Canister Cleaning Practices and Blank VOC Concentrations

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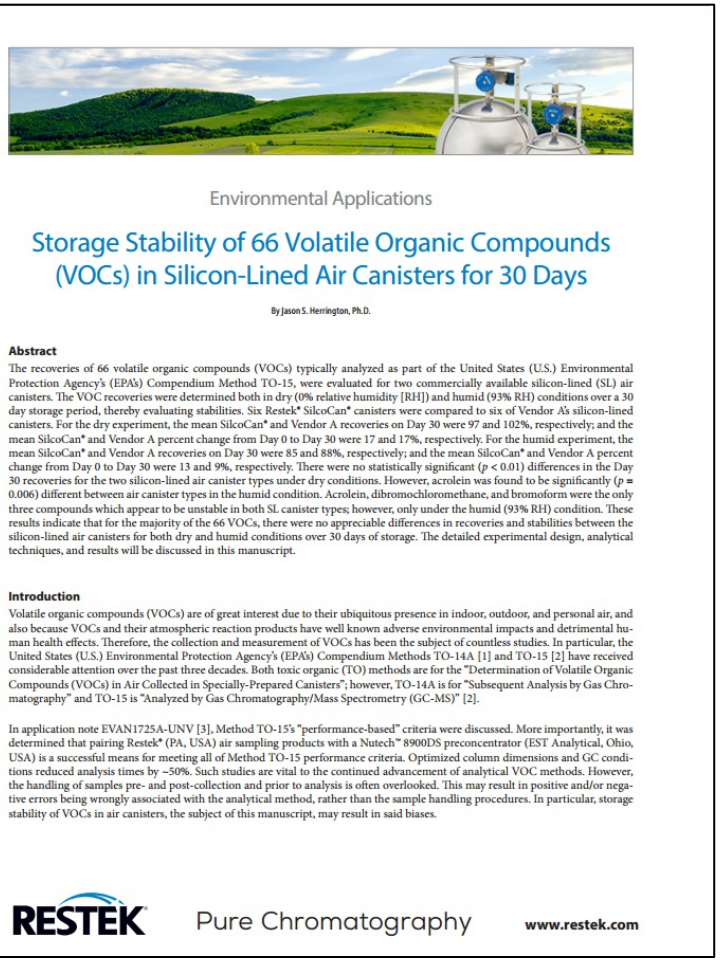
NEMC *2014* Recap on Stabilities

- Most VOCs are stable in a variety of canister types and under various conditions, for up to 30 days of storage.
- Most VOCs exhibit a 24- to 48-hour concentration/ equilibration blip.



Environmental Applications

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

By Jason S. Herrington, Ph.D.

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.

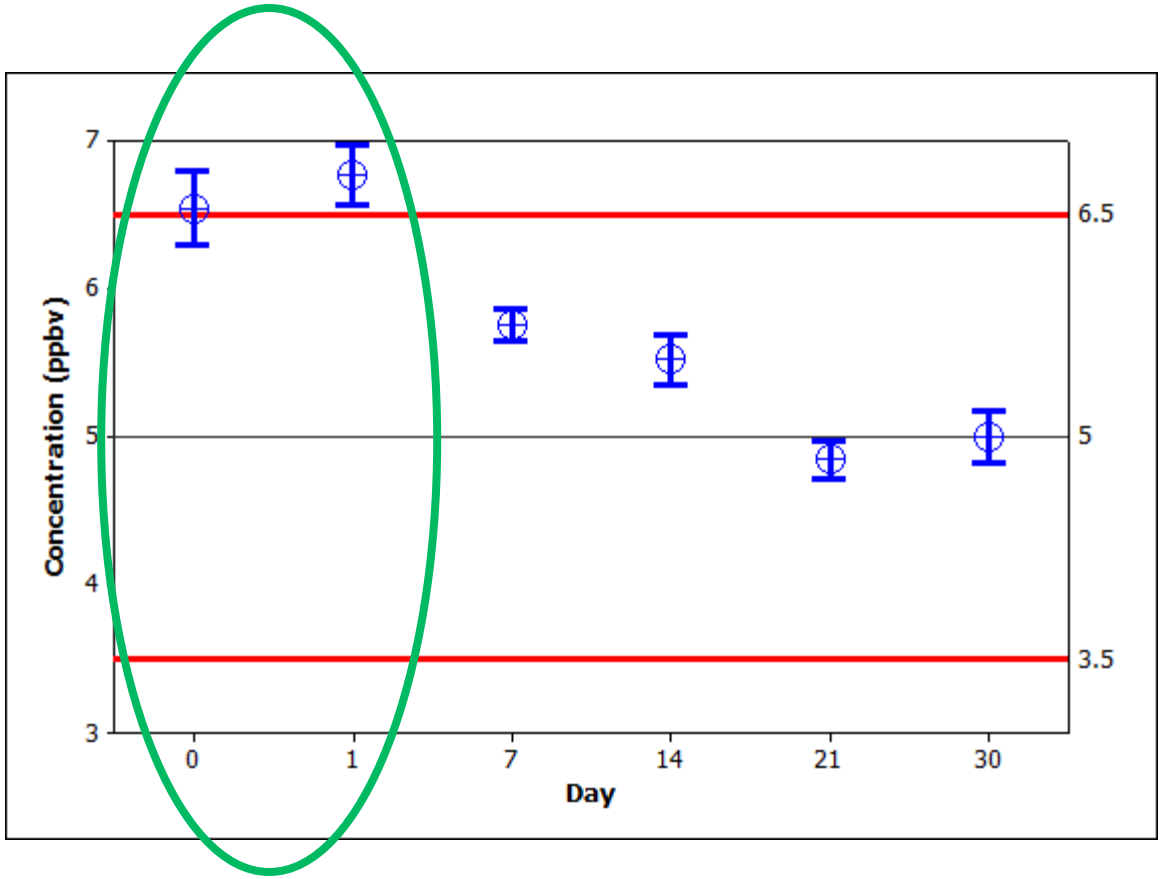
Introduction

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.

RESTEK Pure Chromatography www.restek.com

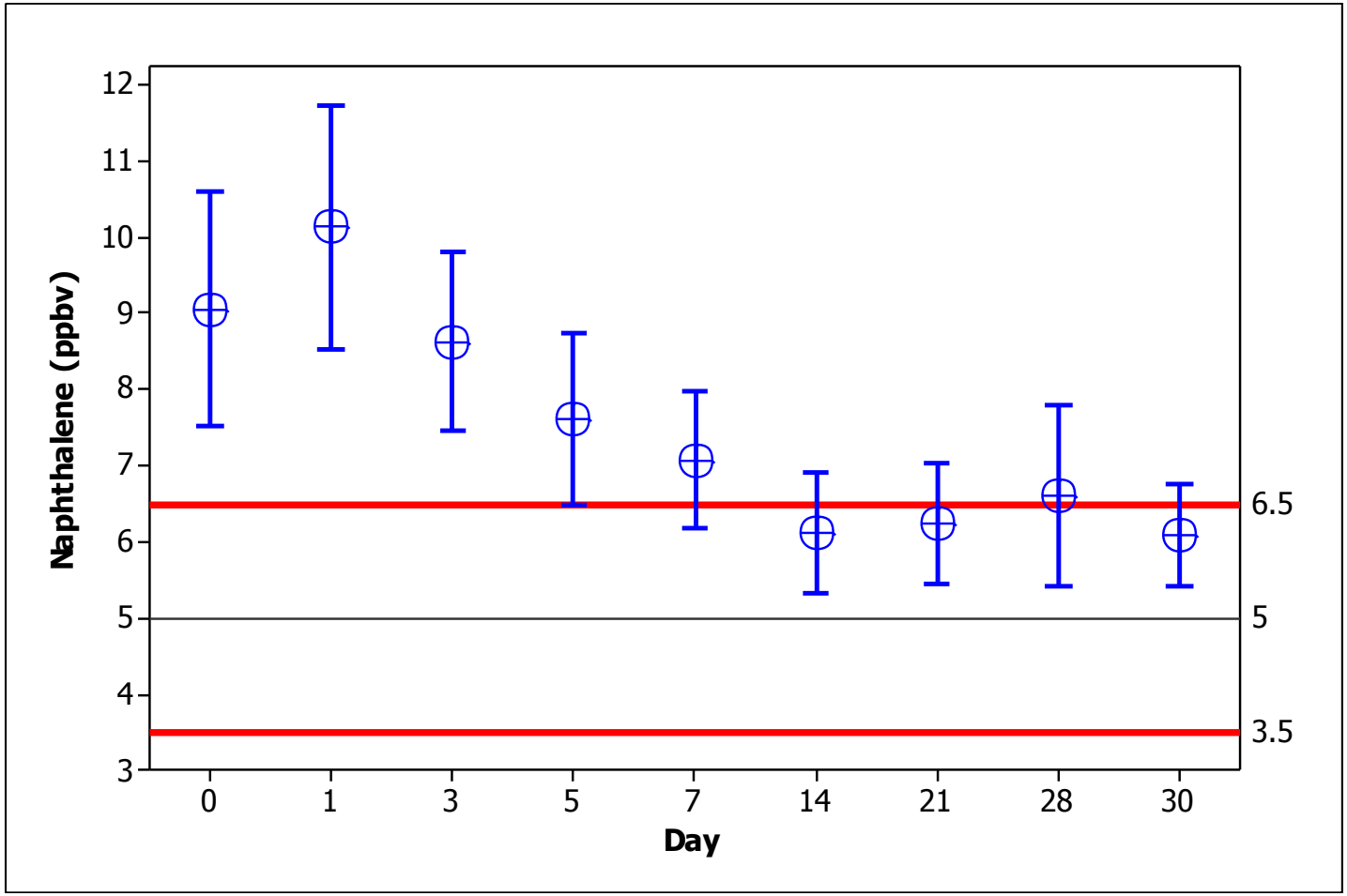
1,1,2,2-Tetrachloroethane



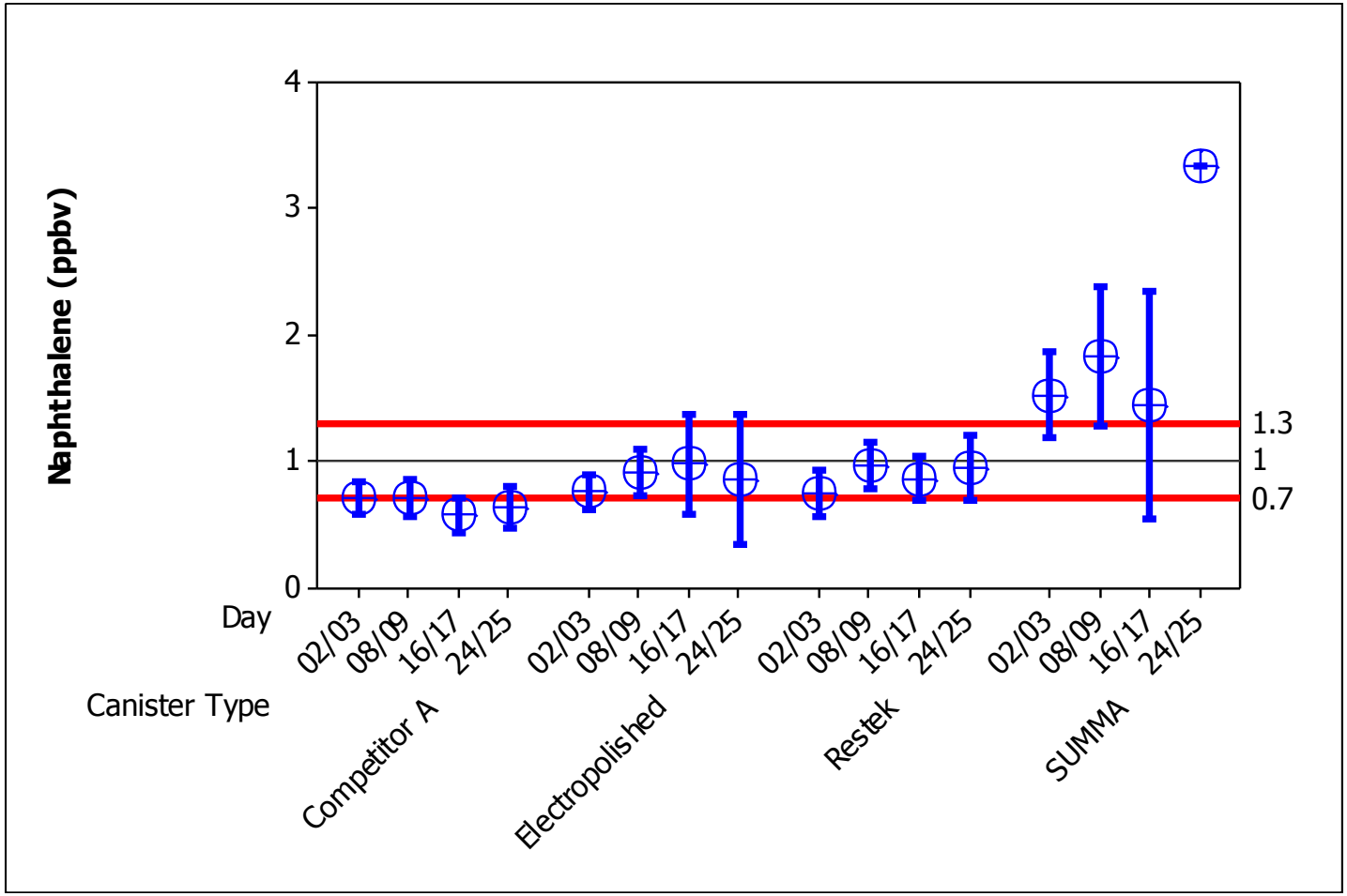
“Misfit” VOCs

Compound	5.00 ppbv @ 30 psig w/ 0% RH								
	Day 0		Day 30		% Change		% Recovery Day 30		*p*-value
	Restek	Competitor A	Restek	Competitor A	Restek	Competitor A	Restek	Competitor A	
Acrolein	6.6	7.1	5.4	6.0	18	16	107	121	0.011
Isopropyl Alcohol	5.2	6.7	5.6	6.2	7	7	112	124	0.164
Benzyl Chloride	6.9	7.7	5.1	5.6	25	28	102	111	0.493
Naphthalene	8.0	10.1	6.4	5.8	21	42	127	116	0.433
Hexachlorobutadiene	6.4	6.9	5.8	6.3	9	8	117	127	0.054
Average	**5.8**	**6.2**	**4.9**	**5.1**	**18**	**17**	**97**	**102**	

Naphthalene @ 0% RH in Silicon-Lined Canister



Canister Type Differences for Naphthalene @ 50% RH



NEMC *2015*

- Evaluate various canister cleaning procedures and the impacts on VOC concentrations in blanks.

- Focus on "misfits":
  - Naphthalene
  - Acrolein

Section 8.4.1 of Method TO-15

- Evacuate down to 500 mTorr
- Hold under vacuum for 60 minutes
- Fill with humidified "zero air" to 30 psig
- Repeat cycle two additional times for a total of three cycles

- **8.4.1.8** As an *option* to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100 -°-C during evacuation of the canister…

Informal Customer Survey

- We do not use a humidified gas…
- We do not use heat…
- We use 14 cycles to clean our canisters…
- We use 6 cycles to clean…
- Etc…

- The various iterations of cleaning schemes goes on at infinitum…

“EPA Combo”

- Evacuate down to 500 mTorr
- Hold under vacuum for 60 minutes
- Fill with humidified “zero *nitrogen*” to 30 psig
- Repeat cycle two additional times for a total of three cycles

- AND… 100 -°-C

Blank Terminology

- **8.4.1.6**
  - At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa ***(30 psig) with humid zero air.*** The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of ***less than 0.2 ppbv of targeted VOCs***) should not be used.

- **10.7.1**
  - To monitor for possible laboratory contamination… A ***laboratory method blank (LMB)*** is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample.

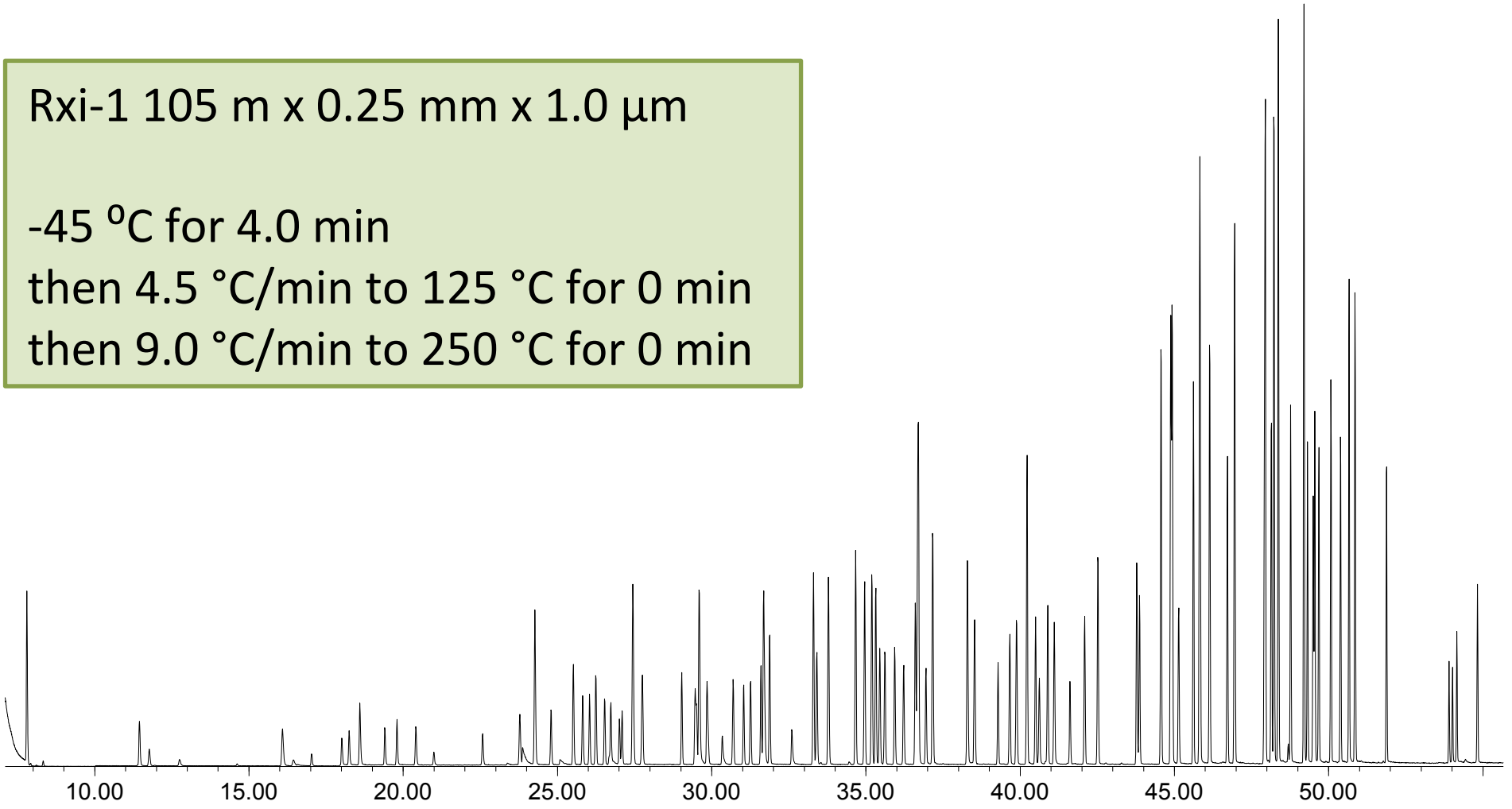
“EPA Combo” on 4 Newer SilcoCans Exposed to 100 ppbv - LMB (i.e., 2.5 psig)

	SilcoCan
Ethylene	0.00
1-Butene	0.00
Chloroethane	0.00
Ethanol	0.00
Acetonitrile	0.00
Acetone	0.09
Tert Butanol	0.00
Vinyl Acetate	0.00
2-Butanone (MEK)	0.00
Benzene	0.00
n-Heptane	0.06
4-Methyl-2-Pentanone (MIBK)	0.00
Toluene	0.00
2-Hexanone (MBK)	0.00
Styrene	0.00
Dodecane	0.00
Naphthalene	0.20
Hexachlorobutadiene	0.00

Ethylene to Hexachlorobutadiene

Rxi-1 105 m x 0.25 mm x 1.0 µm

-45 °C for 4.0 min
then 4.5 °C/min to 125 °C for 0 min
then 9.0 °C/min to 250 °C for 0 min



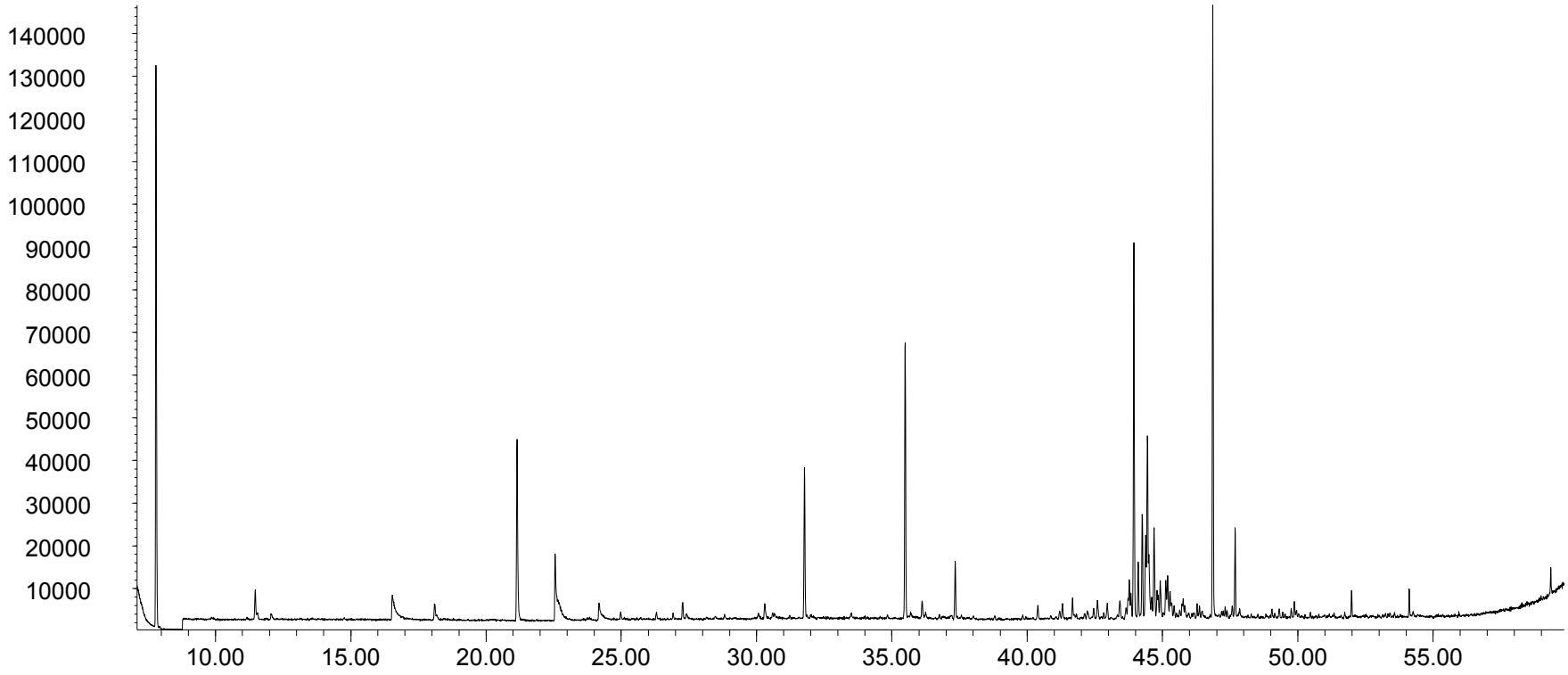
“EPA Combo” on 4 SUMMAs - LMB (i.e., 2.5 psig)

	EPA 1	EPA 2	EPA 3
Ethylene	0.48	0.04	0.00
1-Butene	1.48	0.10	0.04
Chloroethane	0.47	0.00	0.00
Ethanol	31.67	2.38	0.27
Acetonitrile	0.76	0.00	0.00
Acetone	0.91	0.32	0.40
Tert Butanol	0.92	0.00	0.00
Vinyl Acetate	0.57	0.13	0.00
2-Butanone (MEK)	0.68	0.13	0.00
Benzene	0.43	0.00	0.00
n-Heptane	0.19	0.04	0.04
4-Methyl-2-Pentanone (MIBK)	0.13	0.00	0.00
Toluene	0.13	0.00	0.00
2-Hexanone (MBK)	0.13	0.00	0.00
Styrene	0.23	0.00	0.00
Dodecane	0.60	0.00	0.00
Naphthalene	4.55	0.57	0.33
Hexachlorobutadiene	0.00	0.00	0.00

“EPA Combo” on 4 Very Old TO-Cans - LMB (i.e., 2.5 psig)

	EPA Combo
Ethylene	0.60
Acetylene	0.36
1-Butene	0.80
Chloroethane	14.0
Ethanol	3.18
Acetonitrile	0.30
Acrolein	0.20
Isopentane	1.15
Acetone	1.03
2-Butanone (MEK)	0.42
Toluene	0.11
Undecane	0.23
Dodecane	0.65
Naphthalene	0.14

LMB of Very Old TO-Can



“Restek Wash”

- A simple canister cleaning procedure.
- However… I am not at the liberty to divulge any details right now.
  - Next year!?!?

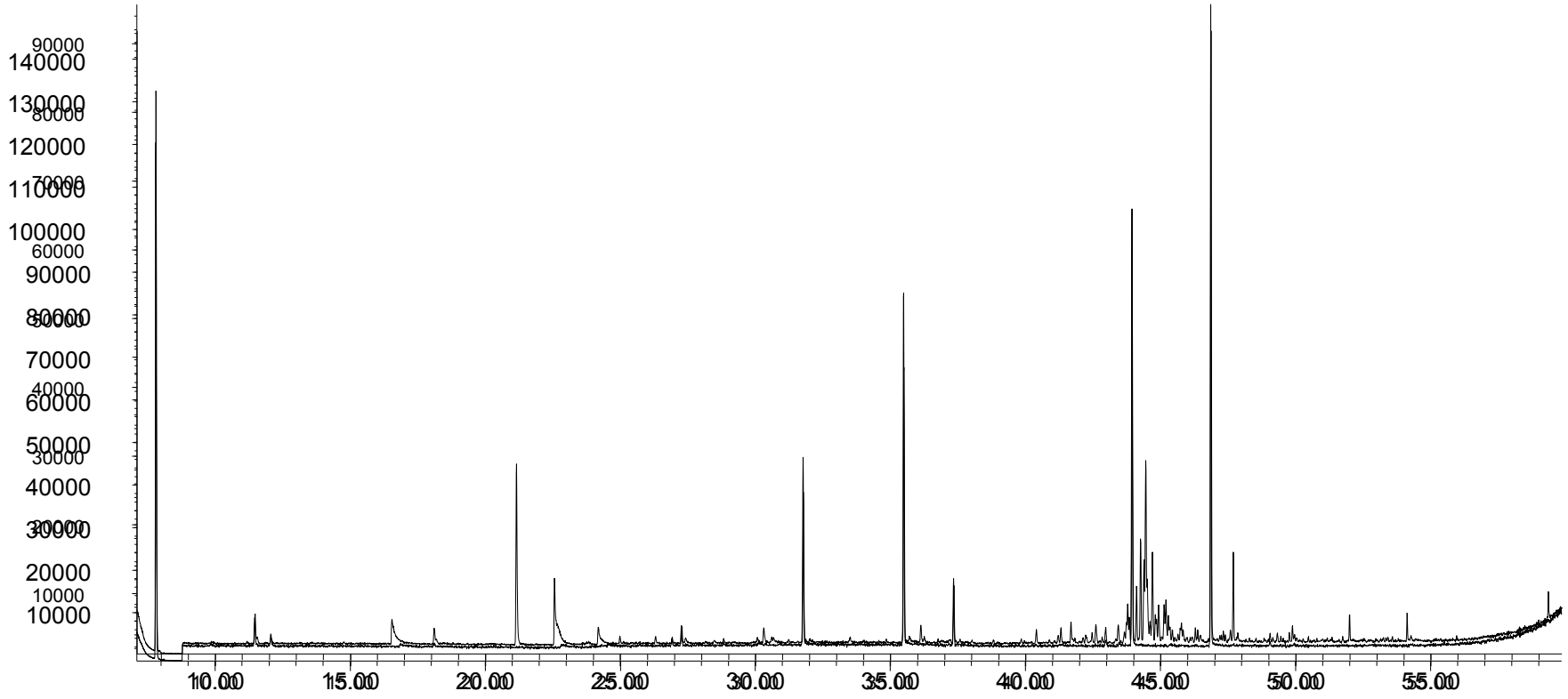
“Restek Wash” on 4 SUMMAs – LMB (i.e., 2.5 psig)

		EPA 1	EPA 2	EPA 1	EPA 2	EPA 3	Restek
	Ethylene	0.48		0.00	0.00	0.00	0.00
	1-Butene	1.48		0.10	0.04	0.04	0.00
	Chloroethane	0.47		0.00	0.00	0.00	0.00
	Ethanol	31.67	2.38		0.27	0.27	0.00
	Acetonitrile	0.76		0.00	0.00	0.00	0.00
	Acetone	0.91	0.32		0.40	0.40	0.17
	Tert Butanol	0.92		0.00	0.00	0.00	0.00
	Vinyl Acetate	0.57		0.13	0.00	0.00	0.07
	2-Butanone (MEK)	0.68		0.13	0.00	0.00	0.00
	Benzene	0.43		0.00	0.00	0.00	0.00
	n-Heptane	0.19		0.04	0.04	0.04	0.01
	4-Methyl-2-Pentanol (MIBK)	0.13		0.00	0.00	0.00	0.00
	Toluene	0.13		0.00	0.00	0.00	0.00
	2-Hexanone (MBK)	0.13		0.00	0.00	0.00	0.00
	Styrene	0.23		0.00	0.00	0.00	0.00
	Dodecane	0.60		0.00	0.00	0.00	0.00
	Naphthalene	4.55	0.57		0.33	0.33	0.13
	Hexachlorobutadiene	0.00		0.00	0.00	0.00	0.00

“Restek Wash” on 4 Very Old TO-Cans

	EPA Combo	EPA Combo Restek V2
Ethylene	0.60	00
Acetylene	0.36	00
1-Butene	0.80	08
Chloroethane	14.0	00
Ethanol	3.18	00
Acetonitrile	0.30	00
Acrolein	0.20	0.00
Isopentane	1.15	00
Acetone	1.03	01
2-Butanone (MEK)	0.42	00
Toluene	0.11	0.01
Undecane	0.23	00
Dodecane	0.65	00
Naphthalene	0.14	0.06

“Restek Wash” on 4 Very Old TO-Cans



2 “Stubborn” and proven “acrolein growing” canisters from colleagues.

	3858	A236
As Received	**1.2**	**0.68**
Restek Wash w/ N2	0.04	0.12
Aged 14 Days	**0.27**	**0.41**
Restek Wash w/ Air	0.11	0.14
Aged 14 Days	0.14	0.18

Conclusions

- Everything here is very preliminary…
- "EPA Combo" appears to work very well on "normally" soiled canisters.
- However, naphthalene continues to be a misfit.
  - Something to consider for TO-15 as a whole, especially when we remember the stabilities from before.
- "Restek Wash" appears to clean up very stubborn canisters.
  - Perhaps a viable option when the "EPA Combo" is not making the grade.

Conclusions (cont'd)

- 2 weeks of storage helps facilitate the growth of acrolein in blanks.
  - Something to consider for TO-15 as a whole, considering blank holding/testing times are not addressed in the method.
- Using air vs. nitrogen for cleaning appears promising.
  - Makes sense given the redox potential differences.
- Future work on "Restek Wash":
  - Soliciting "stubborn" canisters.