Method Optimization of TO-11A

National Air Toxics Monitoring and Data Analysis Workshop 2015

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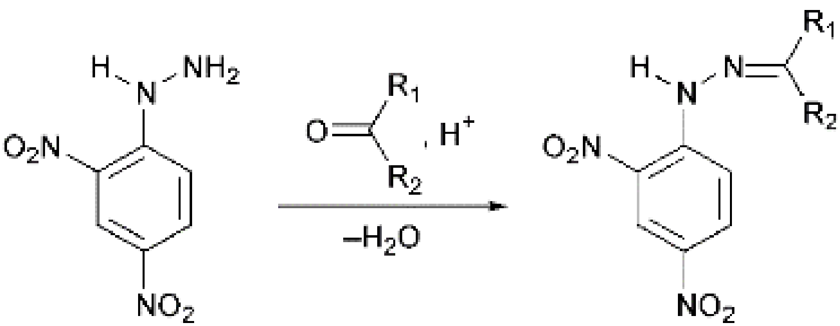
Background and Motivation

- Carbonyl compounds are important to ambient air quality
  - Formaldehyde
  - Acrolein
- Method TO-11a is the ‘gold standard’



R_1, R_2 = H, Alkyl, Aryl

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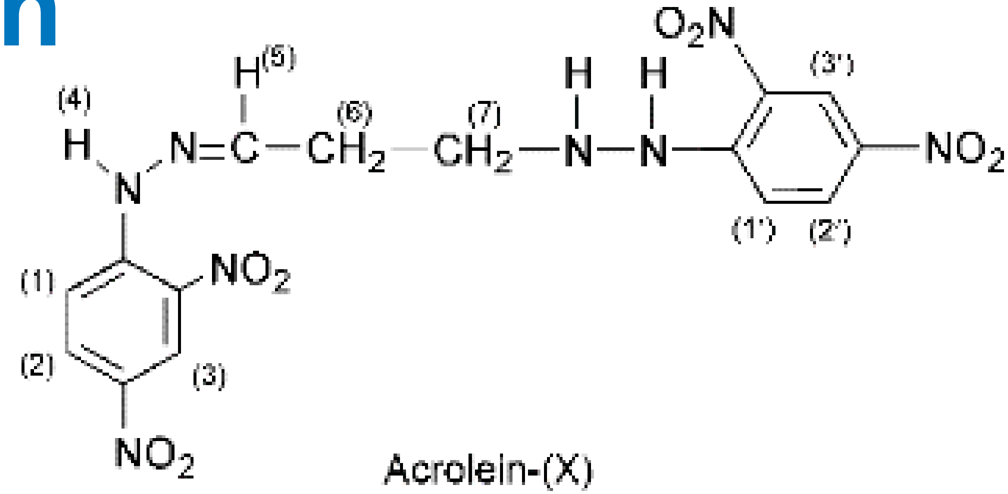
Background and Motivation

- NATTS Network
  - Monitor long-term trends in HAPs concentrations
  - VOCs, carbonyls, PAHs and metals
  - 27 sites around US
- PAMS will again require carbonyls

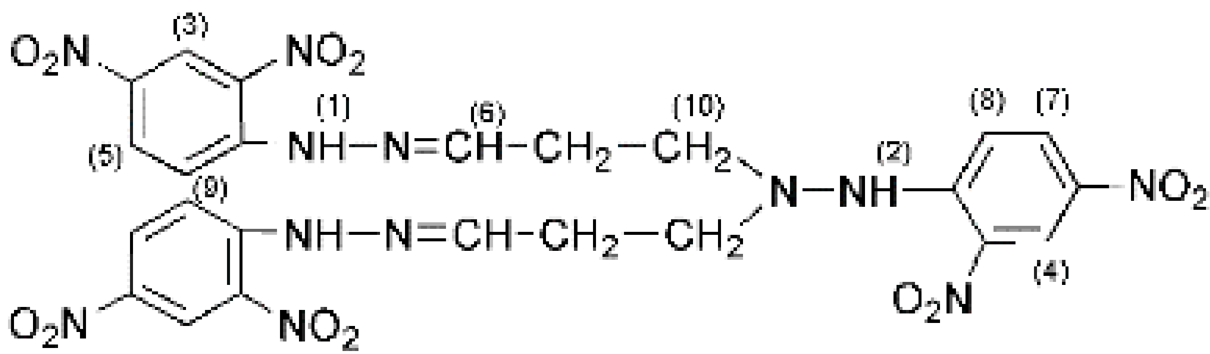
Background and Motivation

- Issues with US EPA Method TO-11a
  - Acrolein
  - Interferences with
    - Ozone
    - Nitrogen dioxide
    - Water
  - Potentially poor, or unknown, collection efficiencies

Acrolein



Acrolein-(X)

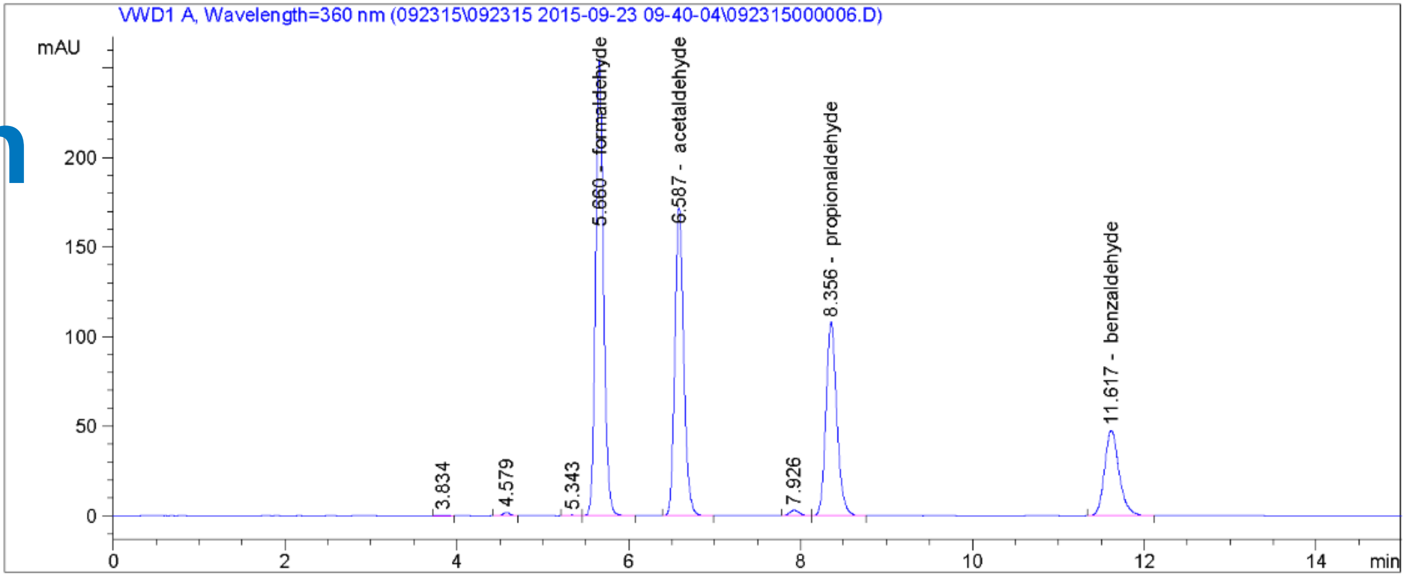


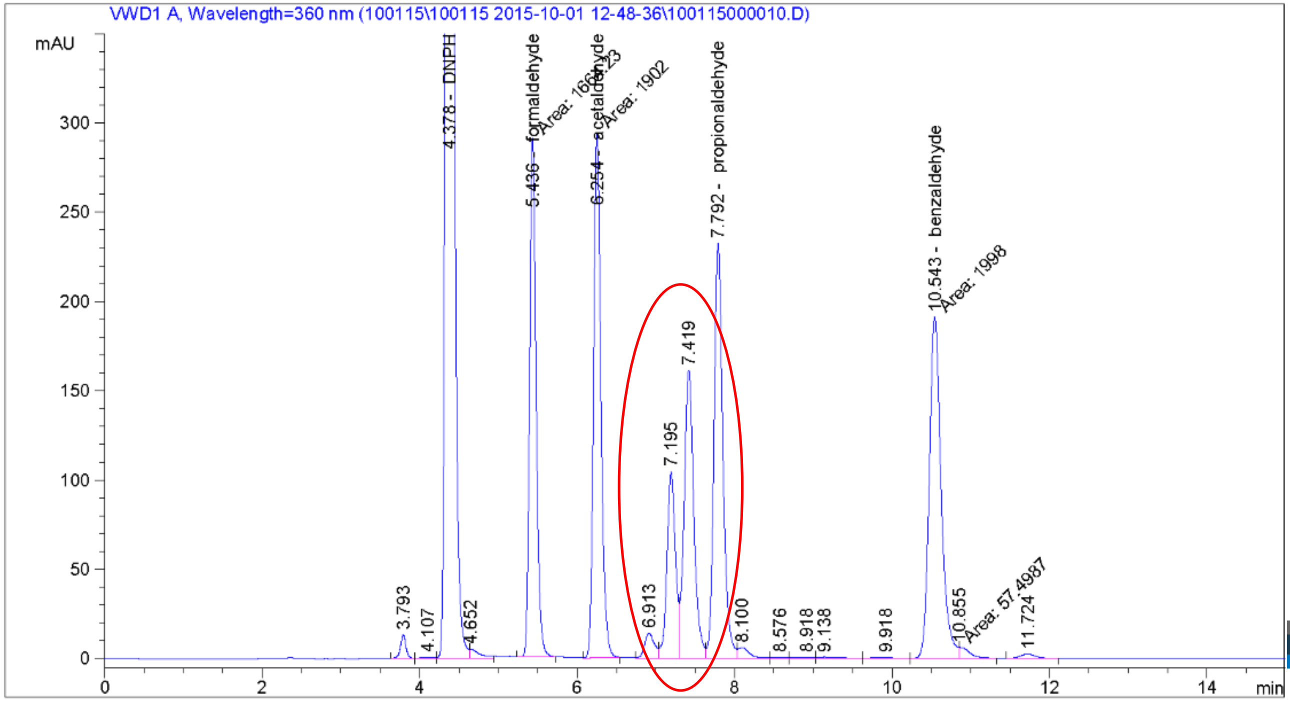
Acrolein-(Y)

Fig. 4 Proposed structures of acrolein-(X) (a) and acrolein-(Y) (b).

Schulte-Ladbeck et al. JEM **3** (2001) 306-310

Acrolein





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Ozone

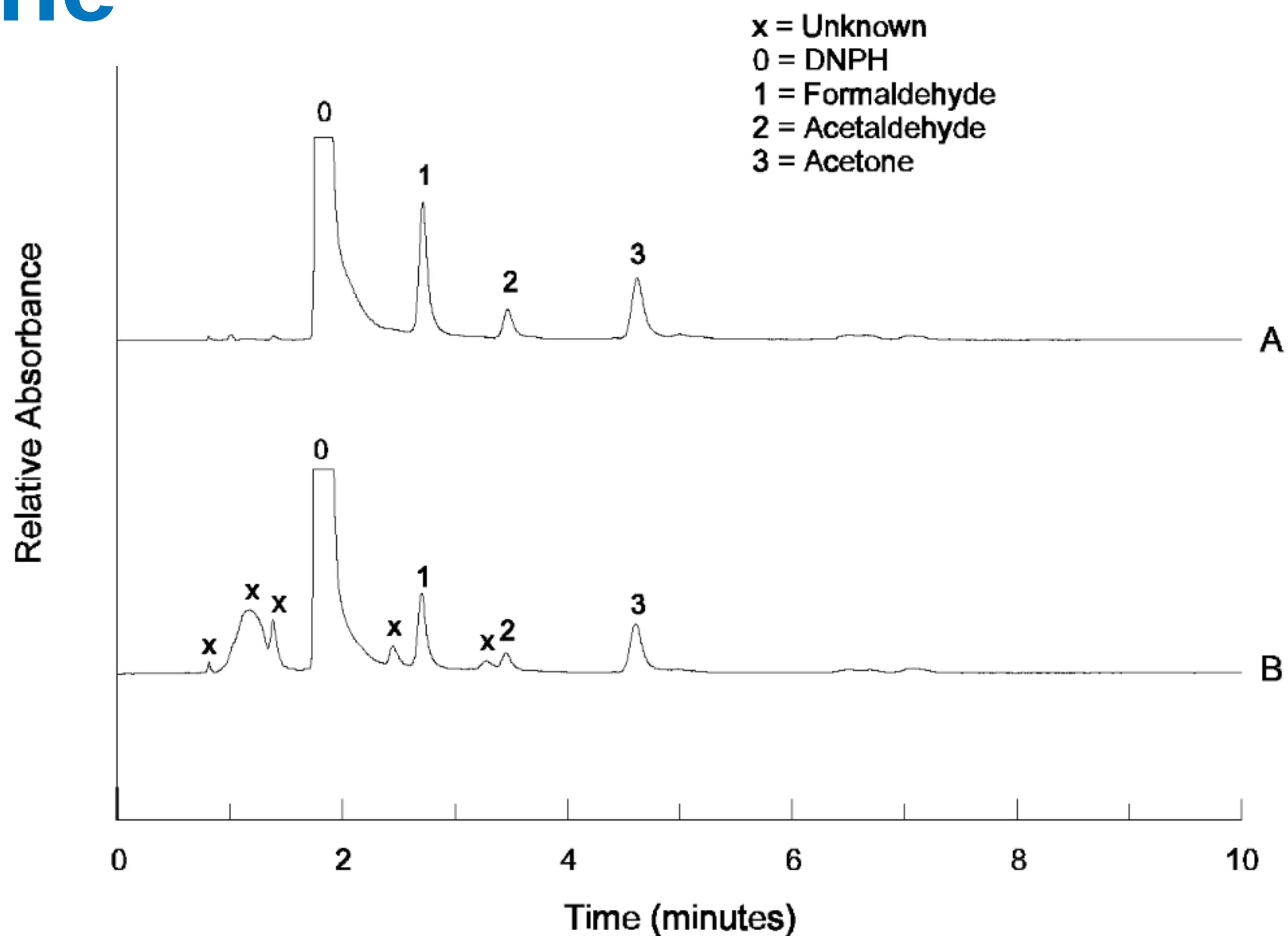


Figure 14. Example of analysis demonstrating DNPH-coated cartridges sampling air with (A) and without (B) ozone denuders, in the determination of formaldehyde.

Nitrogen Dioxide

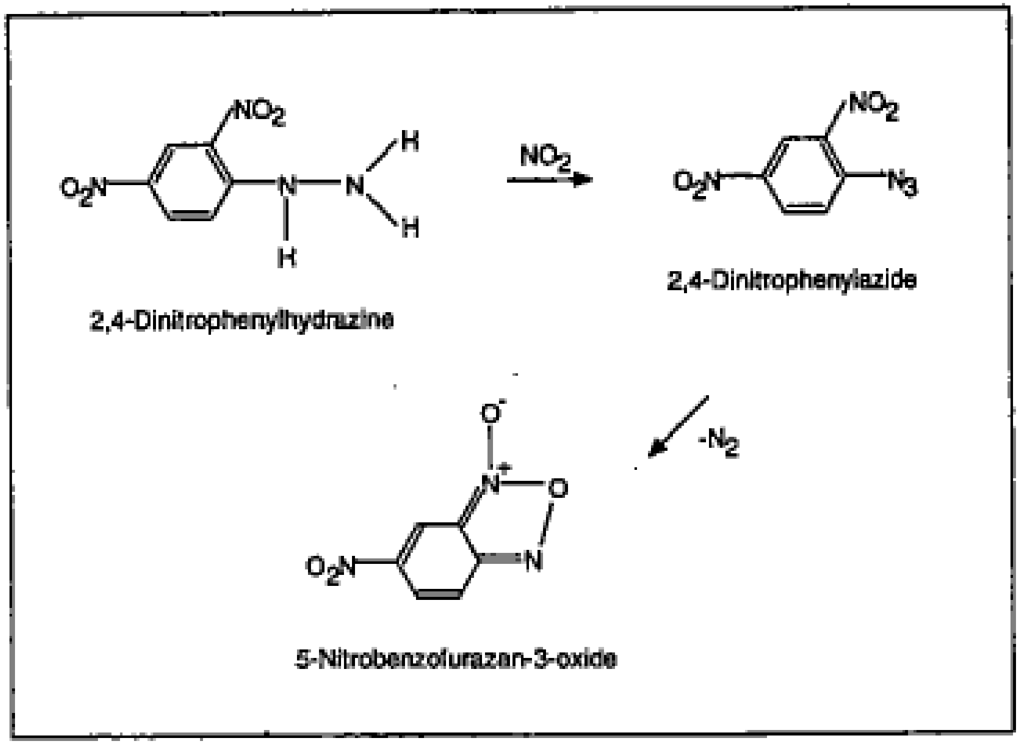
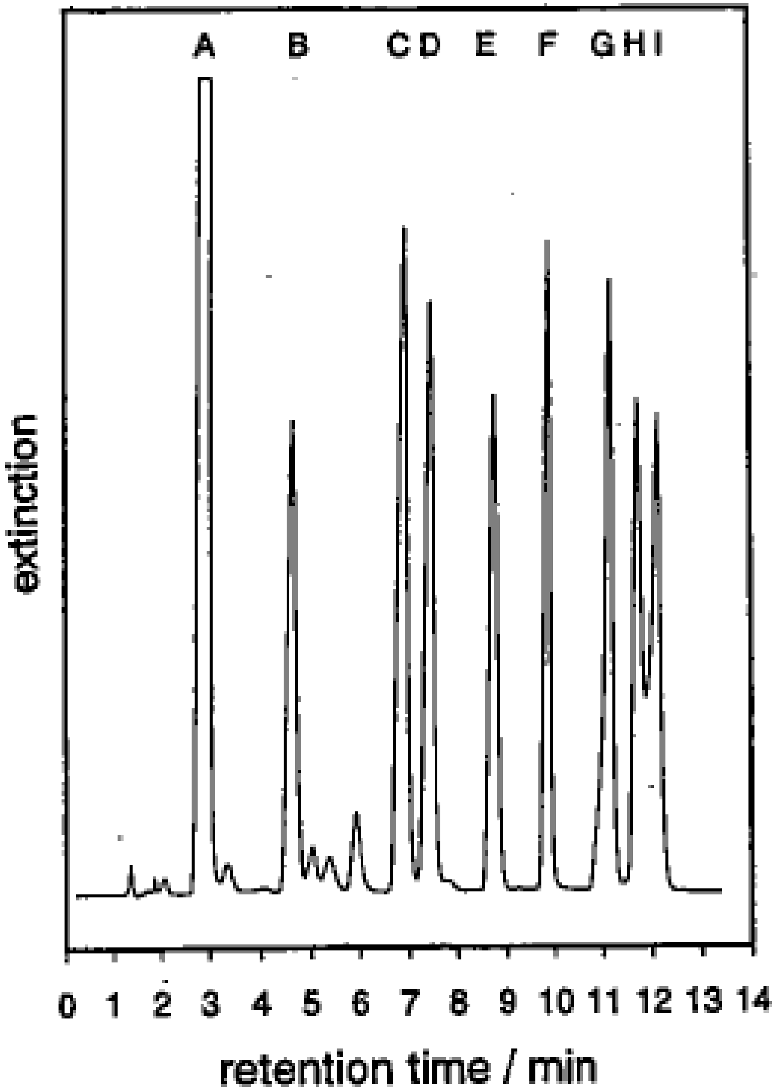


Fig. 6. Reaction scheme of 2,4-dinitrophenylazide



Peak C is 2,4-dinitrophenylazide; Peak D is formaldehyde-2,4-DNP hydrazone

Karst et al. Fresenius J Anal Chem **345** (1993) 48-52

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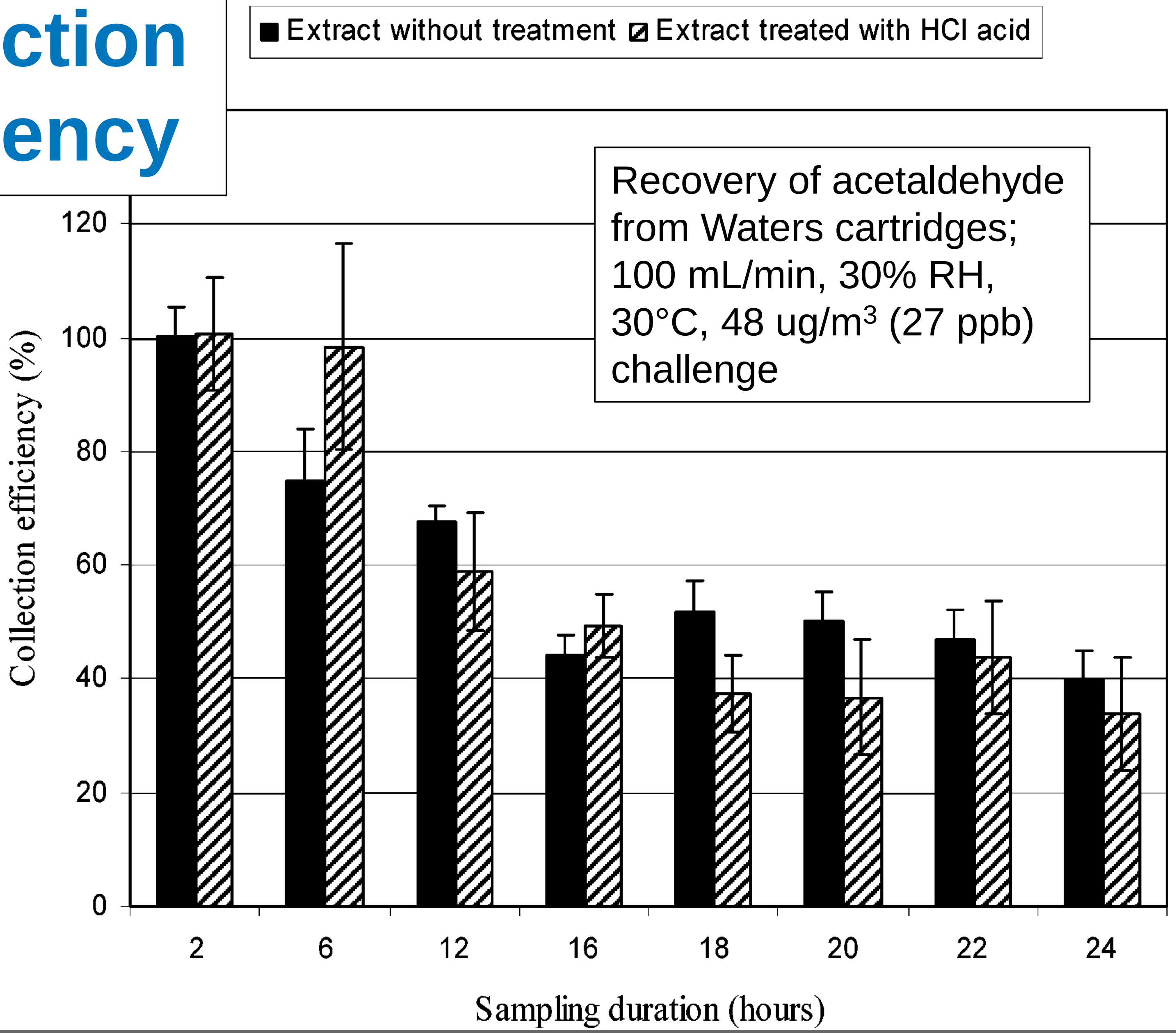
Collection Efficiency



Herrington, et al. ES&T **41** (2007) 580-585

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Objectives

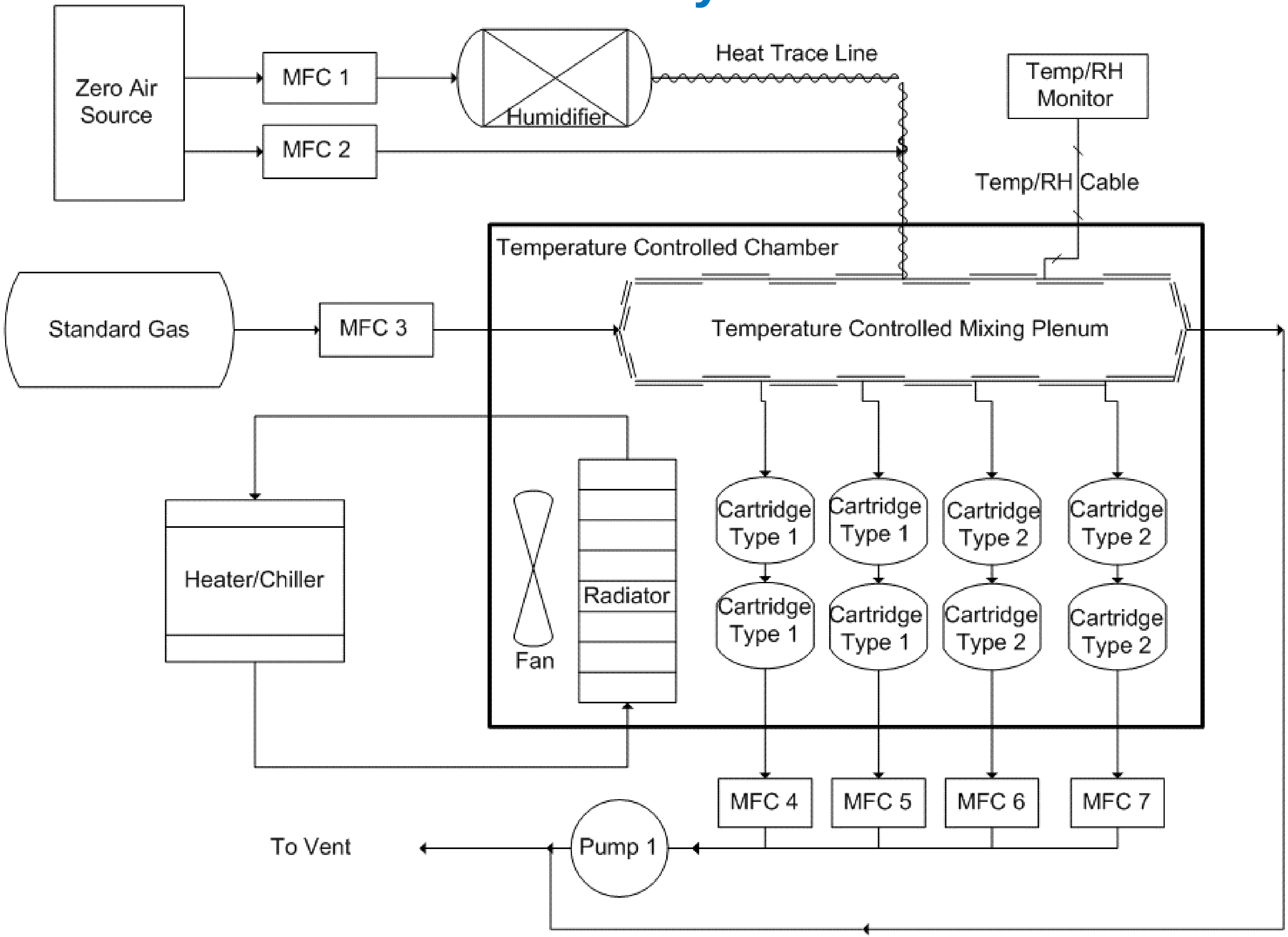
- Evaluate the effect of flow rate, ozone, nitrogen dioxide, and water on Method TO-11A for the measurement of formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde

- Provide updated guidance, as needed, on the implementation of Method TO-11A

Experimental design

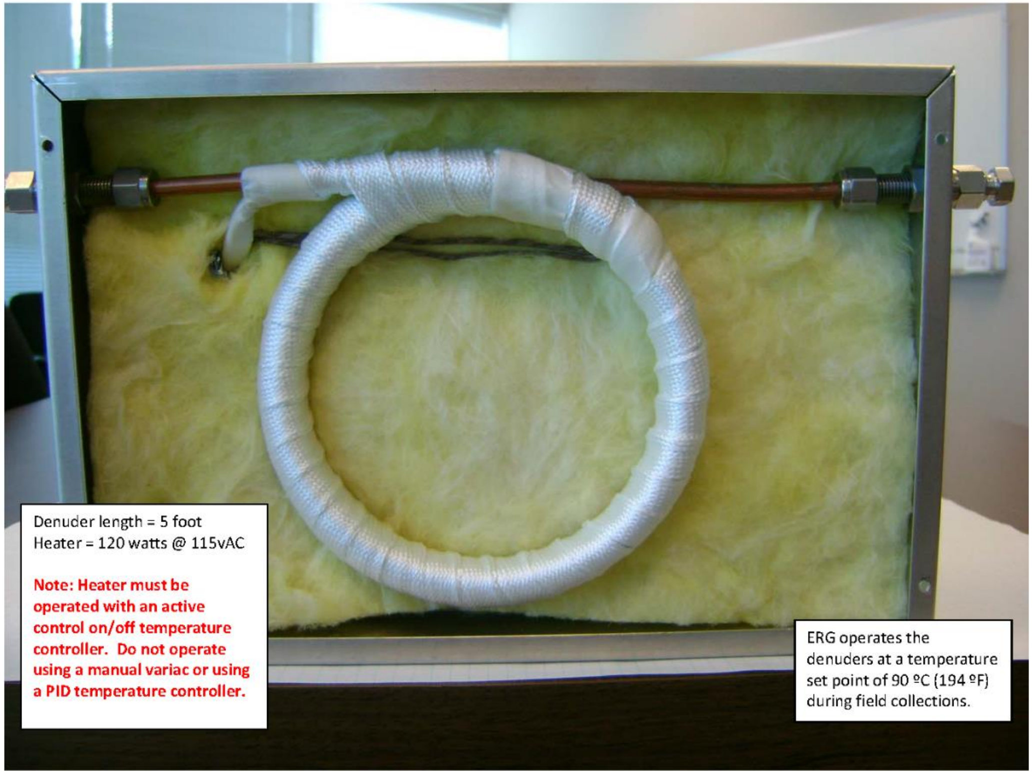
- Part 1: Collection efficiency assessment and flow rate selection
  - Carbonyls generated at ~ 5 ppb with a gas-phase standard
  - Both styles of DNPH cartridges, in duplicate, in series
  - Ideal conditions: zero air without particles, NO_2 or O_3
  - 0.25, 0.5, 0.75, 1.0 and 1.25 L/min @ 25°C, 1 atm
  - 24 hours sampling
  - Tests at 30% and 65% RH @ 25°C
- Goal: investigate CE and select flow rate for future tests

Collection Efficiency Test Fixture



Experimental design

- Part 2: Evaluate ozone scrubbers for capacity and ability to handle short-term high levels of O_3
- Part 3: Evaluate and remediate NO_2 interference
- Part 4: Final method optimization



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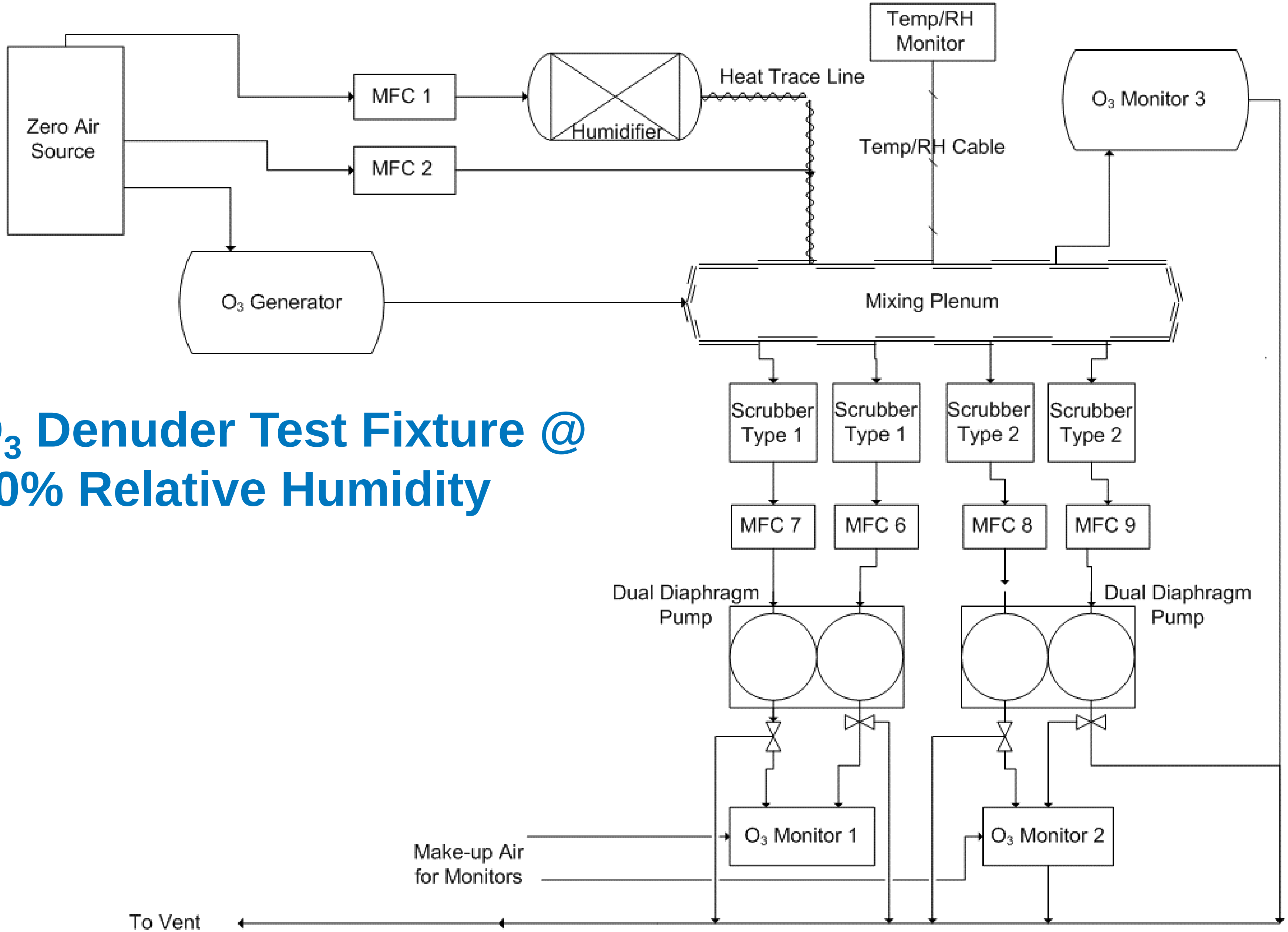
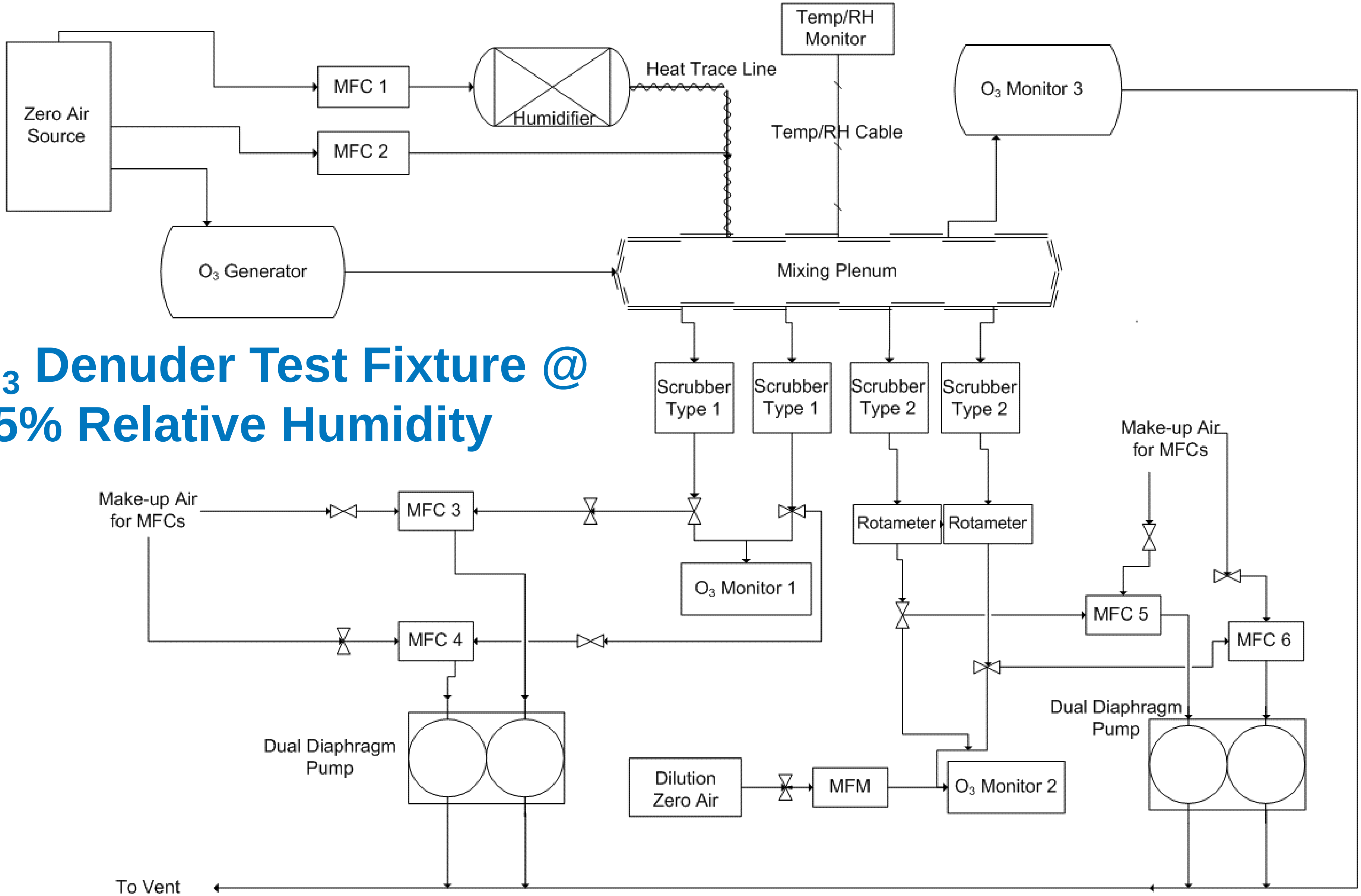
O_3 Denuder Test Fixture @ 30% Relative Humidity



O_3 Denuder Test Fixture @ 65% Relative Humidity



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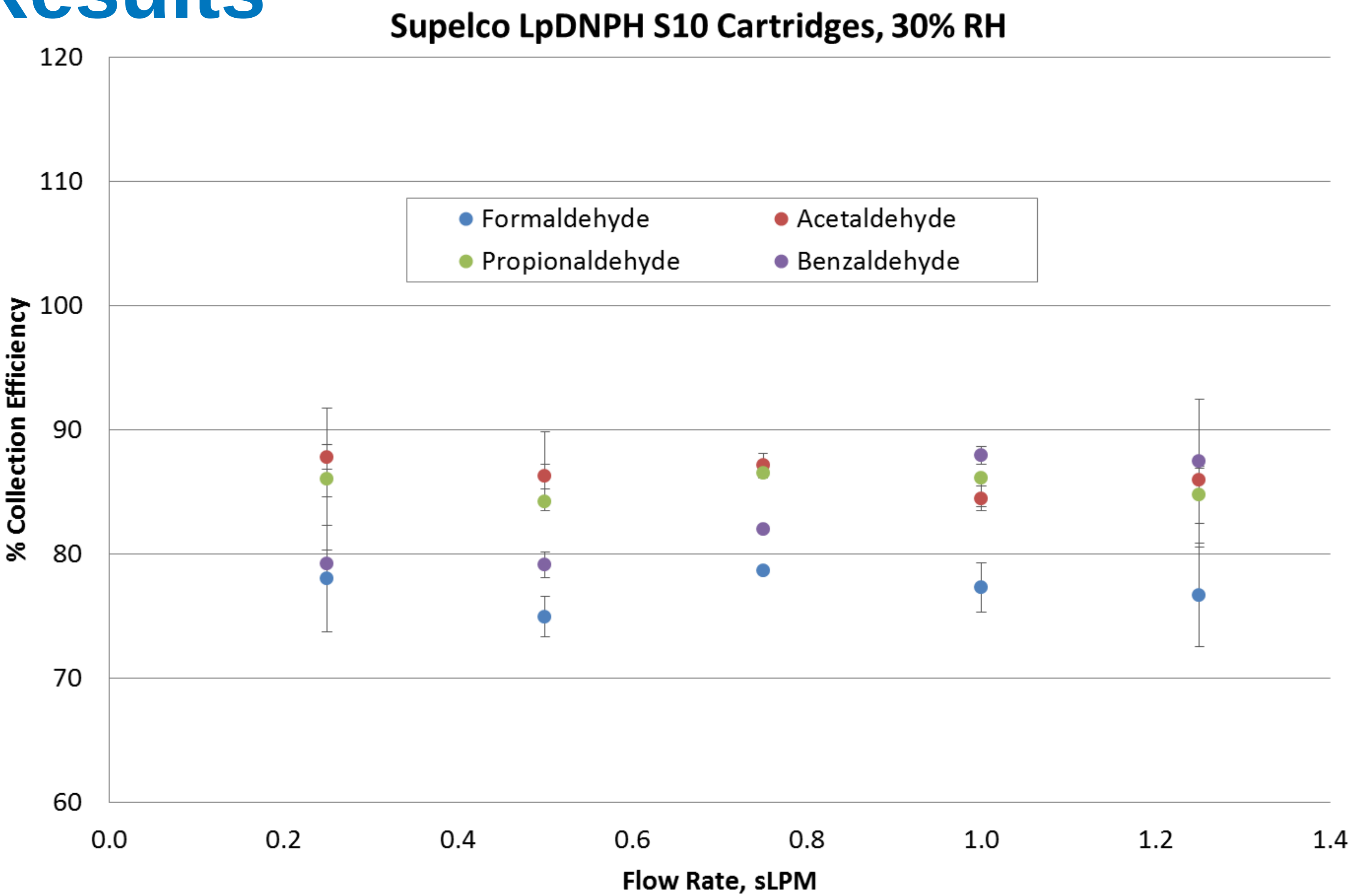
Results



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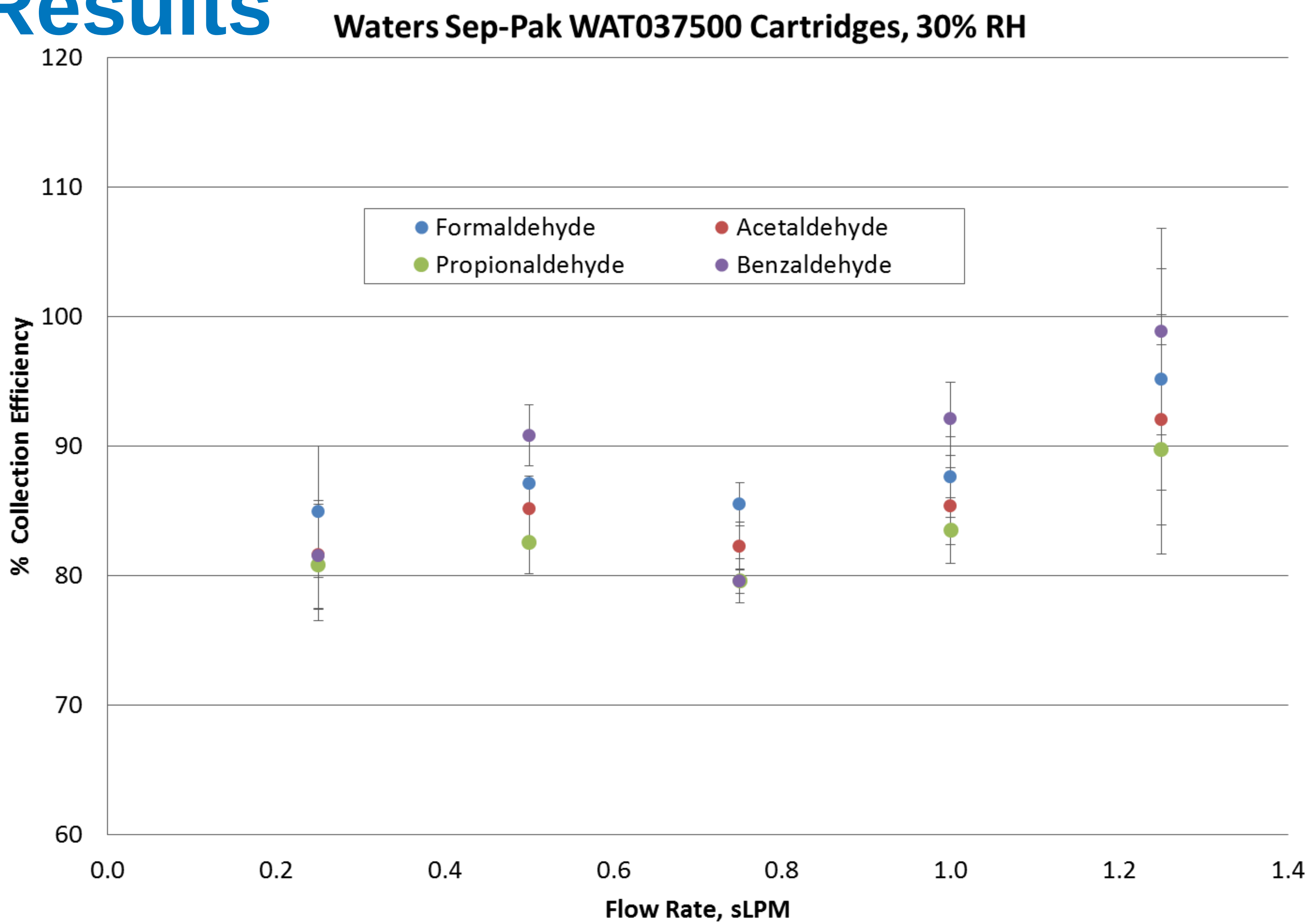
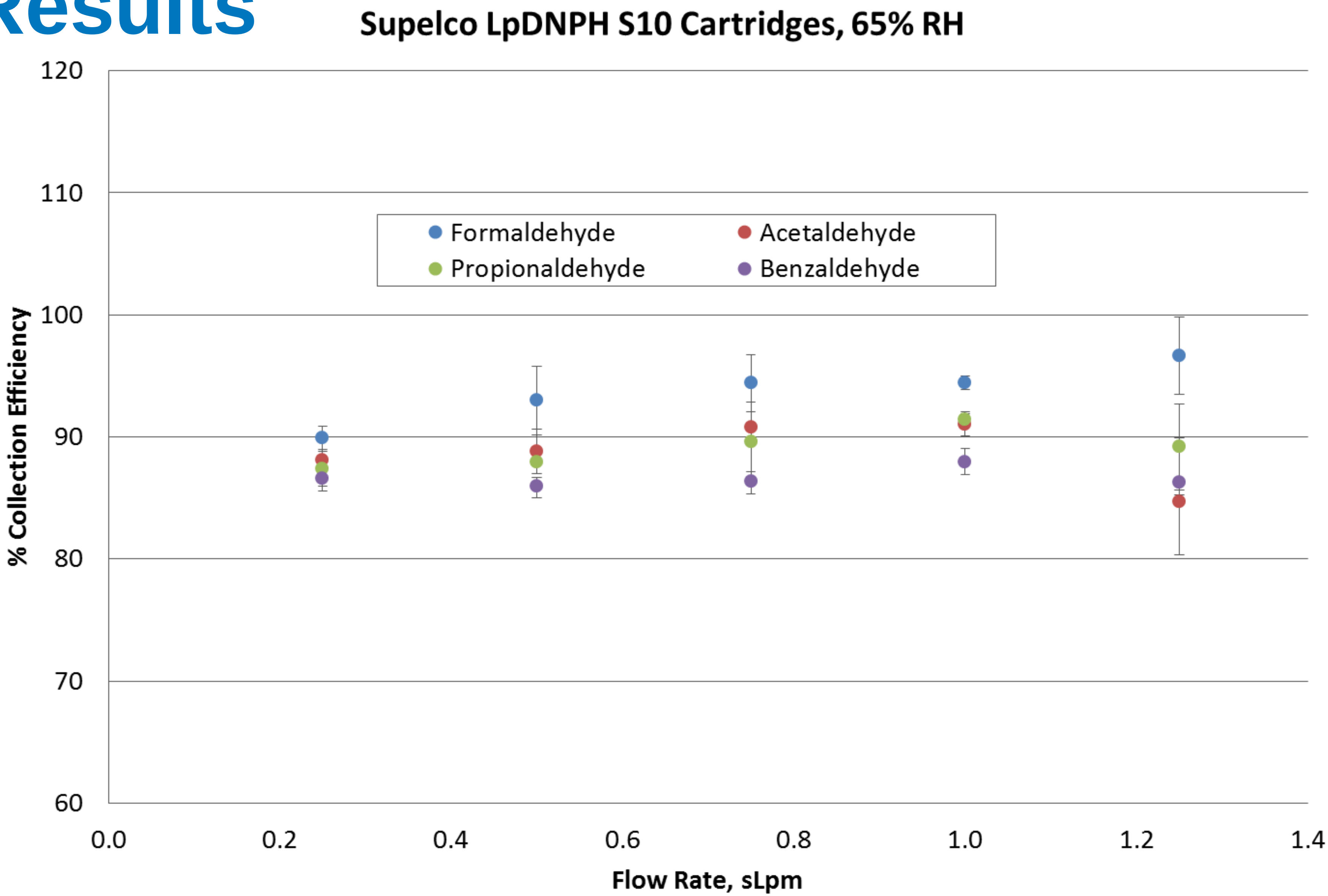
Results

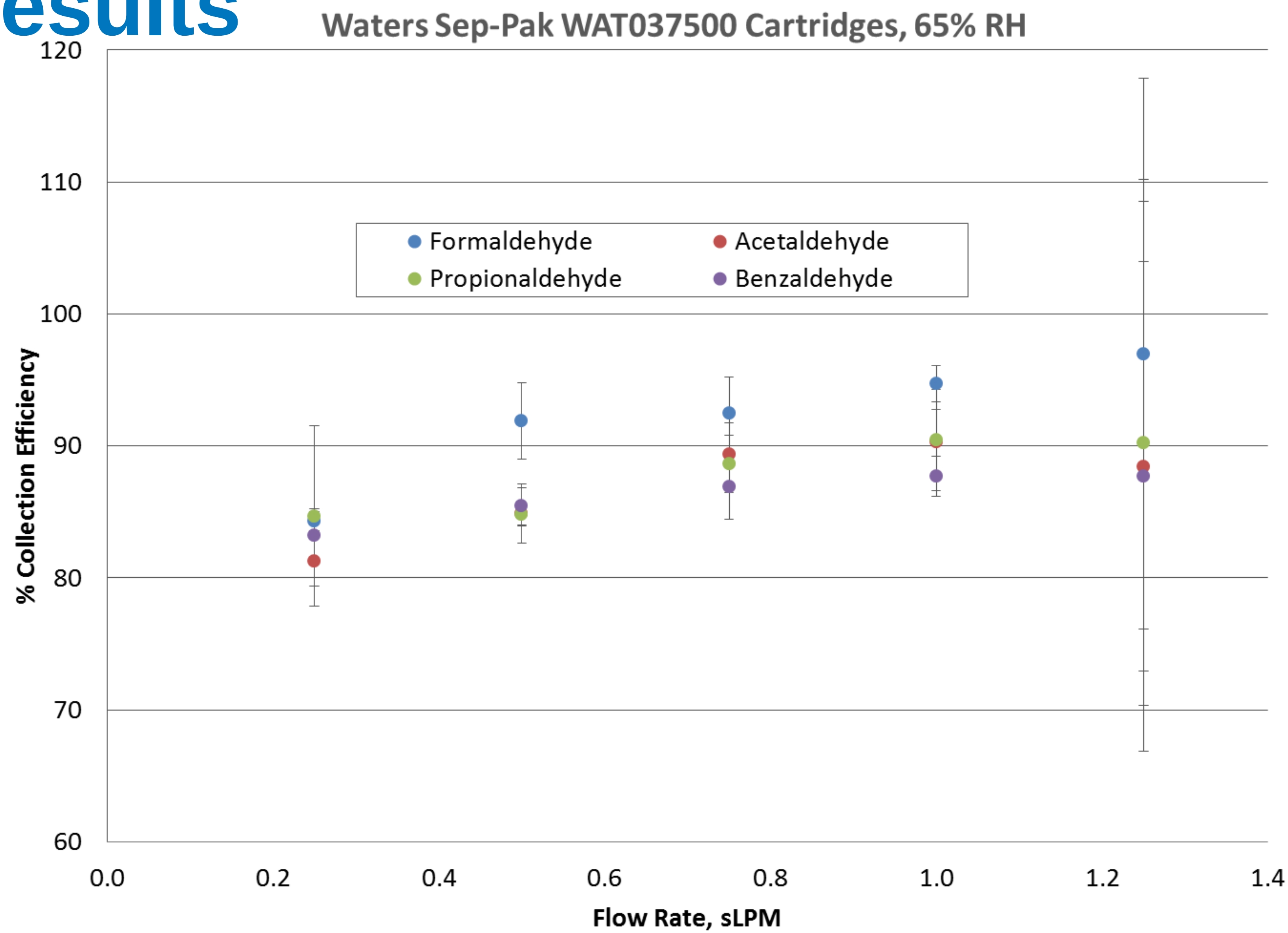


Waters Sep-Pak WAT037500 Cartridges, 30% RH
Formaldehyde
Acetaldehyde
Propionaldehyde
Benzaldehyde
% Collection Efficiency
120
110
100
90
80
70
60
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Flow Rate, sLPM

Results


Supelco LpDNPH S10 Cartridges, 65% RH
120
110
100
90
80
70
60
% Collection Efficiency
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Flow Rate, sLpm
Formaldehyde
Acetaldehyde
Propionaldehyde
Benzaldehyde

Results



Waters Sep-Pak WAT037500 Cartridges, 65% RH
120
110
100
90
80
70
60
% Collection Efficiency
Formaldehyde
Acetaldehyde
Propionaldehyde
Benzaldehyde
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Flow Rate, sLPM

Ozone Denuders

Denuder	Upstream Ozone Challenge, ppb	Downstream Ozone Concentration, ppb
ERG Primary	151.9	-1.0
	255.3	-1.3
ERG Duplicate	154.3	-0.7
	252.9	-1.1
ATEC Primary	155.8	-0.9
	252.4	-0.6
ATEC Duplicate	148.6	-0.5
	246.4	-0.2

Summary of Results to Date

- Good news for the NATTS network!
- Collection efficiency does not appear to vary with flow rates from 0.25 to 1.25 L/min for sampling over 24 hours at either 30 or 65% RH at carbonyl concentrations of ~ 5 ppb
- Effectively no observed breakthrough at flow rates ≤ 1 L/min at both RHs
- Blank corrections small, but important
- Ozone scrubbers: at 30% RH, efficiency > 99% at a 150 and 250 ppb O_3 challenges; capacity > ~108,000 ppb hours

Timeline for Future Work

- Late week of 10/19: Begin Part 2 work @ 65% RH with ozone denuders
- Week of 11/30: Begin Part 3 work with NO_2
- 1st quarter 2016: Complete Part 4 work on final method optimization and write up all results

Acknowledgement

- This work is being by supported by US EPA OAQPS under contract number EP-D-13-005.

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