Method Development Studies for Hexavalent Chromium in Ambient Air Samples

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Introduction

- History of EPA Hexavalent Chromium (Cr(VI) Method)

  http://www.epa.gov/ttnamti1/files/ambient/airtox/hexchromsop.pdf
- 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

Timeline of EPA Method Variations

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

ERG Initial Study (2003-2004)

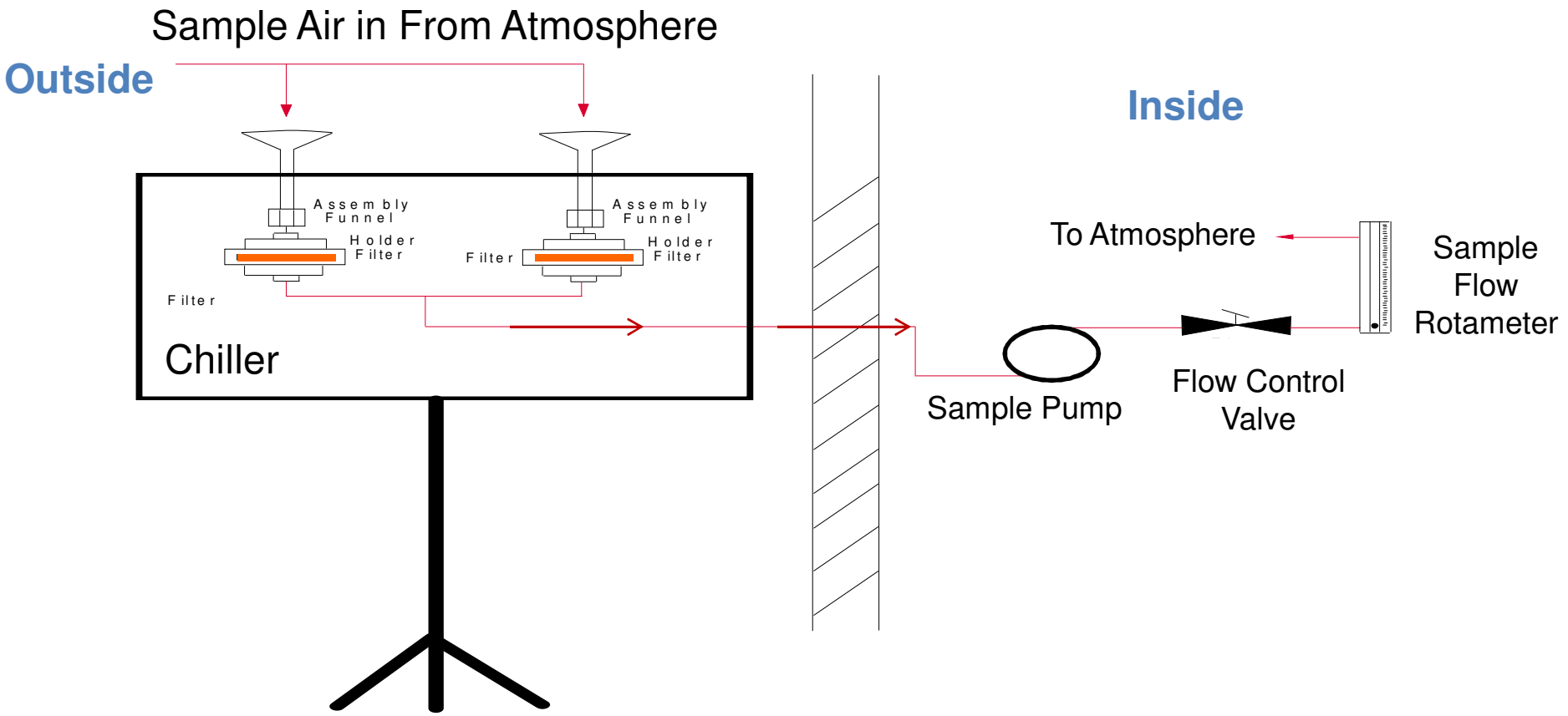
- Incorporated analytical procedure to obtain lowest Method Detection Limits (MDL)
- Investigated filter media
  - Cellulose, Binderless Quartz, PVC, Teflon®
  - Cellulose showed best retention but had high background – had to acid wash in order to obtain low MDL (current MDL = 0.0034 ng/mL)
- Investigated interferences
  - No interference of Cr (III), Fe, Mg

ERG Sampler Study: Chiller (2008-2009)

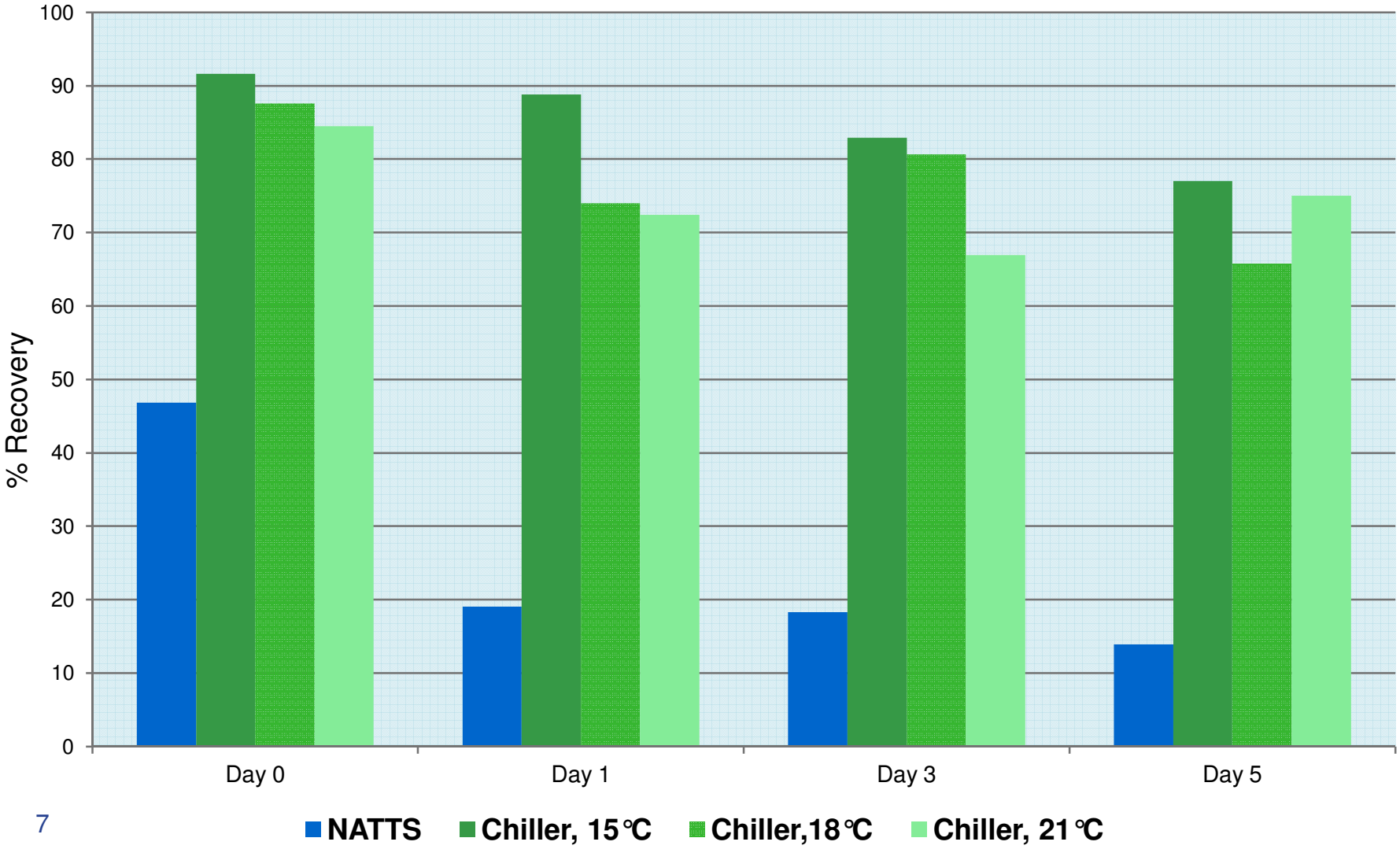
- Added chiller to keep samples frozen while sampling and up to 3 days after sampling
  - Works in laboratory conditions, but collects water at sites with high humidity/high temperature

- 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

Preliminary/Draft

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

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

http://www.epa.gov/ttn/amtic/airtox-daw-2011.html

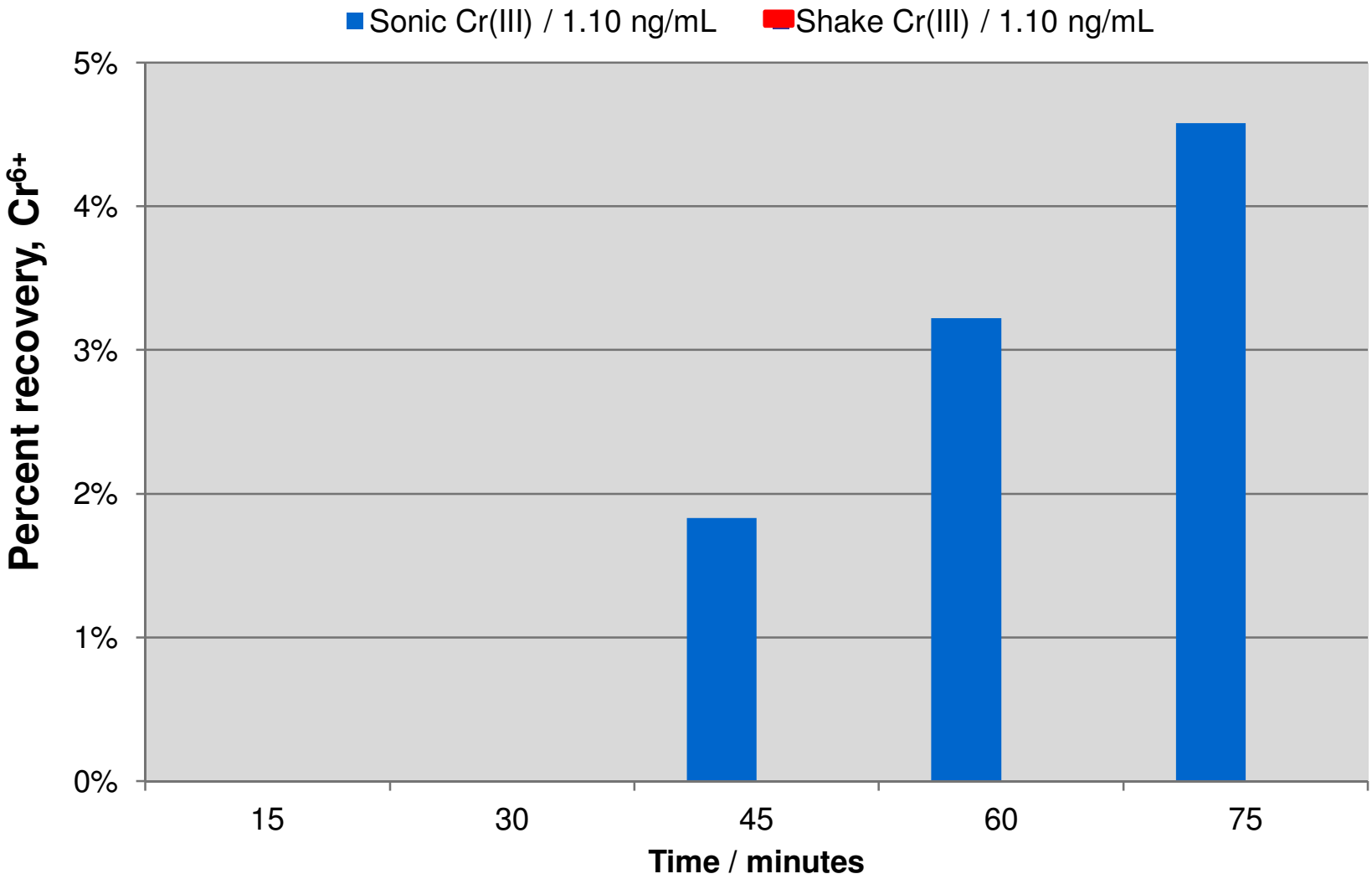
NJ DEP CTI: Sample Preparation Changes

- 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

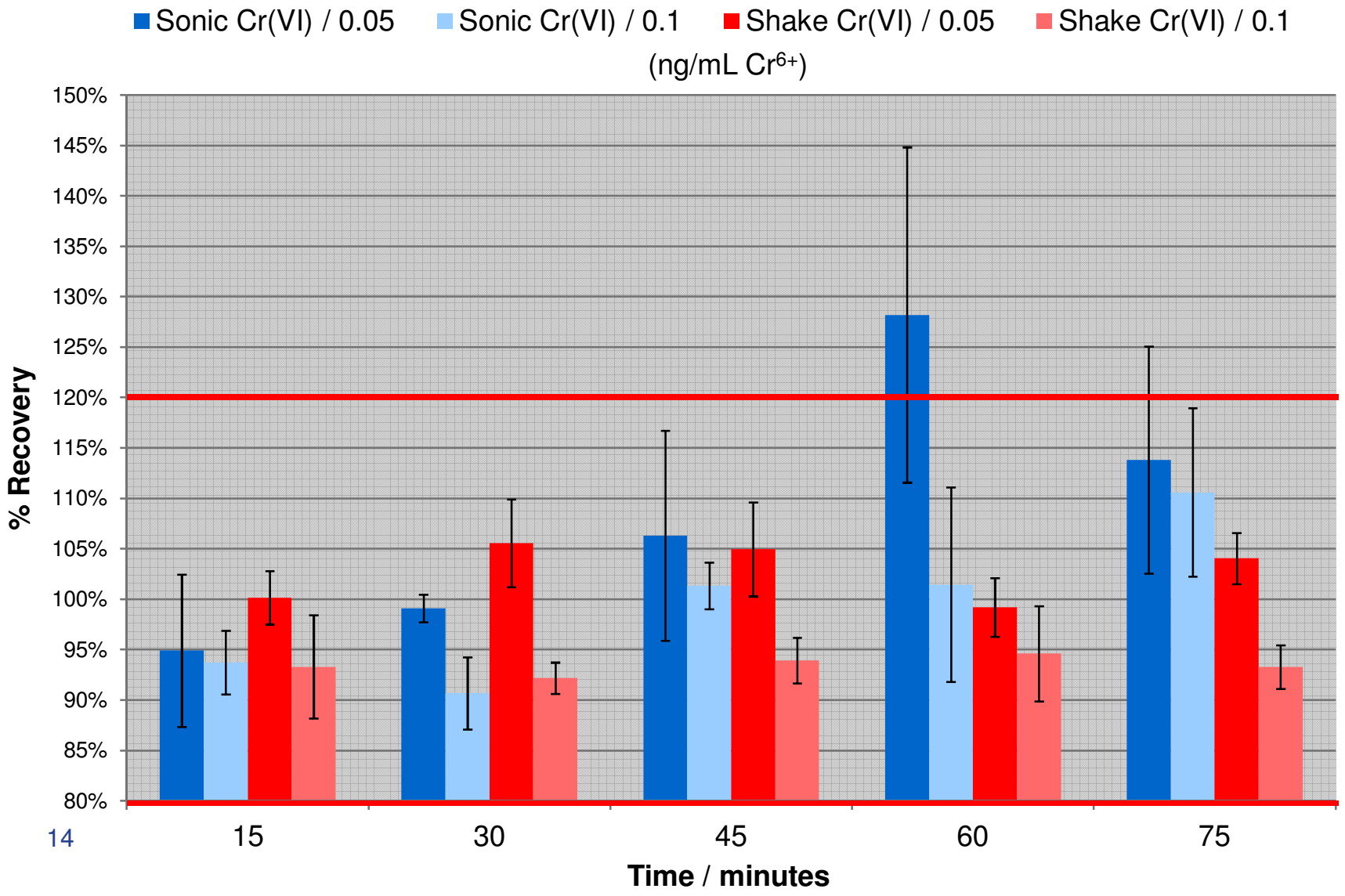
- If sonication is causing a problem, how should samples be prepared?
- Study sample extraction via sonication versus wrist-action shaker
- Data collected comparing sonication to shaking with liquid-spiked filters
  - Cr(III) only
  - Cr(VI) only
  - Cr(VI) and Cr(III)

ERG Study Sonicator vs. Shaker: Cr(III) only

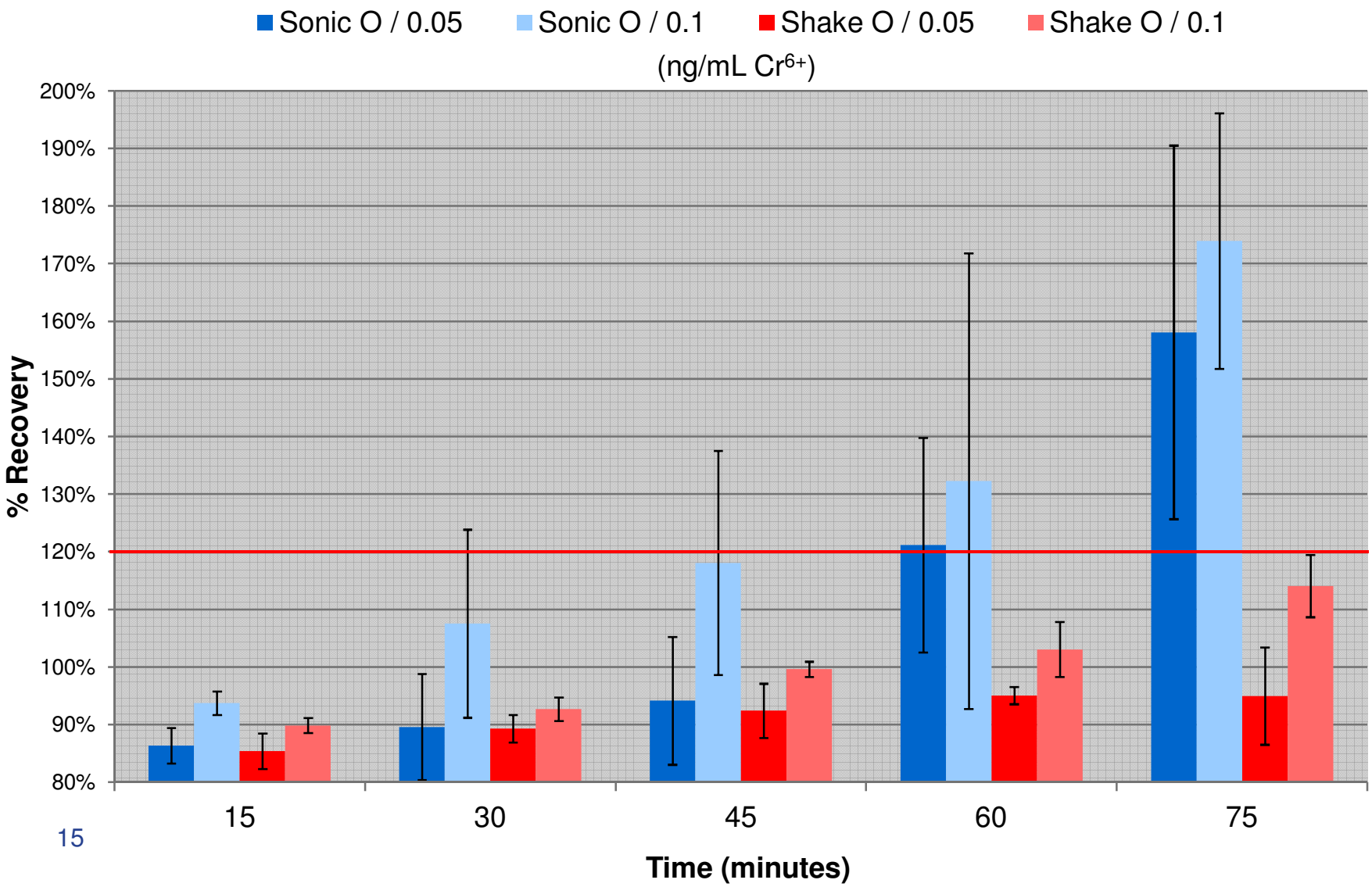


Note: All recoveries for the shaker were zero.

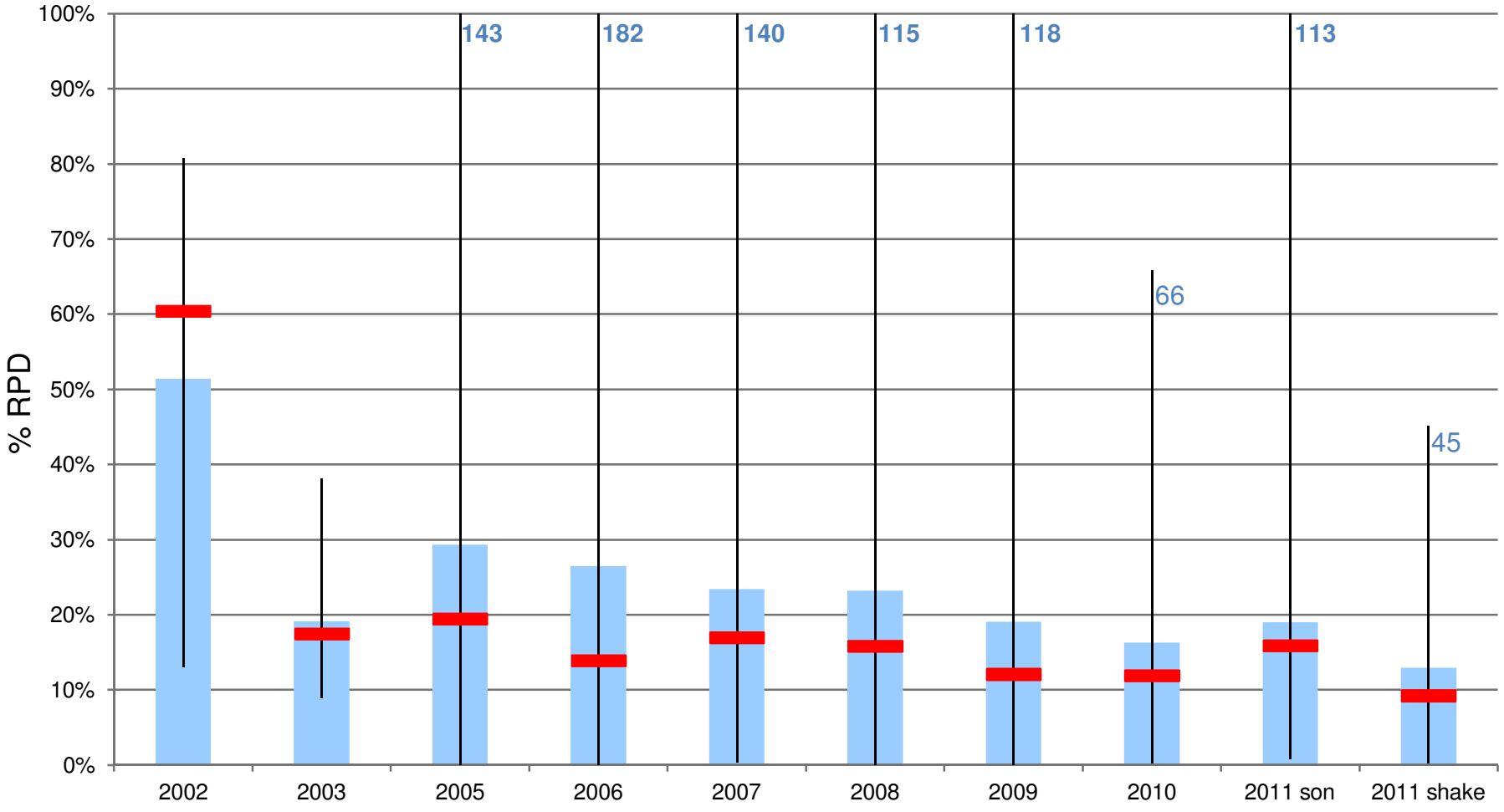
ERG Study Sonicator vs. Shaker: Cr(VI) only



ERG Study Sonicator vs. Shaker: Cr(III) and Cr(VI)



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

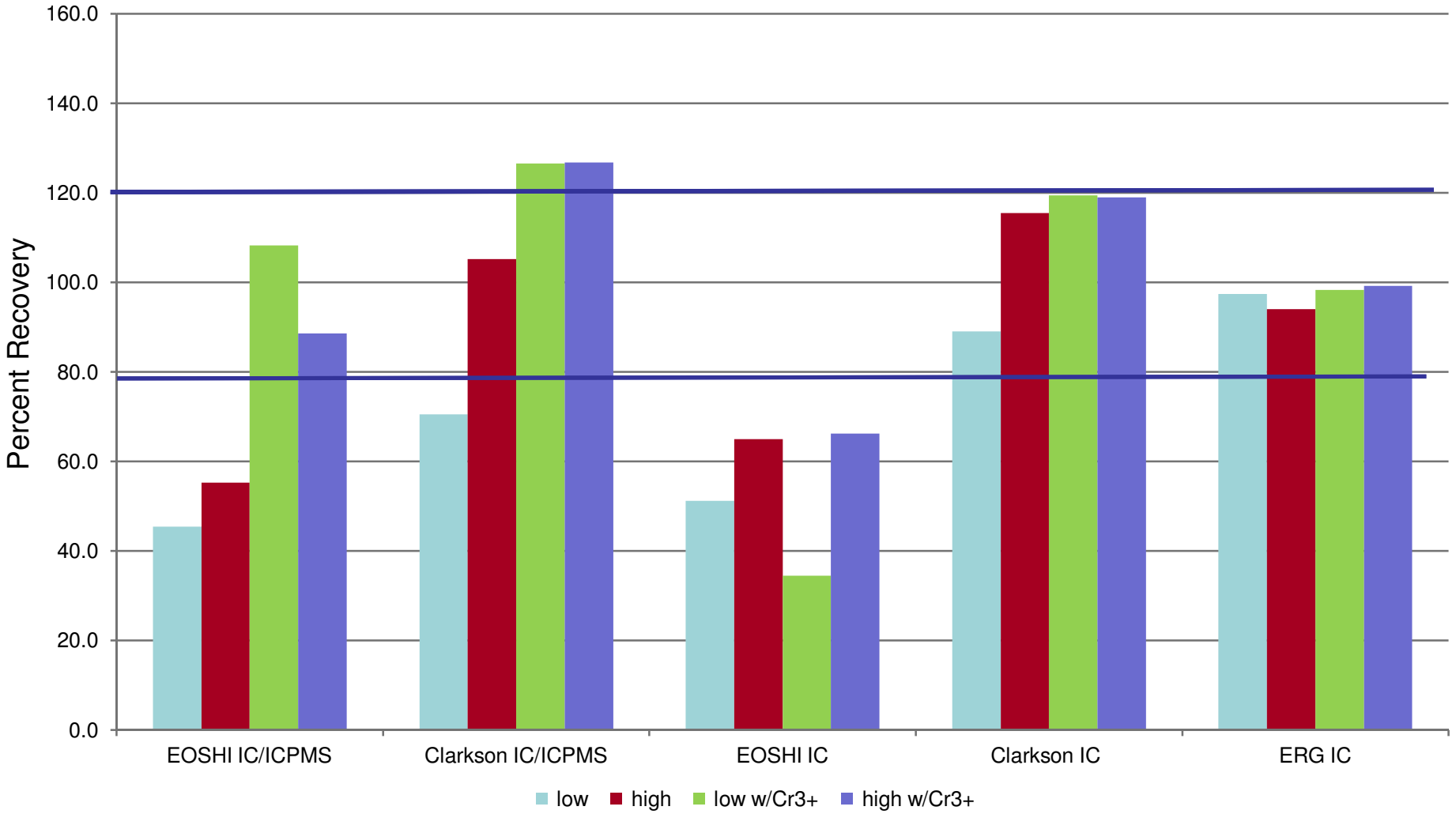
NJ DEP CTI: Analytical Instrumentation

- 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)

NJ DEP CTI: Initial Laboratory Comparisons

- 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 preformed 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)



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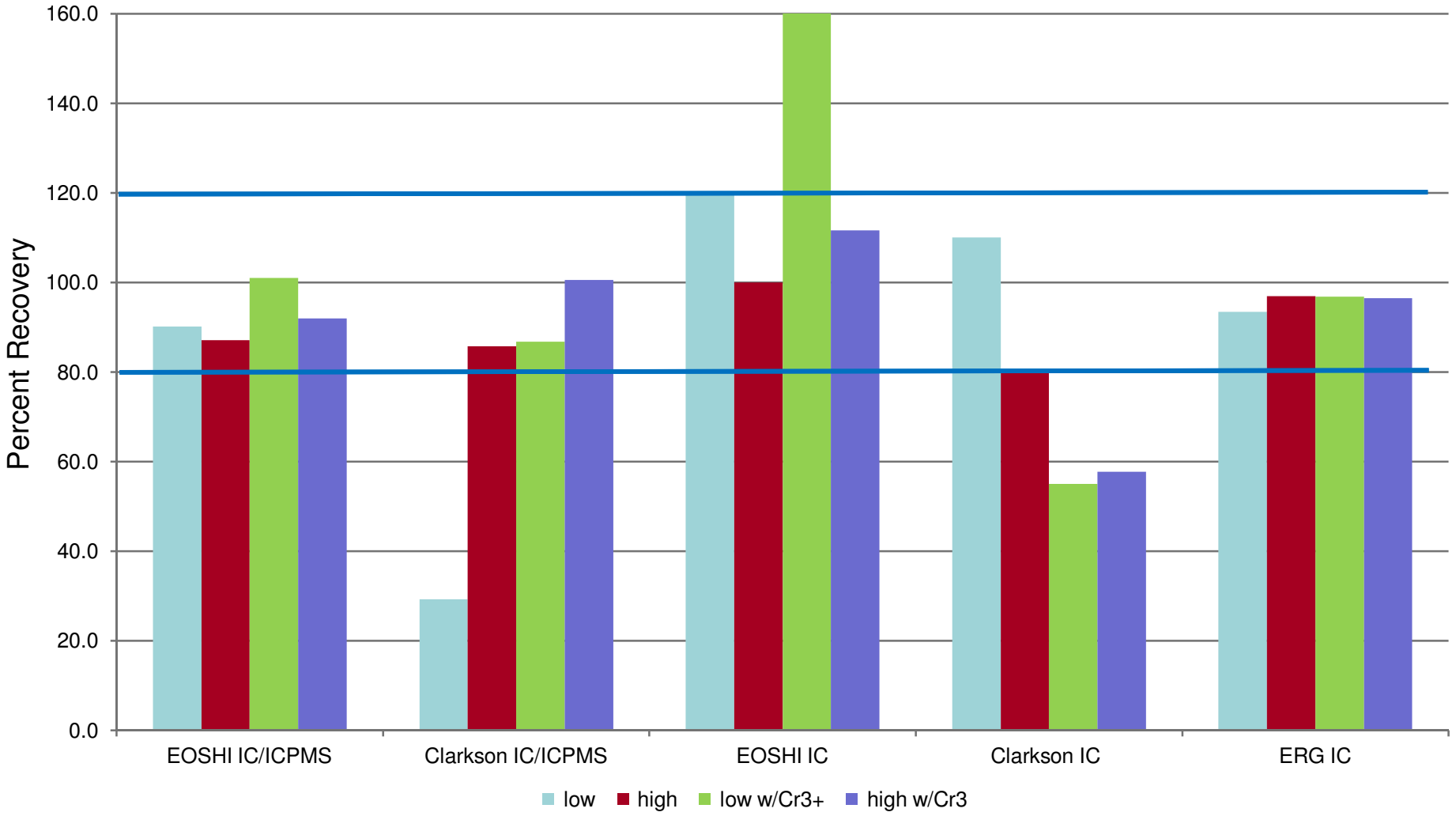
NJ DEP CTI: ERG Audit (September 2011)



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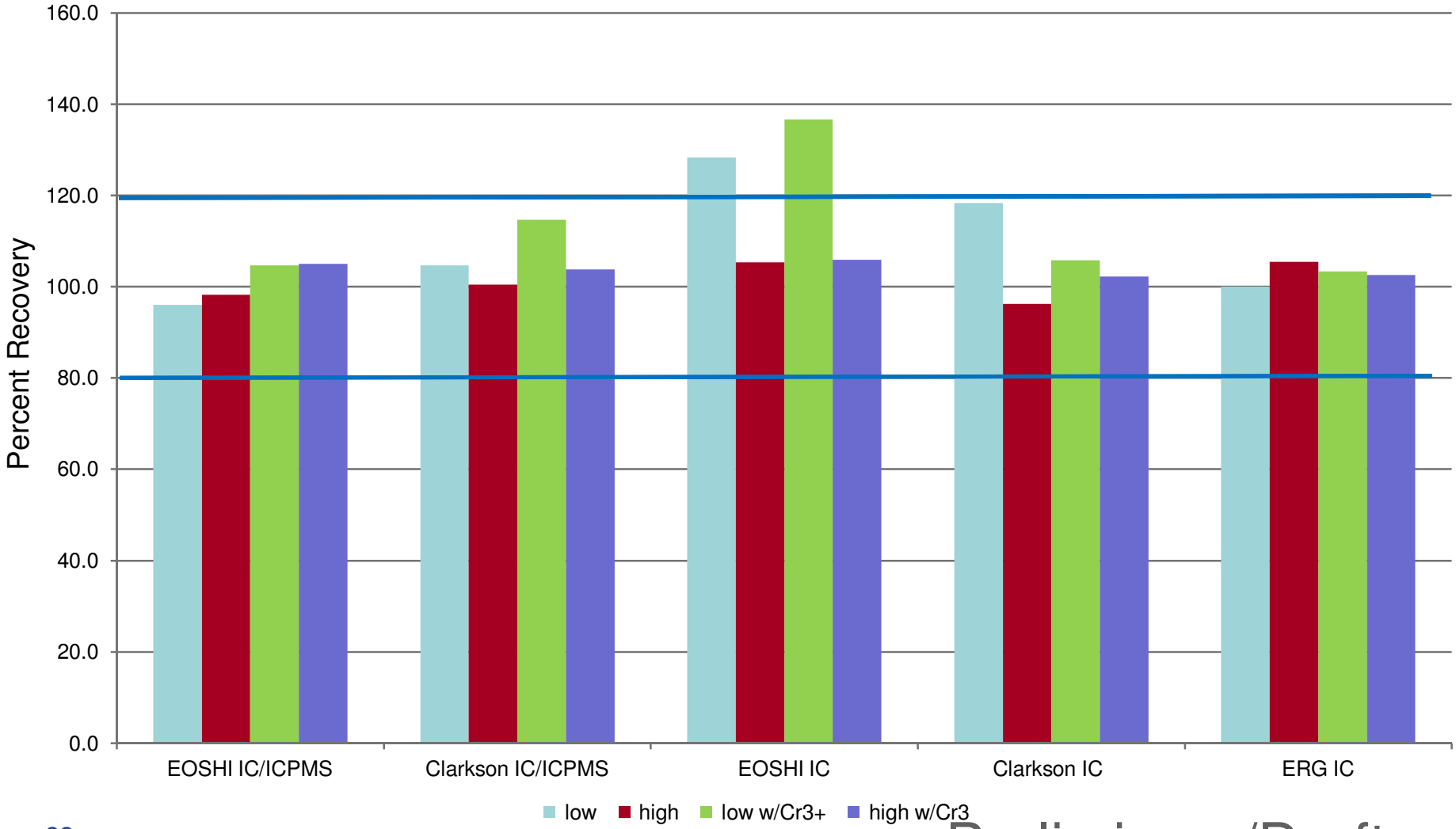
NJ DEP CTI: ERG Audit (October 2011)



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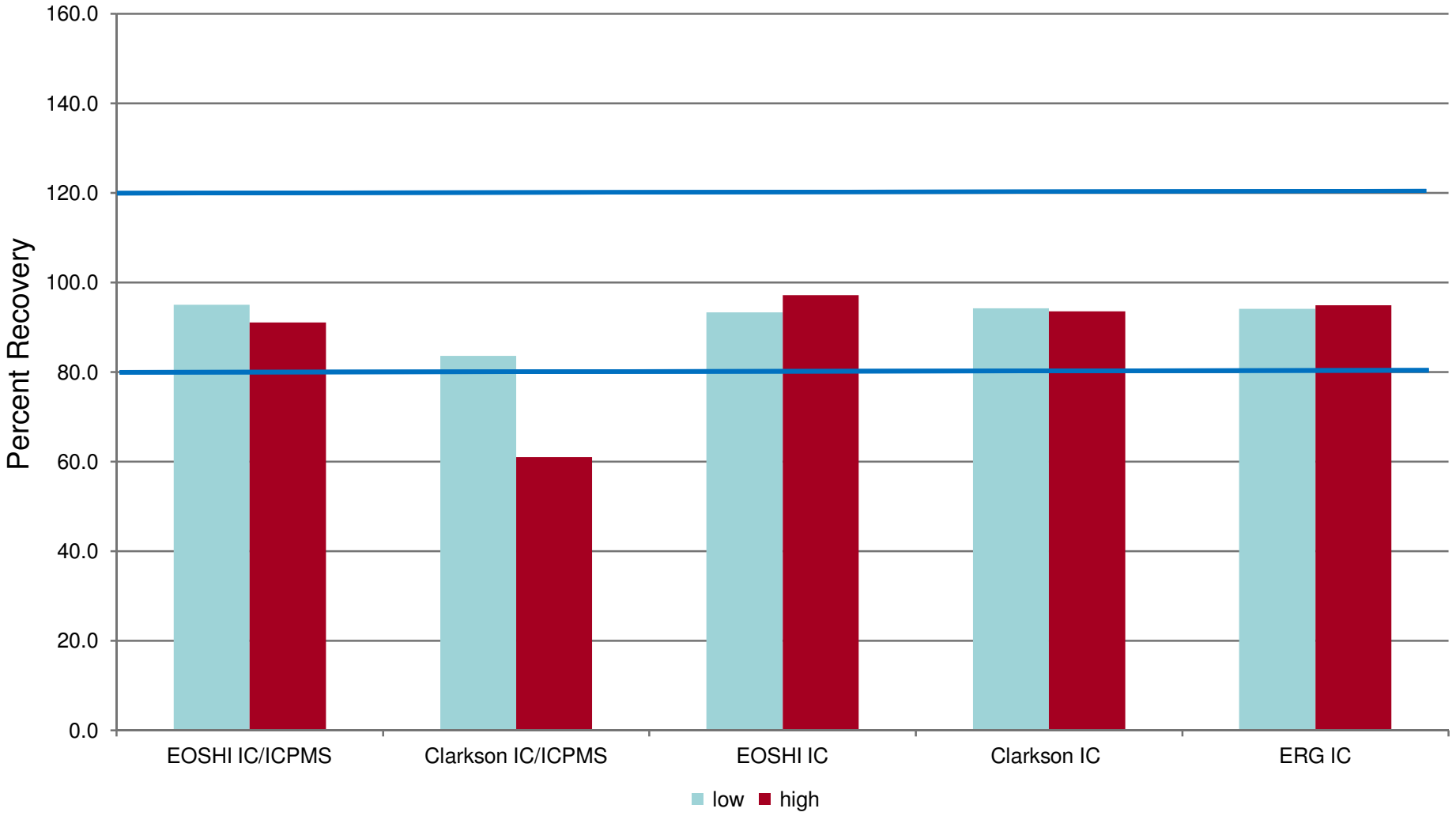
NJ DEP CTI: ERG Audit (January 2012)



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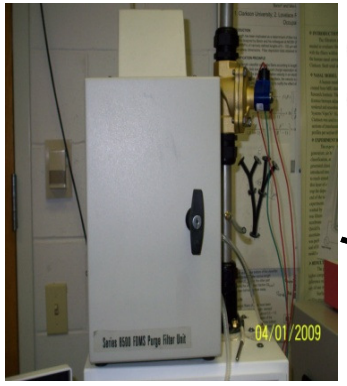
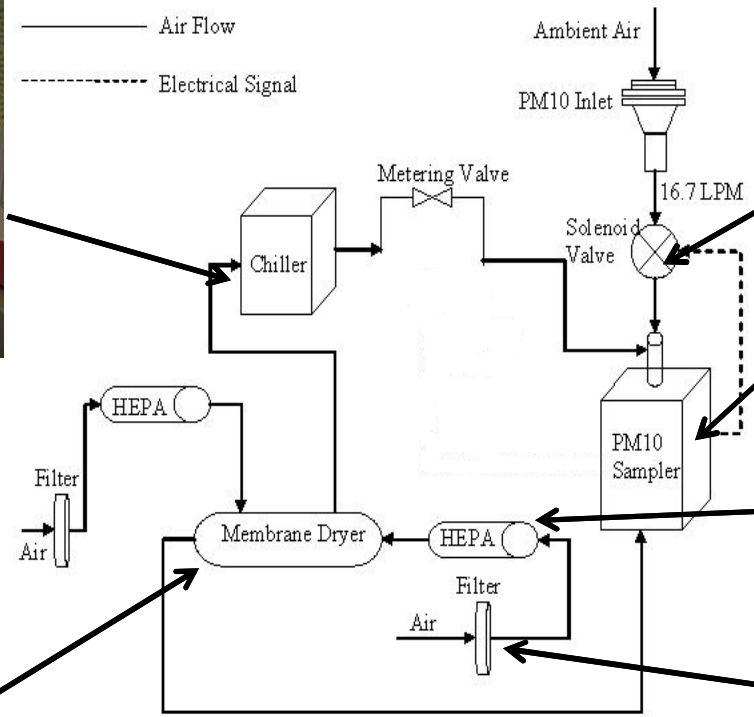
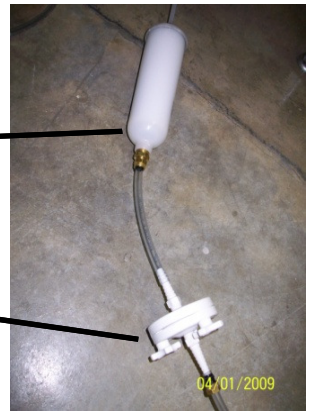
NJ DEP CTI: Summer 2011 Field Results

- 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







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NJ DEP CTI: Winter 2012 Field Results

- 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

NJ DEP CTI: Field Results - Discussion

- 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

Acknowledgements

- The Community Toxics Initiative Grant was funded in part by the US Environmental Protection Agency through a grant to the New Jersey Department of Environmental Protection
- We would like to thank the following people at U.S. EPA:
  - David Shelow, Mike Jones, Joann Rice, Dennis Mikel

Questions?