Update on Work to Optimize US EPA Method TO-11A for Carbonyls

National Ambient Air Monitoring Conference

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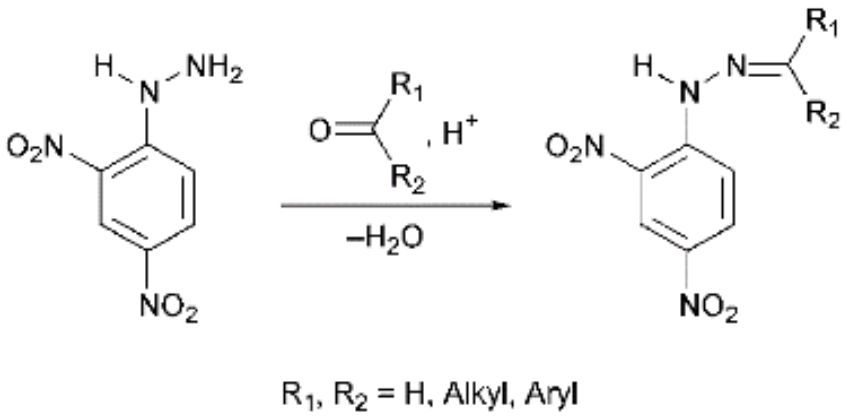
Background and Motivation

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



Background and Motivation

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

Objectives

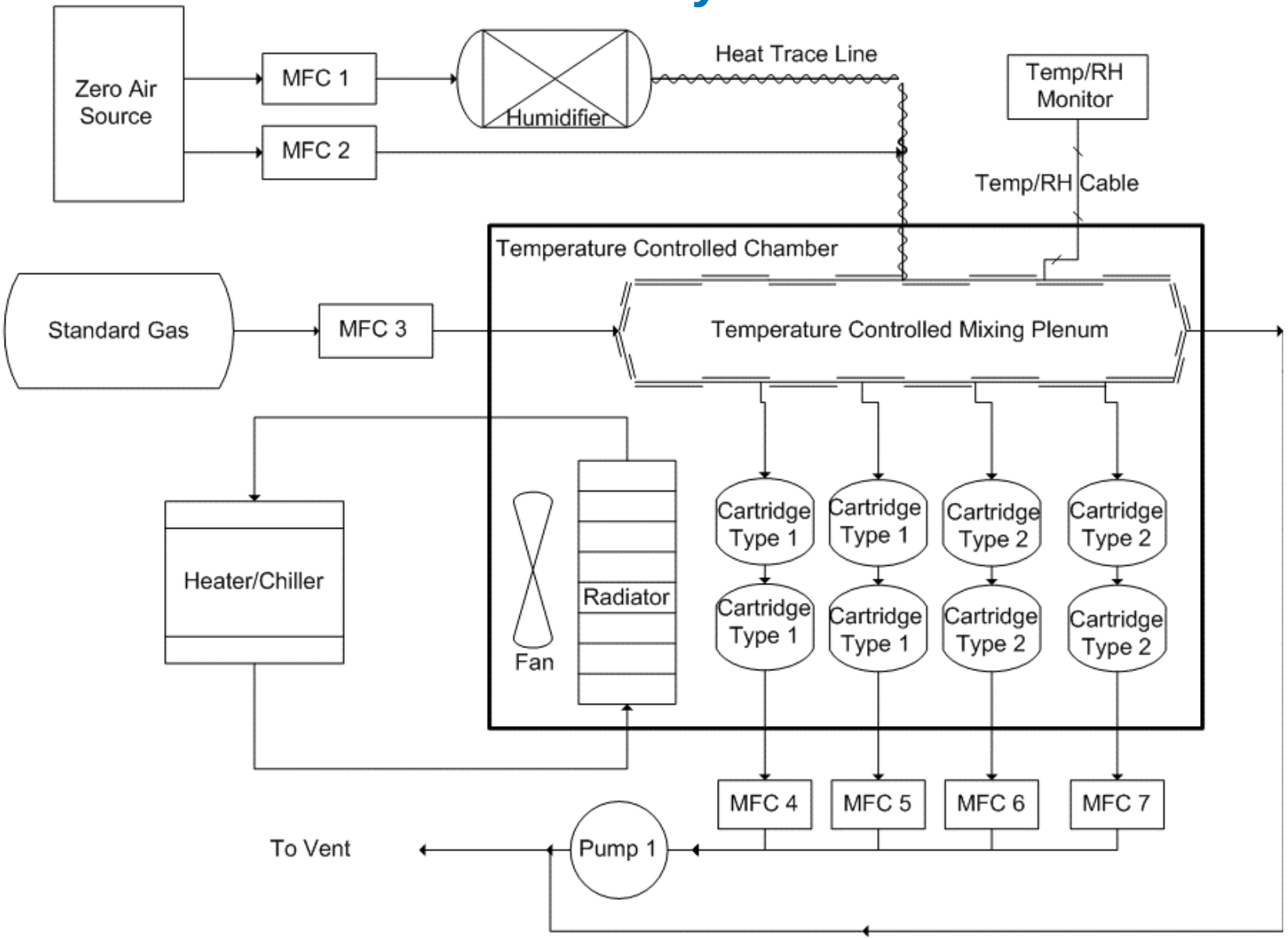
- Evaluate the effect of flow rate, ozone, nitrogen dioxide, and water on Method TO-11A for the measurement of formaldehyde, acetaldehyde, propionaldehyde, and benzaldehyde

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

Experimental design

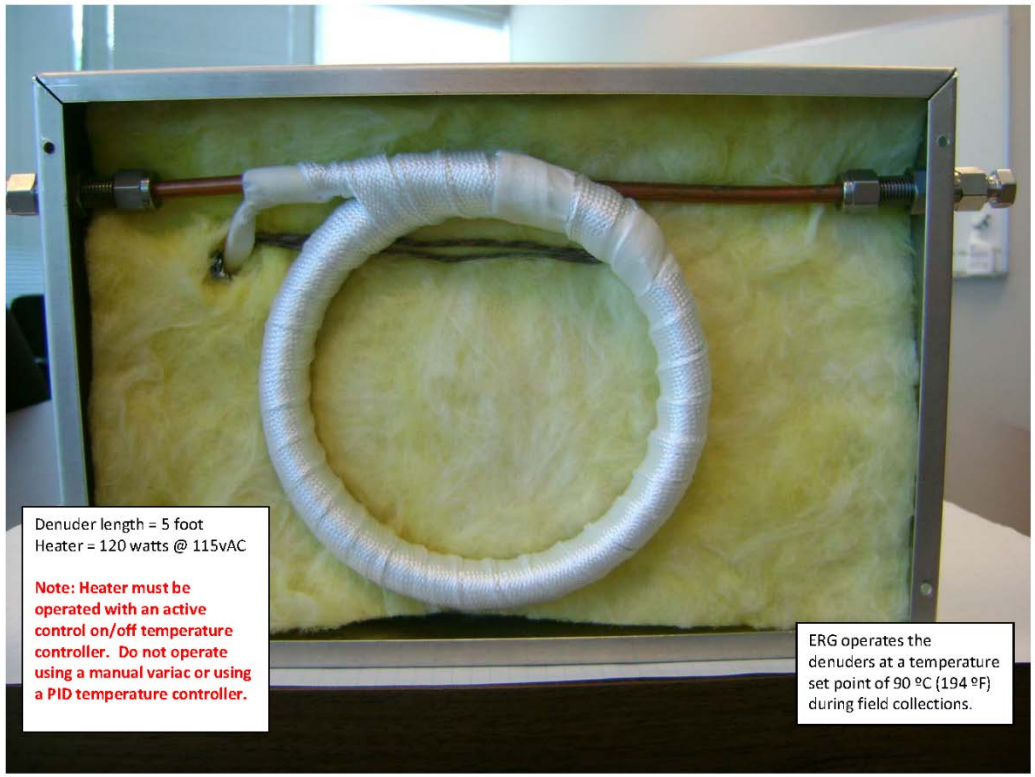
- Part 1: Collection efficiency assessment and flow rate selection
  - Carbonyls generated at ~ 5 ppb with a gas-phase standard
  - Both styles of DNPH cartridges, in duplicate, in series
  - Ideal conditions: zero air without particles, NO_2 or O_3
  - 0.25, 0.5, 0.75, 1.0 and 1.25 L/min @ 25°C, 1 atm
  - 24 hours sampling
  - Tests at 10%, 30%, 65%, and 85% RH @ 25°C
- Goal: investigate CE and select flow rate for future tests

Collection Efficiency Test Fixture

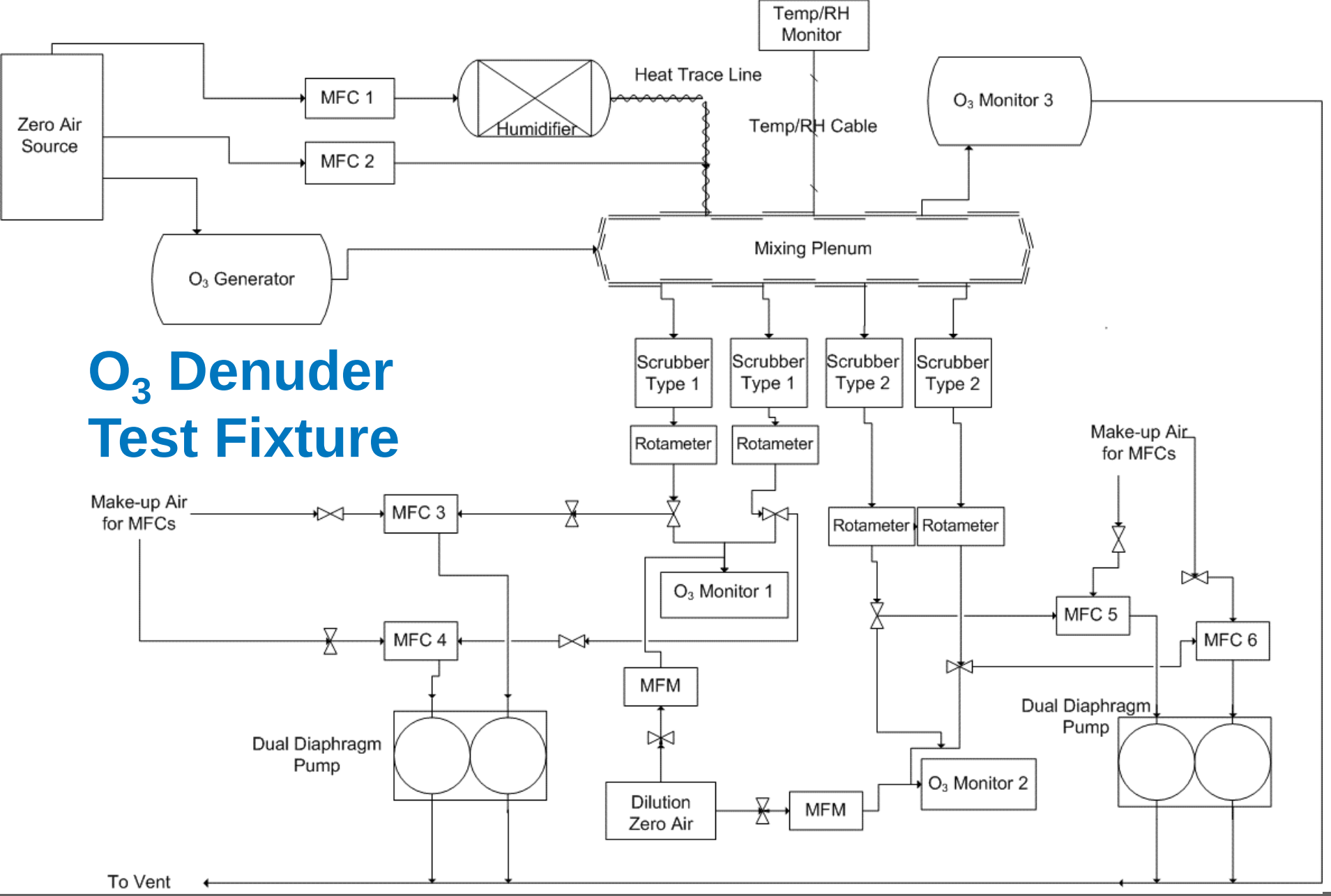


Experimental design

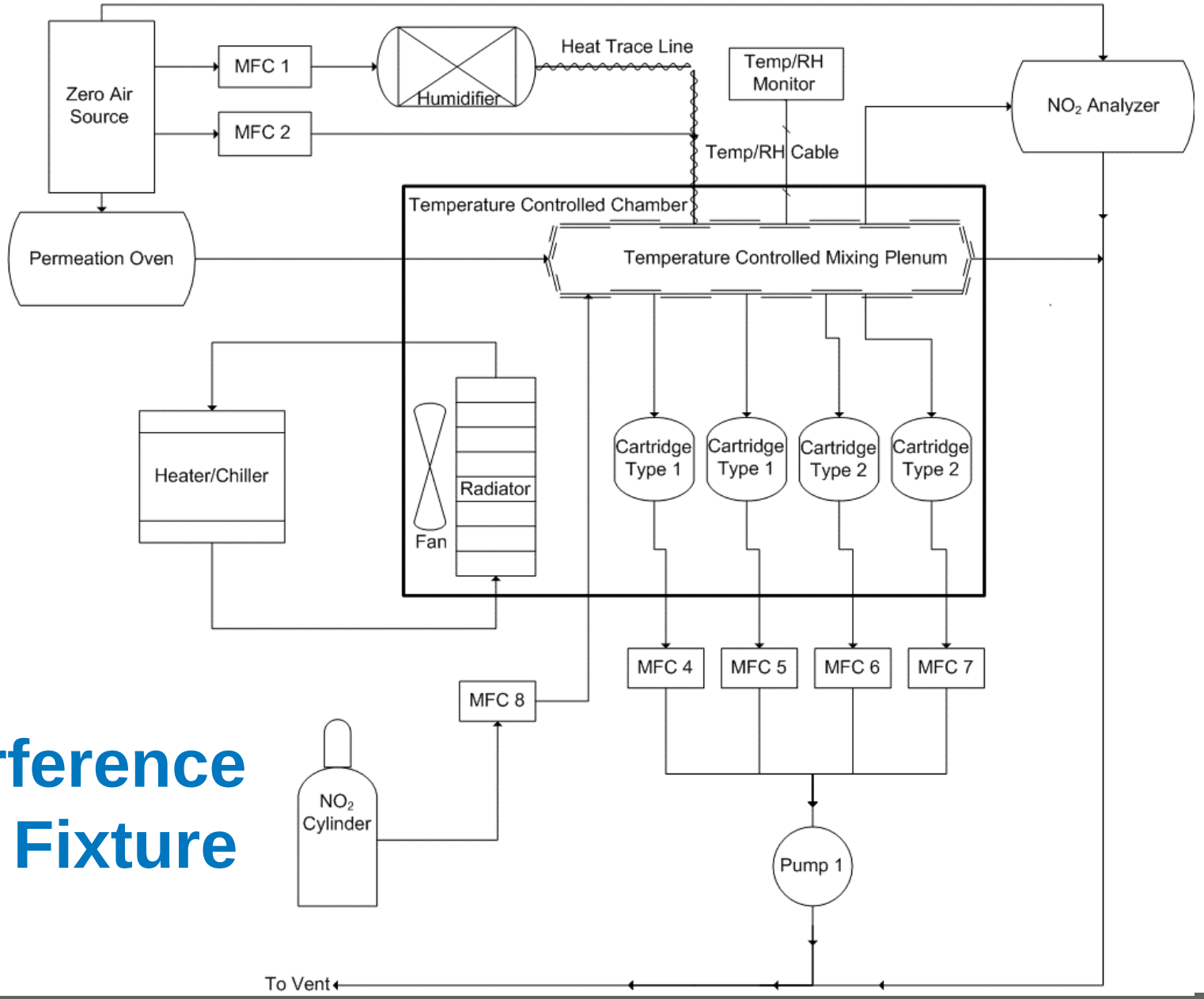
- Part 2: Evaluate at 4 RHs ozone scrubbers' capacity and ability to handle short-term high levels of O_3
- Part 3: Evaluate and remediate NO_2 interference, also at 4 RHs
- Part 4: Final method optimization in the presence of co-collected O_3 and NO_2 and investigation of presence of collection interval bias



O_3 Denuder Test Fixture



NO_2 Interference Test Fixture



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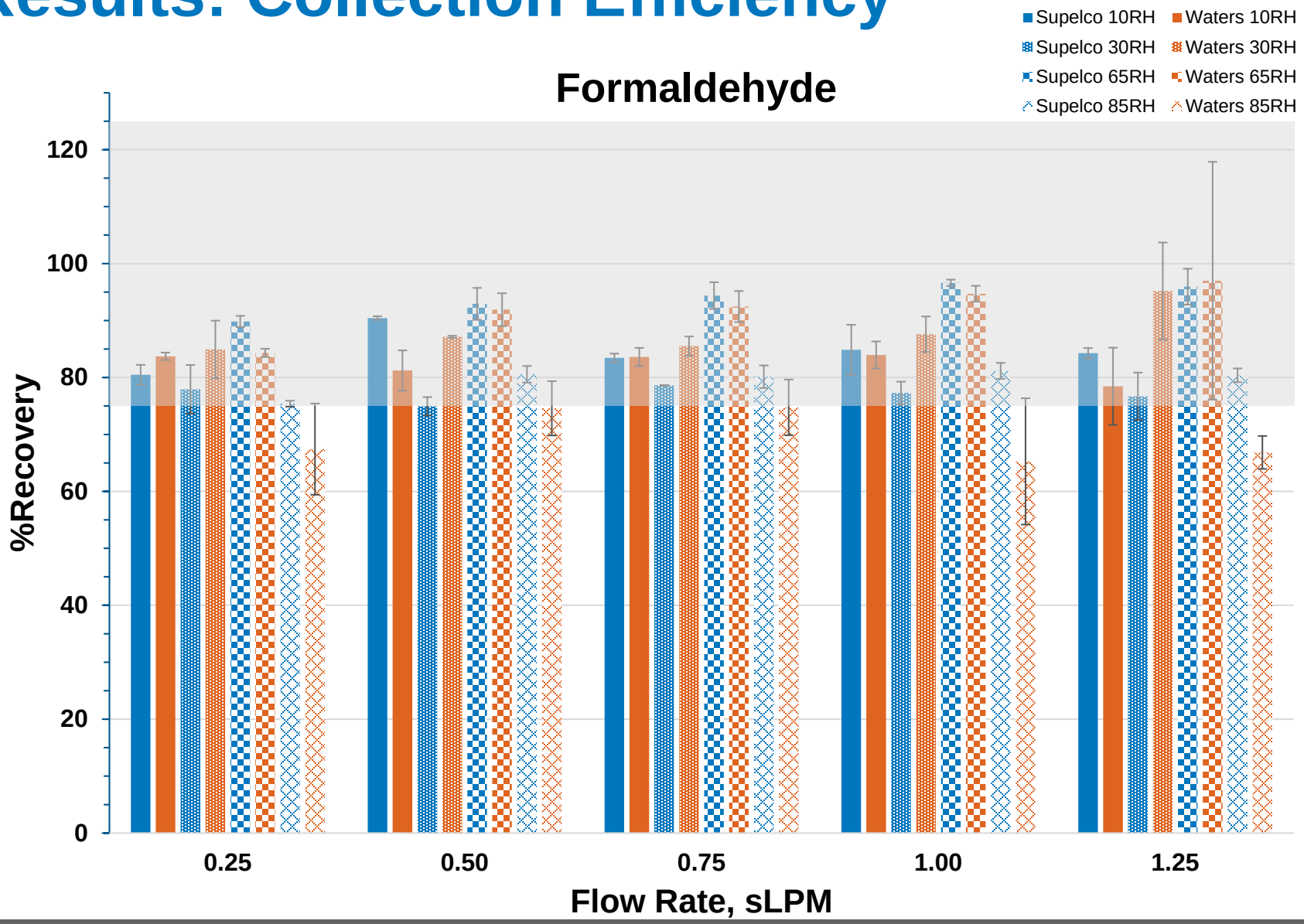
Results: Collection Efficiency



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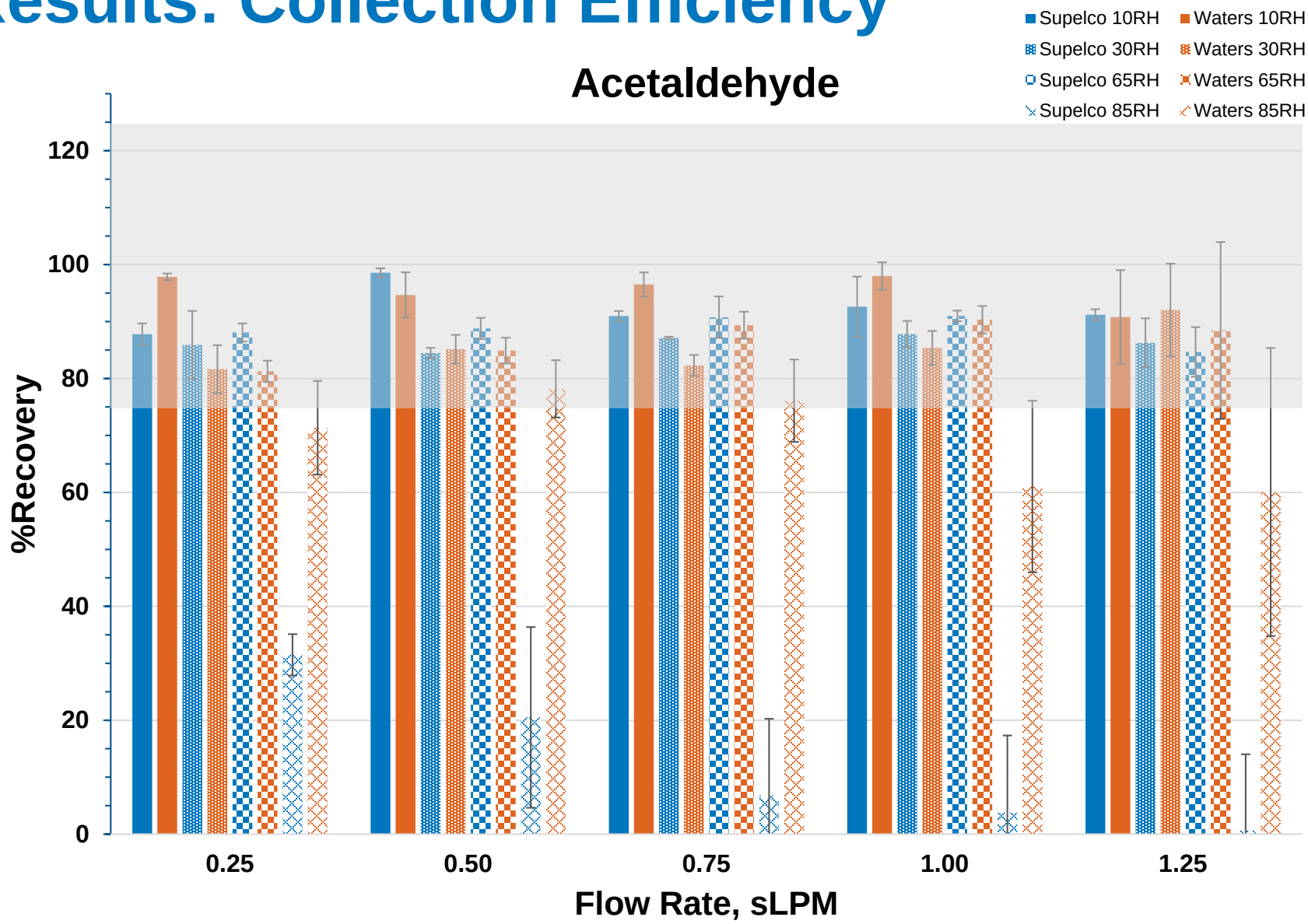
Results: Collection Efficiency



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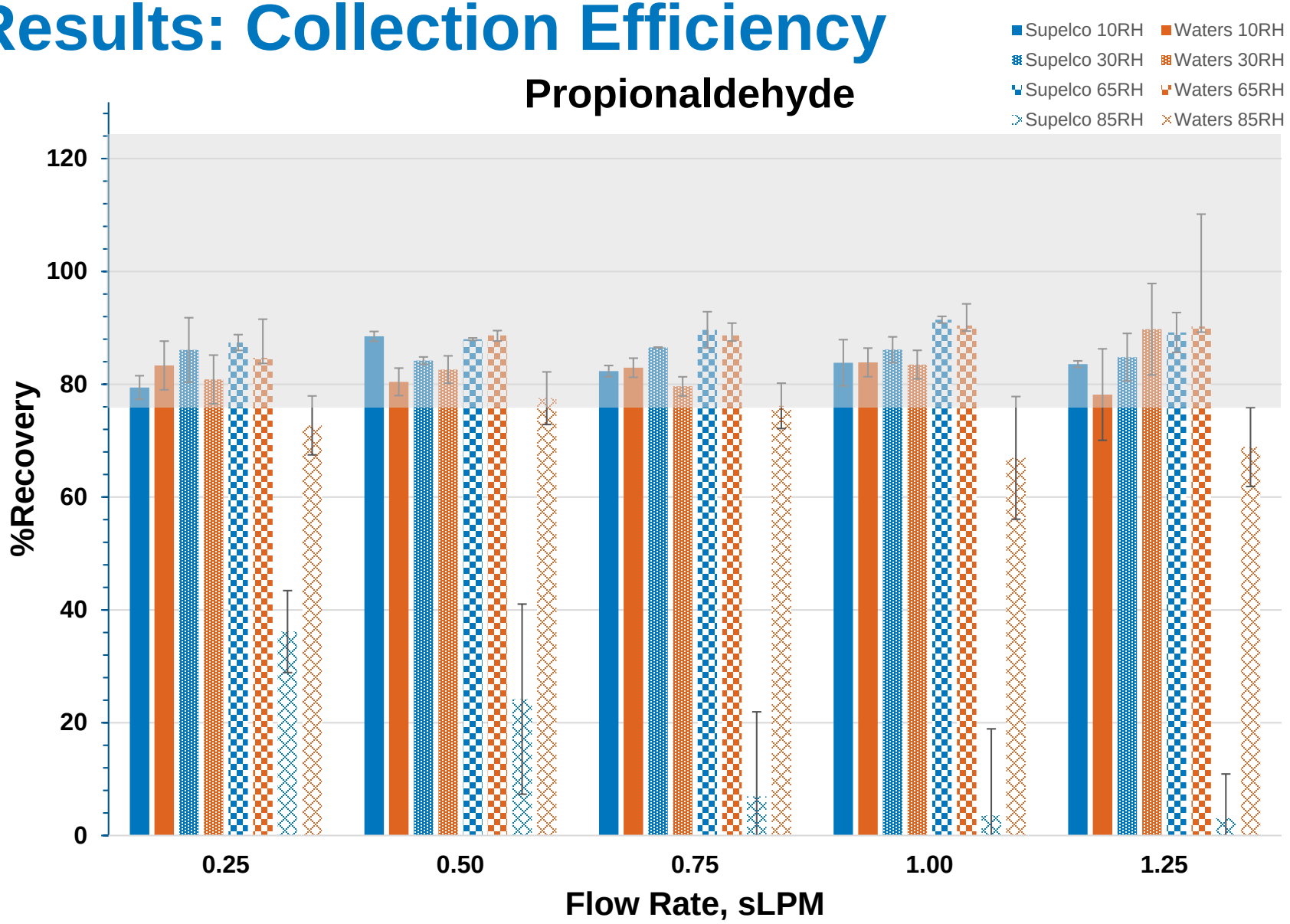

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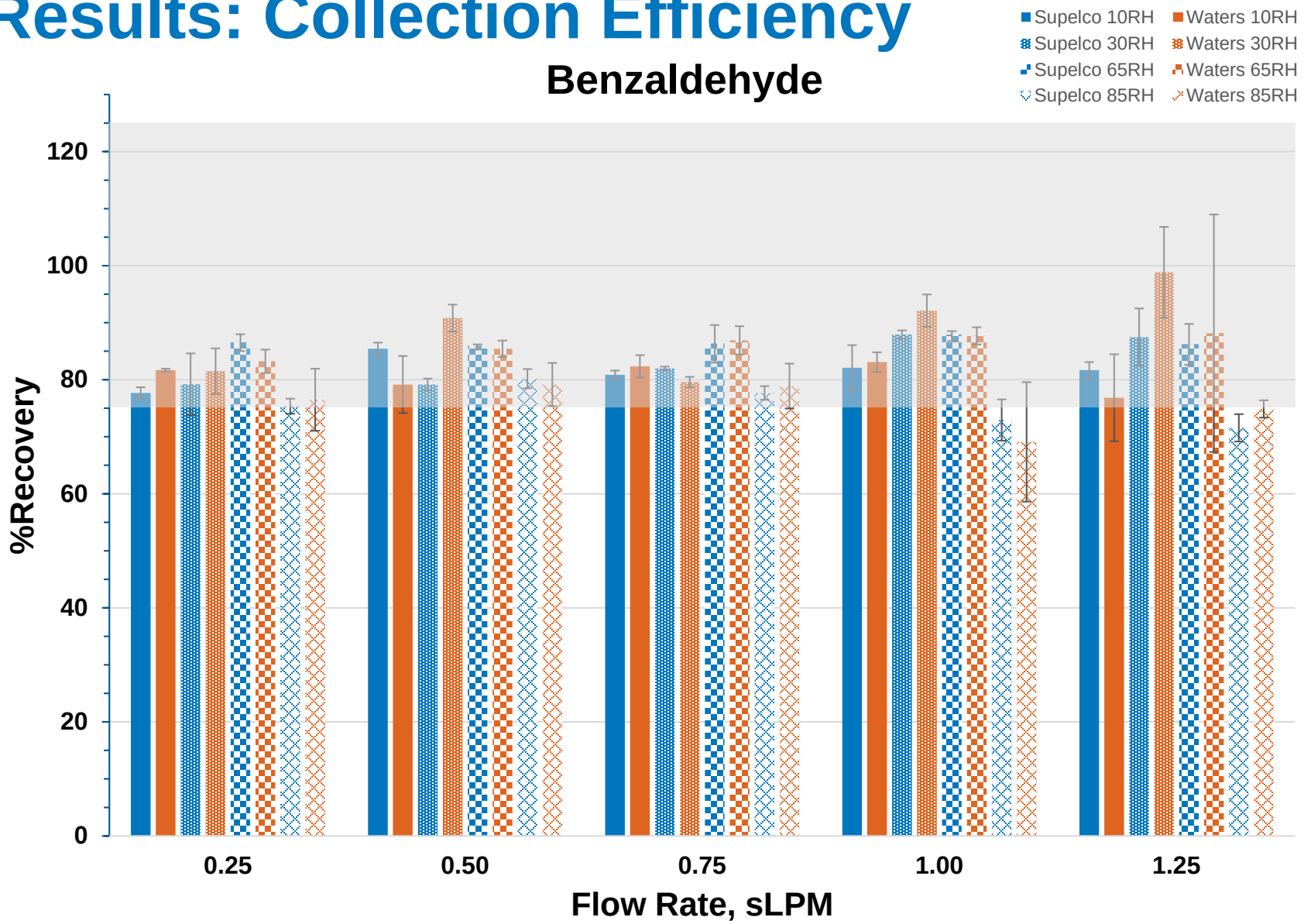
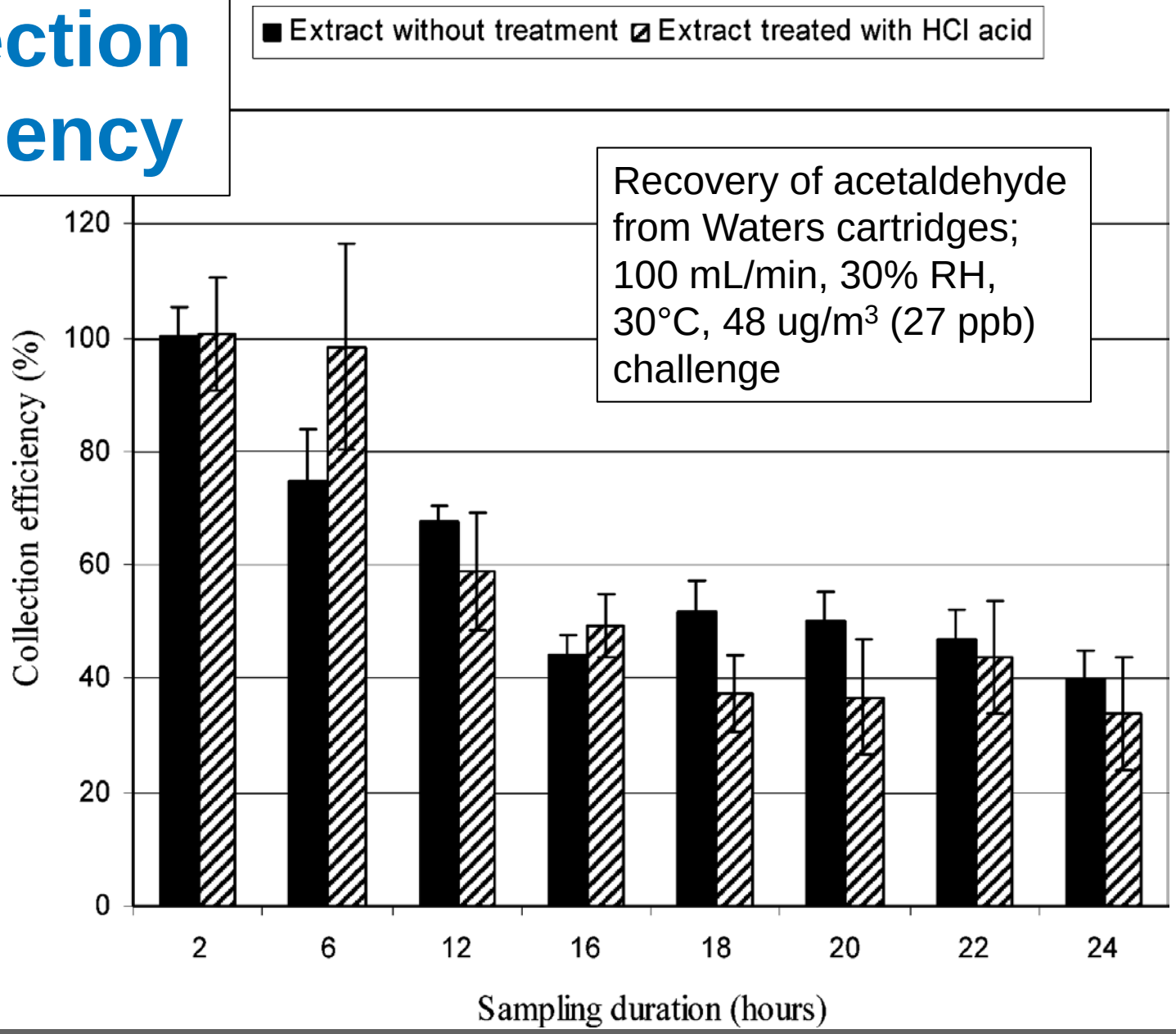


Collection Efficiency



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

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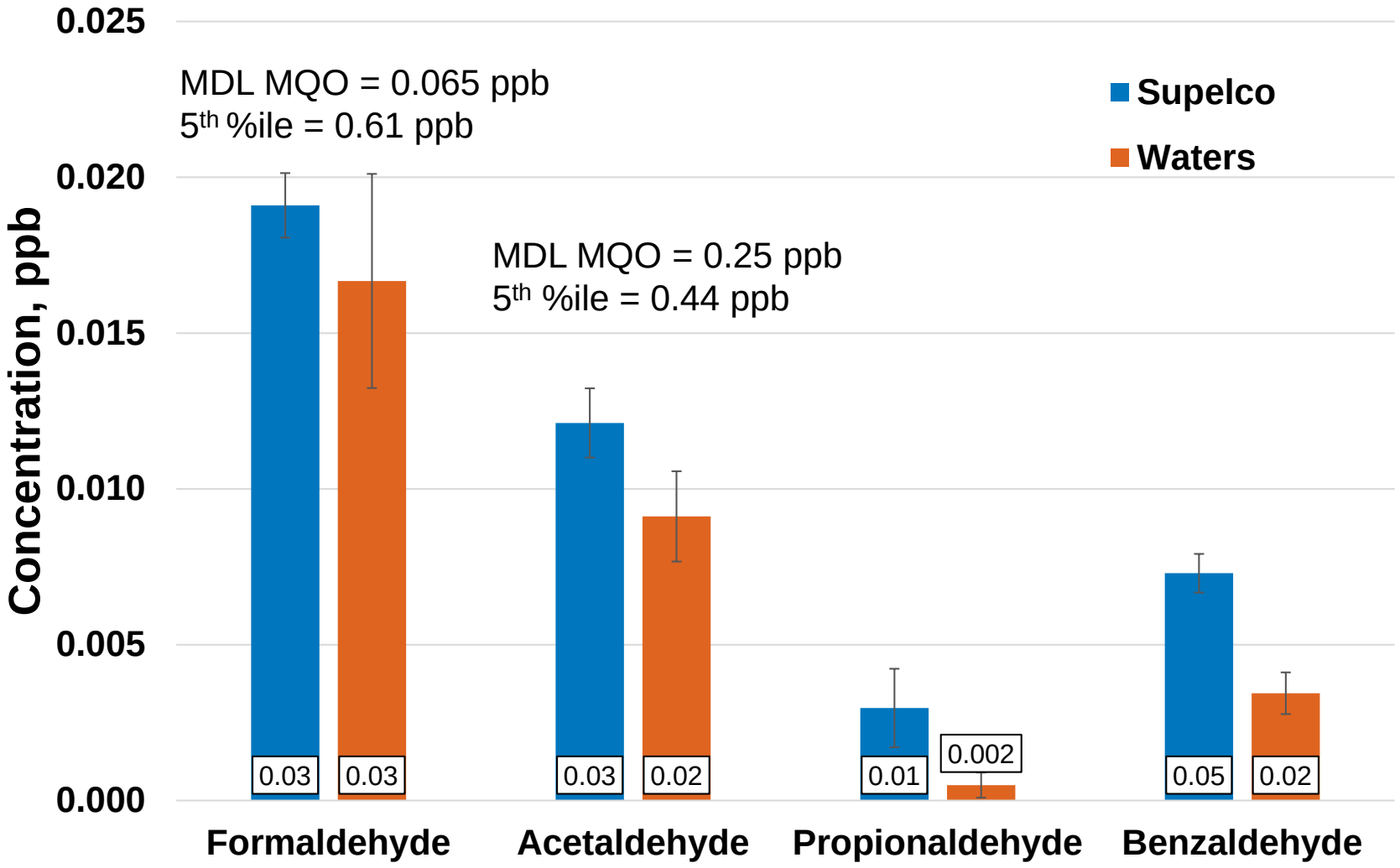
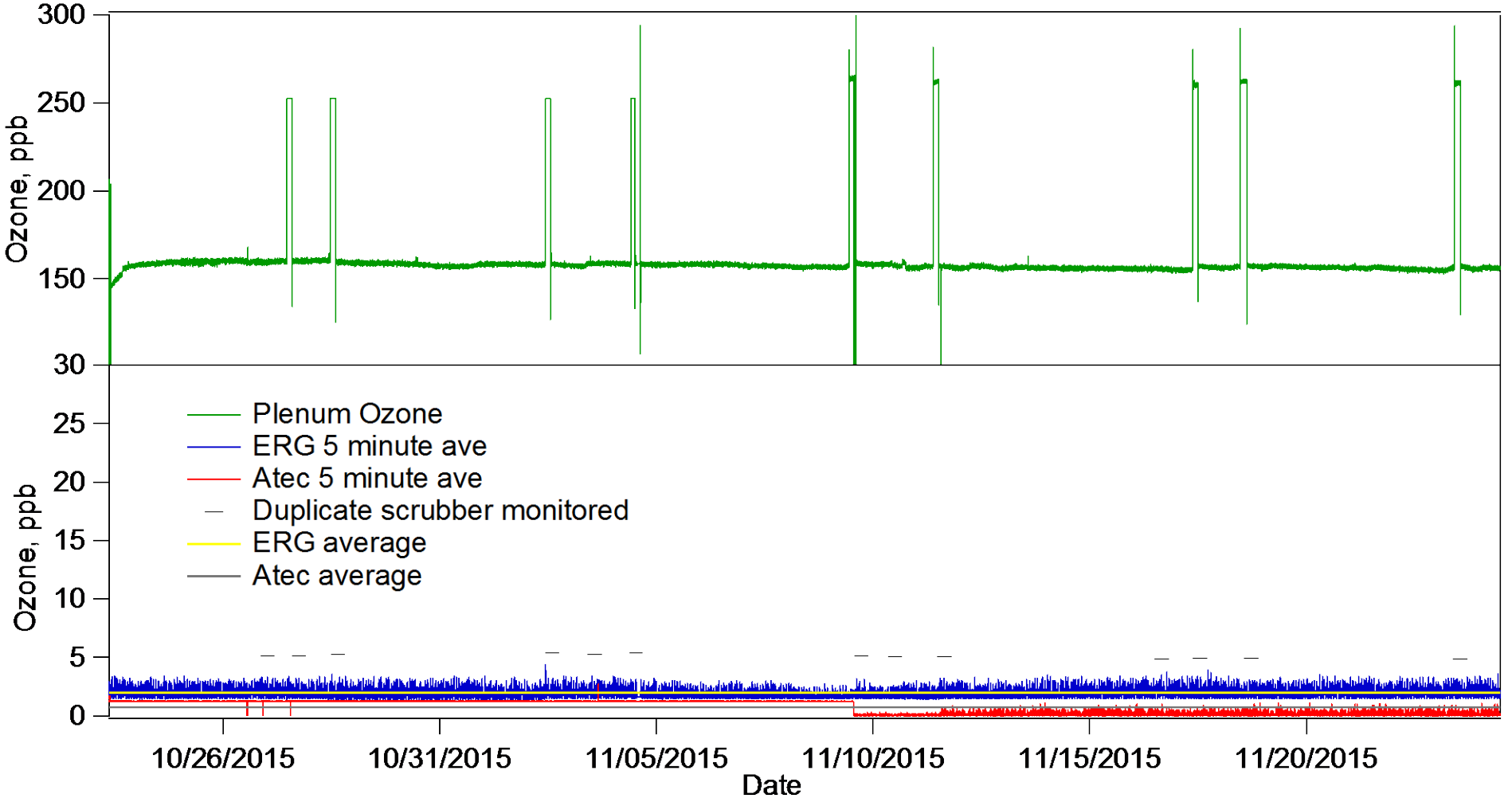
Results: Cartridge Background

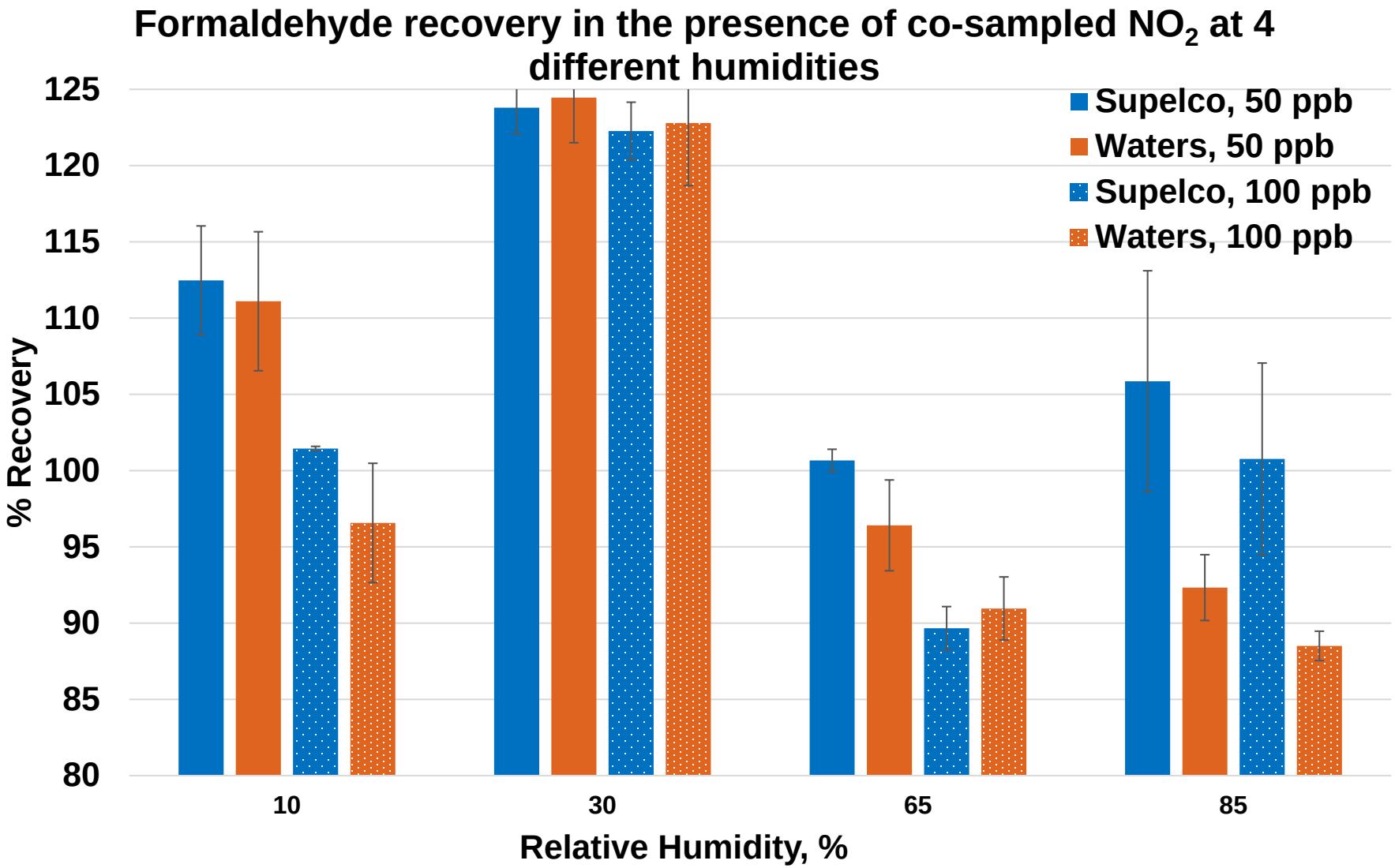


Values inside bars are values in micrograms per cartridge.

Results: 65% RH Ozone Scrubber Evaluation

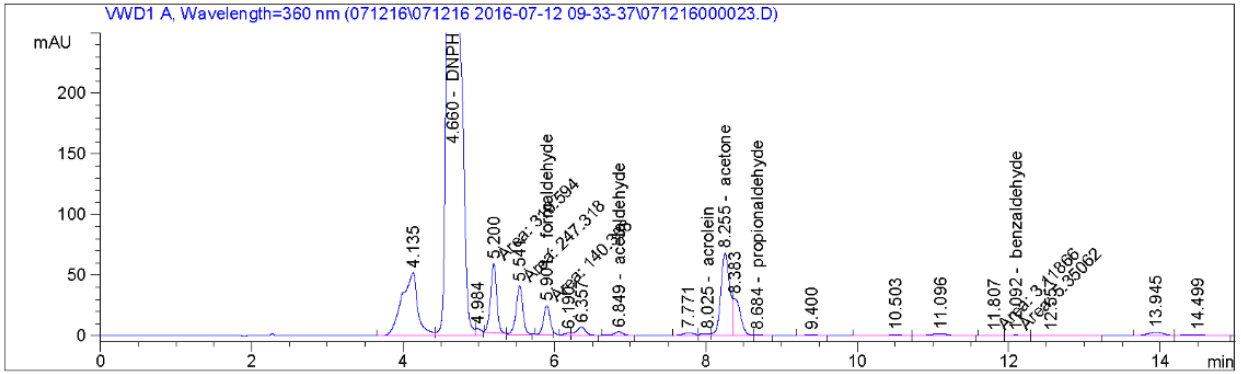


Results: NO_2 Interference Study

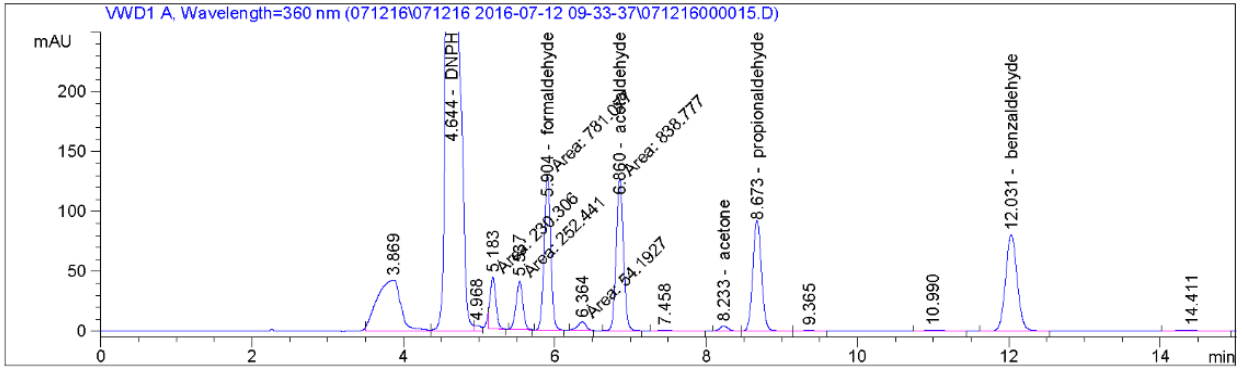


Results: NO_2 Interference Study

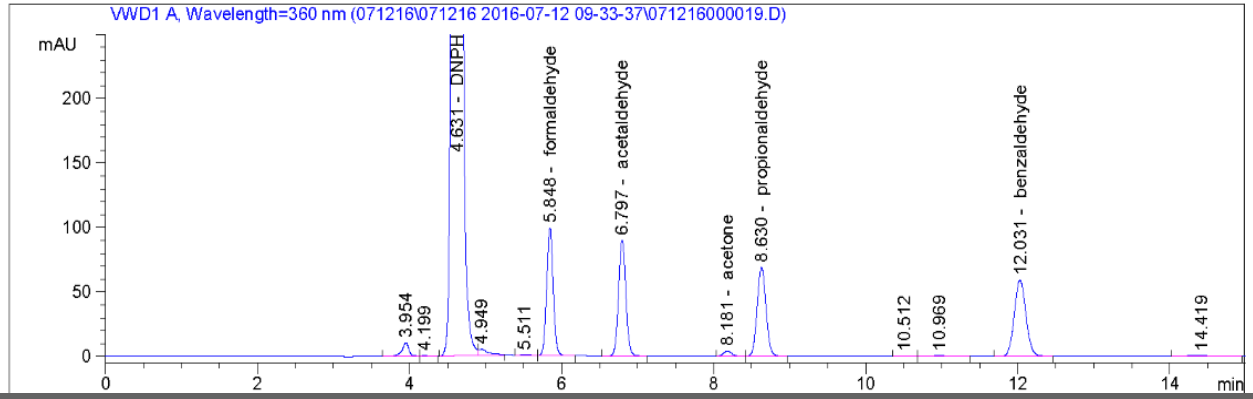
Test 1: 100 ppb NO_2 + 0.5 ppb acrolein



Test 2: 100 ppb NO_2 + 0.5 ppb acrolein + 1.25 ppb target carbonyls

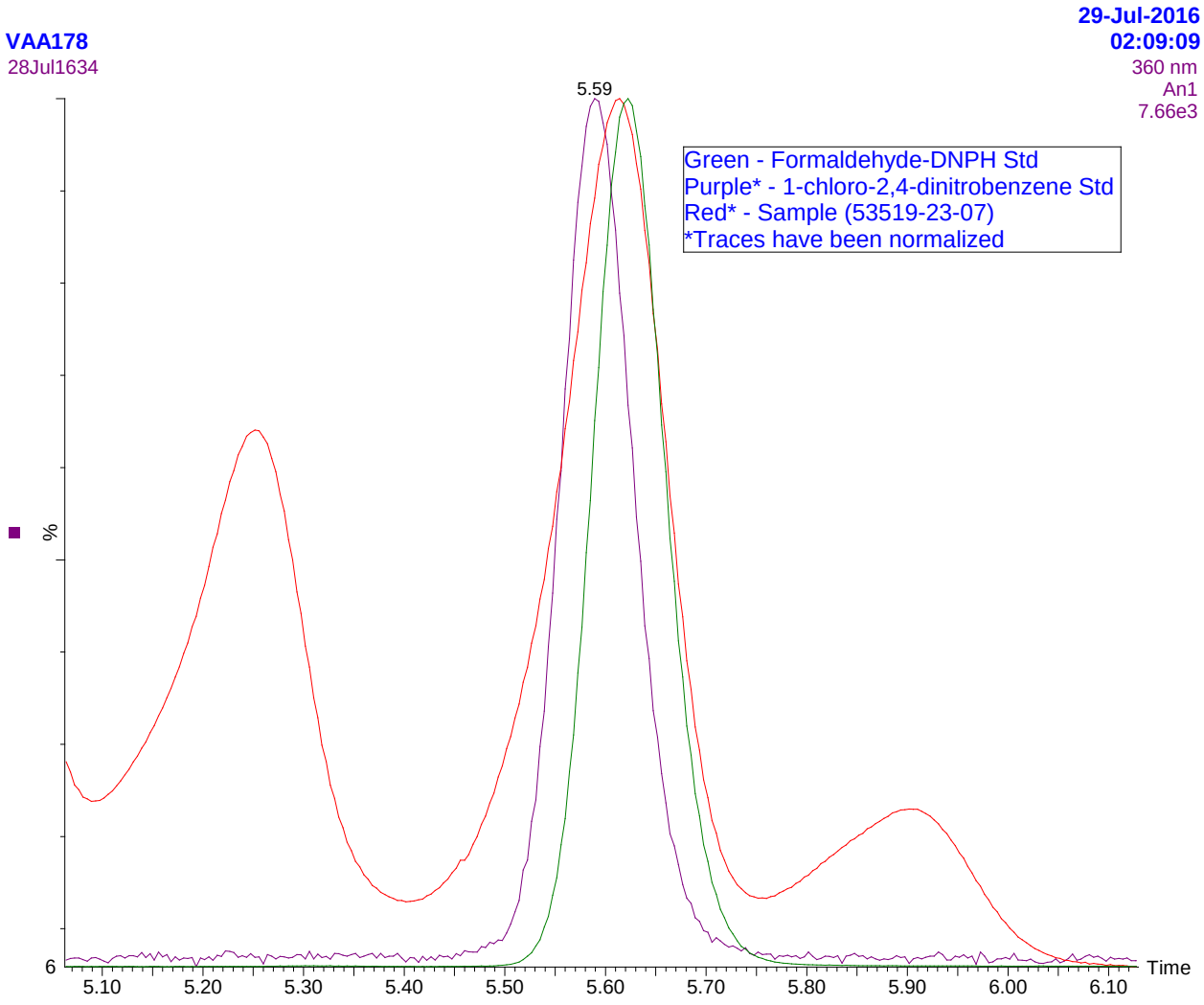


Test 3: 1.25 ppb target carbonyls



Results: NO_2 Interference Study

What is being identified as formaldehyde-DNPH? 2,4-dinitrochlorobenzene!



Summary of Results to Date

- Collection efficiency does not appear to vary with flow rates from 0.25 to 1.25 L/min for sampling over 24 hours at 10, 30, 65, or 85% RH at carbonyl concentrations of ~ 5 ppb for formaldehyde and benzaldehyde
  - Decreases with increasing flow rate at 85% RH for acetaldehyde and propionaldehyde
- Ozone scrubbers: for all RHs efficiency > 99% at a 150 and 250 ppb O_3 challenges; capacity > ~100,000 ppb hours
- DNCB is misidentified as formaldehyde when using a simple isocratic elution method
  - 400 ppb NO2 = 1 ppb formaldehyde (roughly)

Timeline for Future Work

- Beginning method optimization to resolve NO_2 interference
- Complete Part 4 work on final method optimization
  - Combinations of NO2, O3, humidities
  - Compare 3 x 8 hour vs. 24 hour results
- Final report and publication in late 2016

Acknowledgement

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