United States Environmental Protection Agency

# How Well Are We Able to Measure Acrolein, Formaldehyde, and other HAP Carbonyls?

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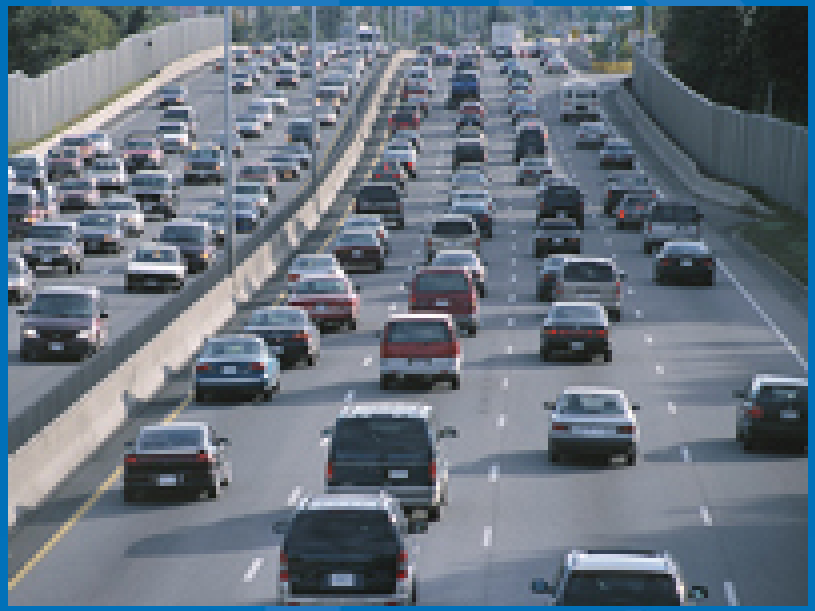


**Office of Research and Development**
National Risk Management Research Laboratory/Air Pollution Prevention and Control Division

# NATTS

National Ambient Air Toxics Trends Stations (NATTS) are to monitor formaldehyde, acetaldehyde, and acrolein once every 6 days, for a 24-hour duration.

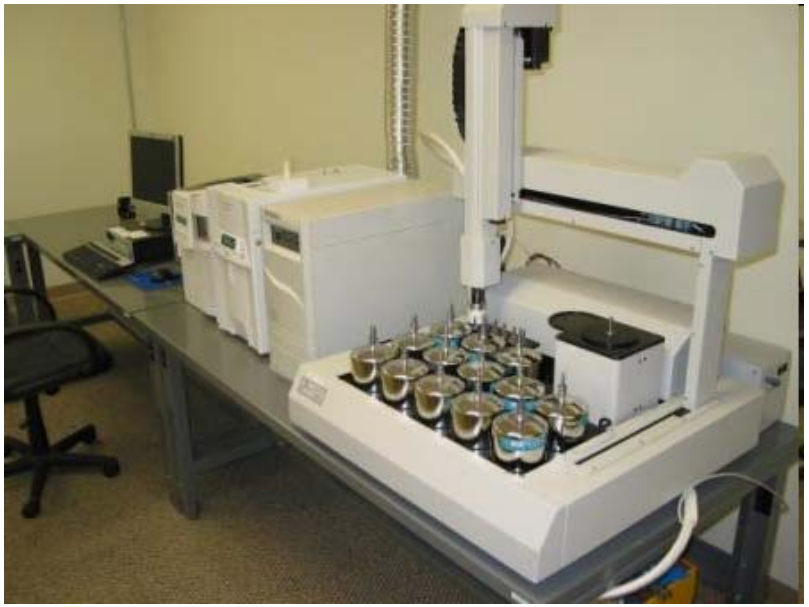
# EPA Compendium Method TO-11A

- Inarguably the most frequently utilized method to date.
- “Gold Standard”
- Utilizes a cartridge packed with acidified 2,4-dinitrophenylhydrazine (DNPH)-coated Silica-Gel.

# EPA Compendium Method TO-15

- Sampling with 6 L silonite coated passivated canisters.

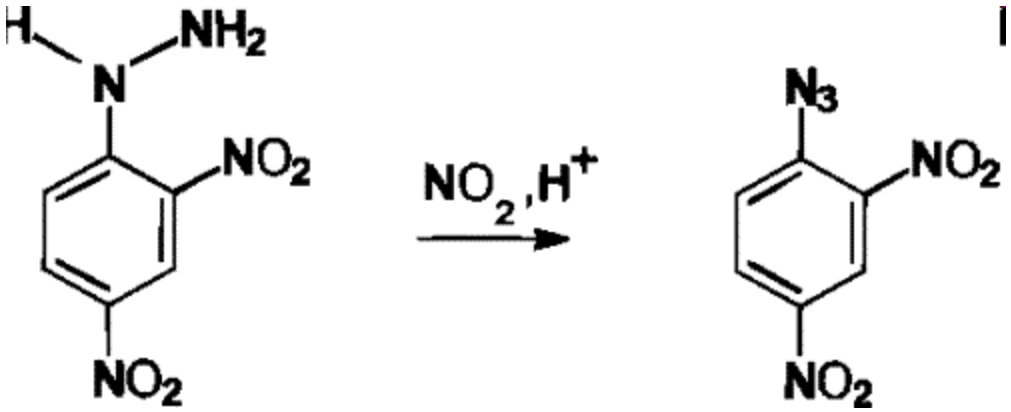
- Recently, utilized for the sampling and analysis of acrolein.



# Formaldehyde

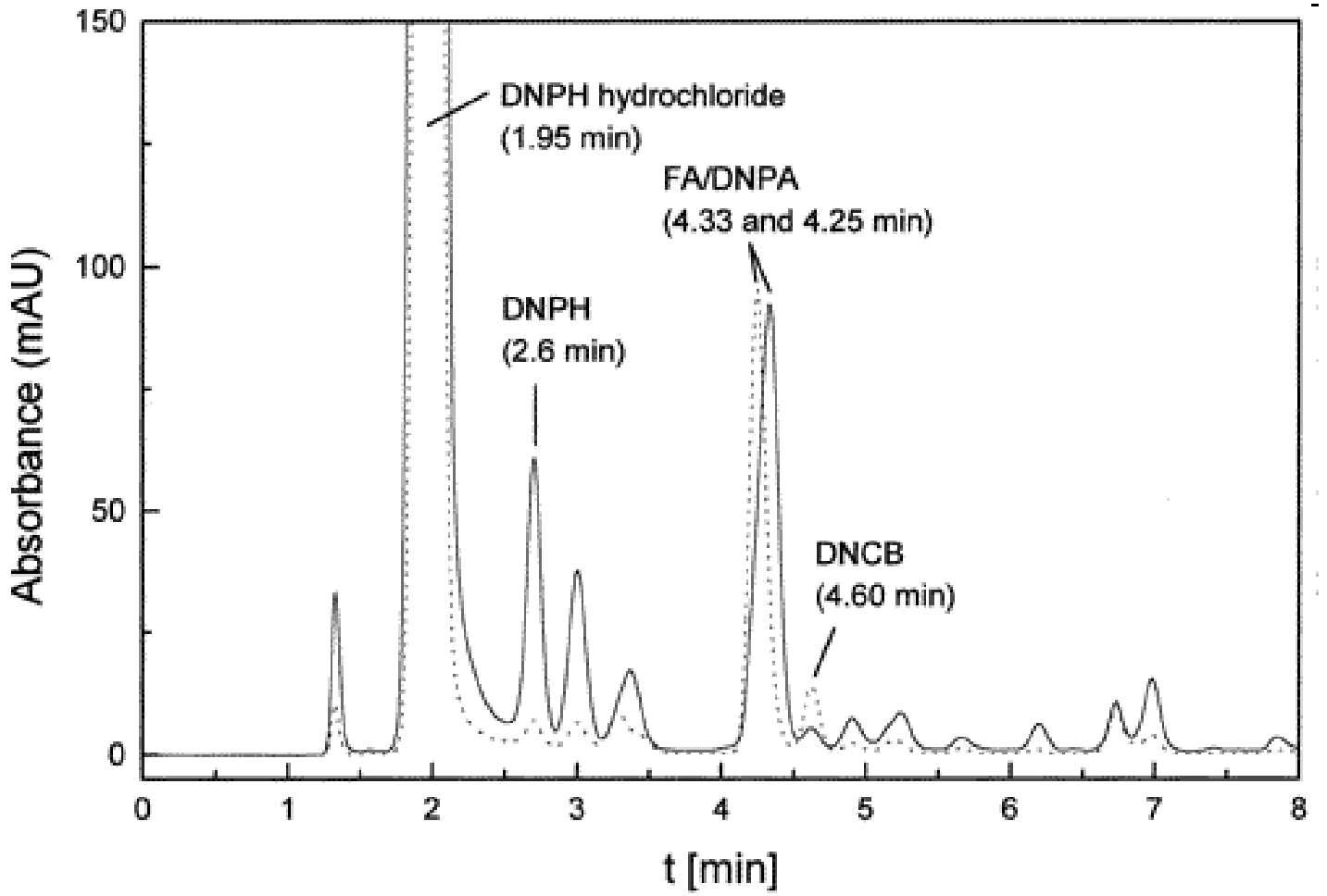
DNPH reacts with $NO_2$ to form 2,4-Dinitrophenyl azide (DNPA).

DNPA coelutes with the formaldehyde-DNPH derivative.




Potter and Karst, 1996

# DNPA






Potter and Karst, 1996

# Formaldehyde

Several studies have capitalized on the formation of DNPA for the sampling of $NO_2$, by altering/optimizing their HPLC gradient.

The use of KI scrubbers to limit $O_3$ intereferences promotes $NO_2$ by the oxidation of NO.

TO11A does not reflect any of the aforementioned information.

# Acetaldehyde

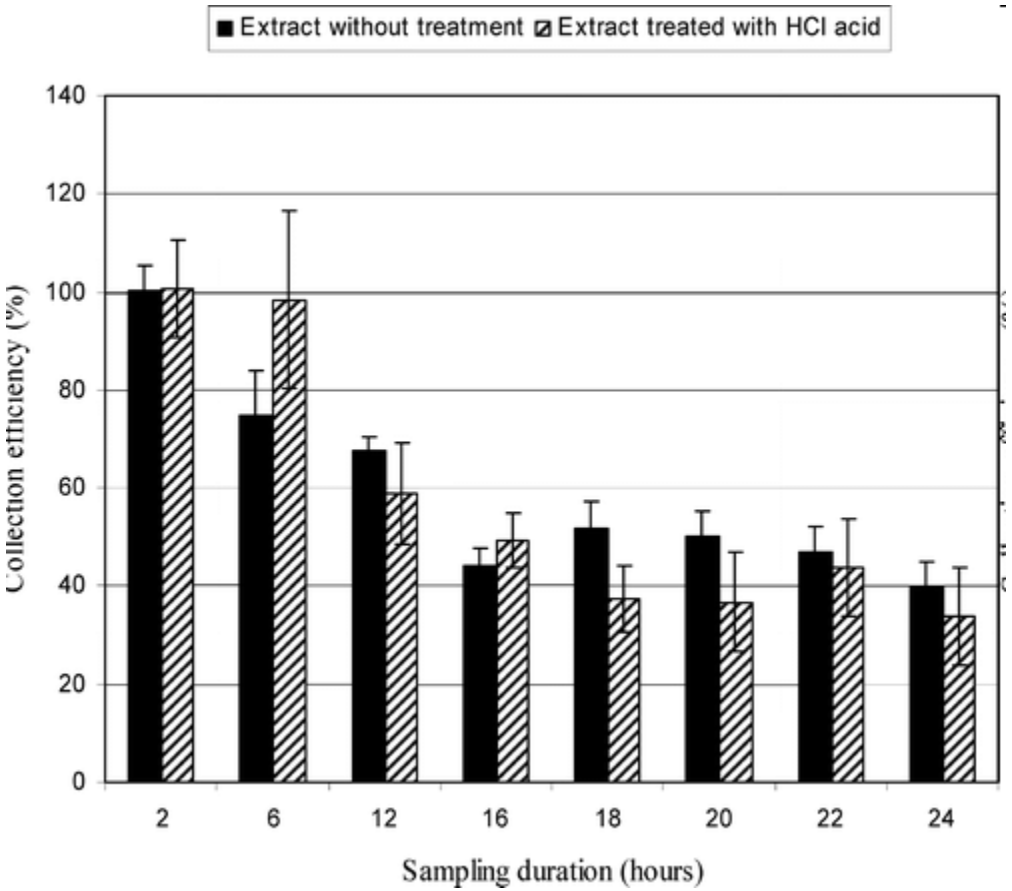
Through an extensive literature search, we were only able to find three studies during which carbonyls other than formaldehyde were evaluated on DNPH-coated solid sorbents for long-term sampling (i.e., 24 h or greater).

Lazarus (*1999*) reported low acetaldehyde collection efficiencies (CE); and Grosjean (*1991*), and Grosjean and Grosjean (*1995*) evaluated breakthrough of the collection media, which does not necessarily reflect CE.

# Acetaldehyde

| Experimental condition | Carbonyl | SUPELCO | WATERS | XPOSURE | HOUSE |
|---|---|---|---|---|---|
| 3 hours at 30% RH | Formaldehyde | 89 ± 10[c] (3) | | | |
| | Acetaldehyde | 93 ± 8[c] (3) | | | |
| 24 hours at 30% RH | Formaldehyde | 83 ± 4 (3) | 87 ± 11 (3) | 111 ± 4 (3) | 104 ± 25 (3) |
| | Acetaldehyde | 39 ± 7 (3) | 43 ± 3 (3) | 62 ± 7 (3) | 1 ± 2 (3) |
| 48 hours at 30% RH | Formaldehyde | 89 ± 8 (3) | 93 ± 4 (3) | 105 ± 19 (3) | 14 ± 8 (3) |
| | Acetaldehyde | 51 ± 22 (3) | 43 ± 2 (3) | 40 ± 11 (3) | 0 (3) |
| 24 hours at 60% RH | Formaldehyde | 101 ± 8 (3) | 101 ± 13 (3) | 121 ± 32 (3) | 133 ± 27 (3) |
| | Acetaldehyde | 27 ± 4 (3) | 29 ± 2 (3) | 30 ± 2 (3) | 9 ± 2 (3) |

# Acetaldehyde

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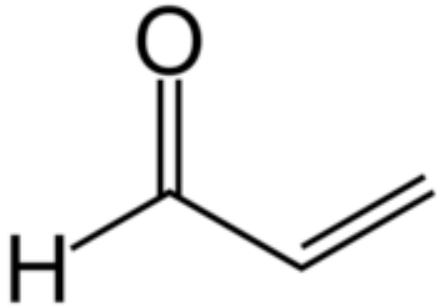
# Acrolein





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# Acrolein by Canisters

- EPA Compendium Method TO-15
  - SUMMA Canisters
  - 24 hour samples
  - Analyzed by GC/MSD
- Recent work (*Heaton, Dann*) has demonstrated growth of acrolein within canisters.
- We designed a small study to investigate



11

# Collocation for Acrolein

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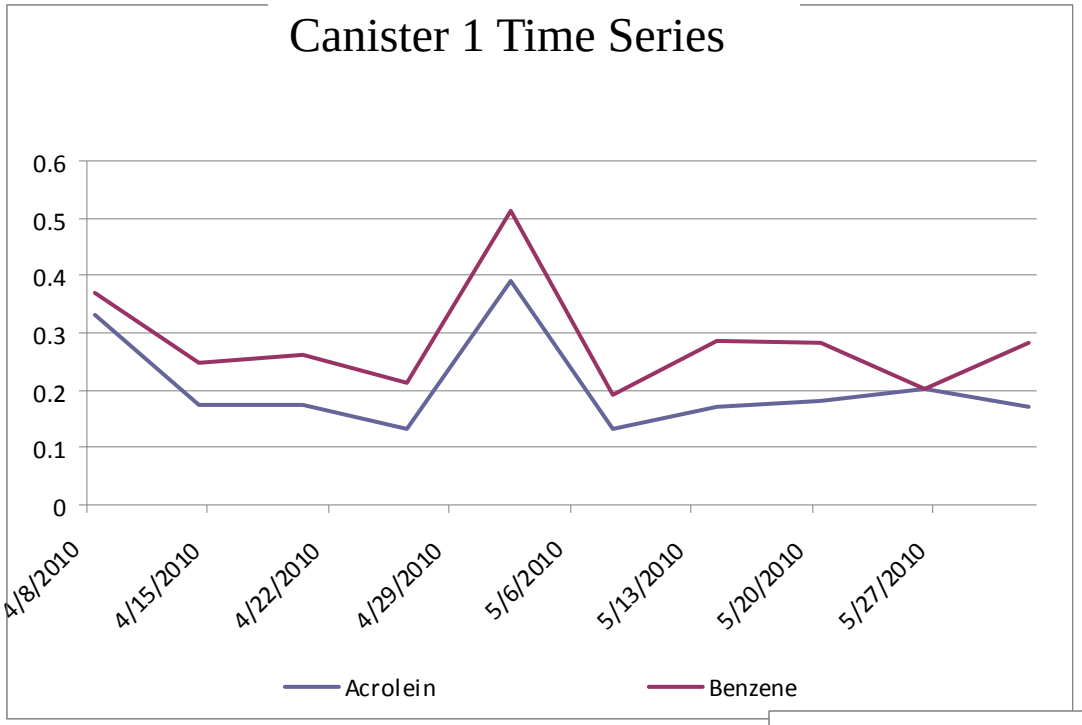
Canister collocation

Can 1

Can 2

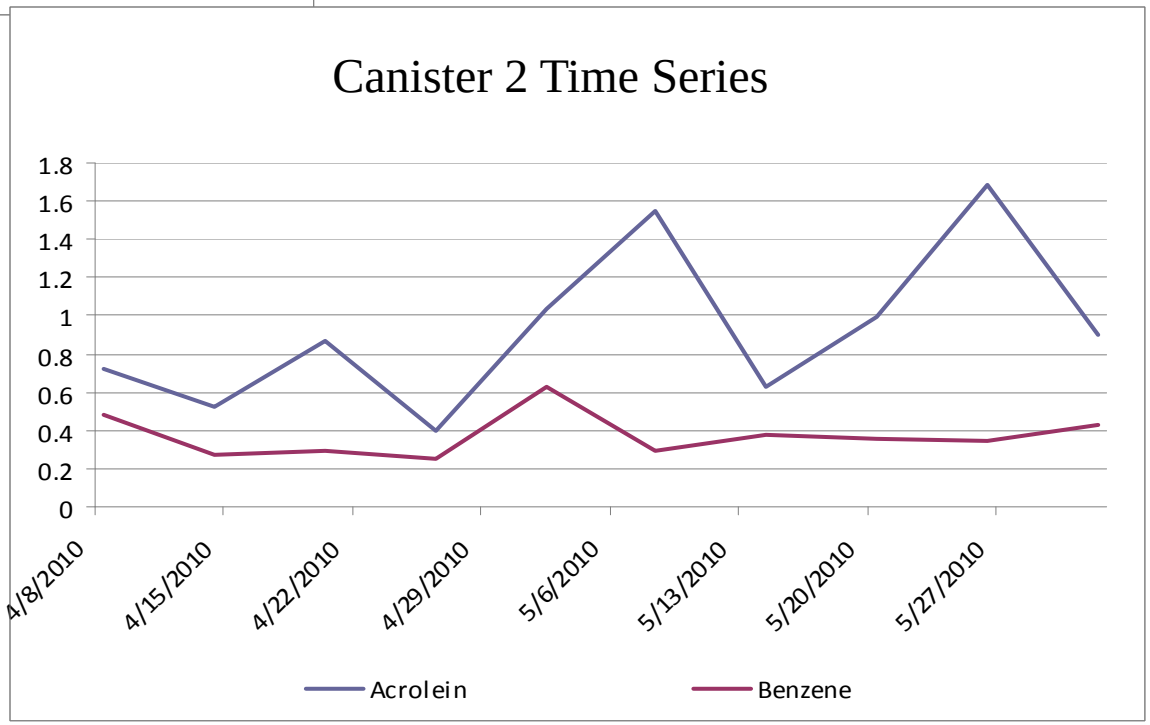

- Same Sample Split to 2 canisters
- 10 sampling events
- 2 different labs prepare and analyze canisters
- Site: Bronx NYC




- Acrolein - As a Mobile Source should tract Benzene
- Typical Acrolein concentration should be lower than benzene

Not the case here –

Why? Canister is contributing to acrolein values.



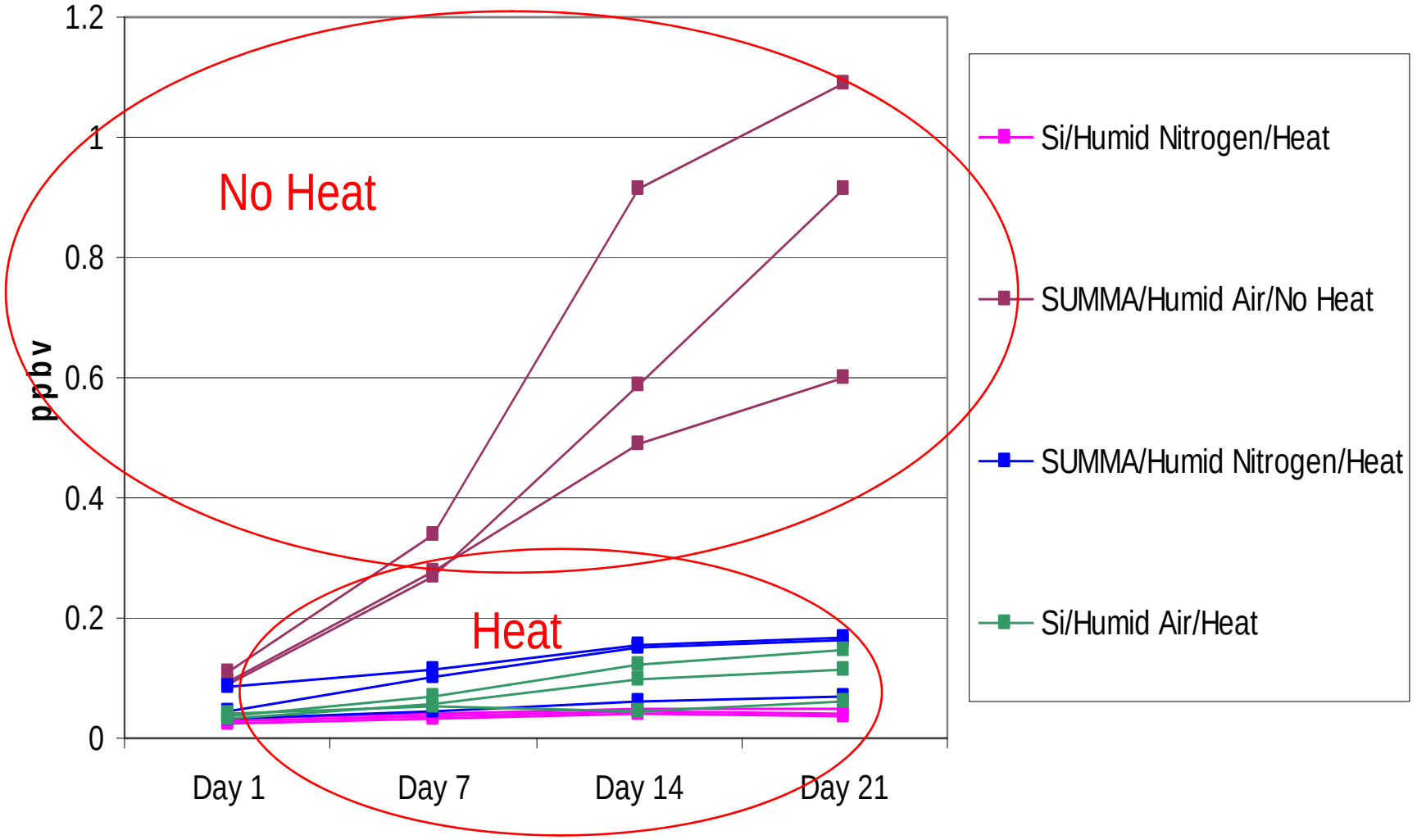
# Acrolein Study

- Experimental Design
  - Variables studied
    1. Canister type and prep (cleaning)
       - Heat vs No-Heat
       - Humidified Air vs Humidified Nitrogen
       - SUMMA canister vs Silco lined
    2. Lab analysis and calibration gas standards

- Test 1: Blank canisters analysis looking at Acrolein growth
  - Test for cleanliness over 21 days
  - Assumption – all SUMMA created equal


14

## Phase 1 Test 1: Blank Canister Analysis for Acrolein (corrected values)



# Recommendations

- Add heat to canister prep. At least 90°C.
- Start with fresh canisters and test **each** canister for cleanliness **over time** to ensure capability for use for Acrolein. (no growth)
- Collocate each sampling event.

# Conclusions

- Laboratory staff need to be aware of DNPA and the possible coelution with the formaldehyde-DNPH derivative.
- Field sampling technicians need to be aware of acetaldehyde collections efficiencies beyond 6 hours of sampling.
- Acrolein-DNPH issues appear to be well known throughout the scientific community.
- Canisters must be cleaned with heat in order to attempt sampling acrolein.