reaction with "active sites" on canister walls [22] and is generally considered a short-term (i.e., takes place on the order of minutes to hours) process [2].

2. Dissolution of soluble compounds in condensed water, which can be exacerbated by the pressurization of canisters [21].

3. Chemical reactions with other gas phase compounds (e.g., ozone), which is generally considered short-term (minutes to hours) [2].

Holdren et al. [14] and Hsieh et al. [22] evaluated the performance of silicon-lined air canisters manufactured by Restek Corporation (Bellefonte, PA, USA) and Ochiai et al. [21] evaluated the performance of SL canisters manufactured by Entech Instruments (Simi Valley, CA, USA). An exhaustive review of the available literature was unable to produce any comparison between different silicon-lined air canister types. In the current study, two commercially available SL canisters were evaluated for recoveries over time (i.e., storage stability). The detailed experimental design, analytical techniques, results, and implications are discussed.

Experimental
Canisters
Six 6-liter SilcoCan® air monitoring canisters (cat.# 24142-650) with Parker® diaphragm valves and gauges (serial numbers H3580, H3581, H3582, H3584, H3585, and H3586) were obtained from Restek Corporation, and six 6-liter canisters with gauges and valves were obtained from Vendor A. Both air canister types and valves were silicon-lined.

Analytical System

The following analytical system was utilized: a Nutech™ 8900DS preconcentrator paired with an Agilent® 6890 gas chromatograph (GC) coupled with an Agilent® 5973 mass selective (MS) detector. The preconcentrator and GC-MS parameters may be found in Tables I and II, respectively. The GC was able to achieve a starting temperature of 32 °C while the Nutech™ 8900DS was preconcentrating the next sample (i.e., sample throughput time was not restricted by waiting for the GC to cool down). The Nutech™ 8900DS preconcentrator utilizes three cryogenically cooled traps to concentrate/focus target analytes (often referred to as "micro-scale purge-and-trap") for delivery to the GC-MS system. In order of sample flow: trap 1 consists of glass beads used to remove water vapor, nitrogen, oxygen, and carbon dioxide (CO_2) from the sample stream; trap 2 consists of Tenax® material used to focus the VOCs and remove any residual water vapor and CO_2; and trap 3 is a proprietary trap used for final analyte focusing and transfer of analytes to the GC column.

Samples were analyzed by preconcentrating 400 mL of sample with 100 mL of the TO-14A internal standard/tuning mix (cat.# 34408) (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and 4-bromofluorobenzene) prepared at 20 ppbv concentrations. Analyzed sample concentrations were calculated from a 5-point calibration curve generated by analyzing a series of volumes of a 10.0 ppbv primary standard (Table III). The 10.0 ppbv primary standard was generated by injecting 180 mL of a 1.00 ppmv TO-15 65 component mix (cat.# 34436) into an evacuated 6-liter SilcoCan® air monitoring canister (cat.# 24142-650) and pressurizing the canister to 30 psig with 50% RH nitrogen. Ochiai et al. [21] determined 50% RH to be optimal for stability. The standard was allowed to age for 7 days.

Table I: Nutech™ 8900DS preconcentrator settings. Default preconcentration volume = 400 mL.

Trap 1 Settings		Internal Standard	
Cooling Temp.	-155 °C	Purge Flow	100 mL/min
Preheat Temp.	5 °C	Purge Time	6 sec
Preheat Time	0 sec	Volume	100 mL
Timeout	10 min	ISTD Flow	100 mL/min
Desorb Temp.	20 °C		
Desorb Flow	5 mL/min	**Sample**	
Desorb Time	360 sec	Purge Flow	100 mL/min
Bakeout Temp.	200 °C	Purge Time	6 sec
Flush Flow	120 mL/min	Sample Flow	100 mL/min
Flush Time	60 sec		
Sweep Flow	120 mL/min	**GC Control**	
Sweep Time	60 sec	Remote Start	Yes
Temp. Target Range	2 °C	GC Run Time	3 min
Stable Time	60 sec	Flush Sample Line	No
Cooling W/He	No	GC Ready Required	Yes
		GC Ready Timeout	1 min
Trap 2 Settings			
Cooling Temp.	-35 °C	**Idle State Configuration**	
Desorb Temp.	190 °C	Cryotrap1	150 °C
Desorb Time	30 sec	Transfer Line	125 °C
Timeout	10 min	Valve Oven	125 °C
Bakeout Temp.	200 °C	Cryotrap2	150 °C
Bakeout Time	10 sec	Sampler Line	125 °C
Temp. Target Range	2 °C	Sampler Oven	125 °C
Stable Time	10 sec	Auxiliary	125 °C
Cooling W/He	No		
Cryofocus Settings			
Cooling Temp.	-160 °C		
Inject Time	140 sec		
Timeout	10 min		
Temp. Target Range	3 °C		
Stable Time	10 sec		

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Table II: Agilent® 6890/5973 GC-MS Parameters

GC Parameters	
Column	Rtx®-VMS, 30 m, 0.25 mm ID, 1.40 µm (cat. # 19915)
Oven	32 °C (hold 1 min) to 150 °C at 8 °C/min to 230 °C at 33 °C/min
Carrier Gas	He, constant flow
Flow Rate	1.2 mL/min
MS Parameters	
Transfer Line Temp.	230 °C
Source Temp.	230 °C
Quad Temp.	150 °C
Electron Energy	70 eV
Solvent Delay Time	1.0 min
Tune Type	BFB
Ionization Mode	EI
Scan Range	35–250 amu
Scan Rate	3.32 scans/sec

Table III: Calibration Curve

Standard (ppbv)	Injection Volume (mL)	Calibration Concentration (ppbv)
10.0	400	10.0
10.0	300	7.50
10.0	200	5.00
10.0	100	2.50
10.0	40	1.00

Air Canister Cleaning

Prior to spiking, all twelve (six Restek® and six Vendor A) canisters were simultaneously cleaned with a TO-Clean canister cleaning system (cat.# 22916). The silicon-lined air canisters were cleaned per the recommended procedures outlined in section 8.4.1 of Method TO-15. Briefly, at 100 °C canisters were evacuated down to 500 mTorr and held under vacuum for 60 minutes; the canisters were then filled with humidified (50% RH) nitrogen to 30 psig. RH values throughout this application note were verified by an EX-TECH hygro-thermometer/datalogger (Model SDL500). This cycle was completed two additional times for a total of three cycles (Table IV). Vacuums/pressures were controlled by the TO-Clean canister cleaning system's internal gauge; however, vacuums/pressures were periodically verified using an Ashcroft® digital test gauge (cat. # 24268).

Table IV: Air canister cleaning procedures were conducted at 100 °C with humidified nitrogen (50% RH).

Cycle	Evacuation Vacuum (mTorr)	Pressurization Pressure (psig)
1	500 (Hold for 60 min)	30
2	500 (Hold for 60 min)	30
3	500 (Hold for 60 min)	30
Final	50	30 (Only for blanks)

Spiking/Recovery/Stability

The twelve canisters were evaluated under "dry" and "humid" conditions at 5.00 ppbv. For the dry experiment, each air canister was spiked with 90 mL of a 1.00 ppmv TO-15 65 component mix (cat.# 34436) and 90 mL of 1.00 ppmv acetonitrile and pressurized to 30 psig with 0% RH nitrogen. For the humid experiment, each air canister was spiked with 90 mL of 1.00 ppmv TO-15 65 component mix (cat.# 34436) and 90 mL of 1.00 ppmv acetonitrile and pressurized to 30 psig with humidified (93% RH) nitrogen. Nitrogen was humidified by sparging the nitrogen through a humidification chamber (cat.# 24282) filled with deionized (DI) water. All canisters were stored at room temperature.

Recovery of each compound was calculated as the determined concentration divided by the spiked concentration (i.e., 5.00 ppbv), expressed as a percentage as follows:

$$Recovery\ (\%): \frac{Determined\ Value}{Spiked\ Value} \times 100$$

Stability was defined as the change in concentration as determined on Day 30 compared to as determined on Day 0. A compound was deemed stable when the % change in concentration was less than Method TO-15's audit accuracy criteria of ±30%.

$$Stability\ (\%): \frac{|\,Day\ 0\ Value - Day\ 30\ Value\,|}{Day\ 0\ Value} \times 100$$

Results and Discussion
Dry Results

The dry experiment (0% RH) results (Table V) indicate the two silicon-lined air canisters exhibited comparable recoveries and stabilities for all 66 VOCs. The mean SilcoCan® and Vendor A recoveries on Day 0 were 115 and 123%, respectively. The mean SilcoCan® and Vendor A recoveries on Day 30 were 97 and 102%, respectively. A multivariate analysis of variance (ANOVA) indicated there were no statistically significant ($p < 0.01$) differences for the 66 VOCs recoveries in the different silicon-lined canister types under dry (0% RH) conditions after 30 days of storage. The mean SilcoCan® and Vendor A percent change values from Day 0 to Day 30 were both 17%. However, only 64 of the 66 compounds were stable (i.e., <30% change) over 30 days of storage in both silicon-lined air canister types. 1,4-dioxane and naphthalene were not stable in Vendor A's canisters, with a 38 and 42% change in concentration from Day 0 to Day 30, respectively

Table V: Day 0 and Day 30 average concentrations of 66 TO-15 components stored in six Restek (SilcoCan®) and six Vendor A canisters spiked at 5.00 ppbv, 30 psig, and 0% RH. Compounds in bold are anomalies, which have been discussed in the text. % Change equals the absolute value of Day 0 minus Day 30, divided by Day 0, and multiplied by 100. p-value from ANOVA of Restek® and Vendor A Day 30 concentrations.

Compound	Day 0 ppbv		Day 30 ppbv		Stability (% Change)		% Recovery Day 30		*p*-value
	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	
Propylene	5.84	5.84	4.63	4.87	21	17	93	97	0.133
Dichlorodifluoromethane (F 12)	5.74	5.73	4.31	4.52	25	21	86	90	0.107
Chloromethane	6.06	6.11	4.93	5.20	19	15	99	104	0.079
1,2-Dichlorotetrafluoroethane (F 114)	5.90	5.90	4.42	4.69	25	21	88	94	0.058
Vinyl chloride	6.01	6.03	4.75	5.02	21	17	95	100	0.152
1,3-Butadiene	5.88	5.87	4.93	5.28	16	10	99	106	0.045
Bromomethane	5.84	5.94	4.74	5.09	19	14	95	102	0.094
Chloroethane	6.33	6.40	5.12	5.48	19	14	102	110	0.095
Ethanol	4.72	5.74	5.55	5.41	18	6	111	108	0.879
Trichlorofluoromethane (R 11)	**7.42**	**7.49**	**5.38**	**5.95**	**28**	**20**	**108**	**119**	**0.099**
Acrolein	**6.55**	**7.14**	**5.35**	**6.03**	**18**	**16**	**107**	**121**	**0.011**
Acetone	4.62	5.37	5.99	5.96	30	11	120	119	0.979
Acetonitrile	5.88	6.09	6.51	6.48	11	6	130	130	0.974
Isopropyl alcohol	**5.24**	**6.65**	**5.61**	**6.20**	**7**	**7**	**112**	**124**	**0.164**
1,1-Dichloroethene	5.84	5.92	4.87	5.20	17	12	97	104	0.111
1,1,2-Trichlorotrifluoroethane (F 113)	5.60	5.65	4.54	4.83	19	14	91	97	0.112

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Compound	Day 0 ppbv		Day 30 ppbv		Stability (% Change)		% Recovery Day 30		*p*-value
	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	
Methylene chloride	6.06	6.09	6.09	6.30	0	3	122	126	0.825
Carbon disulfide	6.12	6.13	5.05	5.30	18	14	101	106	0.102
trans-1,2-Dichloroethene	6.21	6.22	5.00	5.30	19	15	100	106	0.128
Methyl *tert*-butyl ether (MTBE)	5.24	6.07	4.74	5.30	9	13	95	106	0.083
1,1-Dichloroethane	5.75	5.87	4.39	4.67	24	20	88	93	0.107
Vinyl acetate	5.83	6.39	4.78	5.40	18	15	96	108	0.012
2-Butanone (MEK)	4.46	5.36	4.14	4.61	7	14	83	92	0.115
Hexane	6.17	6.39	6.31	6.68	2	5	126	134	0.638
cis-1,2-Dichloroethene	5.88	6.07	4.64	4.93	21	19	93	99	0.130
Ethyl acetate	4.54	5.43	4.26	4.75	6	13	85	95	0.032
Chloroform	6.07	6.12	4.61	4.86	24	21	92	97	0.132
Tetrahydrofuran	4.83	5.66	4.48	4.87	7	14	90	97	0.108
1,1,1-Trichloroethane	5.95	6.00	4.66	4.96	22	17	93	99	0.136
1,2-Dichloroethane	**6.46**	**6.57**	**5.00**	**5.10**	**23**	**22**	**100**	**102**	**0.629**
Benzene	6.08	6.19	4.56	4.83	25	22	91	97	0.158
Carbon tetrachloride	5.38	5.41	4.33	4.66	20	14	87	93	0.048
Cyclohexane	6.13	6.25	4.89	5.17	20	17	98	103	0.166
Heptane	5.93	6.12	4.74	5.09	20	17	95	102	0.108
Trichloroethylene	6.29	6.33	4.87	5.10	23	19	97	102	0.344
1,2-Dichloropropane	**6.35**	**6.53**	**4.63**	**4.96**	**27**	**24**	**93**	**99**	**0.152**
Methyl methacrylate	4.69	5.42	4.08	4.25	13	22	82	85	0.388
1,4-Dioxane	**2.99**	**5.43**	**2.55**	**3.38**	**15**	**38**	**51**	**68**	**0.092**
Bromodichloromethane	**6.62**	**6.79**	**4.92**	**5.28**	**26**	**22**	**98**	**106**	**0.119**
4-Methyl-2-pentanone (MIBK)	3.49	5.22	3.61	4.43	3	15	72	89	0.039
cis-1,3-Dichloropropene	6.01	6.11	4.64	4.93	23	19	93	99	0.121
trans-1,3-Dichloropropene	6.11	6.17	4.74	4.90	22	21	95	98	0.403
Toluene	6.06	6.14	5.18	5.12	15	17	104	102	0.653
1,1,2-Trichloroethane	6.15	6.15	4.78	4.98	22	19	96	100	0.359
2-Hexanone (MBK)	**3.08**	**4.69**	**3.44**	**3.83**	**11**	**18**	**69**	**77**	**0.880**
Dibromochloromethane	6.03	6.06	4.83	5.13	20	15	97	103	0.176
Tetrachloroethene	4.87	4.91	4.41	4.64	9	5	88	93	0.265
1,2-Dibromoethane	5.80	5.85	4.43	4.60	24	22	89	92	0.367
Chlorobenzene	6.18	6.33	4.97	5.11	20	19	99	102	0.447
Ethylbenzene	5.89	6.21	4.80	4.98	18	20	96	100	0.283
m-Xylene	5.90	6.29	4.87	5.02	17	20	97	100	0.303
p-Xylene	5.90	6.29	4.87	5.02	17	20	97	100	0.303
Styrene	5.76	6.06	4.38	4.51	24	26	88	90	0.430
o-Xylene	5.92	6.33	4.86	5.04	18	20	97	101	0.259
Bromoform	5.76	6.05	5.06	5.37	12	11	101	107	0.125
1,1,2,2-Tetrachloroethane	**6.41**	**6.68**	**4.91**	**5.10**	**23**	**24**	**98**	**102**	**0.274**
4-Ethyltoluene	5.60	6.16	4.52	4.61	19	25	90	92	0.494
1,3,5-Trimethylbenzene	5.51	6.24	4.50	4.73	18	24	90	95	0.207
1,2,4-Trimethylbenzene	5.59	6.33	4.55	4.77	19	25	91	95	0.245
1,3-Dichlorobenzene	5.46	5.62	4.76	4.70	13	16	95	94	0.677
Benzyl chloride	**6.87**	**7.73**	**5.12**	**5.57**	**25**	**28**	**102**	**111**	**0.493**
1,4-Dichlorobenzene	5.50	5.59	4.79	4.63	13	17	96	93	0.265
1,2-Dichlorobenzene	5.71	5.93	4.95	4.99	13	16	99	100	0.837
1,2,4-Trichlorobenzene	**7.32**	**7.49**	**6.94**	**6.78**	**5**	**10**	**139**	**136**	**0.314**
Naphthalene	**8.02**	**10.10**	**6.37**	**5.81**	**21**	**42**	**127**	**116**	**0.433**
Hexachlorobutadiene	**6.41**	**6.92**	**5.83**	**6.34**	**9**	**8**	**117**	**127**	**0.054**
Average	**5.77**	**6.16**	**4.86**	**5.12**	**17**	**17**	**97**	**102**	

Although most of the compounds had good recoveries and were stable in the dry condition, there were some noteworthy observations. The majority of the VOCs were recovered close to 100% on Day 0; however, the following compounds had recoveries, which deviated from Method TO-15's audit accuracy criteria of 100±30%: trichlorofluoromethane (R11) (both SL canisters), acrolein (both SL canisters), isopropyl alcohol (Vendor A only), 1,2-dichloroethane (Vendor A only), 1,2-dichloropropane (Vendor A only), 1,4-dioxane (Restek only), bromodichloromethane (both SL canisters), 2-hexanone (Restek only), 1,1,2,2-tetrachloroethane (Vendor A only), benzyl chloride (both SL canisters), 1,2,4-trichlorobenzene (both SL canisters), naphthalene (both SL canisters), and hexachlorobutadiene (Vendor A only) This discrepancy could be due to the fact that all concentrations, and thereby recoveries, were generated from a calibration curve based on an aged (7 days), 50% RH standard. In contrast, the Day 0 canisters were fortified with fresh standards and then analyzed within 24 hours. Therefore, the aforementioned compounds in the spiked samples did not have the same amount of time to react with the canister walls and/or water vapor as they had in the aged, 50% RH standard which was used for calibration. Therefore, the Day 0 concentrations, and consequently the recoveries for these compounds, appear to be artificially high.

Figure 1 provides a visual representation of this equilibration/normalization phenomenon; where the 1,1,2,2-tetrachloroethane concentrations are relatively elevated (compared to the calibration standard) on Day 0 (~6.5 ppbv), but by Day 7 the concentrations decrease to a level more in line with the expected concentrations. Note that the Day 1 concentrations increased relative to Day 0. This was observed in the majority of the 66 VOCs. The equilibration/normalization theory, in particular as it pertains to sample versus standard, is further bolstered by the fact that with storage time, all of the previously mentioned compounds' recoveries receded closer to 100% (i.e., equilibration was complete). With the exception of 1,4-dioxane and 1,2,4-trichlorobenzene, all 66 VOCs were recovered close to 100% on Day 30.

Figure 1: Average 1,1,2,2-tetrachloroethane concentration in six Restek® (SilcoCan®) and six Vendor A canisters spiked at 5.00 ppbv, 30 psig, and 0% RH. Error bars represent 2 standard deviations.
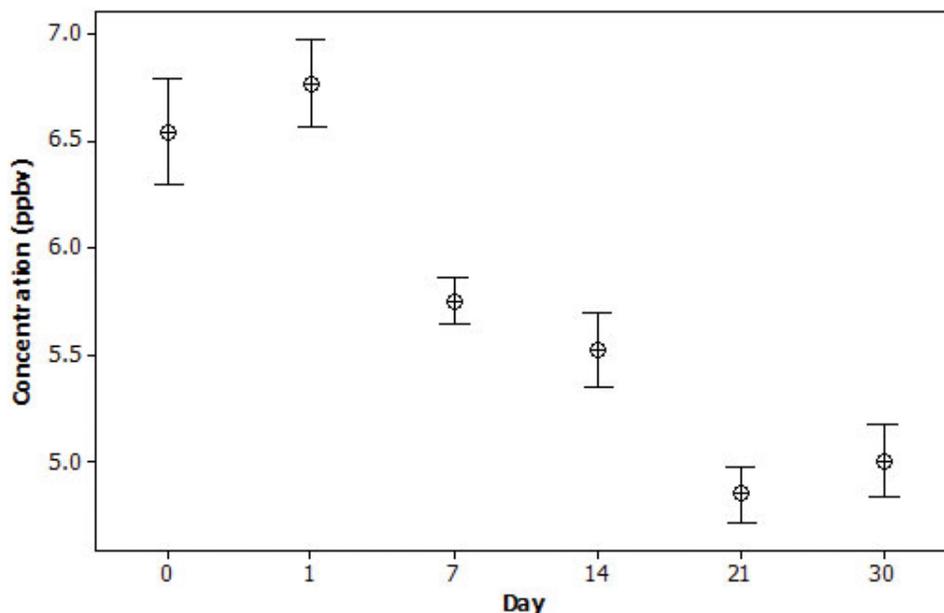
Humid Results

The humid experiment (93% RH) results (Table VII) indicate the two silicon-lined air canisters exhibited comparable recoveries and stabilities. The mean SilcoCan® and Vendor A recoveries on Day 0 were 100 and 97%, respectively. The mean SilcoCan® and Vendor A recoveries on Day 30 were 85 and 88%, respectively. An ANOVA indicated acrolein was the only significant ($p < 0.01$) difference among the 66 VOCs recoveries in the different silicon-lined canister types under humid (93% RH) conditions after 30 days of storage. The mean SilcoCan® and Vendor A percent change values from Day 0 to Day 30 were 13 and 9%, respectively. However, only 60 of the 66 compounds were stable (i.e., <30% change) over 30 days of storage in both SL canister types. Acrolein, dibromochloromethane, and bromoform were not stable in both the SilcoCan® and Vendor A canisters. In addition, acetone and benzyl chloride were not stable in the SilcoCan® canisters, with a 31 and 38% change in concentration from Day 0 to Day 30, respectively. Lastly, vinyl acetate was not stable in the Vendor A canisters, with a 33% change in concentration from Day 0 to Day 30.

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Table VII: Day 0 and Day 30 average concentrations of 66 TO-15 components stored in six Restek® (SilcoCan®) and six Vendor A canisters spiked at 5.00 ppbv, 30 psig, and 93% RH. Compounds in bold are anomalies, which have been discussed in the text. % Change equals the absolute value of Day 0 minus Day 30, divided by Day 0, and multiplied by 100. p-value from ANOVA of Restek® and Vendor A Day 30 concentrations.

Compound	Day 0 ppbv		Day 30 ppbv		Stability (% Change)		% Recovery Day 30		p-value
	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	
Propylene	4.46	4.11	4.33	4.38	3	7	87	88	0.229
Dichlorodifluoromethane (F 12)	4.59	4.28	4.12	4.24	10	1	82	85	0.169
Chloromethane	4.34	4.10	4.07	4.12	6	0	81	82	0.237
1,2-Dichlorotetrafluoroethane (F 114)	4.43	4.14	4.18	4.29	6	4	84	86	0.172
Vinyl chloride	4.32	4.04	4.15	4.36	4	8	83	87	0.136
1,3-Butadiene	4.46	4.11	3.95	4.27	11	4	79	85	0.092
Bromomethane	4.25	4.03	4.10	4.32	4	7	82	86	0.126
Chloroethane	4.23	4.02	4.18	4.33	1	8	84	87	0.159
Ethanol	4.74	2.99	5.95	3.18	25	7	119	64	0.049
Trichlorofluoromethane (R 11)	4.38	4.07	4.89	5.02	12	23	98	100	0.240
Acrolein	**3.37**	**3.72**	**0.10**	**1.20**	**97**	**68**	**2**	**24**	**0.006**
Acetone	**3.70**	**3.91**	**4.85**	**4.45**	**31**	**14**	**97**	**89**	**0.392**
Acetonitrile	4.67	4.21	4.08	4.46	13	6	82	89	0.462
Isopropyl alcohol	**3.32**	**3.49**	**3.31**	**3.91**	**0**	**12**	**66**	**78**	**0.381**
1,1-Dichloroethene	4.47	4.29	3.84	4.09	14	5	77	82	0.117
1,1,2-Trichlorotrifluoroethane (F 113)	4.48	4.24	3.96	4.14	12	2	79	83	0.144
Methylene chloride	4.49	4.48	5.12	5.13	14	15	102	103	0.411
Carbon disulfide	4.53	4.50	4.24	4.86	6	5	85	97	0.115
trans-1,2-Dichloroethene	4.49	4.29	4.05	4.35	10	1	81	87	0.109
Methyl tert-butyl ether (MTBE)	4.26	4.12	3.82	4.13	10	0	76	83	0.086
1,1-Dichloroethane	4.40	4.07	3.94	4.30	11	5	79	86	0.074
Vinyl acetate	**4.75**	**3.69**	**4.33**	**4.92**	**9**	**33**	**87**	**98**	**0.229**
2-Butanone (MEK)	3.89	3.69	4.20	3.89	8	5	84	78	0.848
Hexane	4.38	4.12	3.68	4.25	16	3	74	85	0.930
cis-1,2-Dichloroethene	4.28	4.12	4.06	4.21	5	2	81	84	0.169
Ethyl acetate	4.33	4.17	3.95	4.19	9	0	79	84	0.137
Chloroform	4.25	4.06	4.05	4.20	5	4	81	84	0.164
Tetrahydrofuran	3.92	3.81	3.71	3.95	5	4	74	79	0.132
1,1,1-Trichloroethane	4.34	4.08	3.83	4.04	12	1	77	81	0.127
1,2-Dichloroethane	4.43	4.24	3.69	4.02	17	5	74	80	0.107
Benzene	4.28	3.98	3.85	4.19	10	5	77	84	0.083
Carbon tetrachloride	4.76	4.49	4.35	4.86	9	8	87	97	0.056
Cyclohexane	4.28	4.07	3.92	4.15	9	2	78	83	0.130
Heptane	4.10	3.68	3.85	4.11	6	12	77	82	0.122
Trichloroethylene	4.34	4.10	3.89	4.15	10	1	78	83	0.101
1,2-Dichloropropane	4.49	4.16	3.86	4.20	14	1	77	84	0.074
Methyl methacrylate	4.38	4.33	4.08	4.29	7	1	82	86	0.163
1,4-Dioxane	**3.50**	**3.25**	**3.74**	**3.70**	**7**	**14**	**75**	**74**	**0.355**
Bromodichloromethane	5.08	5.05	3.68	3.93	28	22	74	79	0.325
4-Methyl-2-pentanone (MIBK)	4.47	4.34	3.94	4.07	12	6	79	81	0.237
cis-1,3-Dichloropropene	4.71	4.31	3.79	4.36	19	1	76	87	0.063
trans-1,3-Dichloropropene	5.05	4.83	3.92	4.62	22	4	78	92	0.038
Toluene	4.66	4.27	4.30	4.40	8	3	86	88	0.259
1,1,2-Trichloroethane	4.32	4.07	4.01	4.21	7	3	80	84	0.125
2-Hexanone (MBK)	4.48	4.27	4.52	4.49	1	5	90	90	0.404
Dibromochloromethane	**7.00**	**7.70**	**4.05**	**3.89**	**42**	**50**	**81**	**78**	**0.887**
Tetrachloroethene	4.39	3.93	3.84	4.10	12	4	77	82	0.125
1,2-Dibromoethane	4.62	4.37	3.89	4.21	16	4	78	84	0.099
Chlorobenzene	4.45	4.17	4.09	4.34	8	4	82	87	0.147
Ethylbenzene	4.41	4.21	4.22	4.33	4	3	84	87	0.215
m-Xylene	4.38	4.12	4.21	4.32	4	5	84	86	0.203
p-Xylene	4.38	4.12	4.21	4.32	4	5	84	86	0.203
Styrene	4.66	4.48	4.40	4.57	6	2	88	91	0.192
o-Xylene	4.86	4.65	4.38	4.20	10	10	88	84	0.443

Compound	Day 0 ppbv		Day 30 ppbv		Stability (% Change)		% Recovery Day 30		p-value
	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	Restek	Vendor A	
Bromoform	**18.9**	**28.6**	**4.46**	**4.30**	**76**	**85**	**89**	**86**	**0.438**
1,1,2,2-Tetrachloroethane	5.14	4.83	4.84	4.91	6	2	97	98	0.418
4-Ethyltoluene	4.92	4.66	4.54	4.67	8	0	91	93	0.252
1,3,5-Trimethylbenzene	5.02	4.66	4.56	4.64	9	1	91	93	0.283
1,2,4-Trimethylbenzene	5.11	4.74	4.70	4.80	8	1	94	96	0.306
1,3-Dichlorobenzene	5.22	4.81	5.24	5.09	0	6	105	102	0.542
Benzyl chloride	**12.8**	**11.4**	**7.97**	**8.41**	**38**	**26**	**159**	**168**	**0.634**
1,4-Dichlorobenzene	5.56	5.09	5.09	5.03	8	1	102	101	0.512
1,2-Dichlorobenzene	5.70	5.21	5.20	5.11	9	2	104	102	0.601
1,2,4-Trichlorobenzene	**6.62**	**5.57**	**5.65**	**5.18**	**15**	**7**	**113**	**104**	**0.088**
Naphthalene	**7.28**	**6.21**	**5.26**	**4.64**	**28**	**25**	**105**	**93**	**0.076**
Hexachlorobutadiene	**7.96**	**7.04**	**6.66**	**6.67**	**16**	**5**	**133**	**133**	**0.376**
Average	**4.99**	**4.83**	**4.27**	**4.40**	**13**	**9**	**85**	**88**	

Although most of the compound recoveries were good and deemed stable in the humid condition, there were some notable observations. Most of the VOCs were recovered close to 100% on Day 0. There were several compounds that had recoveries, which deviated from Method TO-15's audit accuracy criteria of ±30%. Dibromochloromethane (both SL canisters), bromoform (both SL canisters), benzyl chloride (both SL canisters), 1,2,4-trichlorobenzene (Restek only), naphthalene (Restek only), and hexachlorobutadiene (both SL canisters) were recovered more than 130% on Day 0. It is hypothesized that excess water vapor passivated the air canister walls to some degree. Recall that the concentrations, and thereby recoveries, were generated from calibration curves based on an aged, 50% RH standard. The fact that benzyl chloride, 1,2,4-trichlorobenzene, naphthalene, and hexachlorobutadiene had high recoveries in both the dry and humid conditions suggests there were calibration issues. Several compounds (ethanol [Vendor A only], acrolein [Restek only], isopropyl alcohol [both SL canisters], and 1,4-dioxane [Vendor A only]) were recovered less than 70% on Day 0. This difference may be due to the dissolution of these polar compounds in excess water. This observation is consistent with what Ochiai et al. [20] had observed. However, the fact that 1,4-dioxane had recovery divergences in both the dry and humid conditions suggests there were calibration issues for this compound.

Overall

The majority of the 66 TO-15 VOCs evaluated in this study were recovered at close to 100% and determined to be stable in both Restek® and Vendor A's silicon-lined air canisters, both under the dry (0% RH) and humid (93% RH) conditions. This observation is consistent with the conclusions previously drawn in Methods TO-14A and TO-15 for most VOCs. These compounds were already deemed stable in electropolished and SUMMA passivated, stainless steel canisters under routine ambient air analysis after storage of up to 30 days [2]. The majority of the apparent discrepancies in recovery and/or storage stability raised in the two previous sections (Dry Results and Humid Results) suggest that the calibration may be responsible. This observation is consistent with Kelly and Holdren's [19] conclusion that further improvements in calibration and analytical methods are needed, because determination of sample stability is dependent upon analytical measurements. Considering that standard preparation practices vary widely among labs and that fresh samples are routinely quantified using standards that vary in age and humidity, this issue deserves further consideration and discussion within the industry.

The only compounds which demonstrated a true instability (i.e., were substantially outside the ±30% acceptance criteria for recovery and/or storage stability under the humid condition for both canister types) were acrolein (Figure 2), dibromochloromethane, and bromoform. Kelly and Holdren [19] did not evaluate acrolein, but indicated that its stability in canisters was questionable due to acrolein's high water solubility, which appears to be responsible for the results in the current study. Brymer et al. [15] found dibromochloromethane to be stable; however, they were using 70% RH. Information on bromoform was not readily available in the current body of literature. The current instability of these compounds appears to be directly related to the dissolution of soluble compounds in condensed water, which was exacerbated by the pressurization of the canisters [21].

The majority of previous studies stressed the importance of humidity (i.e., having a minimum amount of water vapor present) in reducing the loss of VOCs to the air canister walls [19]. However, in the current study the use of silicon-lined air canisters did not demonstrate this dependency. This observation is consistent with Ochiai et al.'s [18] observations of SL canisters and low RH. In the current study, recoveries were higher under dry conditions, which again is probably due to the dissolution of compounds in condensed water under the extremely humid conditions.

Figure 2: Average acrolein concentration in six Restek® (SilcoCan®) and six Vendor A canisters spiked at 5.00 ppbv, 30 psig, and 93% RH. Error bars represent 2 standard deviations.
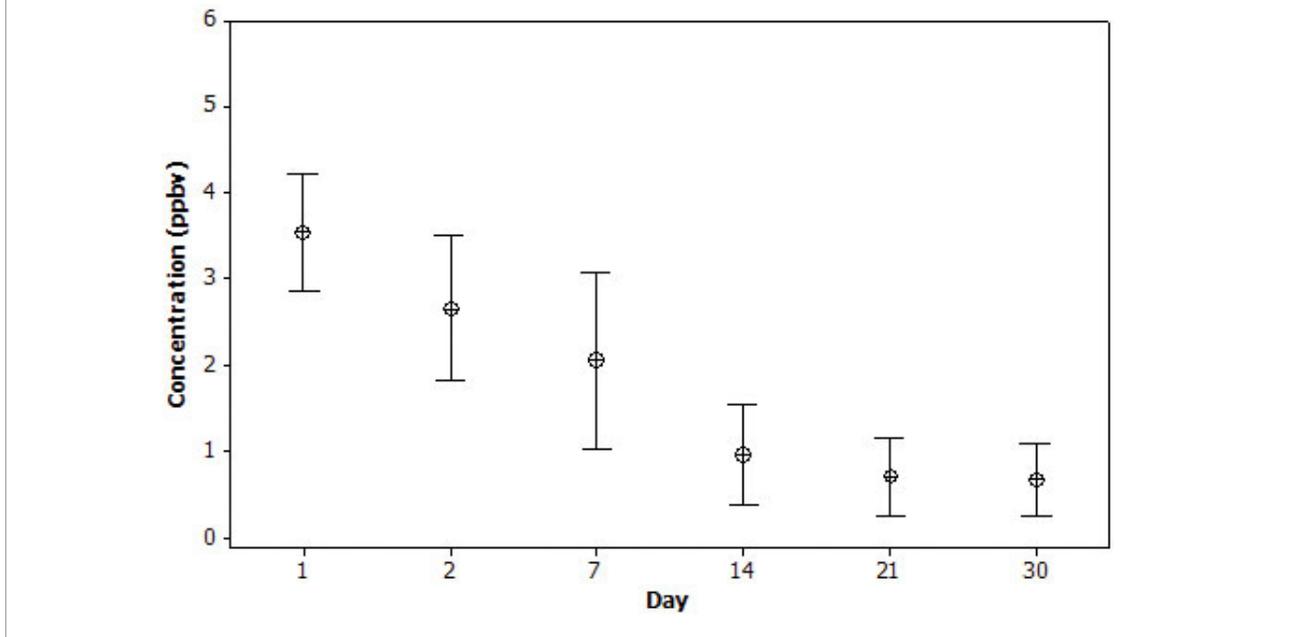
Study Limitations/Future Research

Only six of each type of silicon-lined air canister were used in the current study. In addition, all twelve canisters were brand new. Such a small sample set of new canisters may not be representative of what the typical end user should expect from their used air canisters. Future studies should utilize a larger sample set (i.e., more canisters) and incorporate used silicon-lined air canisters. Lastly, the current study used nitrogen as the fill gas. The current study was only interested in elucidating any differences between silicon-lined canisters. However, future storage stability studies of VOCs in air canisters should utilize air as a fill gas, due to the relatively increased oxidative potential air may have over nitrogen.

Conclusions

The majority of the 66 TO-15 VOCs evaluated in this study were recovered at close to 100%, and deemed stable in both Restek® and Vendor A silicon-lined air canisters, both under the dry (0% RH) and humid (93% RH) conditions. There were no statistically significant ($p < 0.01$) differences in the Day 30 recoveries for the two air canister types under dry conditions. However, acrolein was found to be significantly ($p = 0.006$) different between air canister types in the humid condition after 30 days of storage. The majority of recovery/stability variances appear to be calibration related. Acrolein, dibromochloromethane, and bromoform were the only compounds which appeared to exhibit instability in both SL canister types under humid (93% RH) conditions.

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