
Air Toxics Methods Development Update

Jim Homolya
EPA, OAQPS, Measurement Technology Group
2006 National Air Monitoring Conference
Las Vegas, NV
November 6-9, 2006

Introduction-Acrolein

- Acrolein is listed as one of the core NATTS compounds
 - Because of its reactivity, acrolein in ambient air samples presents an analytical challenge
 - Penetrates biological membranes, strong dermal irritant, inhalation irritant and possible human carcinogen
 - EPA Screening level – $0.002 \mu\text{g}/\text{m}^3$
 - Non-Chronic risk levels – ATSDR Short Term MRL $0.11 \mu\text{g}/\text{m}^3$, CalEPA Acute REL at $0.19 \mu\text{g}/\text{m}^3$
-

Possible Active Methods of Acrolein Determination

- Air samples collected on Dinitrophenylhydrazine (DNPH) cartridges, analyzed by Method TO-11A on an HPLC
 - Air samples collected in stainless steel canisters, analyzed by Method TO-15 on a GC/MS SIM
-

Acrolein Determination by Method TO-11A

- Method TO-11A is based on a specific reaction of organic carbonyls with the DNPH on the sample cartridges in the presence of a strong acid
 - Samples are extracted within 2 weeks of sampling
 - Extracts are analyzed within 30 days of sample preparation
-

Potential Problems with Method TO-11A for Acrolein

- Acrolein appears to break down on the DNPH cartridge to form a second derivative peak after sampling
 - The second peak coelutes with a Method TO-11A target peak
-

Method Development – Method TO-15

- Simulated “real world” conditions by using a gaseous blend of carbonyls
 - Blended a 100 ppbv $\pm 10\%$ gas with clean humidified air to a nominal concentration of 5.92 ppbv
 - Collected duplicate samples through a canister sampler
 - Recovered 90% of acrolein following Method TO-15
-

Acrolein using Method TO-15 (SIM Mode)

- Monitor Ions 56 (Quant Ion), 26, 27, 29, and 55
 - Acceptable calibration from 0.25 ppbv to 15.0 ppbv
 - 2006 Method Detection Limit of 0.08 ppbv (0.18 $\mu\text{g}/\text{m}^3$)
-

Stability Study of Acrolein in Canister Samples

- Sixteen acrolein samples were prepared in canisters
 - Low and high humidity
 - Low and high concentration
 - Samples were analyzed on Days 0, 7, 14, 21, 28
-

Acrolein Initial Stability Study

- Rhode Island Dept of Health Labs reported increase immediately after sampling
 - Performed short-term acrolein stability study
 - Took grab samples on an overpass above a heavily traveled highway
 - Recoveries for 1,3-Butadiene also evaluated because of its close chemical structure to acrolein
 - Samples with nothing detected held for 1 week with no increase in detection (still not detected).
-

Compendium Method Comparison

- Comparison of Methods TO-15 and TO-11A using actual NMP samples from across the country
 - Acrolein recoveries are clearly much higher for Method TO-15 than Method TO-11A
-

Method TO-15 Field Sample Results for Acrolein

- 19 Sites from July '05 to Sept '06
 - 2,044 acrolein measurements
 - 569 of these were from samples during Hurricane Katrina clean-up
 - 59% of the 2,044 were detects
 - 1.7% of the 2,044 had detections less than the MDL
 - Average concentration was 1.49 $\mu\text{g}/\text{m}^3$
 - Median concentration was 1.11 $\mu\text{g}/\text{m}^3$
-

Conclusions

- Higher acrolein recovery using Method TO-15
 - Audit, collocate, duplicate, and replicate samples pass NATTS data quality objectives
 - Results from UATMP and Katrina are relatively the same and show similar trends
 - Need another years data to see if trends are consistent
-

Introduction-Chromium 6

- Chromium is present in several oxidation states
 - Cr^{3+} is naturally occurring, environmentally pervasive and a trace element in man and animals
 - Cr^{6+} is anthropogenic from a number of commercial and industrial sources
-

Hexavalent Chromium

Health Effects

- Penetrates biological membranes
 - Identified as an industrial toxic and cancer substance
 - Inhalation irritant and associated with respiratory cancer
 - EPA Screening level – $0.000083 \mu\text{g}/\text{m}^3$ or $0.083 \text{ ng}/\text{m}^3$
 - Intermediate Risk Factor – $1 \mu\text{g}/\text{m}^3$ or $1000 \text{ ng}/\text{m}^3$
-

Method Development

- Provide cleanest filter media
 - Provide filter media that does not affect background
 - Determine possible interfering elements
 - Stabilize the Cr^{6+} on the filter
 - Recover spiked Cr^{6+} on recommended filter media
-

Filter Media Determination

- Cellulose
 - Binderless Quartz
 - Teflon[®]
 - Polyvinyl Chloride (PVC)
-

Quality Control Criteria

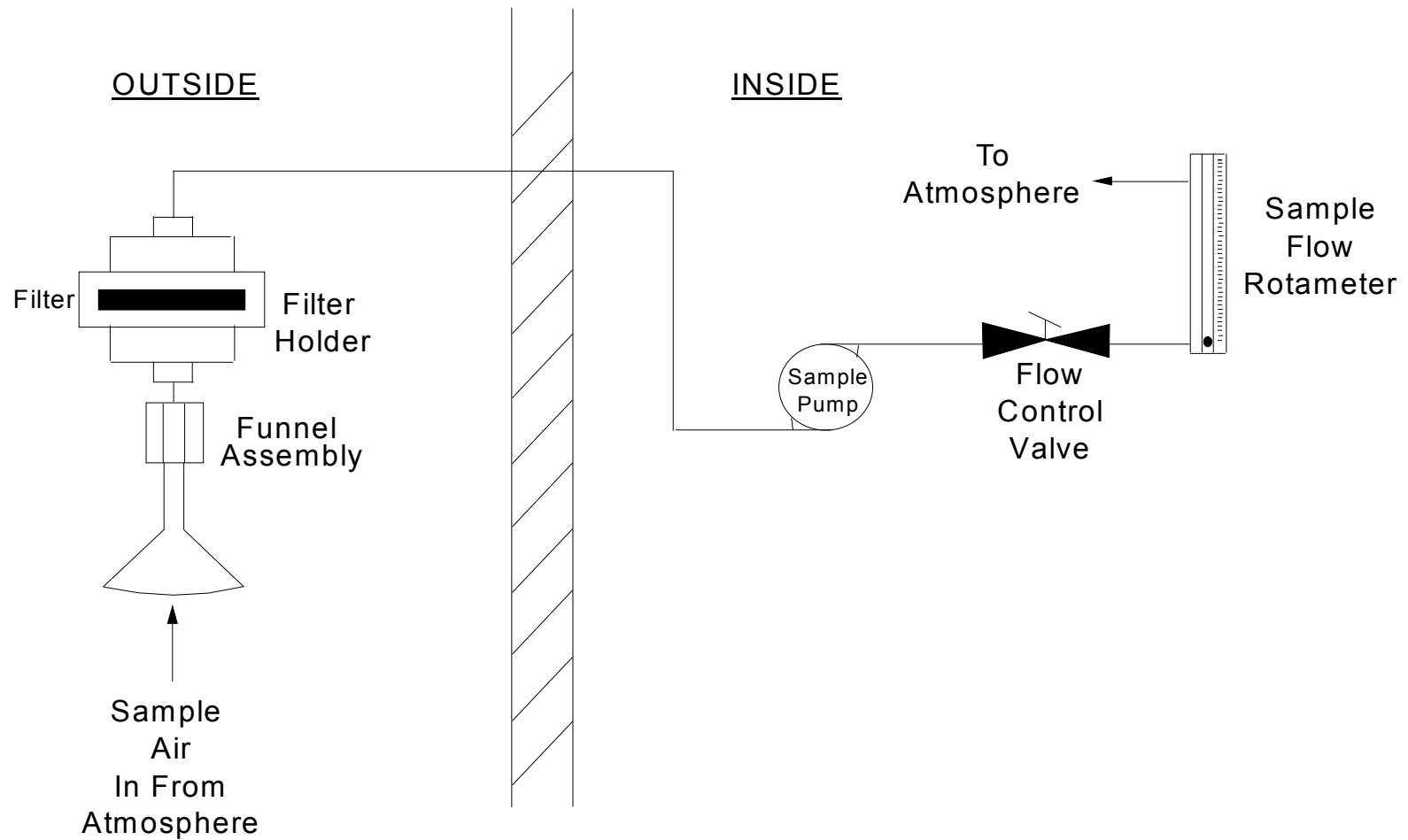
- Relative Percent Difference (RPD) $\pm 25\%$
 - Coefficient of Variation (CV) $\pm 15\%$
 - Percent Recovery $\pm 80\%$
 - Analyzed 4 sets to statistically achieve QA controls
-

Interfering Element Check

- Filters were spiked with 10 total ng of Cr⁶⁺.
- Four sets of filters were spiked with 10 total ng of Cr³⁺, Fe, and Mg.
- Recoveries were within 95.3% ± 13%.

These elements do not pose any interference for the analysis of Cr⁶⁺.

ERG Cr⁶⁺ Sampling System



Sampling Setup

- One filter unspiked (Sample)
- One filter spiked at 2.5 ng
- One trip blank
- One filter spiked at 2.5 ng and left in the filter container - Method Spike

All Samples did not detect Cr⁶⁺.

2005 Field Site Sample Results

- 1,209 Cr⁶⁺ measurements were detected at the 22 NMP
 - 209 of these were taken at 3 sites during the clean up after Hurricane Katrina
 - Of the 1,209 Cr⁶⁺ measurements, 64% of these results were detects and 3% of these concentrations were below the MDL
 - Average Cr⁶⁺ concentration was 0.027 ng/m³.
-

Conclusions

- Cellulose filters collect Cr^{6+} more efficiently than Teflon[®]
 - Sample collection using sodium bicarbonate coated cellulose filters is recommended
 - Filters must be acid washed before coating them with sodium bicarbonate to prevent Cr^{6+} background
-

Conclusions, Cont.

- Samples must be retrieved from the field one day after the sample has been collected to prevent Cr⁶⁺ loss
 - Samples must be frozen after collection to reduce the risk of Cr⁶⁺ loss
 - Collocate and replicate samples pass NATTS data quality objectives
-

Acknowledgments

- US EPA, OAQPS
 - Mike Jones
 - Dennis Mikel
 - ERG
 - Mitch Howell
 - Donna Tedder
 - Ray Merrill
 - Julie Lopez
-