Further Testing of a Newly Developed Method for Low-Level Ambient Air Measurements of Acrolein

Presented by:

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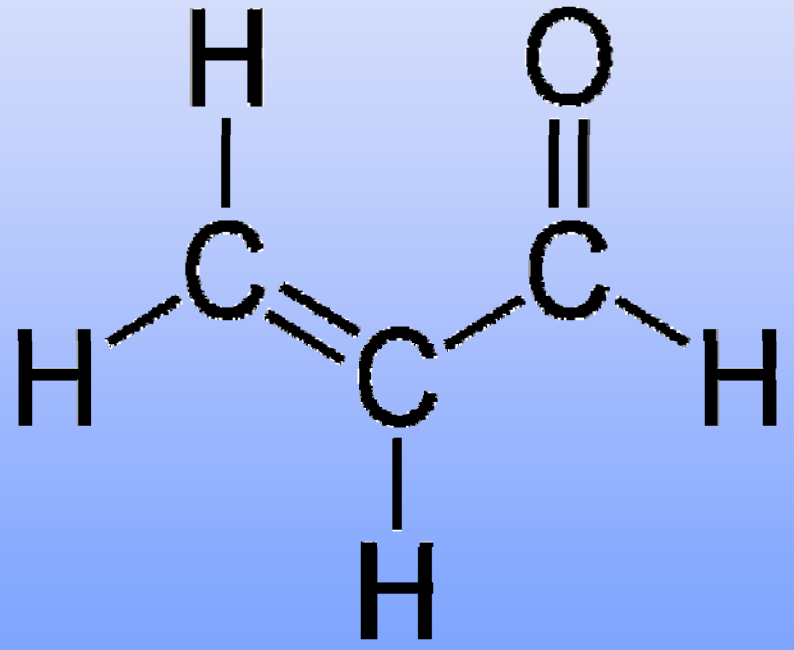
Introduction

- AAC has developed a method for the analysis of Acrolein in ambient air which uses C18 cartridges coated with o-benzylhydroxylamine hydrochloride (BHA)
- Acrolein reacts with BHA on the cartridge to form an Oxime which is then extracted using Hexane and analyzed by GC-NPD
- We are presenting some of our original results plus new results from low-level Acrolein spiking experiments and preliminary ambient air monitoring (Emphasis on 24-hour sampling)

Why Is Acrolein Important?

- Toxicity
- Large variety of sources
- Atmospheric chemistry
- Difficulty in measuring

Acrolein is the simplest unsaturated carbonyl.



Acrolein Toxicity

- Toxic unsaturated carbonyl
- Acute and Chronic Non-Cancerous Toxicity
  - Respiratory tract, skin and eye irritant
  - Can contribute to asthma
- OSHA Permissible Exposure Levels (PEL)
  - Formaldehyde – 0.75ppm
  - Acrolein – 0.1ppm

- Ranks high in most air toxicity assessments due to its low reference concentration (RfC) for chronic inhalation exposure
  - EPA RfC is 0.02µg/m^3 (0.009ppbv)
  - CARB RfC is 0.35µg/m^3 (0.15ppbv)
- Ambient concentrations are typically higher than the reference concentrations

Acrolein Toxicity cont.

- Ranked #37 of 275 hazardous substances on the EPA Superfund priority list (Superfund Sites)
- 1990 Clean Air Act – One of 188 Hazardous Air Pollutants (HAPs)
- EPA NATTS **(National Air Toxics Trends Stations)** – One of 6 core compounds (2003-present)
- Children's Environmental Health Protection Act of 2001(CalEPA) – One of 5 (out of ~200) identified Toxic Air Contaminates which may make children more susceptible to illness
- EPA Schools Monitoring Initiative (2009 ongoing) – One of 16 air toxics measured

Sources of Acrolein

- Point sources include
  - Wood fired boilers
  - Paper mills
  - Municipal solid waste incinerators
  - Petrochemical plants
  - Biocide uses in irrigation canals
  - Acrolein production facilities
  - Wood product facilities
  - Oil seed mills
  - Coffee roasting plants
  - internal/external combustion

- Mobile sources typically account for ~25-75% of Acrolein in urban environments
- Diesel exhaust is a significant source of Acrolein
- Significant indoor exposure sources of Acrolein include residential wood burning, heating of cooking oils and tobacco smoking
- Secondary formation from 1,3-Butadiene plus OH

Problems With Current DNPH Methods

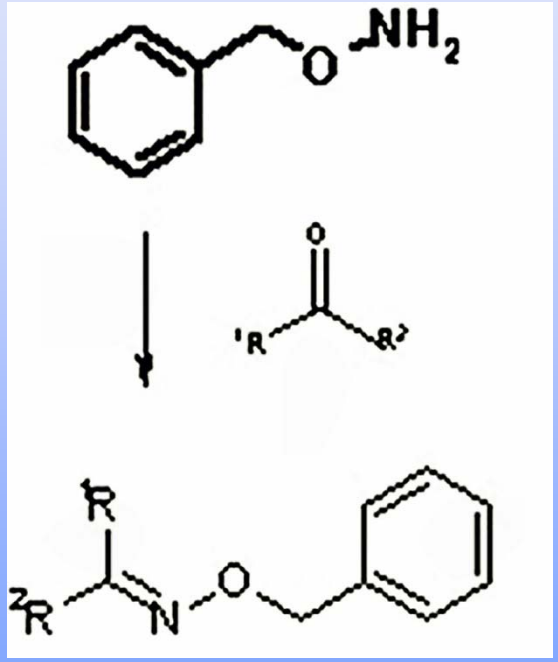
- The standard 2,4-DNPH method (EPA TO-11A/ HPLC-UV) used to measure carbonyls in ambient air is unreliable for measurements of Acrolein
- EPA TO-11A is not approved for Acrolein measurements
- Acrolein and /or once formed Acrolein-2,4-DNPH decompose on the cartridge during and after sampling
- Acrolein reacts with acidified DNPH on cartridges to form two or more peaks with varying ratios that make identification and quantification difficult

Problems With Summa Canisters (TO-15)

- Summa Canister – in some cases have high and variable blank levels of Acrolein (similar to ambient levels), and Acrolein and other carbonyls increase with time after sample collection (up to 10% per day) (EPA Schools Initiative 2009, 2007 Austin TX study, Heaton et al)
- Problems with gas phase standards not being consistent from one brand to another
- EPA has recently(2010) classified all TO-15 Acrolein data as “unverified”

GC Derivatization
BHA

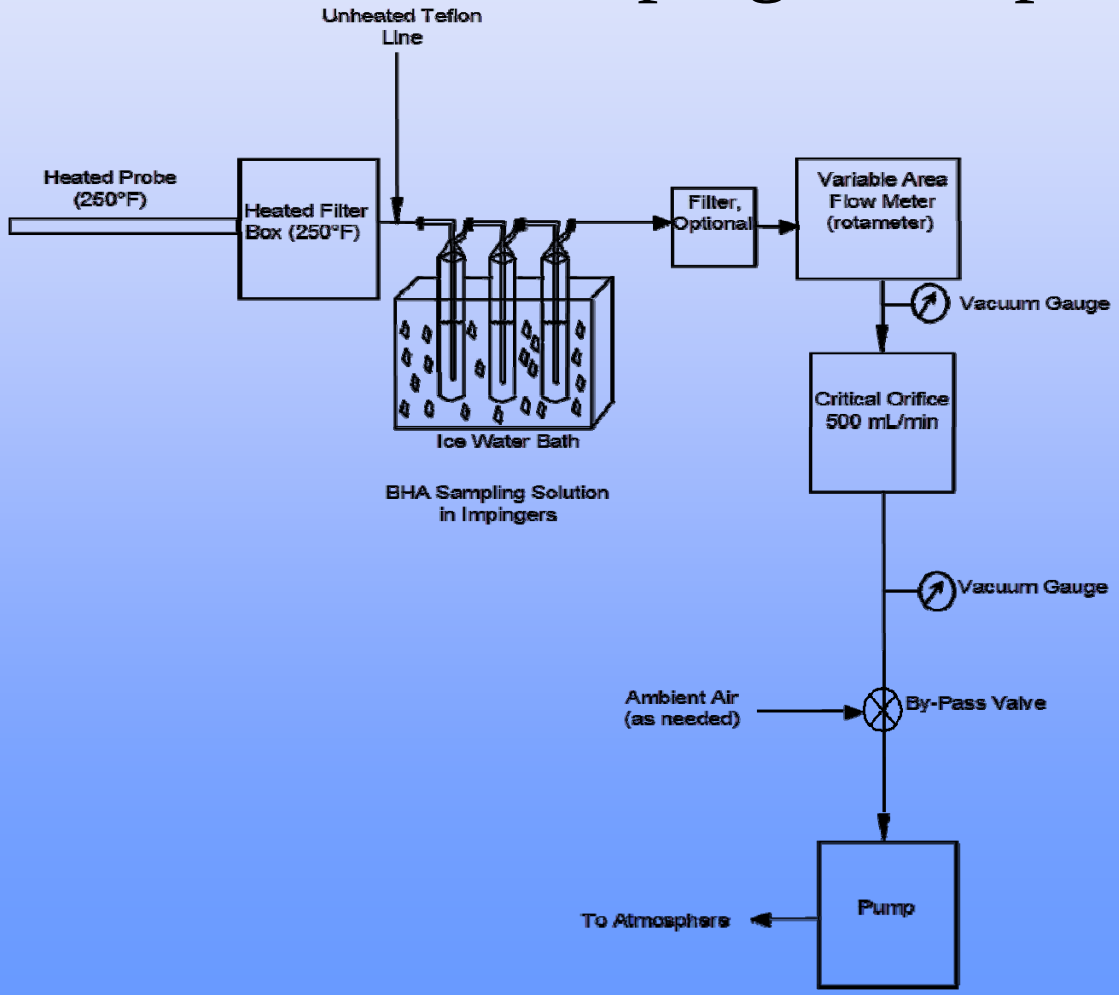
- Used in NCASI Method ISS/FP-A105.01 to analyze:
  - Polar Organics
    - Methanol
    - Phenol
    - Aldehydes and Ketones
      - Acetaldehyde
      - Acrolein
      - Formaldehyde
      - Propionaldehyde



o-Benzylhydroxylamine (BHA)
+
Carbonyl

Impinger Method

NCASI 105.01 impinger setup.



Cartridges

Experimental Details
Liquid Spiking Experiments

- Sampling Media Tested
  - Waters Silica Gel and C18 cartridges
- Cartridges were cleaned using 10mL of HPLC water , coated with 10mL of BHA solution (15g/L) and dried with UHP Nitrogen
- Propanal selected as a non-reactive carbonyl for comparison
- Cartridges were spiked with Acrolein and Propanal solutions made in water

Experimental Details:
Sample Extraction and Analysis

- Each cartridge was sequentially extracted with 2 to 3, 5mL portions of hexane
- Each aliquot was analyzed separately to assess extraction efficiency
- Analysis was done using an Agilent 6890 GC with Nitrogen-Phosphorous Detector (NPD)
- Calibration was done using a seven point calibration curve (0.01-1μg/mL) based on the sum of the peak areas for the two carbonyl-oximes

Acrolein and Propanal Liquid Spiking Results

- 1-3 cartridges spiked per experiment and the cartridges were extracted after 1-18 hours
- Silica Gel cartridges – Acrolein recoveries were ~100%
- C18 cartridges – Acrolein recoveries were ~***70-80***%
- Propanal recoveries were ~100% on the Silica Gel and ~90% on the C18 cartridges

Acrolein Liquid Spiking Results

Table 1. Summary of Acrolein liquid spiking experiments using BHA coated cartridges.

Experiment	Time to Extraction (hrs)	N (a)	Cartridge	Injected Acrolein (µg)	Measured Acrolein Range (µg)	Average % Recovery
1	4	3	Silica Gel	38.8	36.6-38.6	102
2	4	3	Silica Gel	73	75.1-75.8	103
3	4	2	Silica Gel	84	79.6-84.7	98
4	1	2	C18	71.1	56.2-61.8	83
6	18	1	C18	18.3	13.2	72
7	18	2	C18	73.2	63-64	86
8	16	1	C18	68.6	53.3	78

(a) N=Number of samples collected per experiment

Acrolein and Propanal Liquid Spiking Stability Results

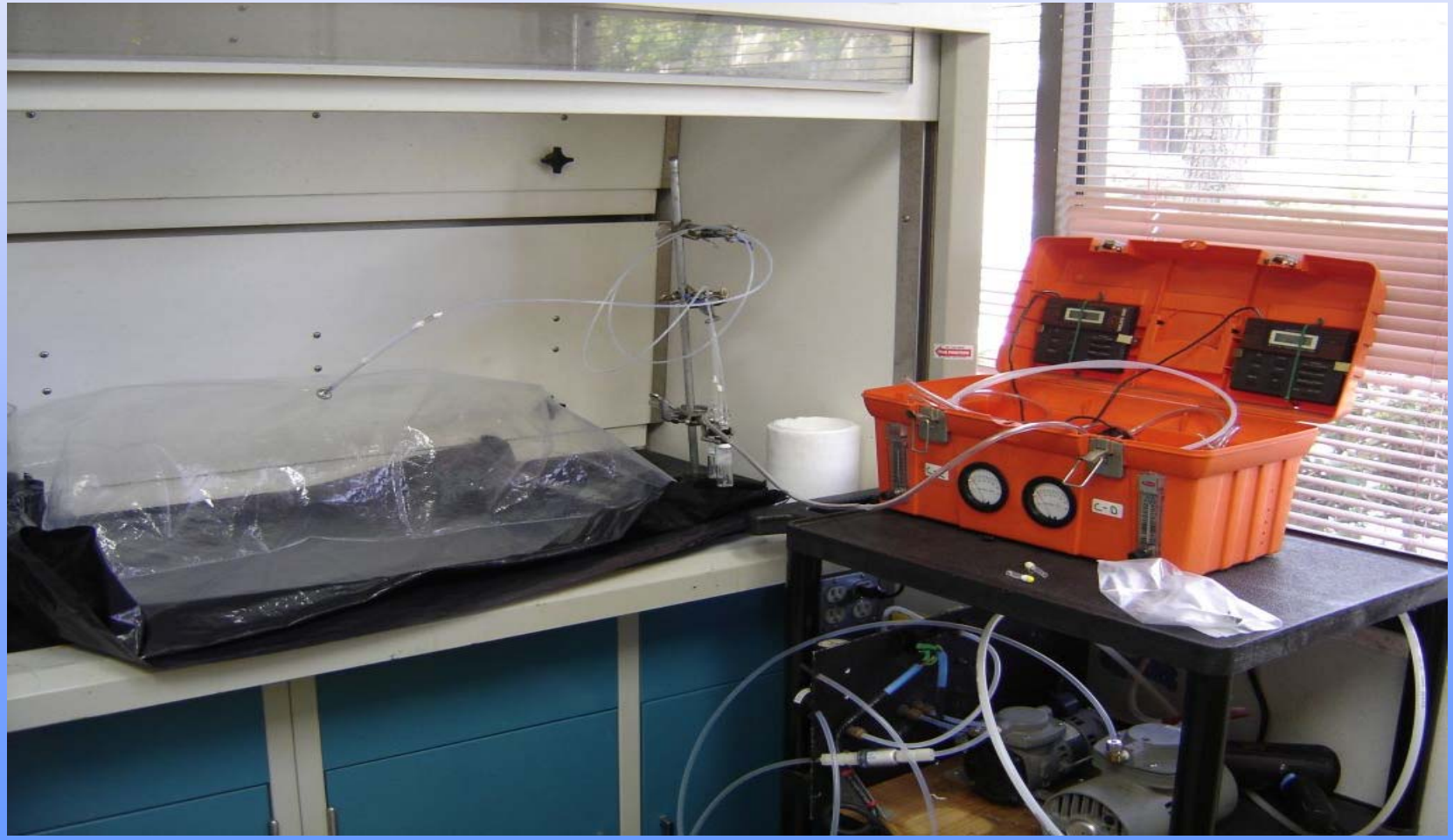
- Stability tested by extracting the cartridges 1-21 days after spiking
- Silica Gel loss rates were 3-13% per day for Acrolein (too high – we discarded the Silica Gel) and ~2% per day for Propanal
- C18 loss rates were ±1% per day for Acrolein and Propanal
- C18 seems the most promising with consistent yields and good stability

Acrolein Liquid Spiking Stability Results

Table 2. Summary of Acrolein liquid spiking stability experiments using BHA coated cartridges.

Experiment	Time to Extraction (days)	N (a)	Cartridge	Injected Acrolein (µg)	Average % Recovery	Loss Rate, % /day
1	1	3	Silica Gel	38.8	97	5.2
2	6	3	Silica Gel	73	80	3.8
3	1	2	Silica Gel	84	85	13.1
4	6	2	Silica Gel	84	65	5.5
5	3	2	C18	71.1	94	**NA**
6	7	2	C18	71.1	102	**NA**
7a	3	1	C18	18.3	72	0
7b	7	1	C18	18.3	77	-0.7
8a	3	2	C18	73.2	86	0.2
8b	7	1	C18	73.2	82	0.6
9	7	1	C18	68.6	83	-0.7
10	14	1	C18	68.6	79	-0.1
11	21	1	C18	68.6	75	0.1
(a) N=Number of samples collected per experiment						

Gas Phase Sampling



Experimental Details
Gas Spiking Experiments

- 74L Teflon Bag filled with purified (50% RH) room air
- Gas phase spiking solutions of Acrolein in methanol or hexane-using heated glass bulb
- 5.8-580ppbv Acrolein
- Sampling for 15-30 minutes at ~1 L/min
- Samples were collected consecutively

Acrolein Gas Phase Spiking Results

Table 3. Summary of Acrolein gas phase spiking experiments using BHA coated cartridges.

Experiment	Time to Extraction (hrs)	N (a)	Cartridge	Injected Acrolein (µg)	Measured Acrolein Range (µg)	Average % Recovery
1	4	3	Silica Gel	0	0	
2	5	3	Silica Gel	14.4	11.5-12.7	84
3	3	2	Silica Gel	14.4	8.1-9.6	62
4	2	2	Silica Gel	14.4	7.5-7.7	54
5	2	2	Silica Gel	0	0	
6	20	3	Silica Gel	13.2	11.4-11.8	87
7	20	2	Silica Gel	0	0	
8	16	2	C18	0	0	
9	16	1	C18	0.99	1	100
10	16	1	C18	9.94	10.5	106
11	16	1	C18	10.1	9.7	96
12	16	1	C18	99.4	90.5	91
(a) N=Number of samples collected per experiment						

•Acrolein recoveries on the C18 cartridge were independent of Acrolein concentration from 5.8-580ppbv

Acrolein Gas Phase Spiking Stability Results

- Stability was tested by extracting the cartridges 3-15 days after spiking
- Silica Gel loss rates were 2-15% per day for Acrolein (discarded)
- Acrolein loss rates on new C18 cartridges were very low-most experiments <1% per day

- **The C18 cartridge is the most promising with consistently high recoveries (~100%) and high stability (most equivalent to >90% after 10 days)**

Acrolein Gas Phase Spiking Stability Results

Table 4. Summary of Acrolein gas phase spiking stability experiments using BHA coated cartridges.

Experiment	Time to Extraction (days)	N (a)	Cartridge	Injected Acrolein (µg)	Average % Recovery	Loss Rate, % /day
1a	3	3	Silica Gel	13	57	15.2
1b	5	3	Silica Gel	13.2	57	7.7
1c	10	3	Silica Gel	13.2	68	2.2
1d	15	3	Silica Gel	13.2	29	4.1
2a	3	1	C18	0.99	88	6.2
2b	7	1	C18	0.99	87	2.3
3a	3	1	C18	9.94	105	0.2
3b	7	1	C18	9.94	101	0.8
4a	3	1	C18	10.1	95	0.3
4b	7	1	C18	10.1	95	0.1
5a	3	1	C18	99.4	89	0.8
5b	7	1	C18	99.4	85	0.9
(a) N=Number of samples collected per experiment						

Low-Level Method Development For Ambient Air

- Establish lowest possible Reporting Levels-optimize GC-NPD, extraction volume etc.
- Repeat the Liquid Spiking experiments at lower concentrations relevant to ambient air (0.1-5ppbv)
- Purchase Acrolein Gas Phase Standard
- Repeat the bag recovery experiments at lower concentrations relevant to ambient air (0.1-5ppbv) using ambient air as a matrix
- Ozone scrubber needed/test ozone scrubber?
- Increase stability studies to ~two weeks
- Make ambient air measurements at AAC in Ventura
- Make ambient air measurements in the South Coast Air Basin or other polluted areas
- Emphasis on 24-hour samples as typical of Toxics Monitoring

Experimental Details: Low-Level Liquid Spiking Experiments

- Sampling Media Tested:
  - Waters C18 cartridges.
- Cartridges were cleaned using 5mL of ACN followed by 10mL of HPLC water and then coated with 10mL of BHA solution (15g/L) and dried with UHP Nitrogen
- Cartridges were spiked with solutions (made fresh and tested before spiking) of Acrolein in water

Low-Level GC-NPD Optimization

- Original method calibration curve from 0.5-100ug/mL
- After GC Optimization a new calibration curve was made from .01-1 ug/mL
- Using the lowest point on the curve (0.01ug/ml) resulted in a reporting limit of 91pptv in a 4-hour sample and 15pptv in a 24-hour sample
- Further improvements can be made by reducing the extraction volume and/or concentrating the samples before analysis.

Acrolein Mid and Low-Level Liquid Spiking and Stability Results

- 2-4 cartridges were spiked per experiment and the cartridges were extracted after 20-504 hours
- Mid-Spike(0.8ug)-Yields were 104% after 20 hours,102% after 6 days, and 97% after 21 days
- Low-Spike(.08ug)-Yields were 99% after 20 hours, 94% after 5 days, and 96% after 19 days
- 2 of the 4 cartridges were sampled with lab air for 3 hours at 1 LPM to test spike stability and extracted after 20 hours- results were 89% for the mid spike and 120% recovery for the low spike showing reasonable stability

Acrolein-BHA Low-Level Liquid Stability Results

- Four low level spiked sample extracts were reanalyzed after 16-19 hours with approximately the same results (102-107% recovery)
- A new aliquot was taken 2-3 days later from the original vial from four low and mid level standards and reanalyzed. Results were 99-107% recovery indicating good stability
- Once derivatized the Acrolein-BHA appears to be stable for at least several days even at very low concentrations

Ambient Measurements

- In order to obtain real low reporting limits all samples were collected at ~0.7LPM
- We initially collected several 10-12 hour samples in Ventura with resulting Acrolein concentrations of 48-84 pptv
- We then collected 4 sets of 24-hour samples at LAX airport using two cartridges in series. The back cartridge contained 30-50% of the total Acrolein (75-100pptv total). In addition the back cartridge contained 50% or more of the Formaldehyde, Acetaldehyde, and Propionaldehyde
- Very large peaks were observed for >C6 aldehydes indicating the possibility of artifact formation from ozone reacting with the C18 substrate (no ozone scrubber was used) and possibly breakthrough issues.

SCAQMD LAX Ambient Samples

Table 5. Summary of Acrolein Data for SCAQMD LAX Samples (collected without an ozone scrubber)

Sample	Flow (LPM)	m^3	Acrolein (ppt)
SCAQMD-1-A-1	0.718	1.03	49
SCAQMD-1-B-1	0.718	1.03	52
SCAQMD-2-A-1	0.716	1.03	49
SCAQMD-2-B-1	0.716	1.03	49
SCAQMD-3-A-1	0.716	1.03	49
SCAQMD-3-B-1	0.716	1.03	29
SCAQMD-4-A-1	0.703	1.01	50
SCAQMD-4-B-1	0.703	1.01	25

Ambient Measurements and Ozone Interference

- We then collected several sets of samples of ~12 hours duration in Ventura, each with two pairs of cartridges in series, one with an ozone scrubber and one without
- The data clearly indicated that Acrolein and other carbonyls were significantly higher on the back cartridge when the ozone scrubber was not used. The samples collected using the ozone scrubber contained no carbonyls on the back cartridge
- Several sets of collocated ~12 hour samples were then collected both using ozone scrubbers with good results, i.e. no Acrolein on the back cartridge.

Ventura Ambient Samples

Table 6. Summary of Acrolein Data for Ventura Samples

Sample	Date	Location	Flow (LPM)	m^3	Acrolein (ppt)
C18-3 C-2 E-1	04/05/11	room air	0.8	0.38	84
C18-3 C-3 E-1	04/06/11	room air	0.8	0.40	83
C18-3 C-4 E-1	04/07/11	room air	0.8	0.45	48
C18-3 C-5-O3-E-1	04/25/11	outdoor air	0.8	0.51	24
C18-3 C-6 E-1	04/25/11	outdoor air	0.8	0.51	8
C18-3 C-7-US-E-1	04/26/11	outdoor air	0.7	0.53	17
C18-3 C-8-DS-E-1	04/26/11	outdoor air	0.7	0.53	16
C18-3 C-9-US-O3-E-1	04/26/11	outdoor air	0.7	0.53	24
C18-3 C-10-DS-O3-E-1	04/26/11	outdoor air	0.7	0.53	0
C18-3 C-11-US-E-1	04/27/11	outdoor air	0.7	0.50	0
C18-3 C-12-DS-E-1	04/27/11	outdoor air	0.7	0.50	0
C18-3 C-13-US-O3-E-1	04/27/11	outdoor air	0.7	0.50	40
C18-3 C-14-DS-O3-E-1	04/27/11	outdoor air	0.7	0.50	0
C18-3 C-15-US-O3-E-1	05/02/11	outdoor air	0.7	0.50	24
C18-3 C-16-DS-O3-E-1	05/02/11	outdoor air	0.7	0.50	
C18-3 C-17-US-O3-E-1	05/02/11	outdoor air	0.7	0.50	24
C18-3 C-18-DS-O3-E-1	05/02/11	outdoor air	0.7	0.50	
C18-3 C-19-US-O3-E-1	05/03/11	outdoor air	0.7	0.50	14
C18-3 C-20-DS-O3-E-1	05/03/11	outdoor air	0.7	0.50	
C18-3 C-21-US-O3-E-1	05/03/11	outdoor air	0.7	0.50	16
C18-3 C-22-DS-O3-E-1	05/03/11	outdoor air	0.7	0.50	
C18-3 C-23-US-O3-E-1	05/04/11	outdoor air	0.7	0.50	27

Ambient Measurements and Ozone Interference cont.

- We then collected 7 sets of 24-hour samples at the downtown LA SCAQMD site, each sample having two cartridges in series and using a sampler containing a built in ozone scrubber. Results ranged from 22-122 pptv with a large portion of the Acrolein being collected on the back cartridge. The same was true for Formaldehyde and Acetaldehyde but most of the Propionaldehyde was collected on the front cartridge.

SCAQMD DOLA Ambient Samples

Table 7. Summary of Acrolein Data for SCAQMD DOLA Samples

Sample	Flow (LPM)	m^3	Acrolein (ppt)
SCAQMD-051511A	0.650	0.94	22
SCAQMD-051511B	0.650	0.94	
SCAQMD-051511	**0.650**	**0.94**	**22**
SCAQMD-051711A	0.790	1.13	5
SCAQMD-051711B	0.790	1.13	21
SCAQMD-051711	**0.650**	**0.94**	**26**
SCAQMD-051911A	0.660	0.95	52
SCAQMD-051911B	0.660	0.95	43
SCAQMD-051911	**0.650**	**0.94**	**95**
SCAQMD-052111A	0.660	0.95	17
SCAQMD-052111B	0.660	0.95	102
SCAQMD-052111	**0.650**	**0.94**	**119**
SCAQMD-052311A	0.770	1.10	18
SCAQMD-052311B	0.770	1.10	35
SCAQMD-052311	**0.770**	**1.10**	**53**
SCAQMD-052511A	0.680	0.98	28
SCAQMD-052511B	0.680	0.98	94
SCAQMD-052511	**0.680**	**0.98**	**122**
SCAQMD-052711A	0.710	1.02	9
SCAQMD-052711B	0.710	1.02	74
SCAQMD-052711	**0.710**	**1.02**	**83**

Conclusions

- AAC has successfully developed a new method for the sampling and analysis of Acrolein in ambient air
- Liquid and gas phase spiking experiments gave promising results
- The BHA coated C18 cartridge had consistently high recoveries (~100%) and high stability (equivalent to >90% after 10 days) for the gas phase Acrolein spikes
- All Method Development Goals were met
- Further validation is required

Conclusions

- AAC has begun further testing of a new method for low-level ambient air measurements of Acrolein
- Analytical improvements resulted in very low detection limits(0.01ug/mL)
- Low level spiking experiments confirmed that Acrolein was 100% recoverable at ~0.1 and 1.0 ug and stable on the BHA C18 cartridge for up to three weeks
- Further testing is required to optimize the coating solution for 24-hour samples

Research in Progress

- Confirm breakthrough level under controlled conditions in the lab for 3 hour, 12 hour and 24 hour samples
- Try to improve the collection efficiency for 24-hour samples using higher BHA loadings, larger cartridges and/or lower flow rates
- Purchase Acrolein Gas Phase Standard
- Repeat the bag recovery experiments at lower concentrations relevant to ambient air (0.1-5ppbv)
- Repeat the bag recovery experiments using ambient air as a matrix

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