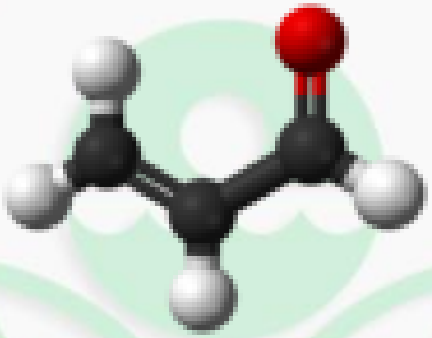
Improving the Analysis of Acrolein in Ambient Air



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Focus

Our research focuses on developing an acrolein method

- that will provide accurate data,
- meet low concentration requirements,
- And that can easily be implemented using the current sampling and analysis infrastructure.

Approach

Chosen approach is to modify Air Toxics Method TO-15 which uses passivated stainless steel canisters for sample collection and analysis.

EPA/RTP Canister Cleaning and Analysis Systems

Acrolein Refresher

- Colorless or yellow liquid with pungent odor
- Causes respiratory irritation
- Byproduct of combustion processes (fires, tobacco smoke, mobile sources), wood product industries, and frying foods
- Formed in the atmosphere from 1,3-butadiene reactions
- Used in the chemical industry as an intermediate for making other chemicals
- Used as a biocide in irrigation canals

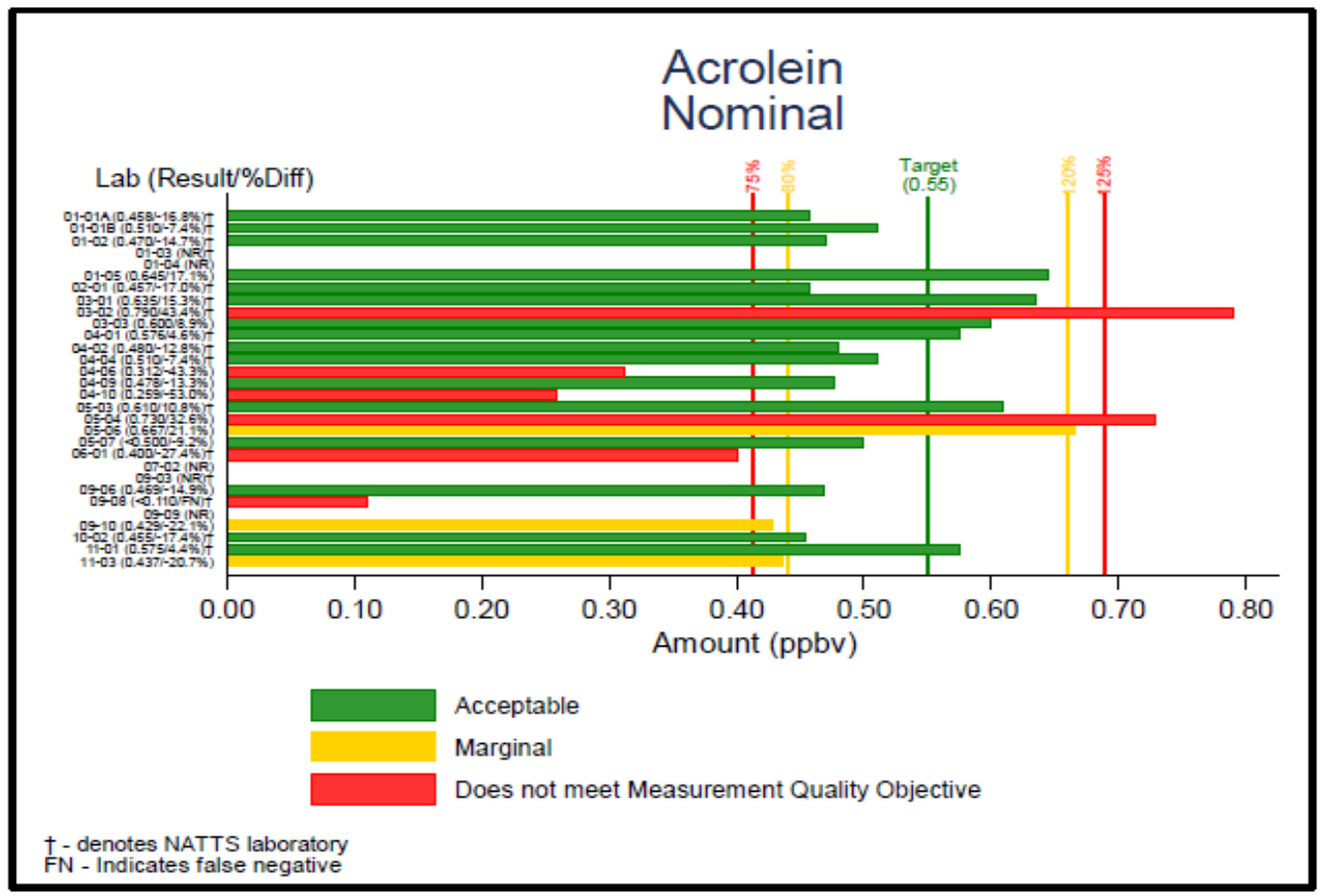
Acrolein Refresher (cont.)

- Acrolein ranks high in air toxicity assessments due to low reference concentration (RfC) and reference exposure levels (REL) determined for chronic exposure
  - EPA inhalation RfC (IRIS 2007) =0.02µg/m^3 (~9 pptv)
  - California (OEHHA 2014)REL= 0.35 µg/m^3 (~150 pptv)
- Based on the EPA values, MDLs need to be in range of 10 pptv

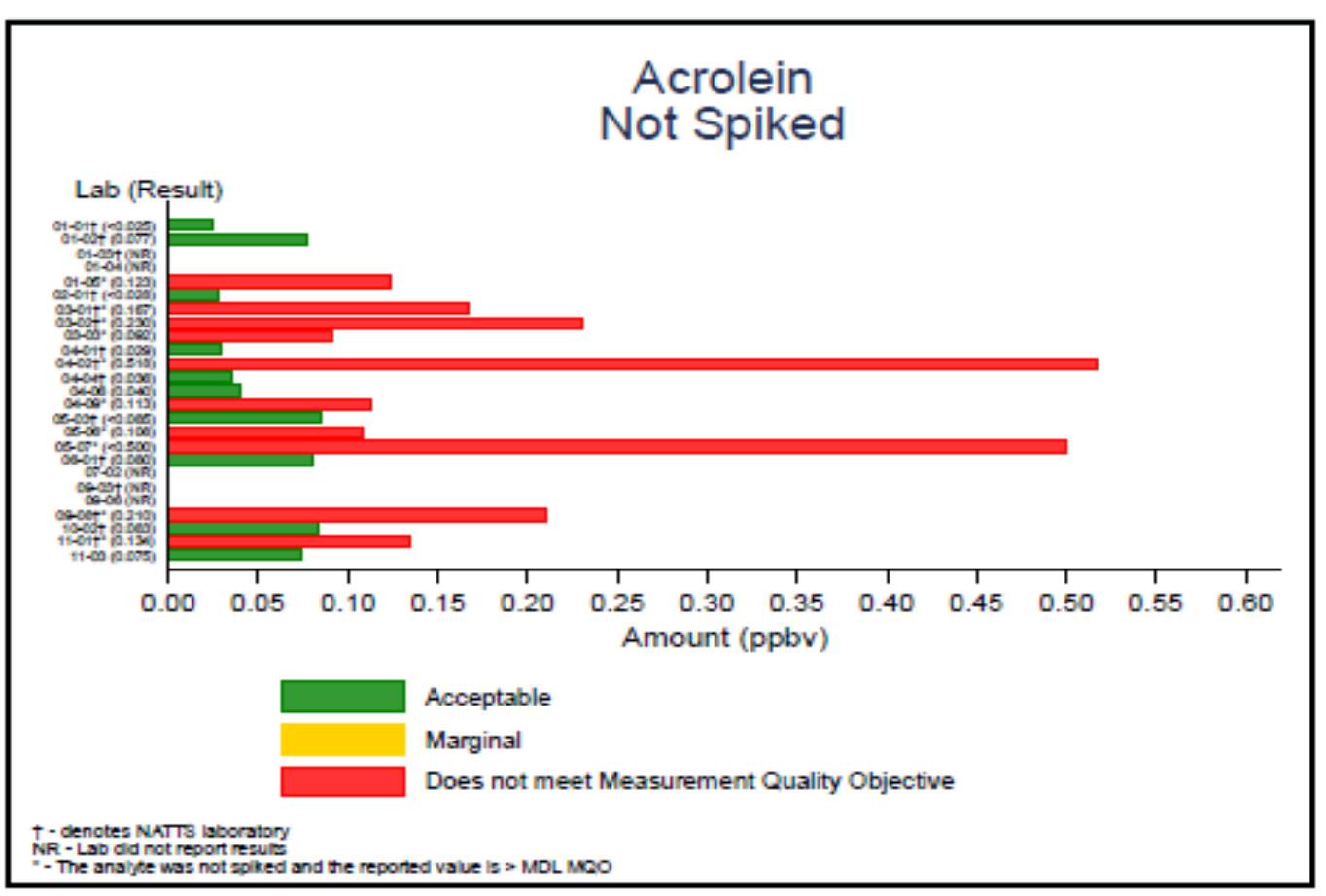
Current Ambient Concentrations

		Avg (pptv)	Range (pptv)
Mist Chamber Method (T. Cahill, 2014)	CA- Remote/ Coastal Sites	17	BDL to 56
	CA- Intermediate	30	MDL(17) to 48
	CA Urban-Northern	44	20 to 78
	CA Urban-LA Basin	139	100 to 178
Rural Samples (2015)	Virginia	40	32 to 44
EPA Parking Lot (2015)	North Carolina	175	149 to 211
Current EPA MDL Value		16	

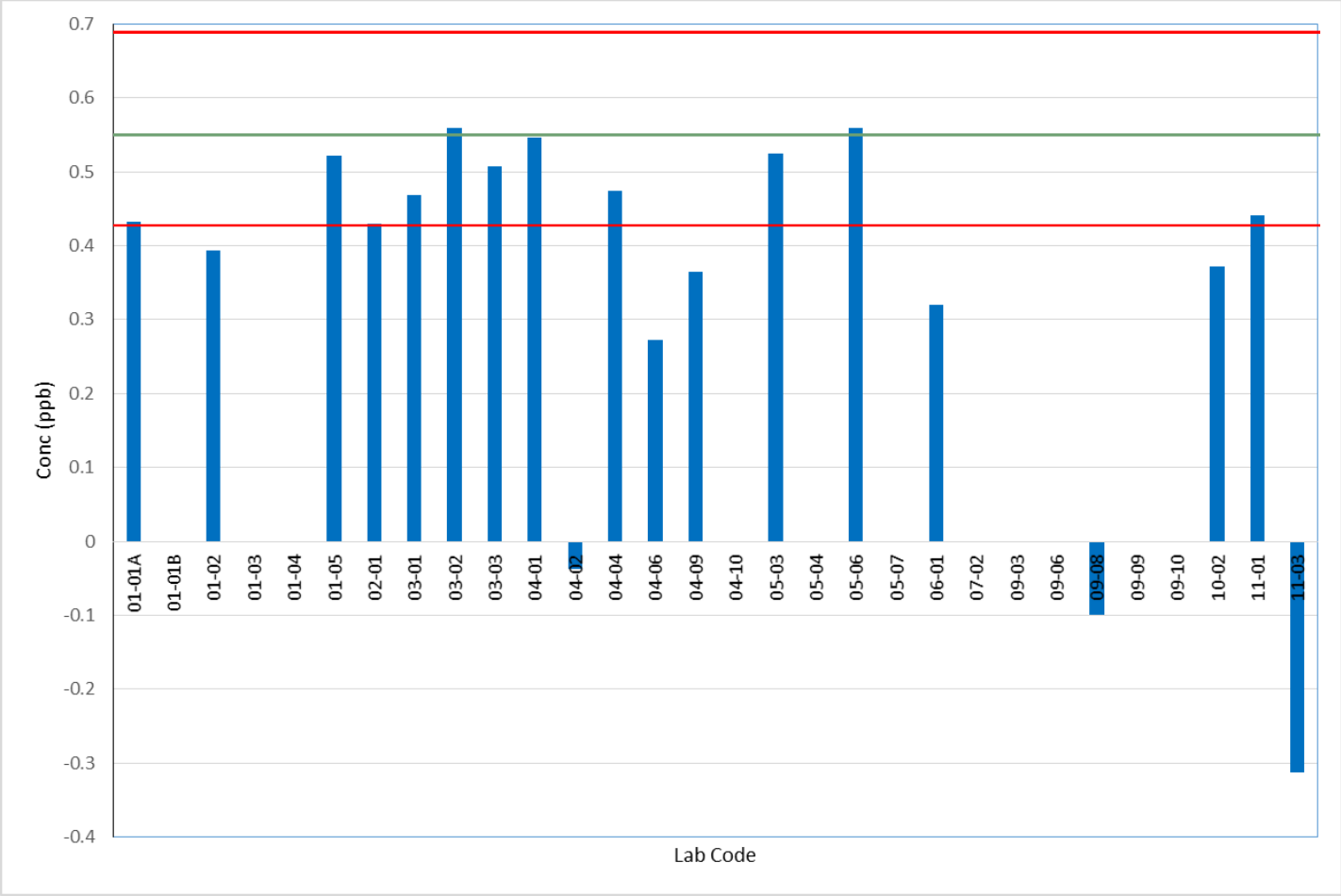
Q1 2015 NATTS Proficiency Testing Results for Acrolein



Q3 2015 NATTS Proficiency Testing Results for Acrolein



Q1 NATTS Acrolein Results Adjusted for Q3 Background Results



Recent Efforts

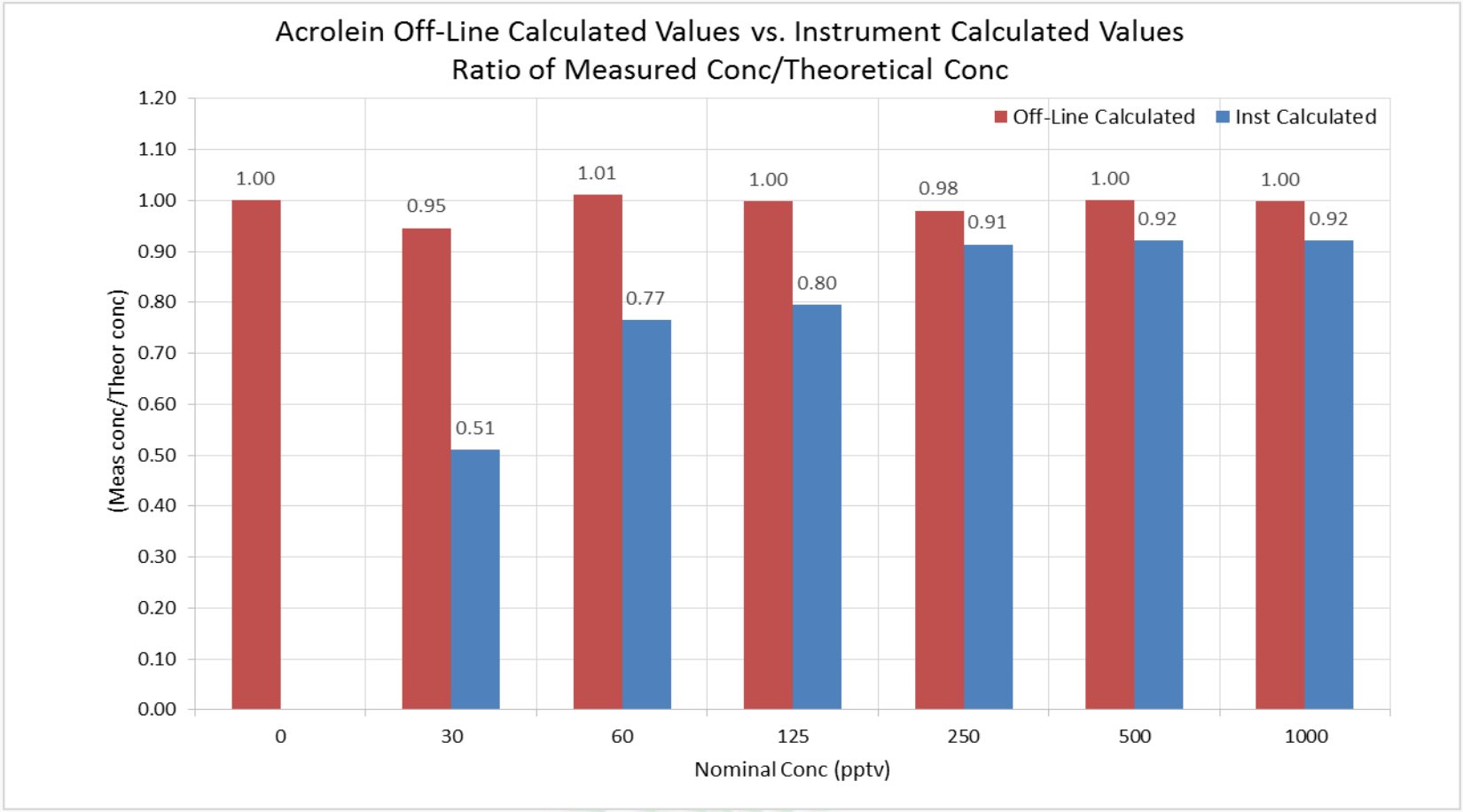
- Upgraded our instrumentation and canister stock
- Conducted a number of experiments to establish the current state of our canister science
- Conducted broad experiments to help focus primary areas of needed improvement

Recent Efforts (cont.)

- Conducted a systematic evaluation of our analytical systems for low-pptv analyses
  - Established that strict attention to details is required to minimize carryover issues
    - Purge regulators and inlet lines when changing standards cans
    - Sequences of humidified air should be analyzed after standards and prior to samples to purge the system
  - Discovered our internal standard canister and/or system has a low but constant acrolein background
  - Developed a quantitation method to improve low pptv results
    - Analyzed internal standard alone as zero calibration point
    - Developed an off-line process that corrects the calibration curve

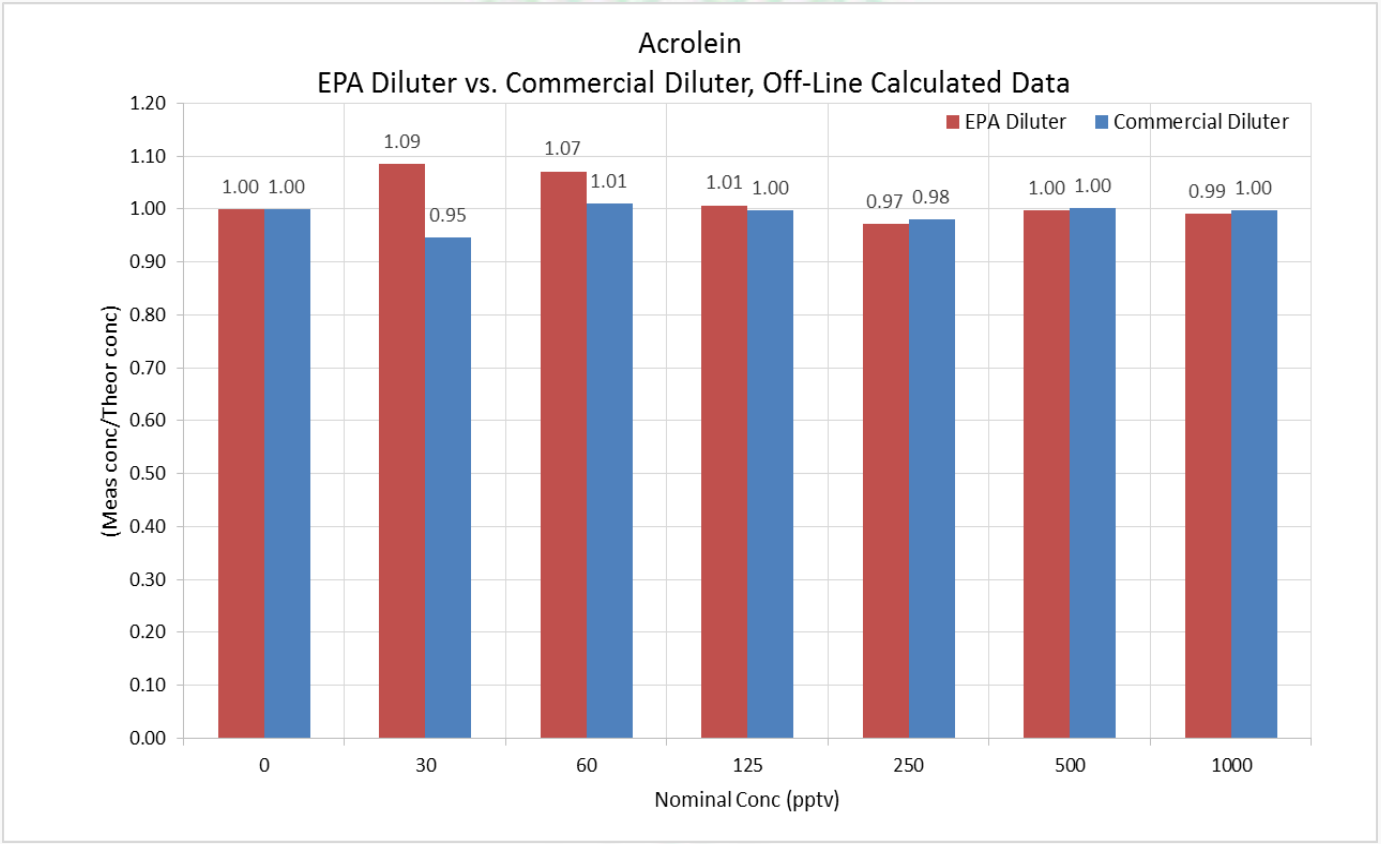
Recent Efforts (cont.)

- Results of improved quantitation method



Recent Efforts (cont.)

- Compared standards prepared on two different dynamic dilution systems



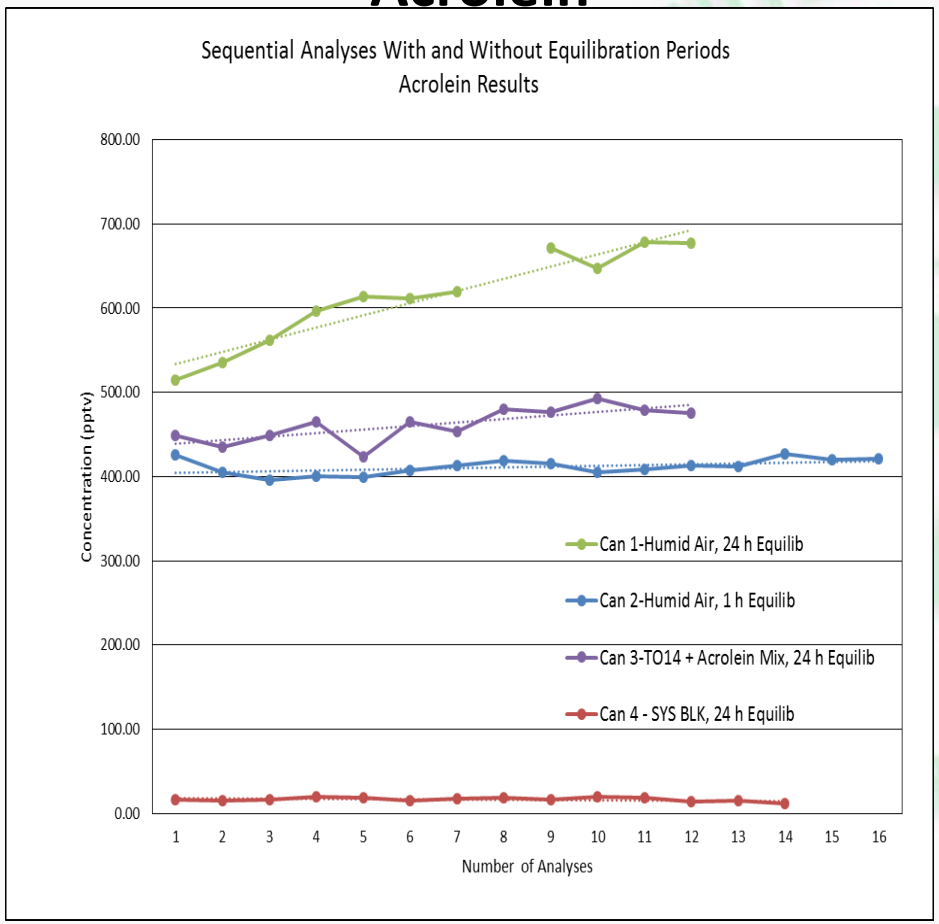
Recent Efforts (cont.)

- Started evaluations of canister cleaning processes
  - Air vs. nitrogen
    - Inconclusive, more testing required
  - Humidifier water source impact
    - Interrupted clean cycle when can filled with humid air
    - Analyzed can
      - » Purged distilled water ~ 130 pptv
      - » Fresh distilled water ~ 480 pptv
  - Cleaning time/cycles
    - Longer time/more cycles appears to be better for acrolein
    - More testing required to determine the optimum
  - Temperature impact
    - To be determined

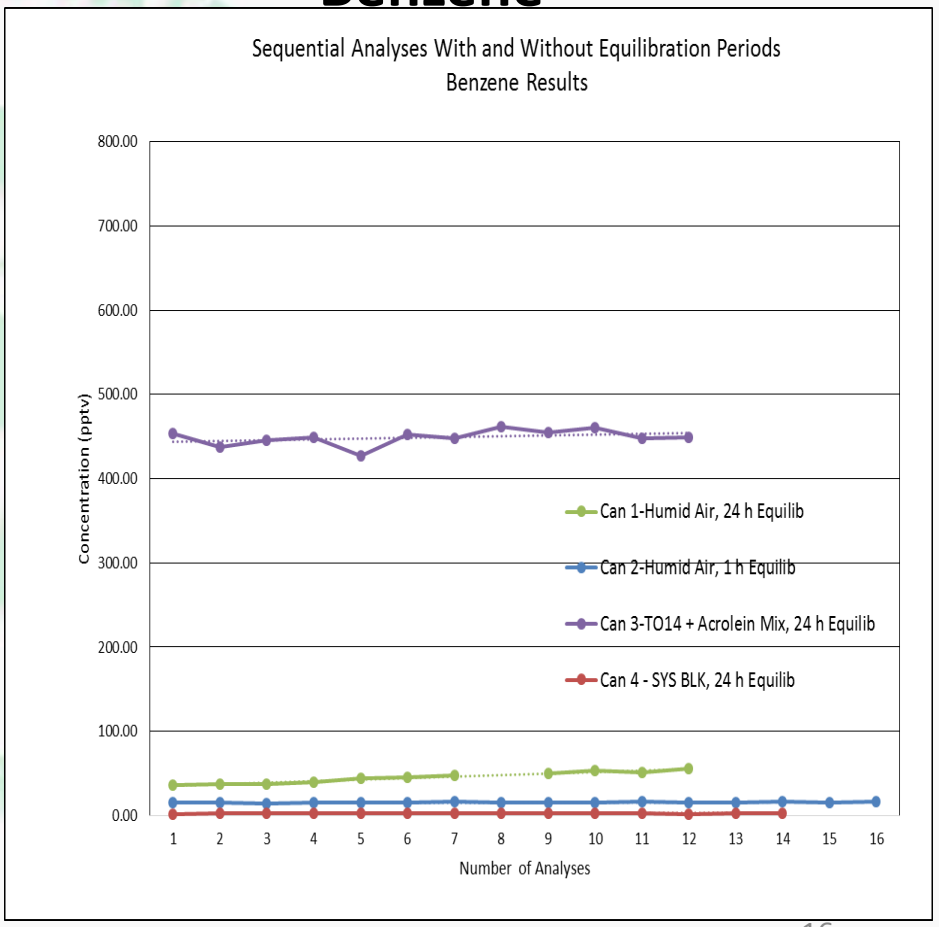
Recent Efforts (cont.)

- Impact of Equilibration Time on Analysis

Acrolein



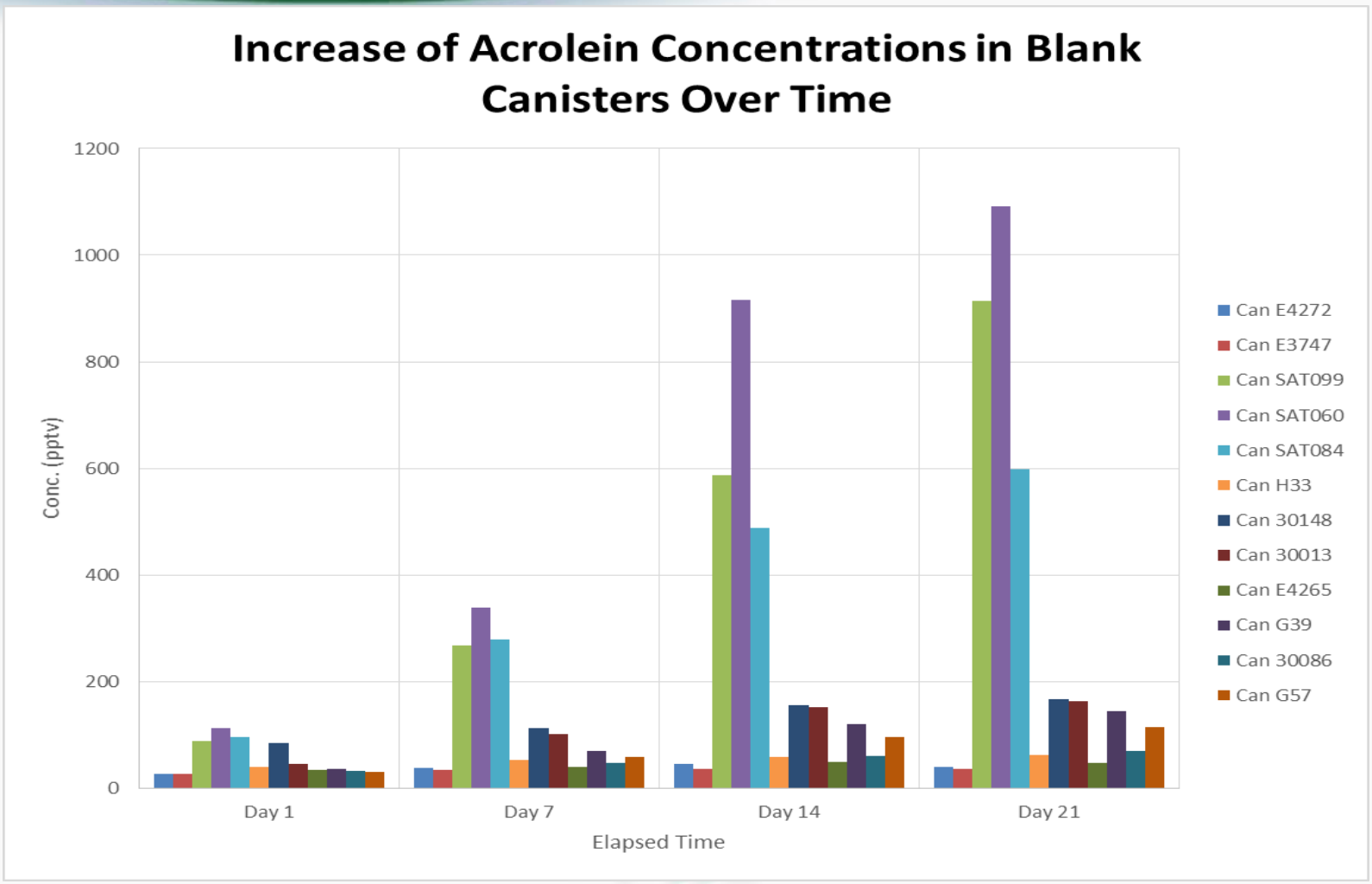
Benzene



Current Research

- First and foremost…
  - Working to improve the canister cleaning process
  - Working to establish an accelerated method to evaluate the cleanliness
  - Evaluating different types of cans
- We will then…
  - Investigate the potential losses to clean canister surfaces
  - Investigate humidity and pressure relationships as they pertain to acrolein recovery from canisters

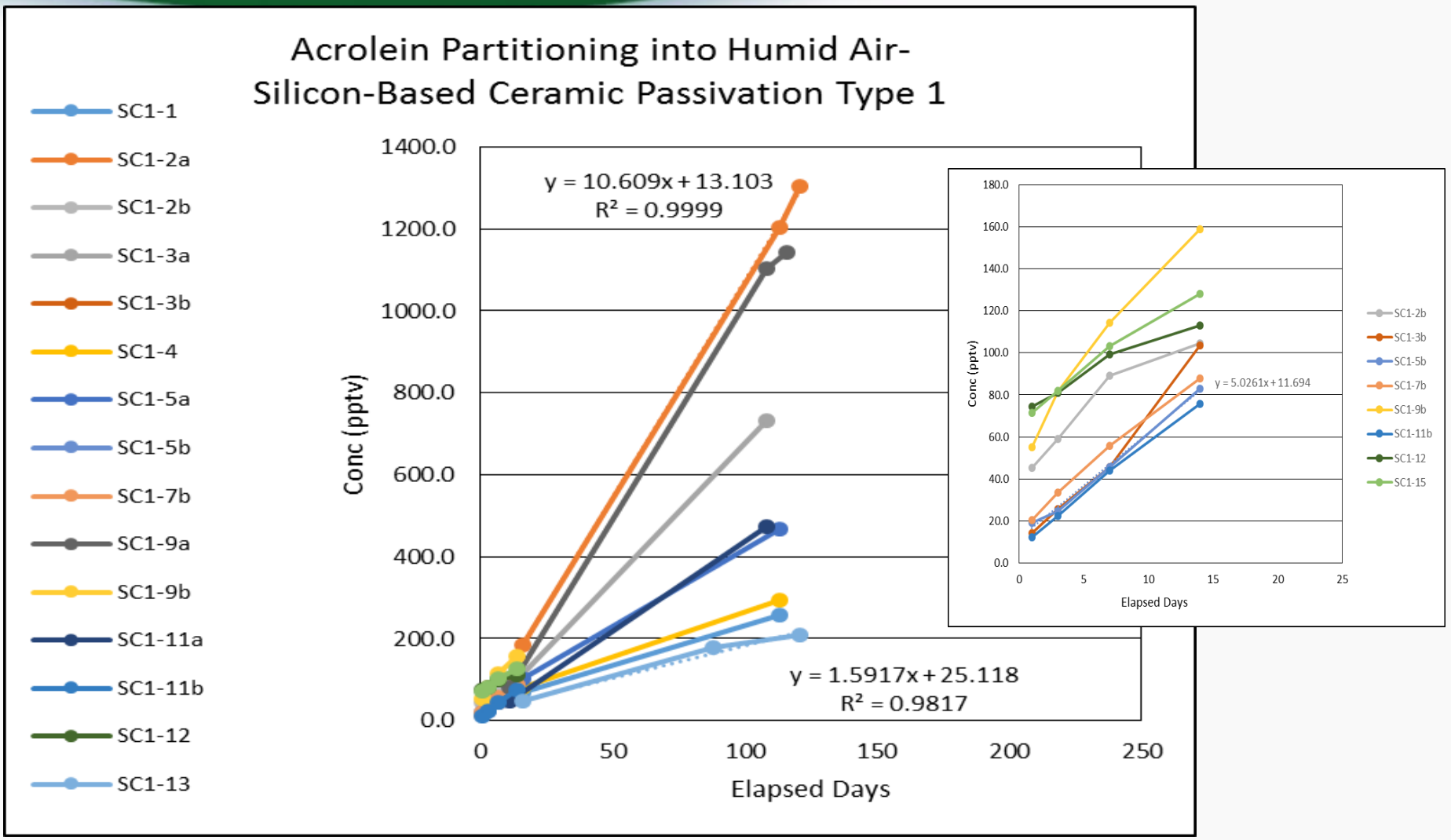
Canister Issues



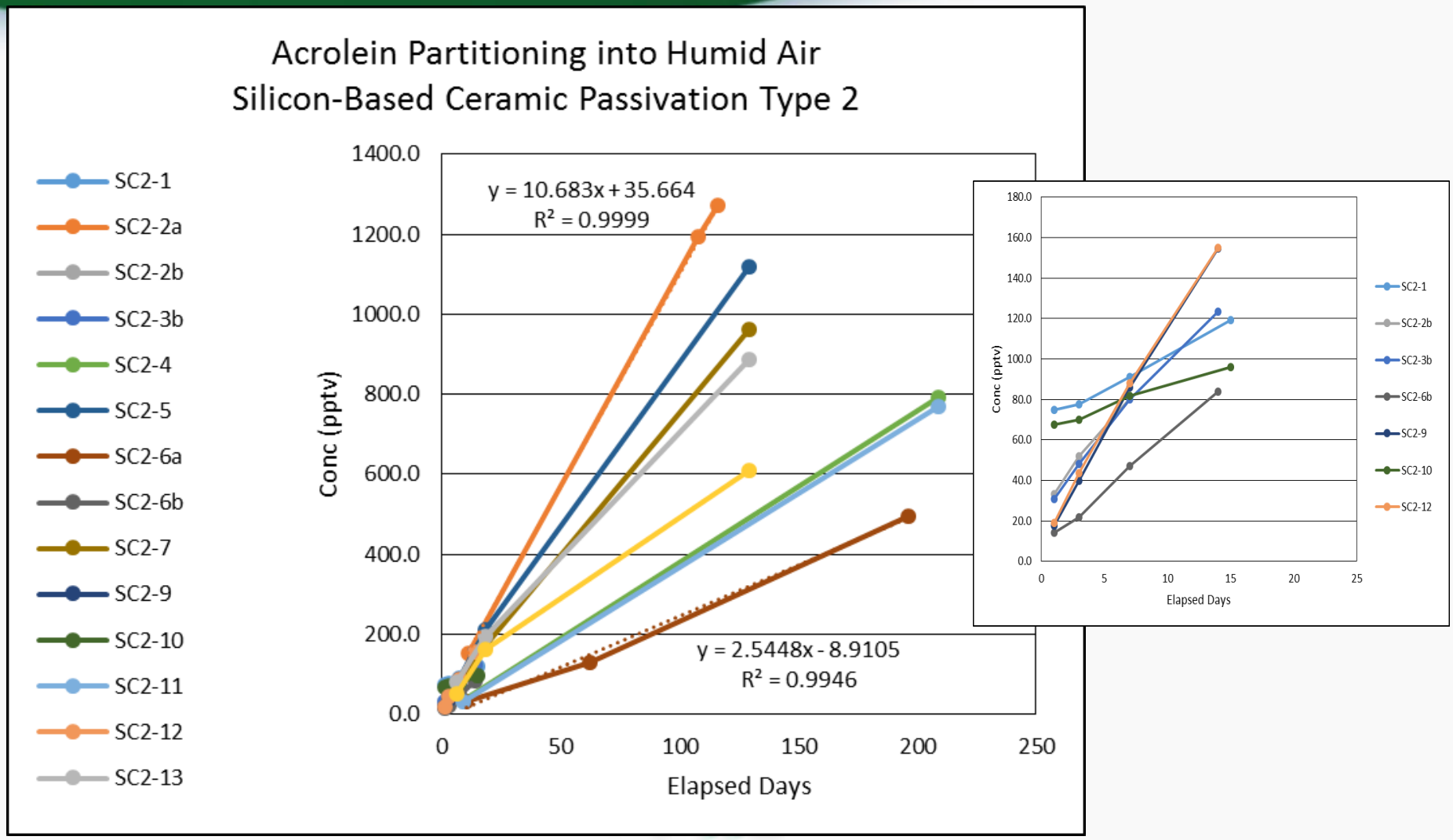
Canister Evaluations

- Currently evaluating silicon-based ceramic passivated cans as well as some older Summa passivated cans
- Clean, fill with 70% RH air to 10 psig, maintain at room temperature, and analyze at various time points (some over 200 days)

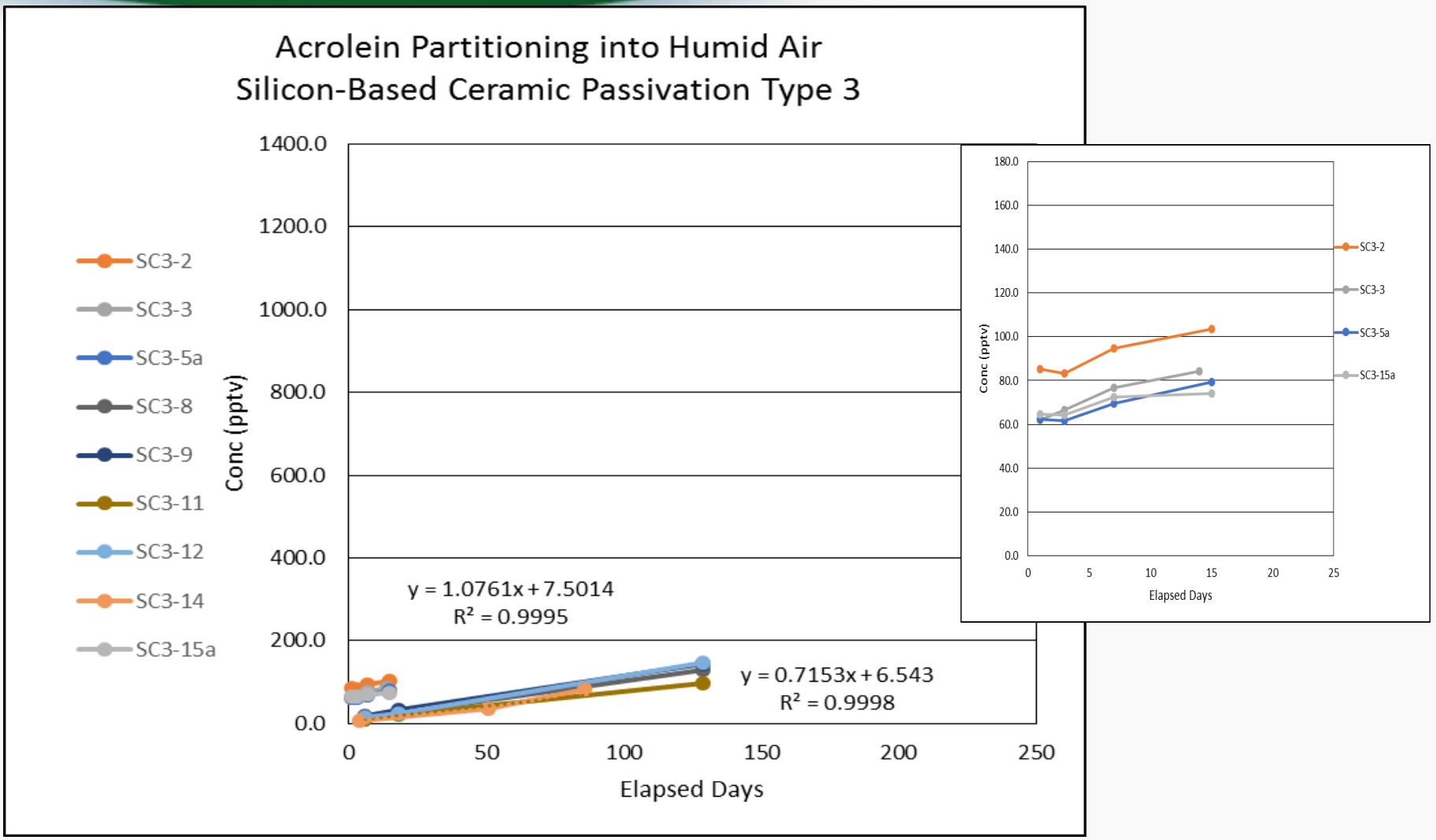
Evaluation Results



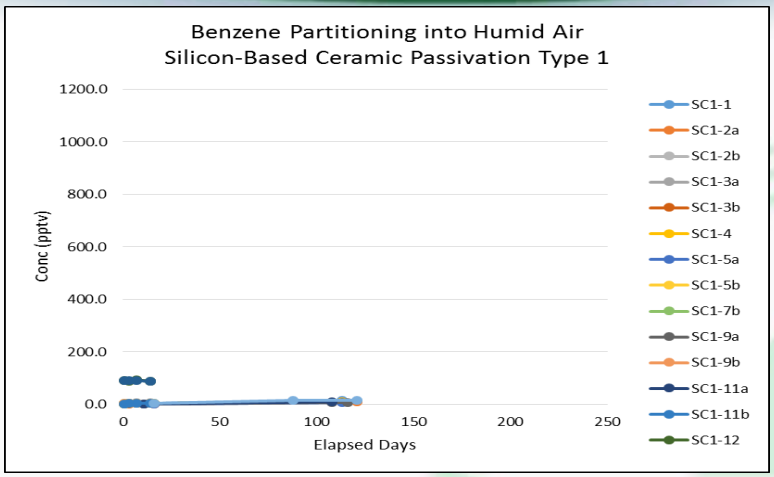
Evaluation Results (cont.)

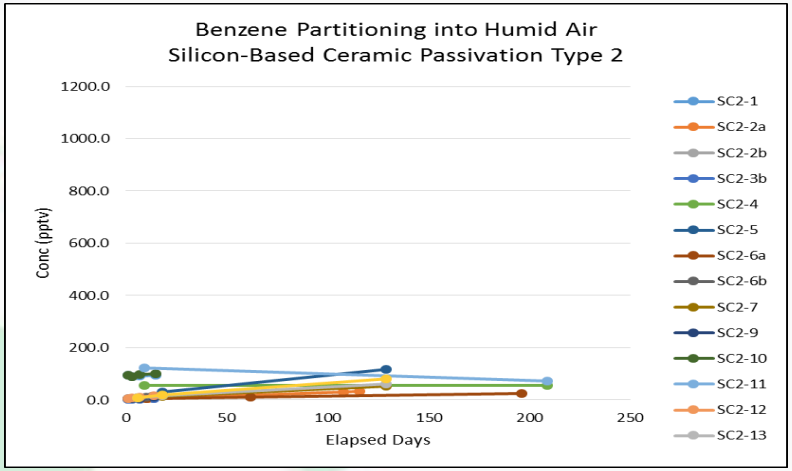


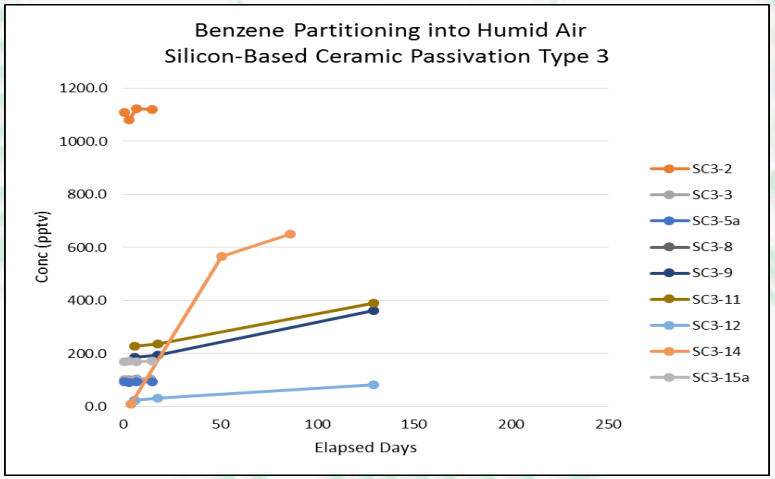
Evaluation Results (cont.)



Evaluation Results (cont.)

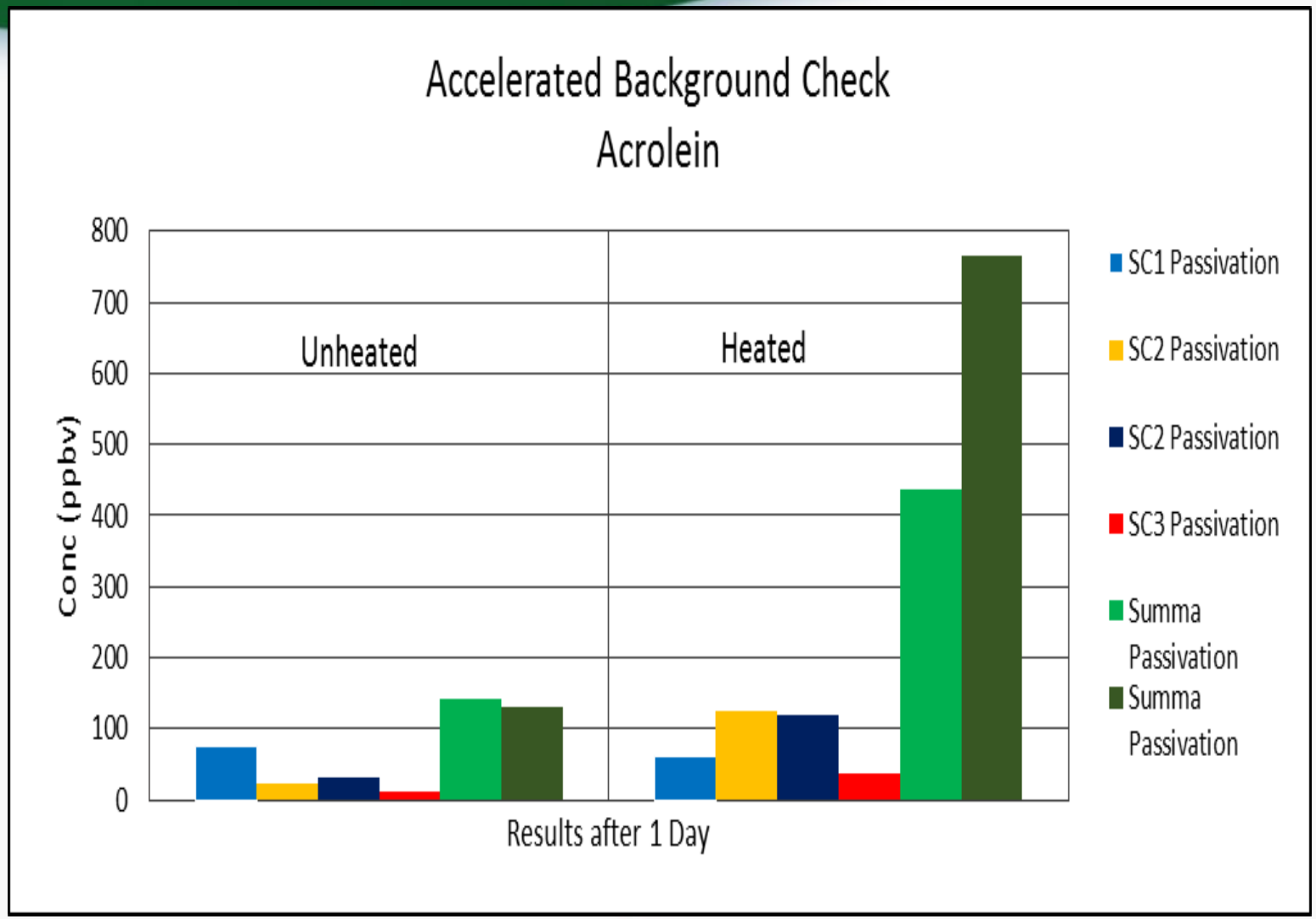


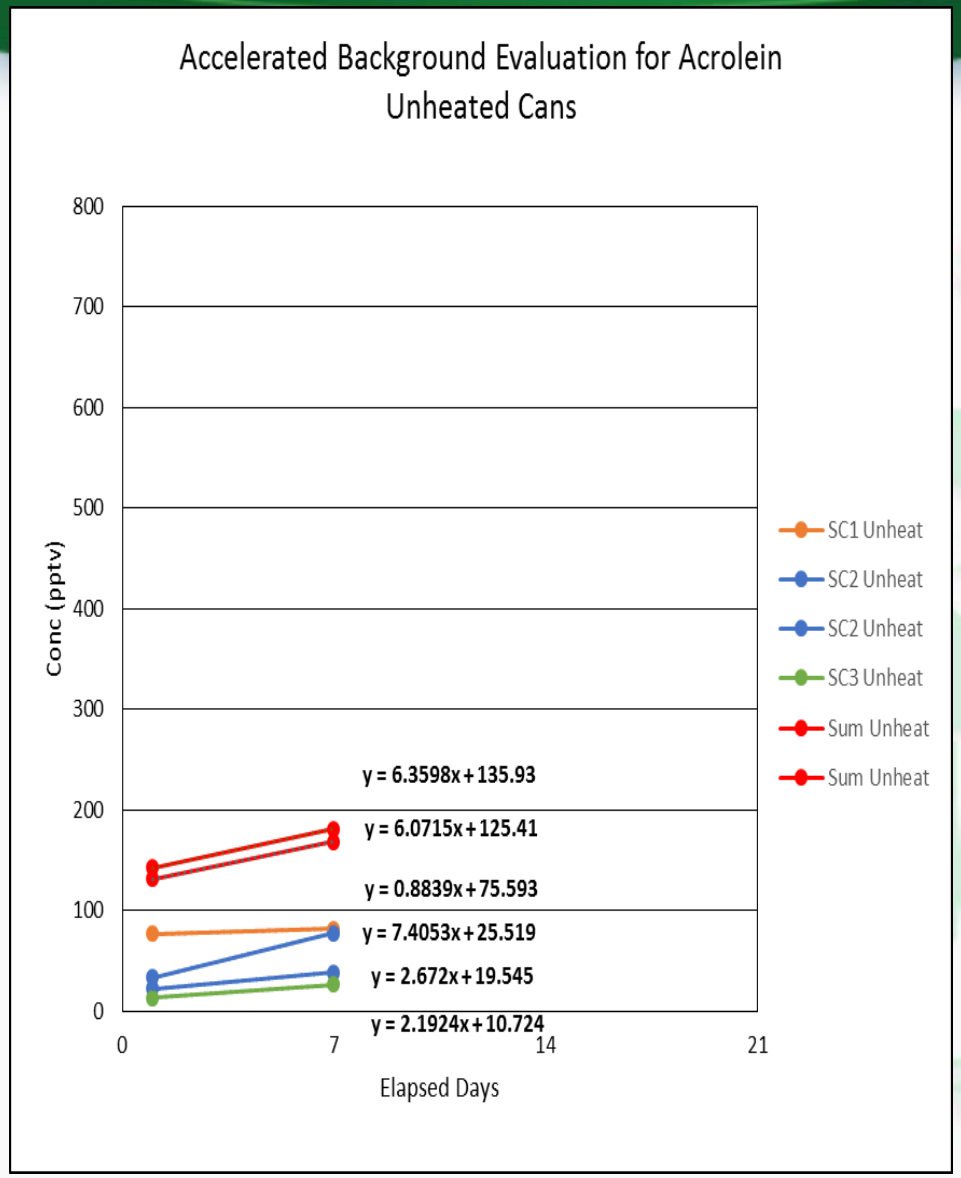


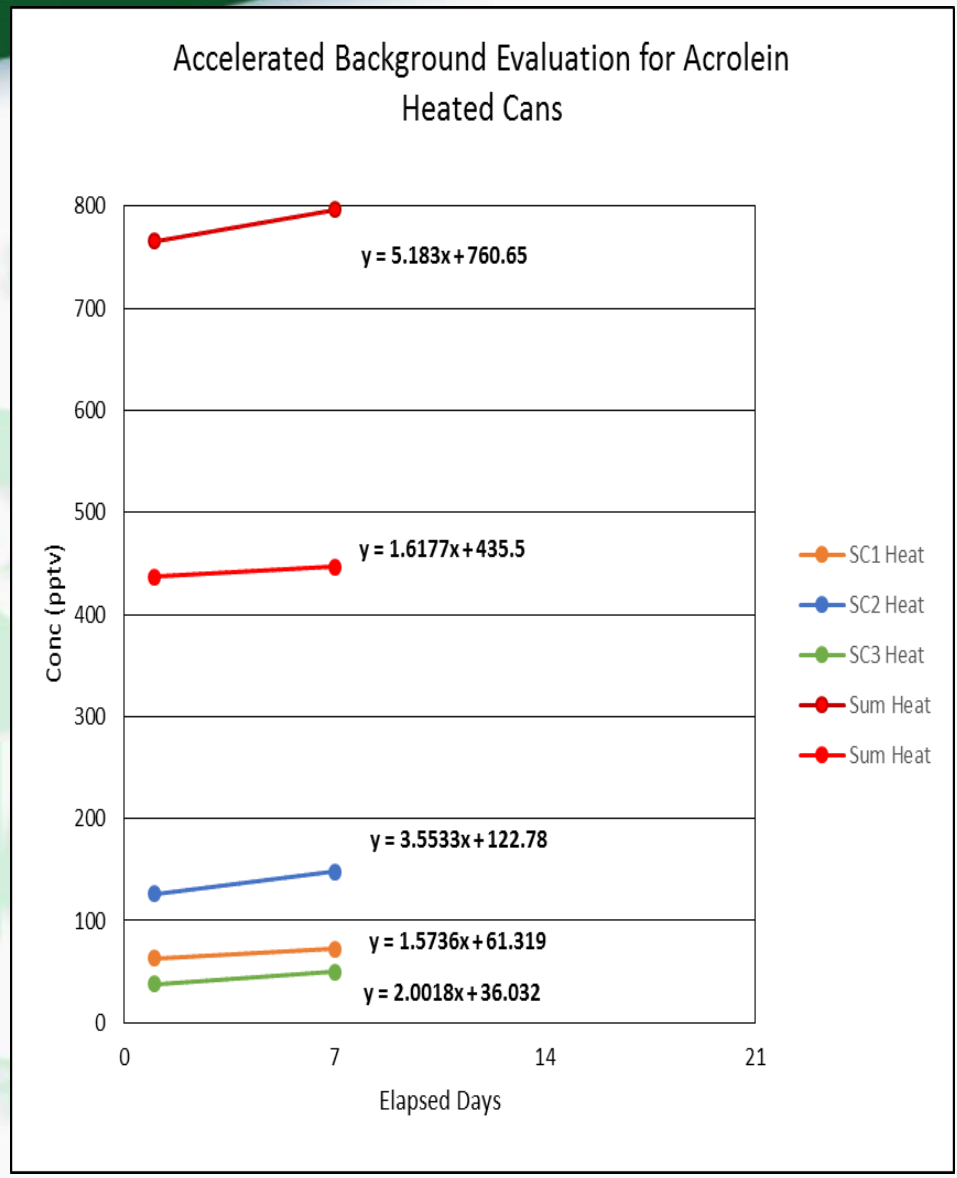


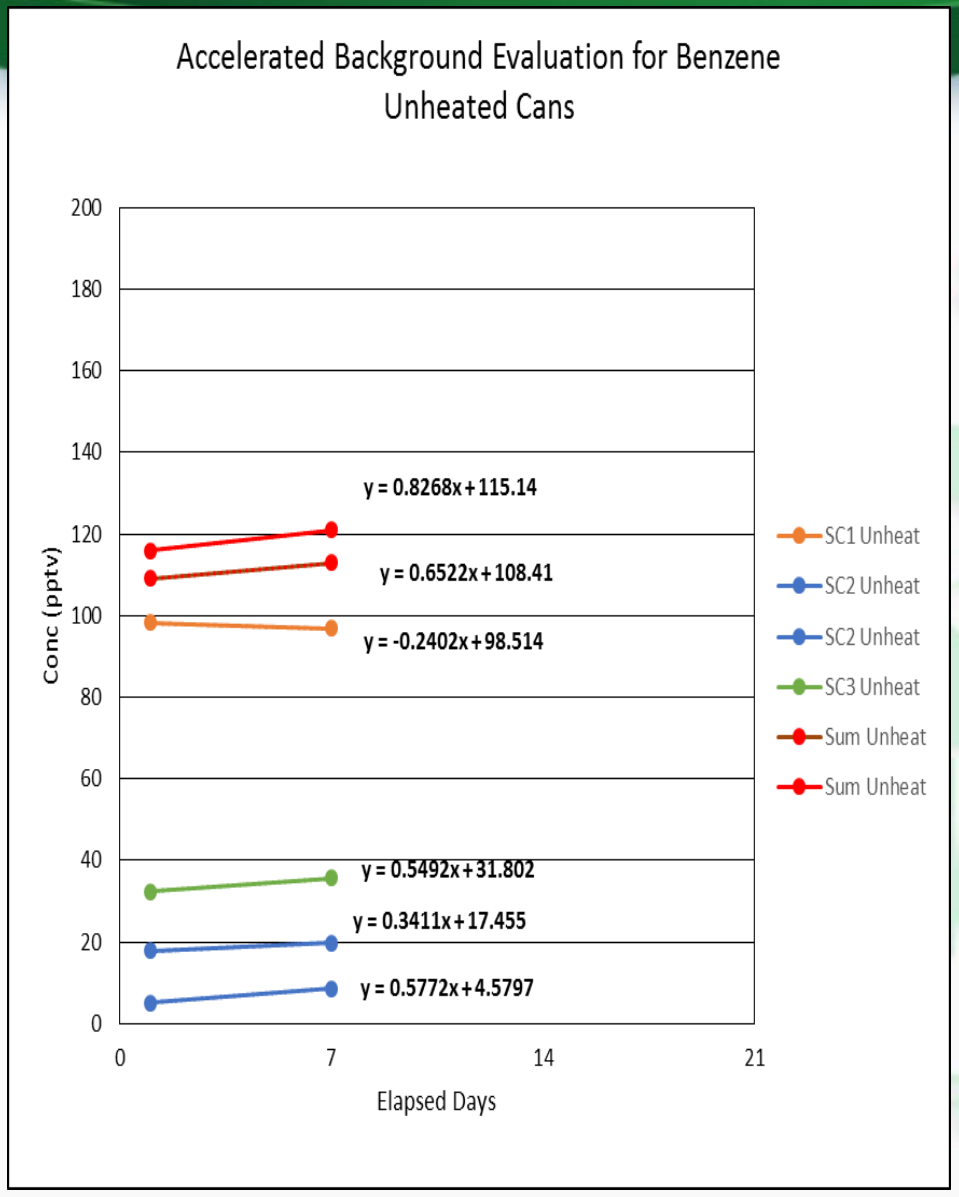
Accelerated Background Check

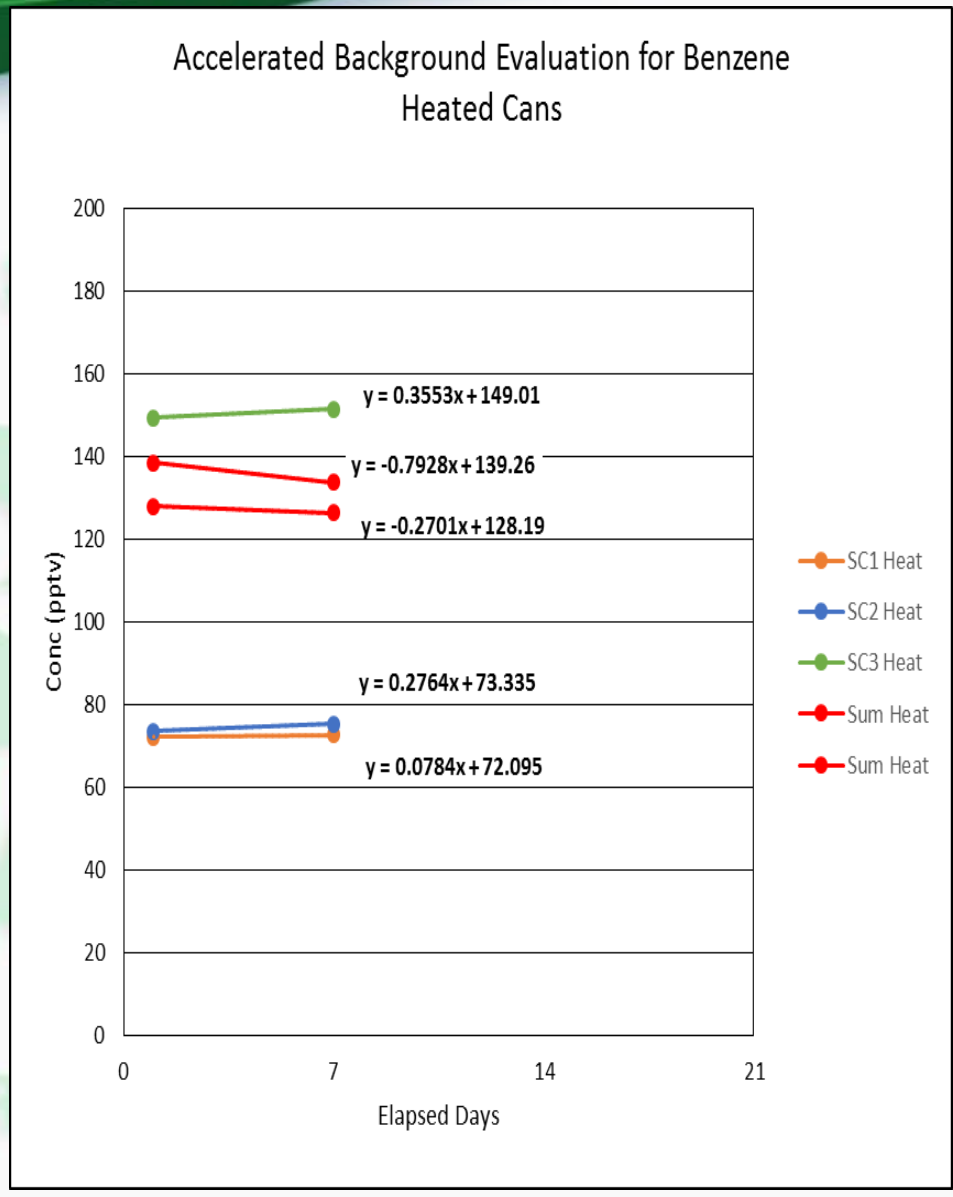
- Don’t want to wait weeks to establish canister status
- Experimental Process
  - Clean cans,
  - fill with 70% RH air to ambient pressure (0 psig),
  - half left at room temperature,
  - half heated to 90 °C for 8 hours,
  - Analyze after 1 day, 7 days, and 14 days


Accelerated Background Check
Acrolein
800
700
600
500
400
300
200
100
0
Conc (ppbv)
Unheated
Heated
Results after 1 Day
SC1 Passivation
SC2 Passivation
SC2 Passivation
SC3 Passivation
Summa Passivation
Summa Passivation


Accelerated Background Evaluation for Acrolein
Unheated Cans
800
700
600
500
400
300
200
100
0
Conc (pptv)
0
7
14
21
Elapsed Days
y = 6.3598x+135.93
y = 6.0715x+125.41
y = 0.8839x+75.593
y = 7.4053x+25.519
y = 2.672x+19.545
y = 2.1924x+10.724
SC1 Unheat
SC2 Unheat
SC2 Unheat
SC3 Unheat
Sum Unheat
Sum Unheat


Accelerated Background Evaluation for Acrolein
Heated Cans
800
700
600
500
400
300
200
100
0
Conc (pptv)
0
7
14
21
Elapsed Days
y = 5.183x+760.65
y = 1.6177x+435.5
y = 3.5533x+122.78
y = 1.5736x+61.319
y = 2.0018x+36.032
SC1 Heat
SC2 Heat
SC3 Heat
Sum Heat
Sum Heat


Accelerated Background Evaluation for Benzene
Unheated Cans
Conc (pptv)
Elapsed Days
y = 0.8268x+115.14
y = 0.6522x+108.41
y = -0.2402x+98.514
y = 0.5492x+31.802
y = 0.3411x+17.455
y = 0.5772x+4.5797
SC1 Unheat
SC2 Unheat
SC2 Unheat
SC3 Unheat
Sum Unheat
Sum Unheat


Accelerated Background Evaluation for Benzene
Heated Cans
Conc (pptv)
Elapsed Days
y = 0.3553x+149.01
y = -0.7928x+139.26
y = -0.2701x+128.19
y = 0.2764x+73.335
y = 0.0784x+72.095
SC1 Heat
SC2 Heat
SC3 Heat
Sum Heat
Sum Heat

Can we solve the puzzle?

Final Thought …For Now

A process must be established that provides reliably clean canisters for acrolein in the low pptv (10-20) range and that exhibits little or no "growth" before we can proceed with future acrolein canister method evaluations.

Acknowledgments

Thanks to Maribel Colon and Lillian Alston for laboratory support.