Method Development Studies for Hexavalent Chromium in Ambient Air Samples

Julie L. Swift
Eastern Research Group, Inc.
Julie.swift@erg.com
Introduction

- History of EPA Hexavalent Chromium (Cr(VI) Method)
- Analytical preparation method change
- Improvements in precision after method change
- Evaluation of EPA Method vs. other analytical techniques (IC/UV vs. IC/ICPMS)
- Evaluation of EPA/NATTS sampler vs. sampler developed by NYS and Clarkson University
2003 - ERG started working on method
2004 - EPA contracted ERG to study CARB 039 method
   - ERG authored Method Development paper
2006 - ERG authored an SOP (http://www.epa.gov/ttnamti1/airtox.html)
2008 - ERG modified NATTS sampler to add chiller
2009 - ERG modified filter preparation technique before sampling – stable <15 °C (60 °F) for 3 days
2011 - ERG modified sample preparation technique – sonication vs. shaking
2012 - New study with NJ DEP CTI Grant
Incorporated analytical procedure to obtain lowest Method Detection Limits (MDL)

Investigated filter media
- Cellulose, Binderless Quartz, PVC, Teflon®
- Cellulose showed best retention but had high background – had to acid wash in order to obtain low MDL (current MDL = 0.0034 ng/mL)

Investigated interferences
- No interference of Cr (III), Fe, Mg
Added chiller to keep samples frozen while sampling and up to 3 days after sampling
  – Works in laboratory conditions, but collects water at sites with high humidity/high temperature

ERG modified filter preparation technique before sampling – stable for up to 3 days at <15°C (60°F)
ERG Sampler Study: Chiller (2008-2009)
ERG Sampler Study: Chiller (2008-2009)
NJ DEP CTI: Newest Study (2009 - present)

- Community Toxics Initiative Grant
  - NJ DEP CTI grant (funds from US EPA)
    - Dr. Linda Bonanno – Principal Investigator at NJDEP

  “Evaluation of Two Analytical Methods and Sampling Trains for the Measurement of Hexavalent Chromium in Ambient Air”

  - In conjunction with University of Medicine and Dentistry of NJ (EOHSI), Clarkson University and ERG
    - Compare Analytical Instrumentation
      - IC/UV
      - IC/ICPMS
    - Compare Sampling Systems (added ERG Prototype)
      - EPA/NATTS Sampler
      - Clarkson/State of NY
      - ERG Prototype
NJ DEP CTI: Research Team

- New Jersey Department of Environmental Protection:
  - Dr. Linda Bonanno

- Clarkson University:
  - Dr. Philip Hopke, Dr. Lin Lin, Mehdi Amouei Torkmahalleh

- EOHSI:
  - Dr. Tina Fan, Chang Ho Yu

- ERG:
  - Julie Swift, Victoria Genther, Dr. Laura Krnavek, Randy Mercurio, Ariel Atkinson, Donna Tedder

Preliminary/Draft
NJ DEP CTI: New Study Analytical Module Objective

- Evaluate the 2 analytical methods
  - All cellulose filters are prepared at ERG
  - Spiked filters were prepared by EOHSI and sent to Clarkson, ERG and kept in-house
  - Presented at 2011 National Air Toxics Monitoring & Data Analysis Workshop

Previously prepared samples for analysis by sonicating filters in sodium bicarbonate solution

- Studies with NJDEP/EOHSI/Clarkson have detected Cr(VI) when Cr(III) was spiked on filters
- In previous ERG studies, we did not see this problem
- However, spiking concentration in new study is higher
  - Recoveries showed need to reevaluate the preparation procedure
  - Dr. Phil Hopke suggested that the presence of hydroxyl ions may cause conversion of Cr(III) to Cr(VI) during sonication
ERG Study: Sonicator vs. Shaker

- If sonication is causing a problem, how should samples be prepared?
- Study sample extraction via sonication versus wrist-action shaker
- Data collected comparing sonication to shaking with liquid-spiked filters
  - Cr(III) only
  - Cr(VI) only
  - Cr(VI) and Cr(III)
ERG Study Sonicator vs. Shaker: Cr(III) only

Sonic Cr(III) / 1.10 ng/mL
Sonic Cr(III) / 1.10 ng/mL

Note: All recoveries for the shaker were zero.
ERG Study Sonicator vs. Shaker: Cr(VI) only

![Graph showing recovery of Cr(VI) over time for different conditions.](image)

- **Sonic Cr(VI) / 0.05**
- **Sonic Cr(VI) / 0.1**
- **Shake Cr(VI) / 0.05**
- **Shake Cr(VI) / 0.1**

Time / minutes:
- 15
- 30
- 45
- 60
- 75

% Recovery:
- 80%
- 85%
- 90%
- 95%
- 100%
- 105%
- 110%
- 115%
- 120%
- 125%
- 130%
- 135%
- 140%
- 145%
- 150%

Recovery of Cr(VI) in ng/mL Cr^6+ for different conditions and time intervals.
ERG Study Sonicator vs. Shaker: Cr(III) and Cr(VI)

![Graph showing comparison of recovery times for Cr(III) and Cr(VI) using Sonicator and Shaker at different concentrations and time points.](image-url)
ERG Study Sonicator vs. Shaker: Increased Precision

Maximum values for %RPD are in blue
ERG Study Sonicator vs. Shaker: Conclusions

- Detected Cr(VI) on filters spiked with high levels of Cr(III) extracted via sonication
- Found that filters spiked with both Cr(III) and Cr(VI) extracted via shaking show acceptable recoveries and variability
- Duplicate filters extracted via shaker show good %RPD
- Changed extraction method to shaking for 45 minutes instead of sonicating for one hour
Compared the IC/UV to IC/ICP-MS
- Standard NATTS method uses IC/UV
- New method uses IC/ICP-MS

IC/ICP-MS method uses same filter as IC/UV (Sodium bicarbonate coated cellulose filters)
- Coated after acid washed, clean enough for low concentration ambient samples
- Causes background on IC/ICP-MS for Cr(VI)
- Sodium Bicarbonate causes Cr(III) to precipitate (only able to detect Cr(VI), not Cr(III) and Cr(VI) on IC/ICPMS)
Audits were put in place in order to confidently evaluate the different analytical techniques
  – External audits obtained by Wibby Environmental
  – Internal audits prepared by ERG

Method Detection Limits were performed on each analytical system.
  – IC/UV lower than IC/ICPMS (background interference on IC/ICPMS does not allow lower MDL)
  – ERG IC/UV results 3-4 times lower

Laboratory techniques improved over time
NJ DEP CTI: Wibby Audit (August 2011)
NJ DEP CTI: ERG Audit (September 2011)

Preliminary/Draft
NJ DEP CTI:
ERG Audit (October 2011)
NJ DEP CTI: ERG Audit (January 2012)

Percent Recovery

Low [light blue] High [dark red]

- EOSHI IC/ICPMS
- Clarkson IC/ICPMS
- EOSHI IC
- Clarkson IC
- ERG IC

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NJ DEP CTI: Summer 2011 Field Results

- Sampler set up
  - Sampler installation – 6 samplers (8 ports)
    • Plus ERG Prototype sampler
  - Instrument design challenges
    • Clarkson sampler also had water on filters but was a sampler error and was easily corrected
    • ERG prototype collected water and was removed from study

- Not enough valid samples but did get some information
  - Use only Teflon® screens in samplers (Clarkson)
  - Tighten all filter holders (NATTS)
NJ DEP CTI: NYS-Clarkson Sampler

Air Flow

Electrical Signal

16.7 LPM

FM10 Inlet

Solenoid Valve

Membrane Dryer

Filter

Air

HEPA

Filter

HEPA

Chiller

Metering Valve

Ambient Air

FM10 Sampler

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All samples taken were sent to each laboratory
  - Each set included 8 samples
    • 2 NATTS samplers – each sampler able to sample primary and collocated
    • 4 Clarkson samplers – for study, 2 considered primary, 2 considered collocated
  - Two whole sets sent to each laboratory
    • EOHSI and Clarkson analyzed by IC/UV and IC/ICPMS
    • ERG analyzed by IC/UV only
  - Two sets sent to all 3 laboratories
    • EOHSI analyzed by IC/UV and IC/ICPMS
    • Clarkson and ERG analyzed by IC/UV only
Only the IC/ICPMS & IC/UV final Cr(VI) results can be compared.

At this point, have not been able to compare the interconversion of Cr(VI)/Cr(III) by IC/ICPMS and IC/UV.

- Different sample preparation techniques used:
  - IC/ICPMS – acidified Nitric Acid extraction before analysis
  - IC/UV – basic Sodium Bicarbonate extraction before analysis

Blanks – IC/ICPMS appear to have interferences at low levels with the sodium bicarbonate filters.

- Could this be a problem for IC/ICPMS for low concentration samples?
ERG Recent Development (2012)

- EPA Approved Cr(VI) Method developed by ERG was approved as an ASTM International Standard
  - Began process in 2008
  - Modified draft in 2011 to incorporate new preparation technique (shaker instead of sonicator)
  - Received approval on May 7, 2012!

Standard Test Method for
Determination of Total Suspended Particulate (TSP) Hexavalent Chromium in Ambient Air Analyzed By Ion Chromatography (IC) and Spectrophotometric Measurements
Conclusions

- ERG Prototype sampler collects water in humid/rainy conditions. It does give good recoveries for samples left out for multiple days.

- Shaker converts less Cr(III) to Cr(VI) for spiked filters that contain Cr(III) over time.

- More studies are needed to compare Clarkson and NATTS sampler Cr(VI) recoveries.
  - Summer study not conclusive – too many variables but did learn from it.
  - Winter study had low concentrations. Need more samples to obtain any definitive conclusions.

- Now have a ASTM Cr(VI) method.
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  - David Shelow, Mike Jones, Joann Rice, Dennis Mikel
Questions?