Canister Cleaning Practices and Blank VOC Concentrations

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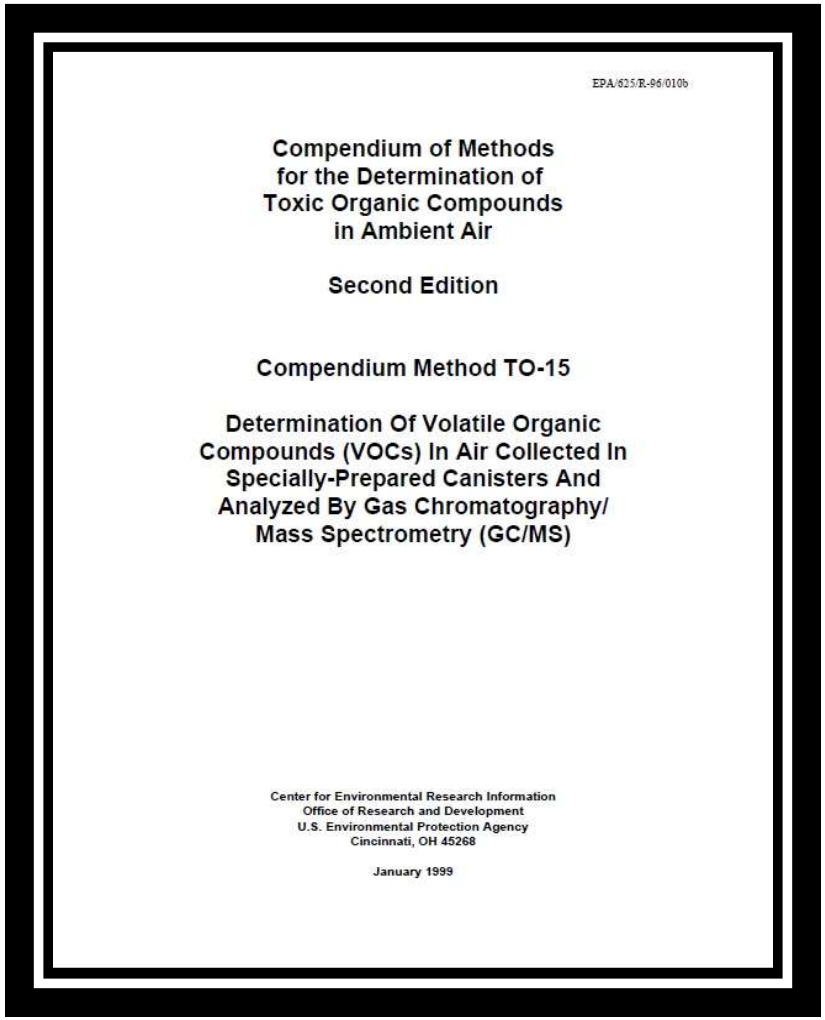
U.S. EPA Method TO-15

- A "*guidance document*" for a Performance Based Method (PBM)
- Means a laboratory can meet performance criteria by hook or crook



EPA/625/R-96/010b

Compendium of Methods
for the Determination of
Toxic Organic Compounds
in Ambient Air

Second Edition

Compendium Method TO-15

Determination Of Volatile Organic
Compounds (VOCs) In Air Collected In
Specially-Prepared Canisters And
Analyzed By Gas Chromatography/
Mass Spectrometry (GC/MS)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

TO-15 Blank Criteria

- **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.

“Guidance” for Canister Cleaning

- **8.4.1** 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…
- We use nitrogen, not air…
- Etc…
- The various iterations of cleaning regimens goes on at infinitum…

So why today's talk?

- Assu[illegible]dures are [illegible]..
- No r[illegible]
- BUT.

Compound	1-in-1-million cancer risk (pptv)	Noncancer effects (pptv)
Acrolein	NA	9
Naphthalene	5.6	570
Propylene Dichloride	11	870
1,3-Butadiene	15	900
Acrylonitrile	6.8	920
Ethylene Dibromide	0.22	1200
Methyl Bromide	NA	1300
Benzene	39	9200
Carbon Tetrachloride	26	16000
Vinyl Chloride	44	38000
1,4-Dichlorobenzene	15	133000
Ethylbenzene	92	230000
1,1,2,2-Tetrachloroethane	2.5	NA
Ethylene Dichloride	9.5	NA
Tetrachloroethylene	25	NA
Trichloroethylene	93	NA

Current Study

- Last Summer @ NEMC - Wayne Whipple (U.S. EPA Region 5) and I coincidentally presented on canister cleaning

- Both of us had limited sample sets and/or test parameters

- So for today I evaluated 30 brand new electropolished stainless steel canisters under various cleaning regimens

Objectives

- Time Dependence
  - Only one obscure reference to blank holding times prior to analysis in Method TO-15. Specifically, in section 8.4 "Cleaning and Certification Program" it states ***12 hours*** of aging.
  - The only other time TO-15 mentions an ageing period is in section 6 "Interferences and Contamination," where the method states that canisters should be aged for ***24 hours***; however, this is for the qualification of "new" canisters.

Objectives (cont'd)

- Sweep Gas
  - Method TO-15 routinely states **"zero air."** However, most laboratories are using nitrogen from the headspace of their liquid nitrogen dewars, which are used for the air concentrators.

- Heat
  - Clearly listed as an ***"option,"*** which some laboratories are taking advantage of.

Experimental Design

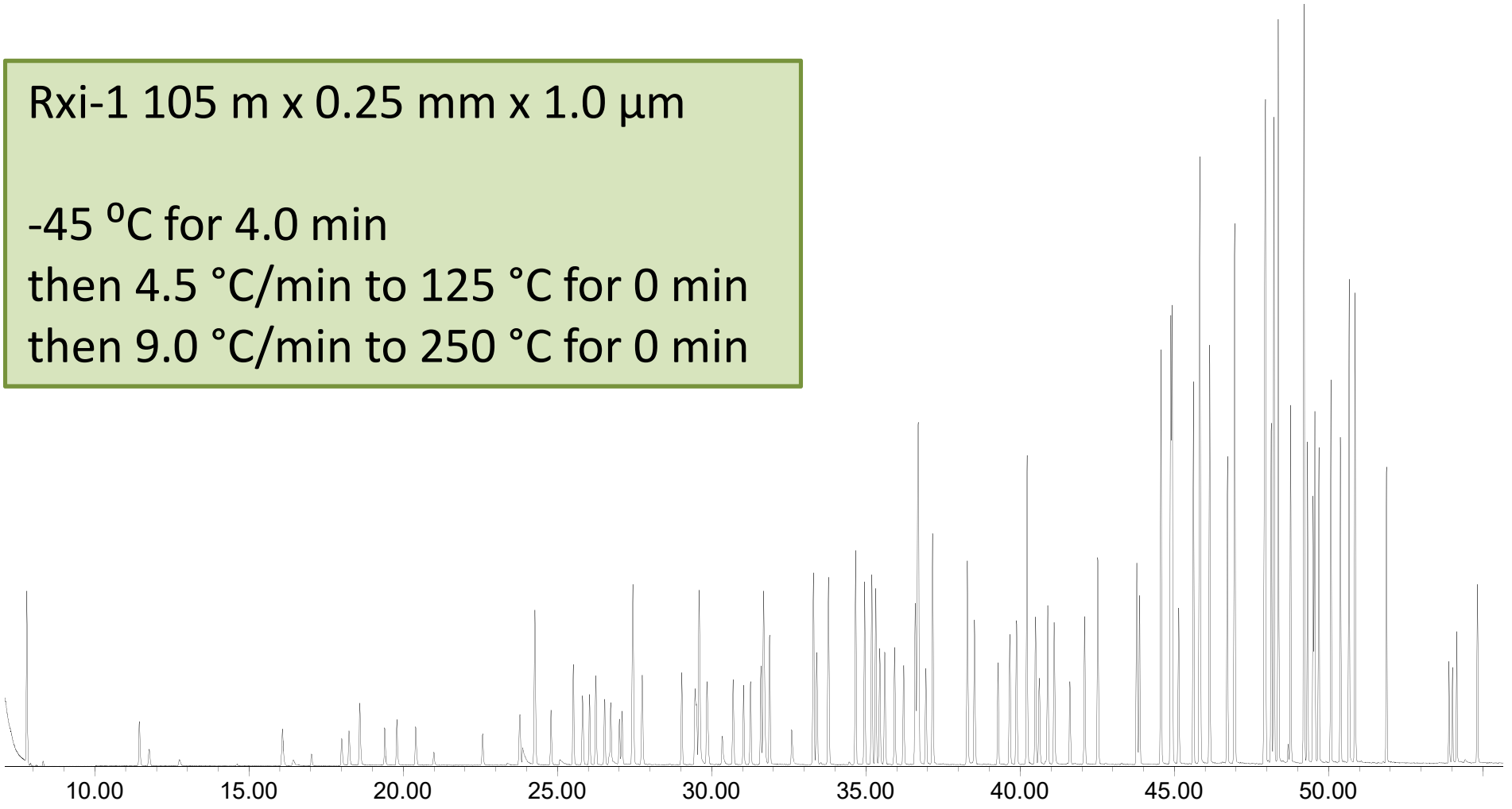
Experiment	Sweep Gas	Humidification	Heat	# of Cycles
N_2/NO-H_2O/25	Nitrogen	0% RH	25 °C	1
N_2/H_2O/100	Nitrogen	50% RH	100 °C	12
Air/H_2O/100	Air	50% RH	100 °C	12
Air/H_2O/ 25	Air	50% RH	25 °C	12
Proprietary	Air	50% RH	100 °C	12

- All canisters filled to 30 psig with 50% RH zero air
- 800 mL sample volumes
- SIM calibrated from 10 to 300 pptv
- Analyzed on Day 0 and 14

Ethylene to Hexachlorobutadiene

Rxi-1 105 m x 0.25 mm x 1.0 µm

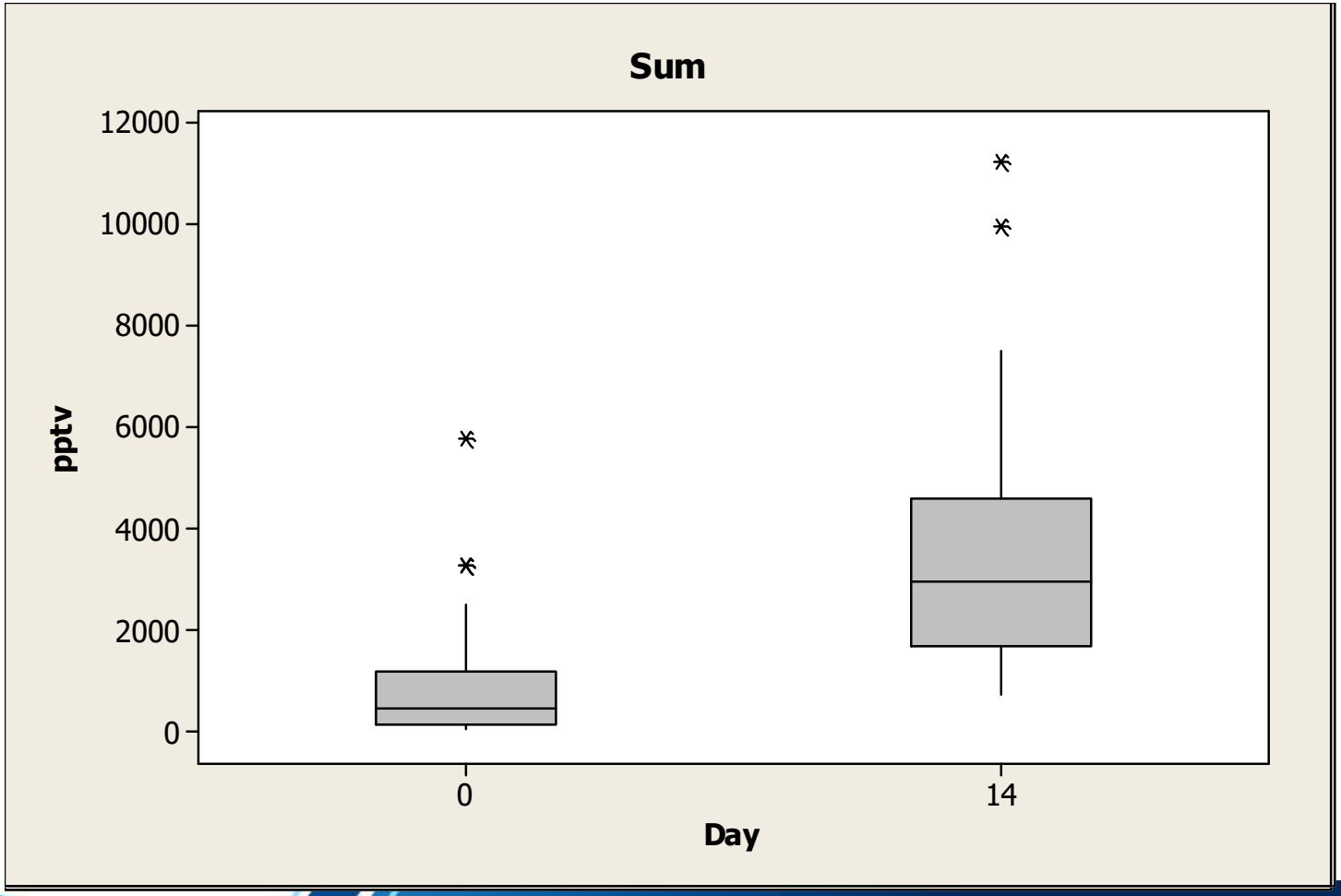
-45 °C for 4.0 min
then 4.5 °C/min to 125 °C for 0 min
then 9.0 °C/min to 250 °C for 0 min



“Usual Suspects”

Compound	W. Whipple	Me
Acetone	x	x
Acrolein	x	x
Benzene	x	x
Benzyl Chloride	x	x
Dichlorodifluoromethane (F12)	x	x
Ethanol	x	x
Hexachlorobutadiene	x	x
Isopropyl Alcohol	x	x
Methylene Chloride	x	x
Naphthalene	x	x
Propylene	x	x
1,2,4-Trichlorobenzene	x	x
2-Butanone (MEK)	x	x
2-Hexanone (MBK)	x	x

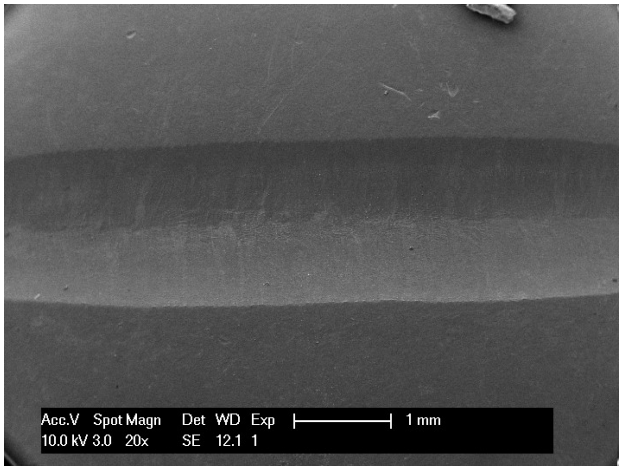
Time

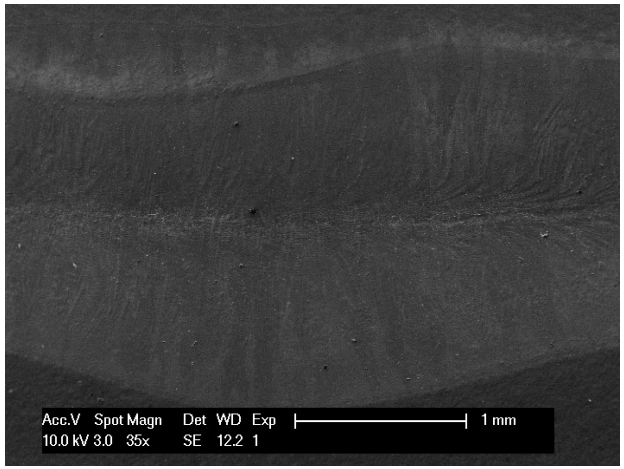


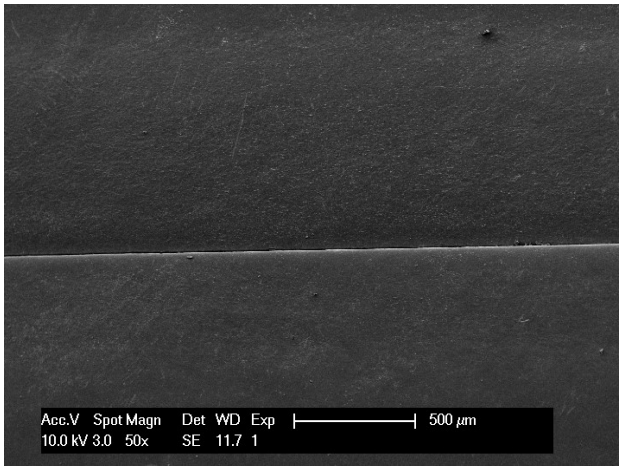
Time (cont'd)

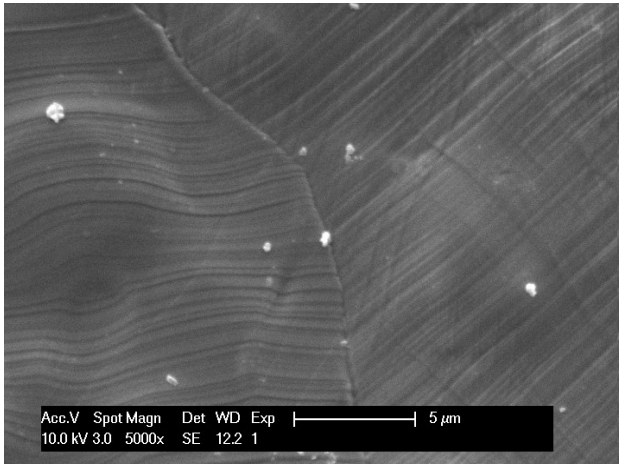
- Observation:
  - Most VOCs "grow" significantly with time… not just acrolein
- Explanation:
  - KISS: The VOCs and/or precursors are still on the canister walls at low levels and take time to volatilize and/or react
- Recommendation:
  - Blank aging/holding times need to be more in line with sample turn-around time

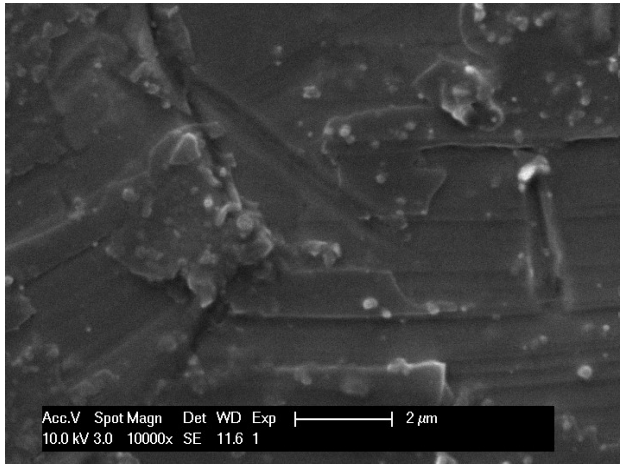
VOC Sinks

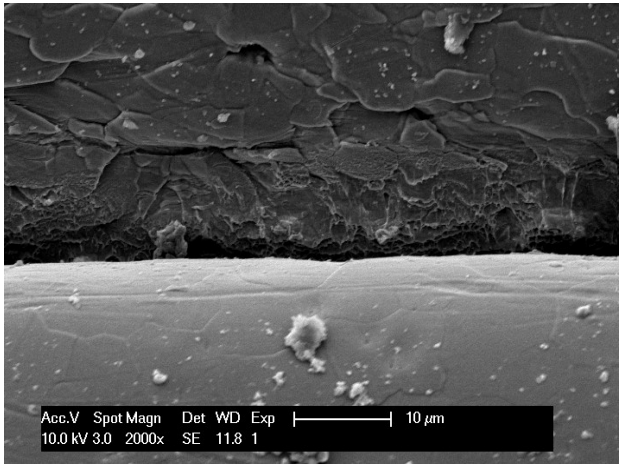

Acc.V Spot Magn Det WD Exp 1 mm
10.0 kV 3.0 20x SE 12.1 1


Acc.V Spot Magn Det WD Exp 1 mm
10.0 kV 3.0 35x SE 12.2 1

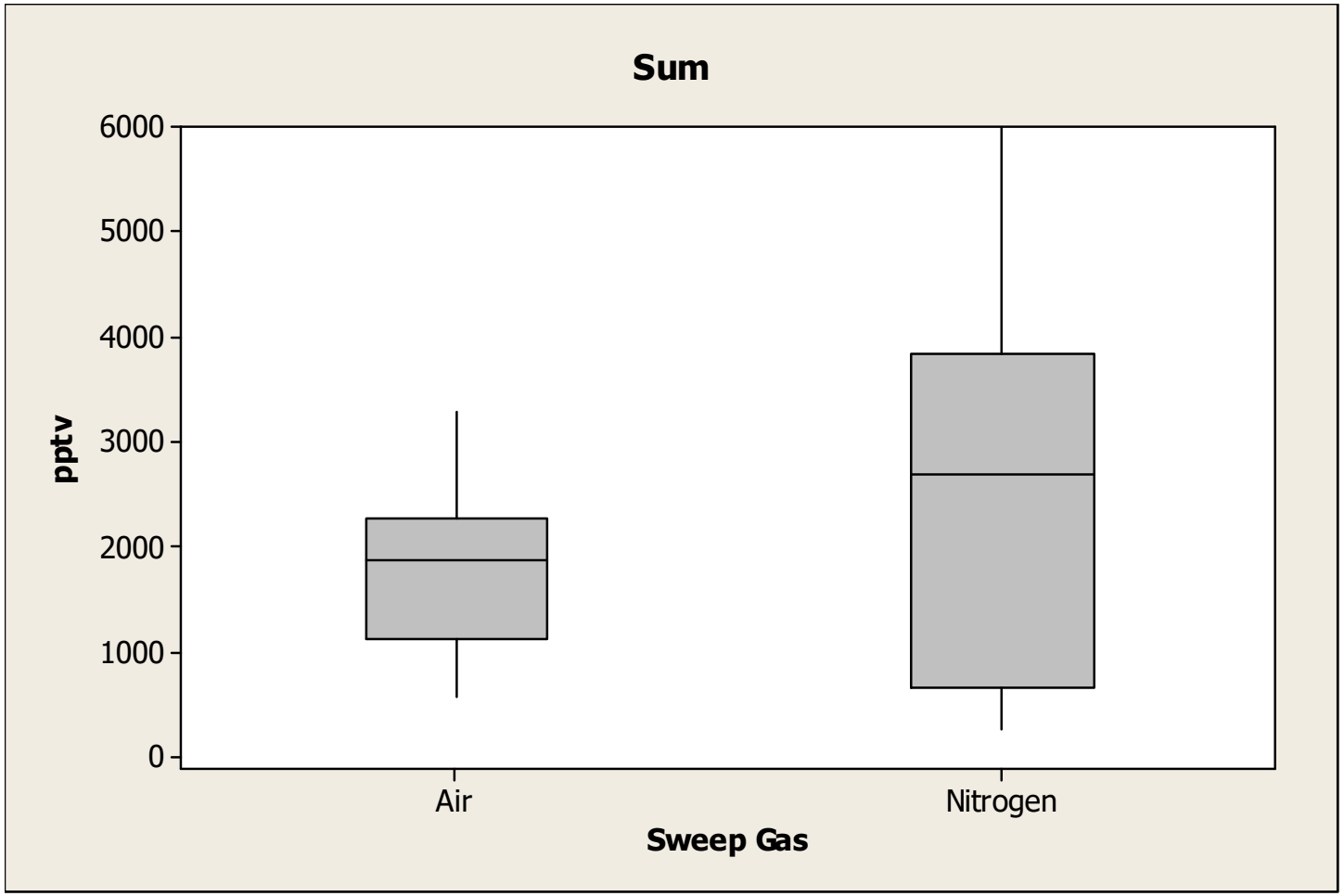

Acc.V Spot Magn Det WD Exp 500 µm
10.0 kV 3.0 50x SE 11.7 1


Acc.V Spot Magn Det WD Exp 5 µm
10.0 kV 3.0 5000x SE 12.2 1

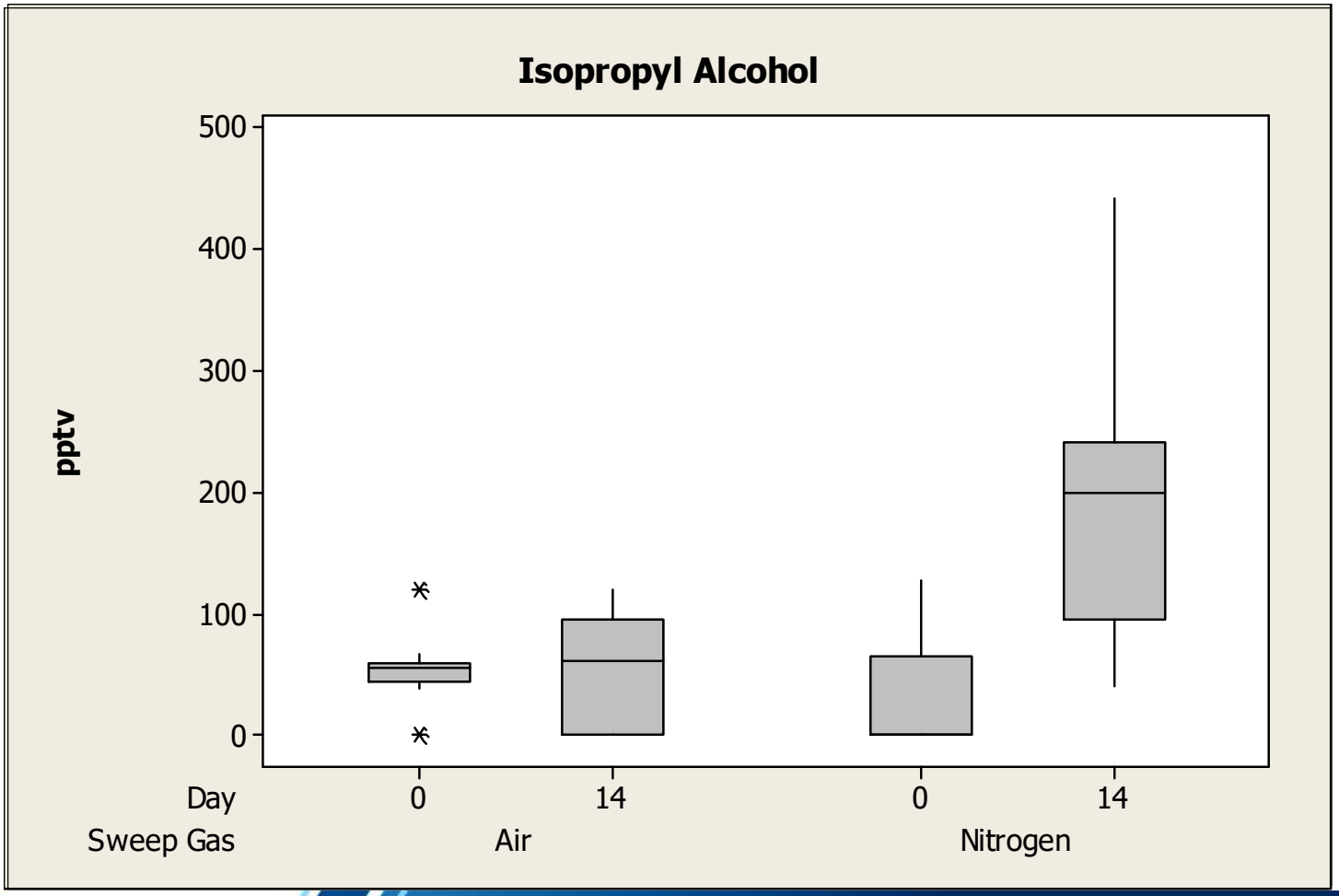

Acc.V Spot Magn Det WD Exp 2 µm
10.0 kV 3.0 10000x SE 11.6 1


Acc.V Spot Magn Det WD Exp 10 µm
10.0 kV 3.0 2000x SE 11.8 1

Sweep Gas


Sum
6000
5000
4000
3000
2000
1000
0
pptv
Air
Nitrogen
Sweep Gas

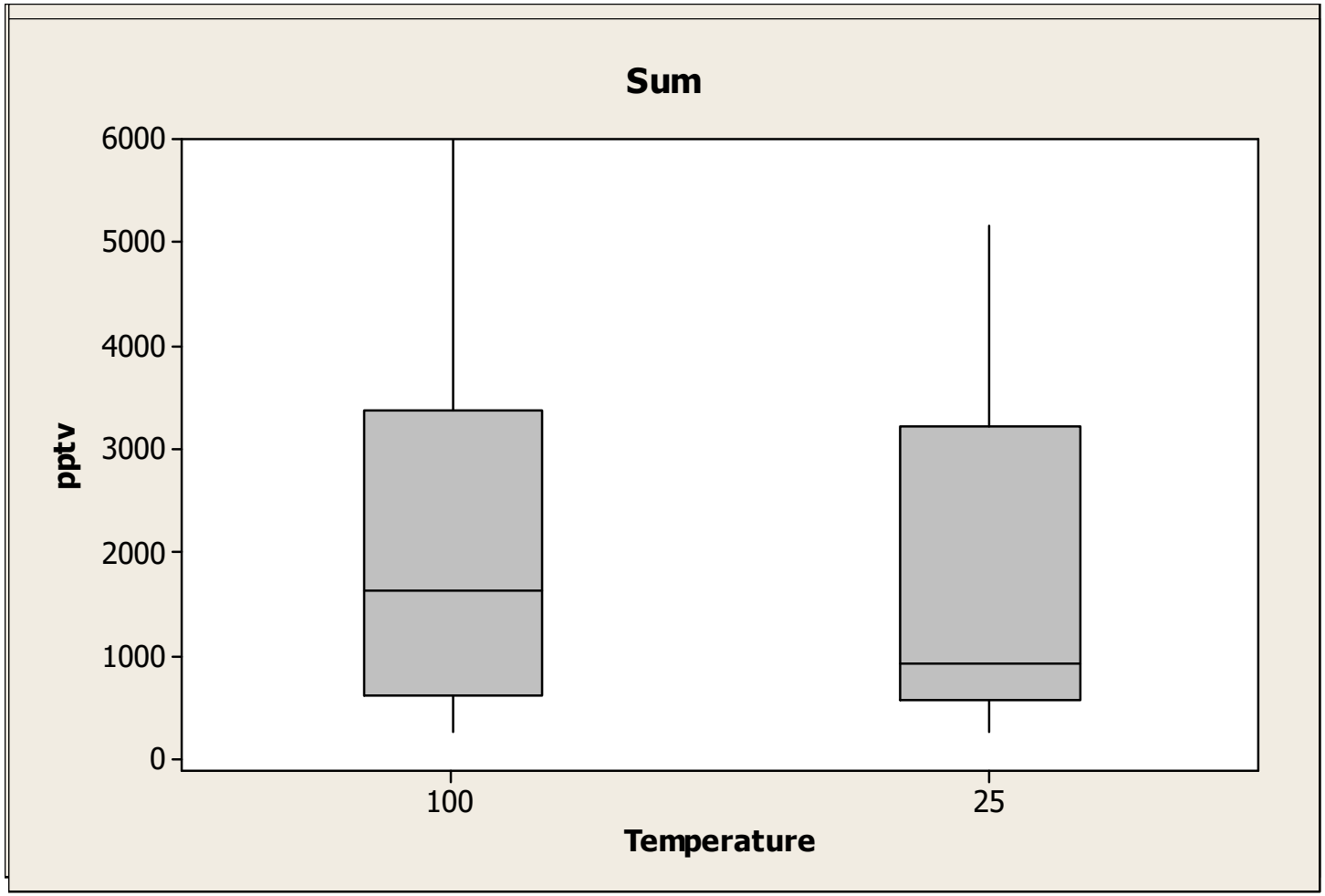
Sweep Gas w/ Time



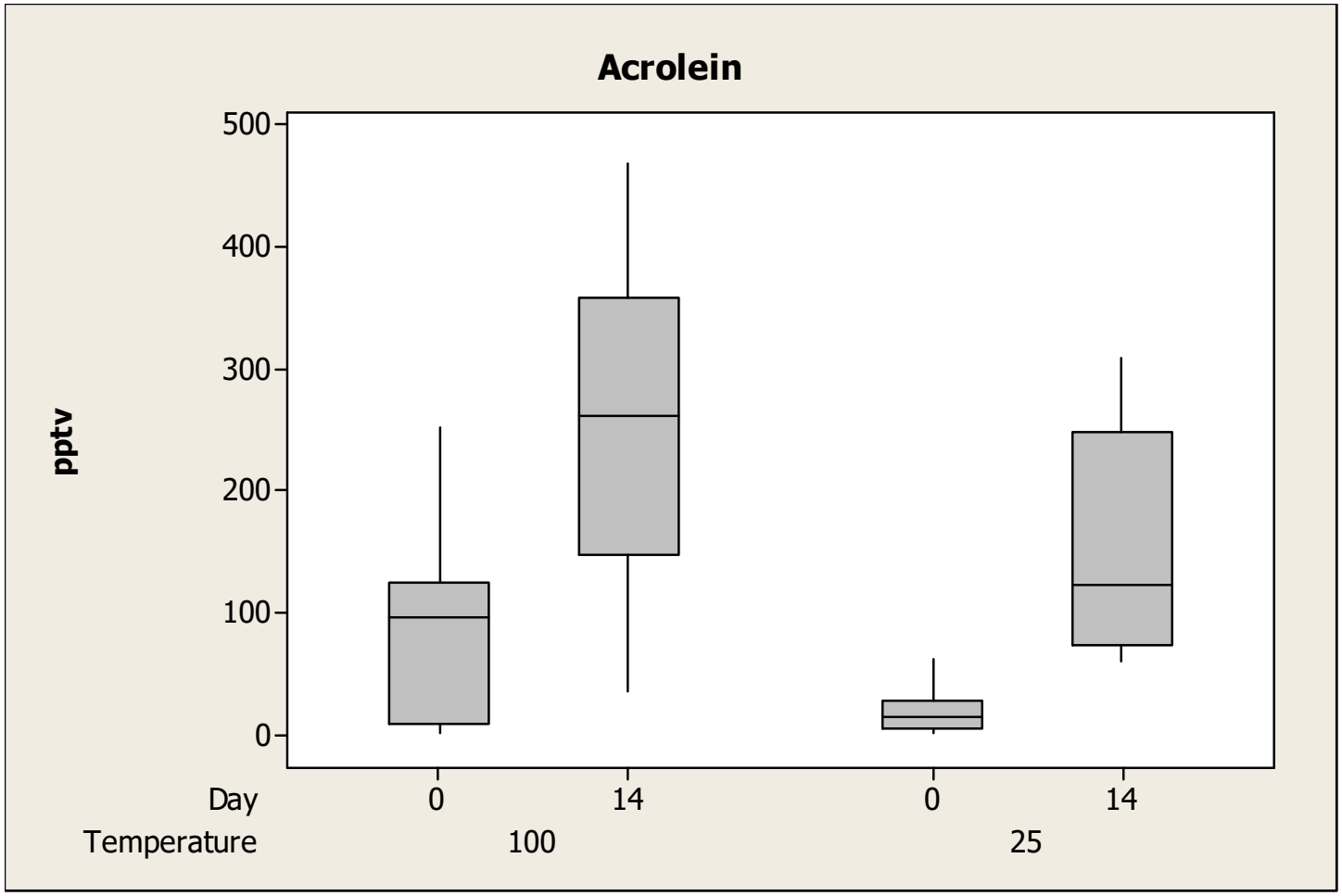
Sweep Gas (cont'd)

- Observation:
  - Using air as a sweep gas appears to work better relative to nitrogen, especially over time
- Explanation:
  - KISS: Air has oxygen, which carries an oxidative potential nitrogen lacks
- Recommendation:
  - Use air… as suggested years ago

Temperature



Temperature w/ Time



Temperature (cont'd)

- Observation:
  - No clear trend

- Explanation:
  - No KISS…
  - We know what 100 °C means for H2O. This resulted in an absence of water vapor on the canister walls, thereby allowing polars to stick.
  - Final vacuum/heat stage

Temperature (cont'd)

- Recommendation:
  - Utilize a more moderate temperature (e.g., 70 – 80 °C)
  - Evaluate the potential of a final "cool" evacuation
  - Extend canister cleaning evaluation to silicon-lined canisters

Conclusions/Future Work

- Everything here is very preliminary…
- Time plays a major roll for most VOCs
- Use air as a sweep gas
- Heat needs further evaluation
- Evaluate silicon-lined canisters with new information at hand
- Evaluate more cleaning cycles