National Contract Lab
Analytical Method
Development Updates

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2011 National Air Toxics Monitoring and Data Analysis Workshop
Introduction

- Overview of the EPA contract
- Compendium TO-15 canister method development
  - Canister Cleaning for select compounds
  - Greenhouse Gas compound additions?
- Compendium IO-3.5 metals method development
  - Includes Pb TSP FEM
- EPA Hexavalent Chromium method development
  - Sampling
  - Analytical preparation
Overview of the EPA Contract

- Provides Analysis
  - VOC (TO-15)
  - Speciated Hydrocarbons
  - Carbonyls (TO-11A)
  - PAH (TO-13A)
  - Metals (IO-3.5)
  - Hexavalent Chromium (EPA Method)

- Provides Site Support
  - VOC
  - Carbonyls
  - Hexavalent Chromium

- Provide QA Support
  - Audits
  - Sampler Recertification
  - PAMS Cylinders
  - Report Development
  - AQS Data Entry
TO-15 Canister Cleaning and Method Development
TO-15 Canister Cleaning Method Development

- Canister cleaning with no heat since 1984
- Polar compounds added to TO-15 in 1999
- Recent EPA study showed heated systems removed polar compounds (acrolein) better than non-heated
  - EPA recommended change to heated cleaning
- Purchased heated cleaning system in January 2011
  - Still developing the approach/procedure
Canister Cleaning – Acrolein
No Heat Cleaning Approach

History of high acrolein values from 2005 - 2010
what does "History of high acrolein values" mean? Could you just put the time frame "2005 -2010"?

was this a study? Should the title be Can Cleaning Study?

Donna Tedder, 3/31/2011
Canister Cleaning – MEK
No Heat Cleaning Approach
History shows this canister is trending upwards in concentrations.

First time canister was used.
DST4

History shows the acrolein concentration in this can is trending upwards.

What does "First time canister was used" mean? new can? first can from that manufacturer? first time the can was sent to the field for sampling?

Donna Tedder, 3/31/2011
Canister Cleaning – MEK
Heat Cleaning Approach

![Graph showing MEK cleaning approach]

- Areosphere Line 1
- Areosphere Line 2
- Anderson Line 3
- Anderson Line 4
- New Star Line 5
- New Star Line 6
- Restek Line 7
- Restek Line 8
- SSI Line 9
- SSI Line 10
- Demaray Line 11
- Demaray Line 12
## Batch Blank Comparison – 349 Batch Blanks in 2010

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average (ppbv)</th>
<th># of Detections</th>
<th>% Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>0.111</td>
<td>341</td>
<td>97.7</td>
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<tr>
<td>Methyl Ethyl Ketone</td>
<td>0.072</td>
<td>326</td>
<td>93.4</td>
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<td>87.7</td>
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<td>Carbon Disulfide</td>
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<td>Chloromethane</td>
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<td>29.2</td>
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# Batch Blank Comparison w/ Heat

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<th>% Detected</th>
<th>Average (ppbv)</th>
<th>% of Detections</th>
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</table>
TO-15 Method Development – Current List

- Green house gas compound list – 11 compounds
  - Trichloromonofluoromethane (CFC-11)
  - Dichlorodifluoromethane (CFC-12)
  - 1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)
  - 1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC-114)
  - 1,1,1-Trichloroethane
  - Carbon tetrachloride
  - Chloroform
  - Methyl chloride
  - Methylene chloride
  - Methyl bromide
  - Bromodifluoromethane
TO-15 Method Development – Potential Addition

- Green house gas compound list
  - Decafluorobutane
  - 1,1,1-Trifluoroethane
  - Pentafluoroethane
  - Chloropentafluoroethane
  - Bromotrifluoromethane
  - 1,1,1,2-Tetrafluoroethane
  - 1,1-Difluoroethane
  - 1,1,1,2,2,2-Hexafluoropropane
  - Tetradecafluorohexane
  - 1,-Chloro-1,1-difluoroethane
  - Bromochlorodifluoromethane
  - 2,2-Dichloro-1,1,1-trifluoroethane
  - 1,1-dichloro-1-fluoroethane
  - 1,2-dibromo-1,1,2,2-tetrafluoroethane

Potential addition of 14 more compounds?
Metals Method Development
Compendium Method IO-3.5 for National Contract

- For the EPA contract
  - Antimony
  - Arsenic
  - Beryllium
  - Cadmium
  - Chromium
  - Cobalt
  - Lead
  - Manganese
  - Mercury
  - Nickel
  - Selenium
Compendium Method IO-3.5 Method Development

- Previous procedure
  - Digest all filter samples in a sonicator
    - Low Vol 47mm Teflon®
    - High Vol TSP/PM$_{10}$ Quartz 8” x 10” filters
- Tested NIST 1648 – Urban Particulate Matter
  - Recoveries were not as good we would like
- Hot Block vs. Sonicator
  - Sonicator – HNO$_3$ only
  - Hot Block – various times and acids
IO-3.5 Method Development - ERG Sonicator (3hr) 4% HNO3
IO-3.5 Method Development - ERG Hot Block Study

HNO₃ and HCl

HNO₃, HCl & HF

HNO₃, HCl, HF & H₂O₂

Teflon

Quartz

% Recovery

(1 hr) HNO₃ & HCl
(2 hr) HNO₃ & HCl
(3 hr) HNO₃ & HCl
(4 hr) HNO₃ & HCl
(3 hr) HNO₃, HCl & HF
(2.5 hr) HNO₃, HCl & HF, H₂O₂
(2.5 hr) HNO₃, HCl & HF, H₂O₂

Chromium
Manganese
Cobalt
Nickel
Arsenic
Cadmium
Antimony
Lead
IO-3.5 Method Development – Pb TSP FEM Approval

Because of the new NAAQS rule for lead (2008), ERG is proposing a new FEM for analysis by ICPMS

- Currently have TSP filters in-house
- Expected to submit to the EPA in April (?)
- Need to obtain PM10 filters at high enough concentrations

Difference between our method and others?

- Acid combination in order to get all of the NATTS elements + lead
IO-3.5 Method Development – Pb TSP FEM Approval

- ERG Proposed FEM
  - Acids used:
    - HNO₃
    - HCl
    - HF
    - H₂O₂
  - Hot Block (not sonicator)
  - Recoveries for Urban Dust 1648 Pb with new method ranges from 80-100%
- Also able to provide other NATTS elements with the use of these additional acids
IO-3.5 Method Development – ERG Hot Block Study (extended list)

% Recovery

(1 hr) HNO₃ & HCl
(2 hr) HNO₃ & HCl
(3.5 hr) HNO₃ & HCl
(4 hr) HNO₃ & HCl
(4.5 hr) HNO₃ & HCl
(3 hr) HNO₃, HCl & HF
(2.5 hr) HNO₃, HCl & HF, H₂O₂
(2.5 hr) HNO₃, HCl & HF, H₂O₂

Aluminum  Iron  Copper  Zinc  Magnesium  Cadmium  Manganese  Barium  Uranium

Teflon  Quartz
IO-3.5 Method Development – Elements Added

- Aluminum
- Barium
- Calcium
- Copper
- Iron
- Magnesium
- Molybdenum

- Rubidium
- Silver
- Strontium
- Thallium
- Thorium
- Uranium
- Zinc
Hexavalent Chromium Method Development
Hexavalent Chromium

- Sampling for hexavalent chromium (Cr⁶⁺) since 2005
- Collection on 47mm Sodium Bicarbonate coated cellulose filters – TSP collection
- Analysis on Ion Chromatography - derivatize and measure at 530 nm
- Method Development on sampling system and on sample preparation (before analysis)
Hexavalent Chromium - Sampling

Currently collect samples at ambient conditions

- Filters are stored frozen before analysis
- More stable when stored at temperatures $<15^\circ$C
- Samples must be recovered day after sampling
- New modified sampler collects samples at reduced temperatures
  - Shows increased recoveries as temperatures decrease
  - Need to control moisture during collection
Hexavalent Chromium – Sampling Study

% Recovery

Day 0  Day 1  Day 3  Day 5

NATTS Avg  Chiller, 15°C  Chiller, 18°C  Chiller, 21°C
Is this a study? If so, I would add it to the title.

does this graph show that for NATTS the % recovery is less than 50% even at Day 0? Hope not. Doesn't that leave present hen chrom values open to criticism?

Donna Tedder, 3/31/2011
Hexavalent Chromium – Sample Prep

Currently prepare samples for analysis by sonicating filters in NaBicarb solution

- Studies with NJ DEP/Rutgers/Clarkson have detected $Cr^{6+}$ when $Cr^{3+}$ was spiked on filters
  - In previous ERG studies, we did not see this problem
  - However, spiking concentration in new study are higher
    - Recoveries showed need to reevaluate the preparation procedure
    - Presence of hydroxyl ions may cause oxidation of $Cr^{3+}$ to $Cr^{6+}$ during sonication
Hexavalent Chromium – Sample Prep

- If sonication is causing the problem, how do we prepare the samples?
  - Had OLD shaker in lab from 1980’s!
  - Established study to compare
    - Sonication vs. Shaking
      - Cr$^{6+}$ only
      - Cr$^{6+}$ and Cr$^{3+}$
    - Established study to compare NIST SRM (test)
      - Sonication
      - Shaking
      - SW846 Method 3030
Hexavalent Chromium –
Sonication vs. Shake – Cr\textsuperscript{6+} Only

<table>
<thead>
<tr>
<th>Time / minutes</th>
<th>Sonic Cr(VI) / 0.05</th>
<th>Sonic Cr(VI) / 0.1</th>
<th>Shake Cr(VI) / 0.05</th>
<th>Shake Cr(VI) / 0.1</th>
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</tr>
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</table>
Hexavalent Chromium –
Sonication vs. Shake – $\text{Cr}^{6+}$ & $\text{Cr}^{3+}$

% Recovery

Time / minute

80% 90% 100% 110% 120% 130% 140% 150% 160% 170% 180% 190% 200%

15 30 45 60 75

Sonic O / 0.05  Sonic O / 0.1  Shake O / 0.05  Shake O / 0.1
Hexavalent Chromium –
Sonication vs. Shake – SRM soil test

NOTE: Standard not verified by NIST. This is a low concentration soil that ERG was given to validate. Concentration has decreased over time, but was verified with sonicator extraction.
Hexavalent Chromium – Method Development Summary

- New sampler being developed that chills samples during collection
  - Will keep samples cold up to 3 days after sampling
  - Need to control moisture

- Noted conversion on high concentration Cr\(^{3+}\) samples.

- Developed new method that shakes the filters during sample prep (instead of sonication)
Acknowledgements

- **US EPA**
  - Mike Jones, OAQPS
  - Dennis Mikel, OAQPS
  - Dave Shelow, OAQPS

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  - **VOCs**
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    - Chris Kopp
    - Mitchell Howell
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    - Scott Sholar
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    - Randy Mercurio
    - Jennifer Colby
  - **QA**
    - Donna Tedder
  - **Hexavalent Chromium**
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    - Ariel Atkinson
    - Laura Krnavek