

Updates on EPA Method TO-11a for the Measurement of Airborne Carbonyls

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Ian MacGregor
Battelle

David Shelow
US EPA OAQPS

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Background and Motivation

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



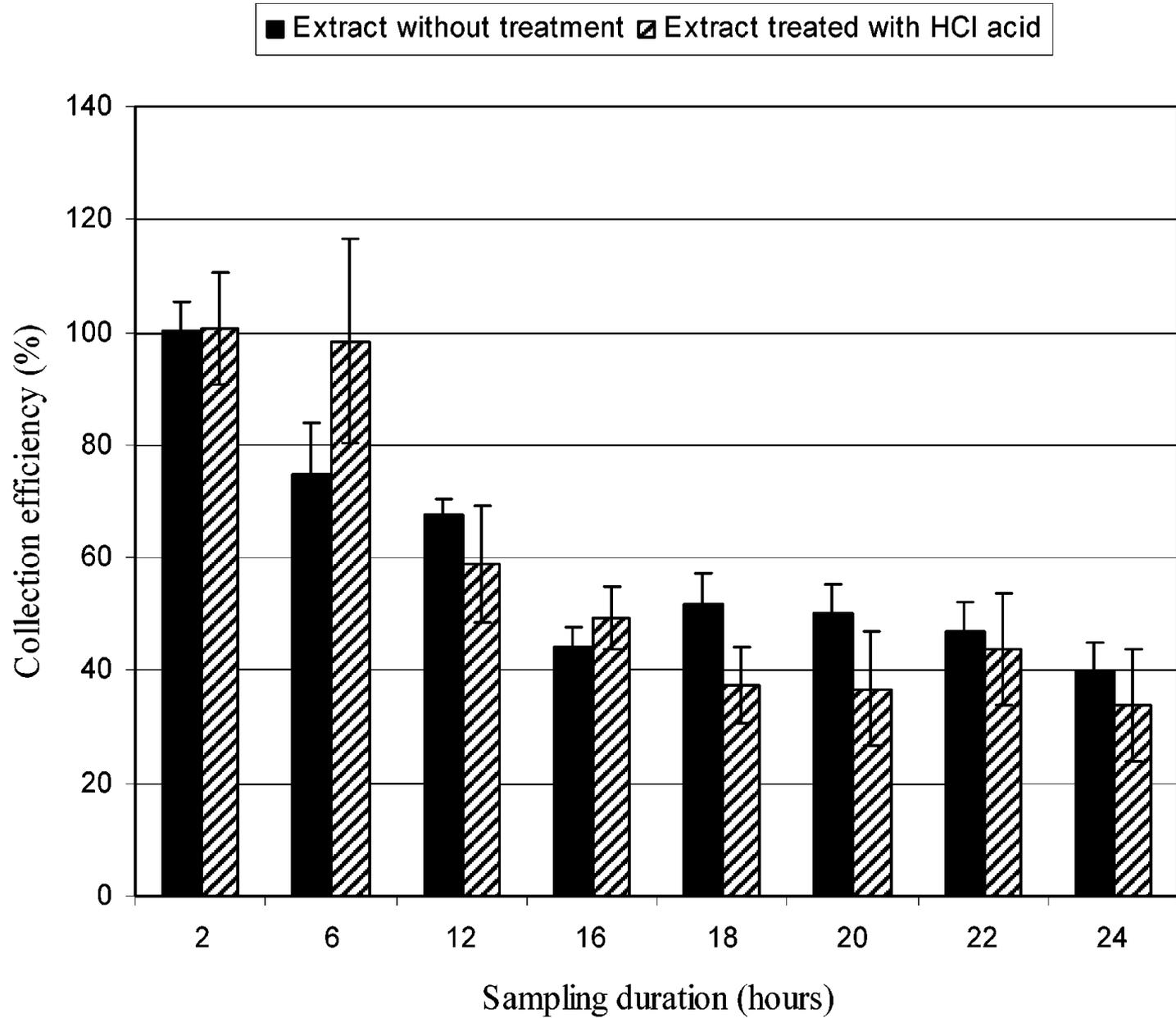
Background and Motivation

- NATTS Network
 - Monitor long-term trends in HAPs concentrations
 - VOCs, carbonyls, PAHs, metals, hexavalent chrome
 - 27 sites around US



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 ozone, nitrogen dioxide, and water on Method TO-11a for the measurement of formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde
- Determine optimal collection efficiency for use over a 24 hour sampling period
- Ultimate goal: provide updated guidance on the implementation of Method TO-11a

Experimental design

- Part 1: Evaluate ozone scrubber for capacity and ability to handle O₃ transients
 - 2 types of KI denuders
 - 150 ppb at 1 L/min for 30 days, in duplicate
 - First at ~30% RH
 - Then at ~65% RH
 - Continuous upstream and downstream ozone monitoring
 - Transient high (>200 ppb) levels



Experimental design

- Part 2: Evaluate NO₂ interference and start collection efficiency assessment
 - Carbonyls generated at 1 to 10 ppb using permeation tubes
 - Both style of DNPH cartridges, in series, in duplicate
 - 1 L/min for 24 hours @ 25°C
 - With KI denuder present
 - Modify HPLC method to address DNPA interference, if observed
 - Confirm applicability of modified method at higher humidity

Relative Humidity (%)	NO ₂ (ppb)
30 ± 5	0
30 ± 5	25
65 ± 5	0
65 ± 5	25

Experimental design

- Part 3a: Collection efficiency assessment
 - Carbonyls generated at 1 to 10 ppb using permeation tubes
 - Both style of DNPH cartridges, in series, in duplicate
 - Without NO₂ or O₃
 - ~0.3, ~0.5, ~0.75, ~1.25 and ~1.5 L/min
 - 24 hours sampling
 - 30% RH @ 25°C
- Goal: balance maximizing CE with maintaining required MDLs

Experimental design

- Part 3b: Final method optimization
 - Carbonyls generated at 1 to 10 ppb using permeation tubes
 - Both style of DNPH cartridges, in series, in duplicate
 - 24 hours @ optimal flow rate for maximized CE
 - 25°C, with KI denuder present

Relative Humidity (%)	O ₃ (ppb)	NO ₂ (ppb)
First at 30, then at 65	0	0
	30	0
	100	0
	0	10
	0	25

Timeline

- Begin experimental work in September, results by spring 2015

Acknowledgement

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