National Contract Lab Analytical Method Development Updates

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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

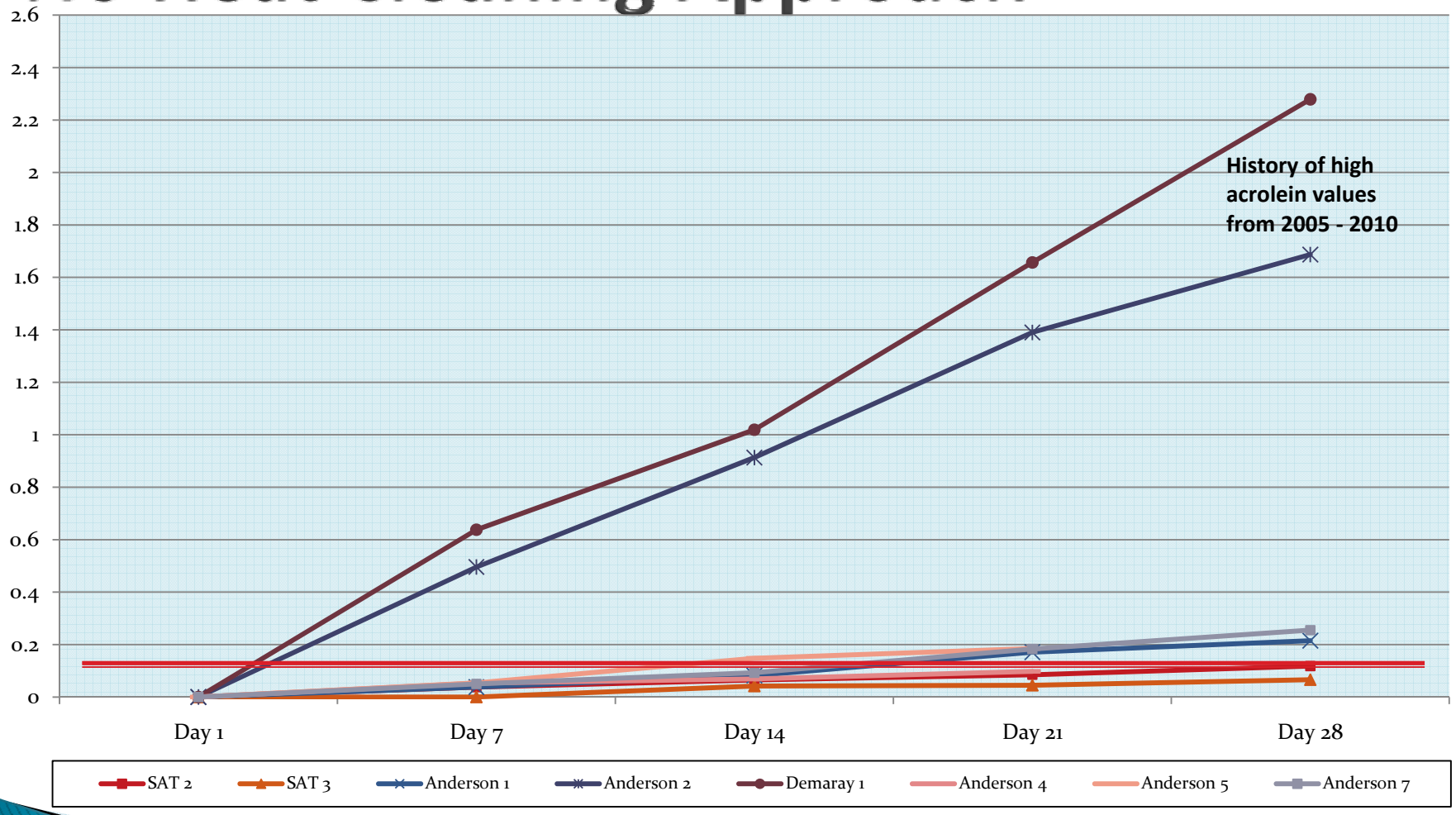
- Provides Analysis
  - VOC (TO-15)
  - Speciated Hydrocarbons
  - Carbonyls (TO-11A)
  - PAH (TO-13A)
  - Metals (IO-3.5)
  - Hexavalent Chromium (EPA Method)
- Provides Site Support
  - VOC
  - Carbonyls
  - Hexavalent Chromium
- Provide QA Support
  - Audits
  - Sampler Recertification
  - PAMS Cylinders
  - 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



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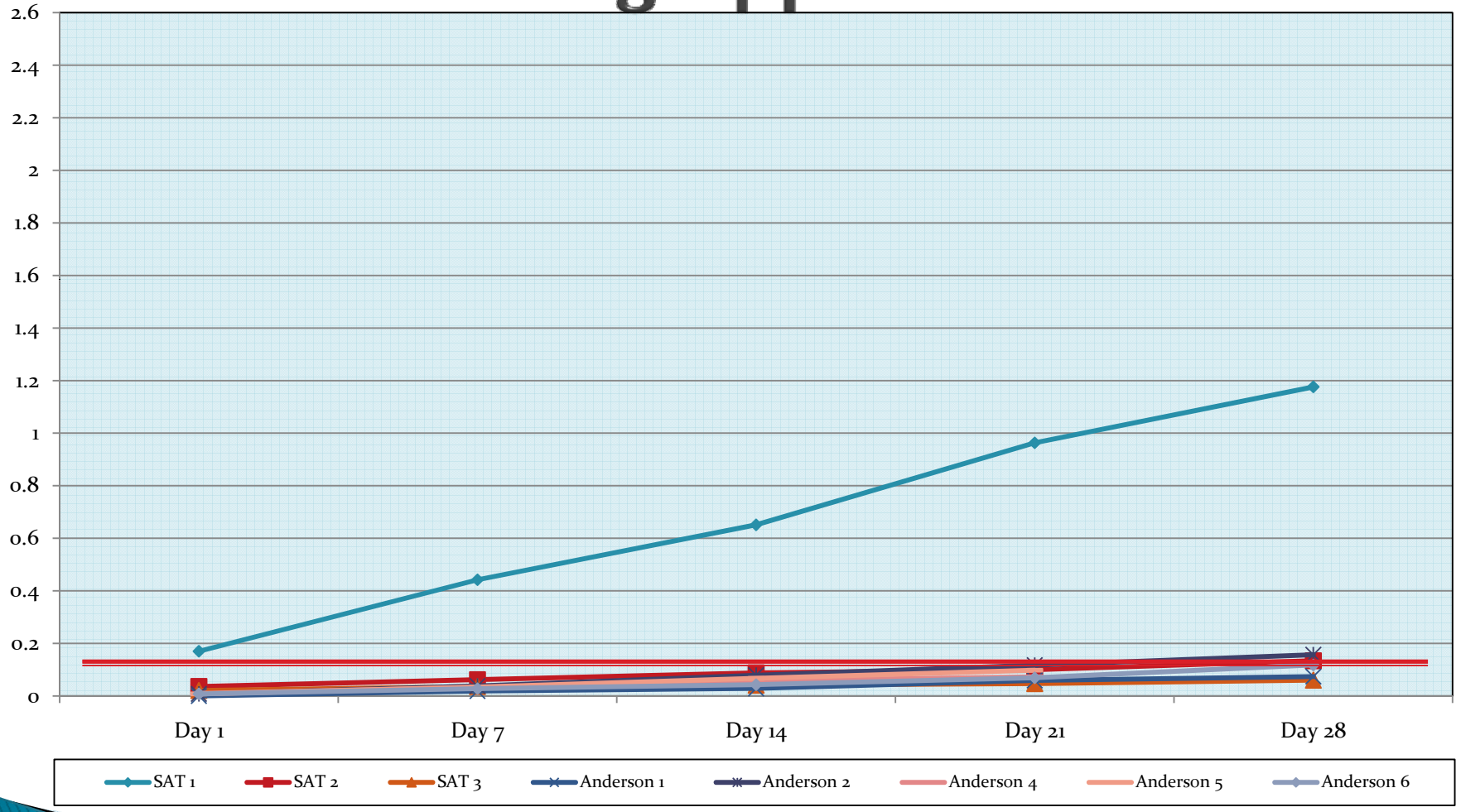
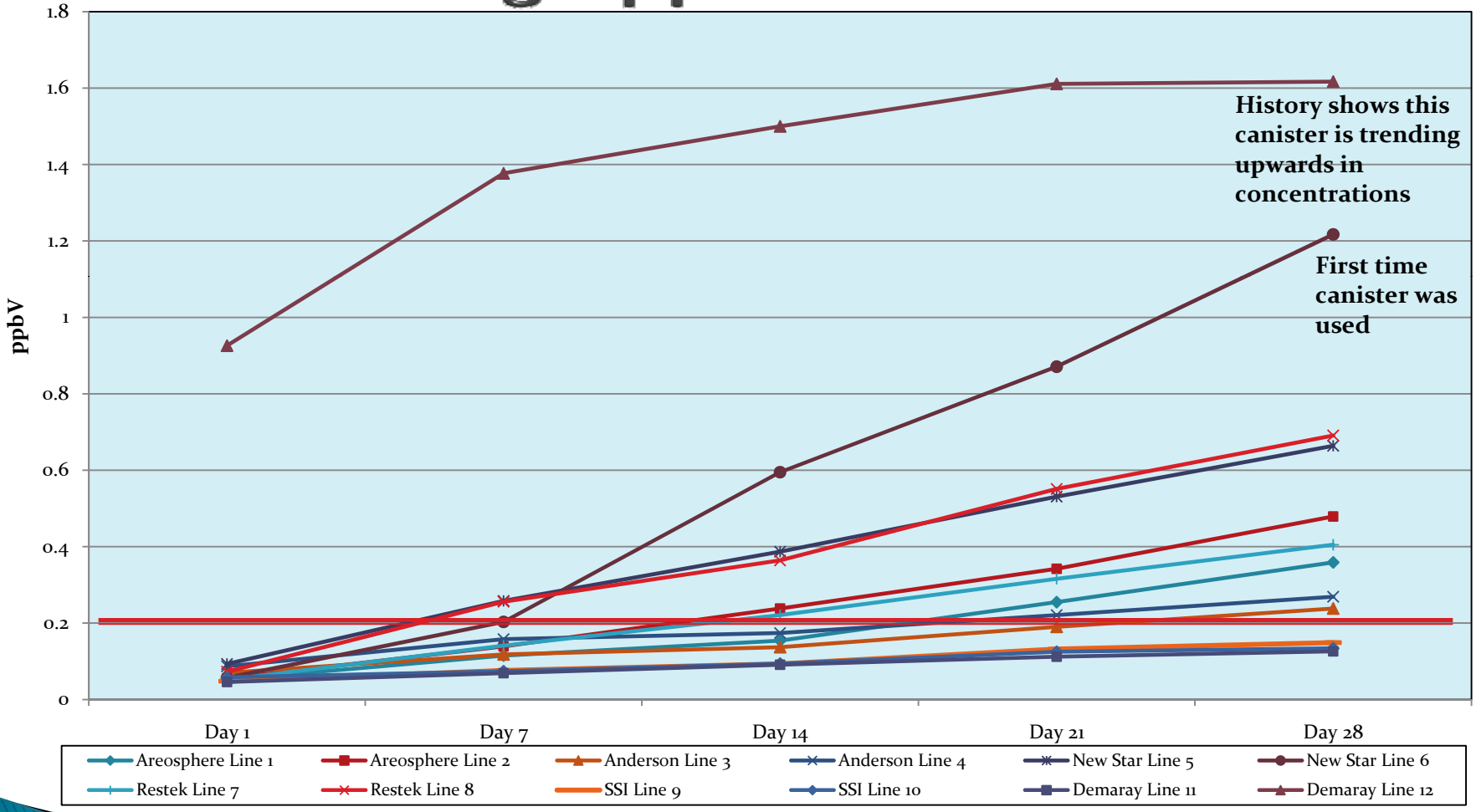
DST3 what does "History of high acrolein values" mean? Could you just put the time frame "2005 -2010"?

was this a study? Should the title be Can Cleaning Study?
Donna Tedder, 3/31/2011

Canister Cleaning – MEK
No Heat Cleaning Approach



Canister Cleaning – Acrolein Heat Cleaning Approach



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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?
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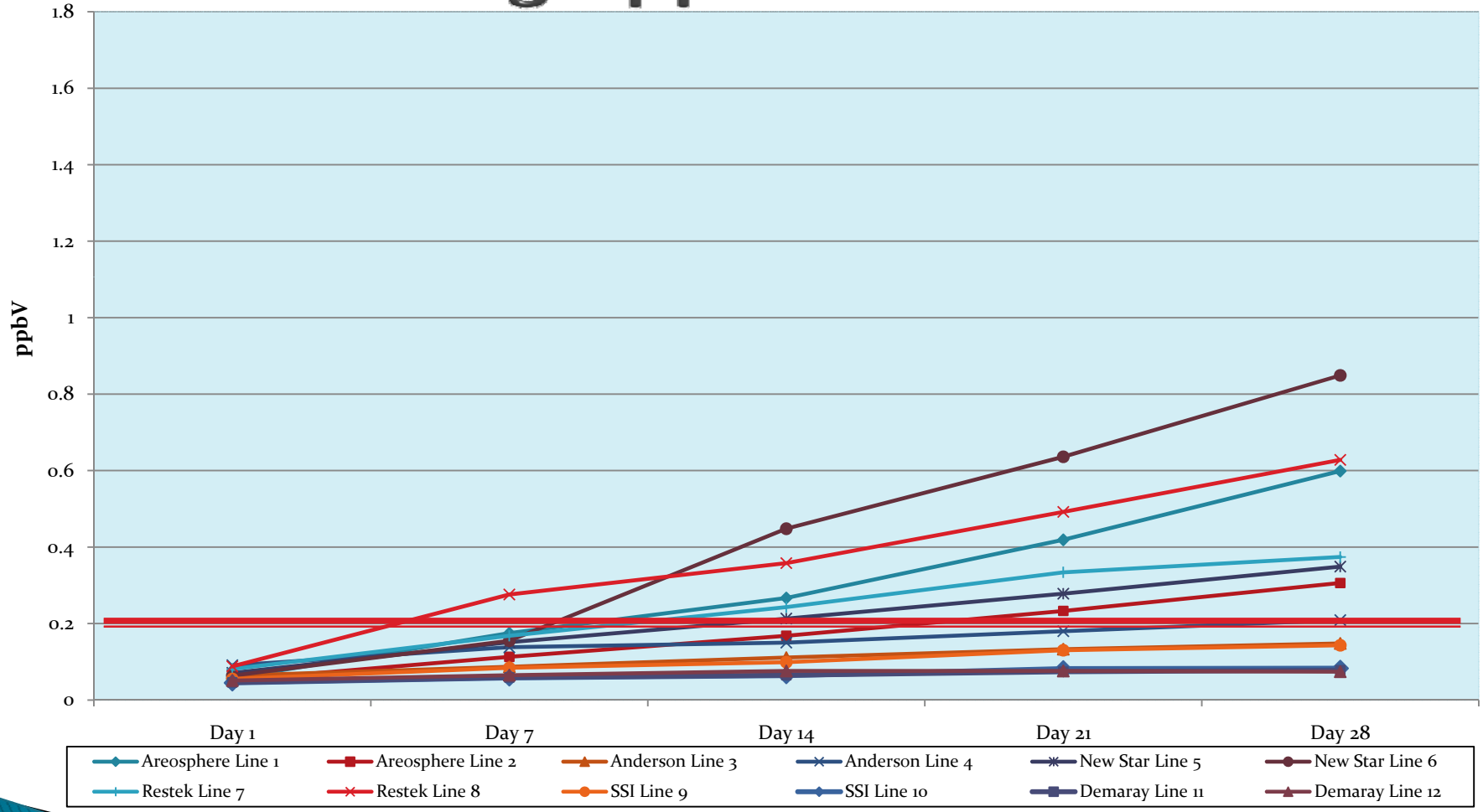
Canister Cleaning – MEK Heat Cleaning Approach



Batch Blank Comparison – 349 Batch Blanks in 2010

Compound	Average (ppbv)	# of Detections	% Detected
Propylene	0.111	341	97.7
Methyl Ethyl Ketone	0.072	326	93.4
Methyl Methacrylate	0.024	323	92.6
Benzene	0.020	306	87.7
Carbon Disulfide	0.025	253	72.5
Acetylene	0.050	211	60.5
Acrolein	0.071	199	57.0
Acetonitrile	0.030	174	49.9
Toluene	0.054	143	41.0
Chloromethane	0.037	102	29.2

Batch Blank Comparison w/Heat

NO HEAT (349 blanks)				HEAT (4 blanks)		
Compound	Average (ppbv)	# of Detections	% Detected	Average (ppbv)	% of Detections	% Detected
Propylene	0.111	341	97.7	0.109	4	100
Methyl Ethyl Ketone	0.072	326	93.4	0.037	4	100
Methyl Methacrylate	0.024	323	92.6	0.029	3	75
Benzene	0.020	306	87.7	0.048	4	100
Carbon Disulfide	0.025	253	72.5	0.008	3	75
Acetylene	0.050	211	60.5	0.039	4	100
Acrolein	0.071	199	57.0	0.106	4	100
Acetonitrile	0.030	174	49.9	0	0	0
Toluene	0.054	143	41.0	0.019	4	100
Chloromethane	0.037	102	29.2	0.007	1	25

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

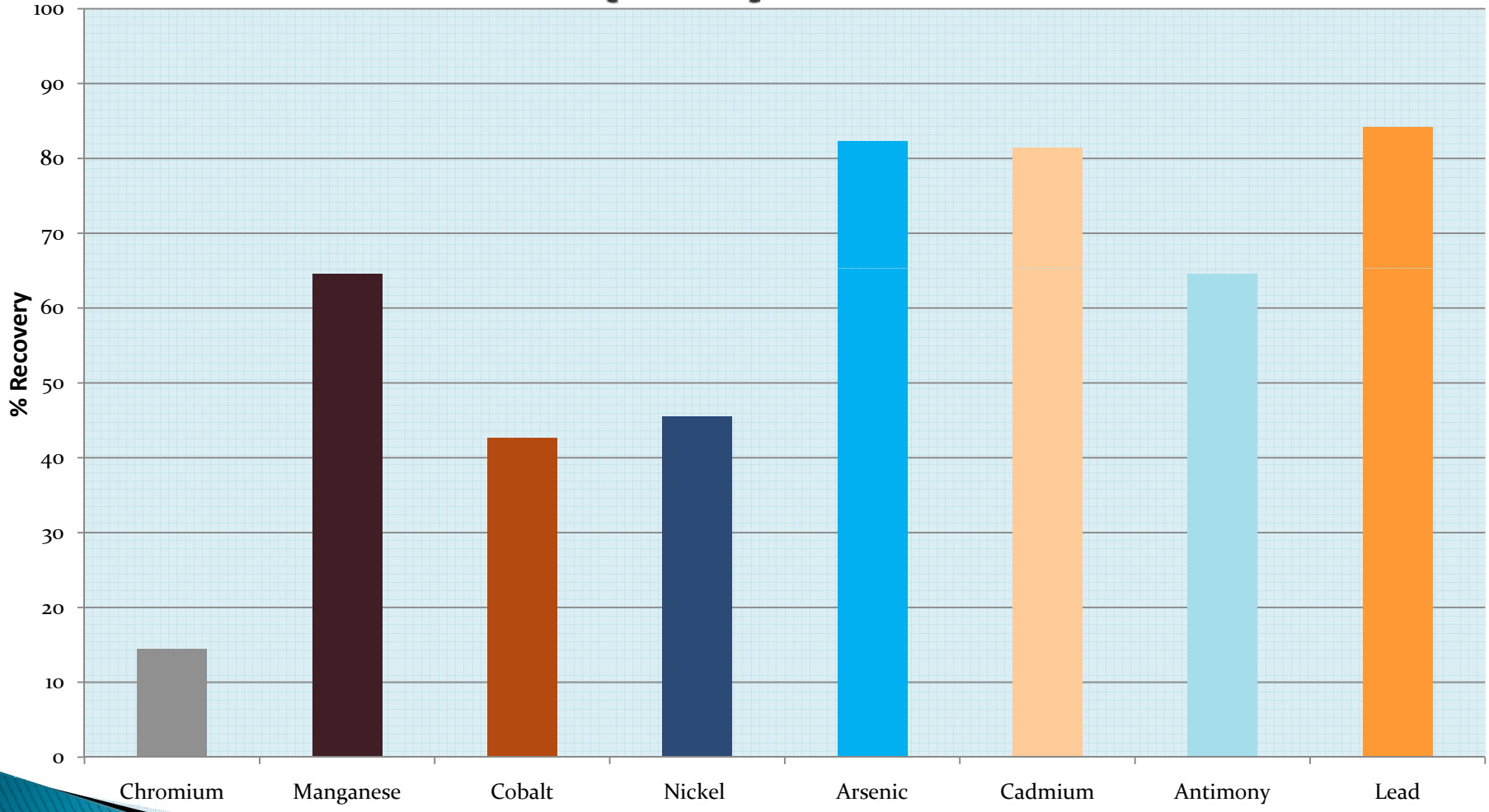
Compendium Method IO-3.5 for National Contract

- For the EPA contract
  - Antimony
  - Arsenic
  - Beryllium
  - Cadmium
  - Chromium
  - Cobalt
  - Lead
  - Manganese
  - Mercury
  - Nickel
  - Selenium

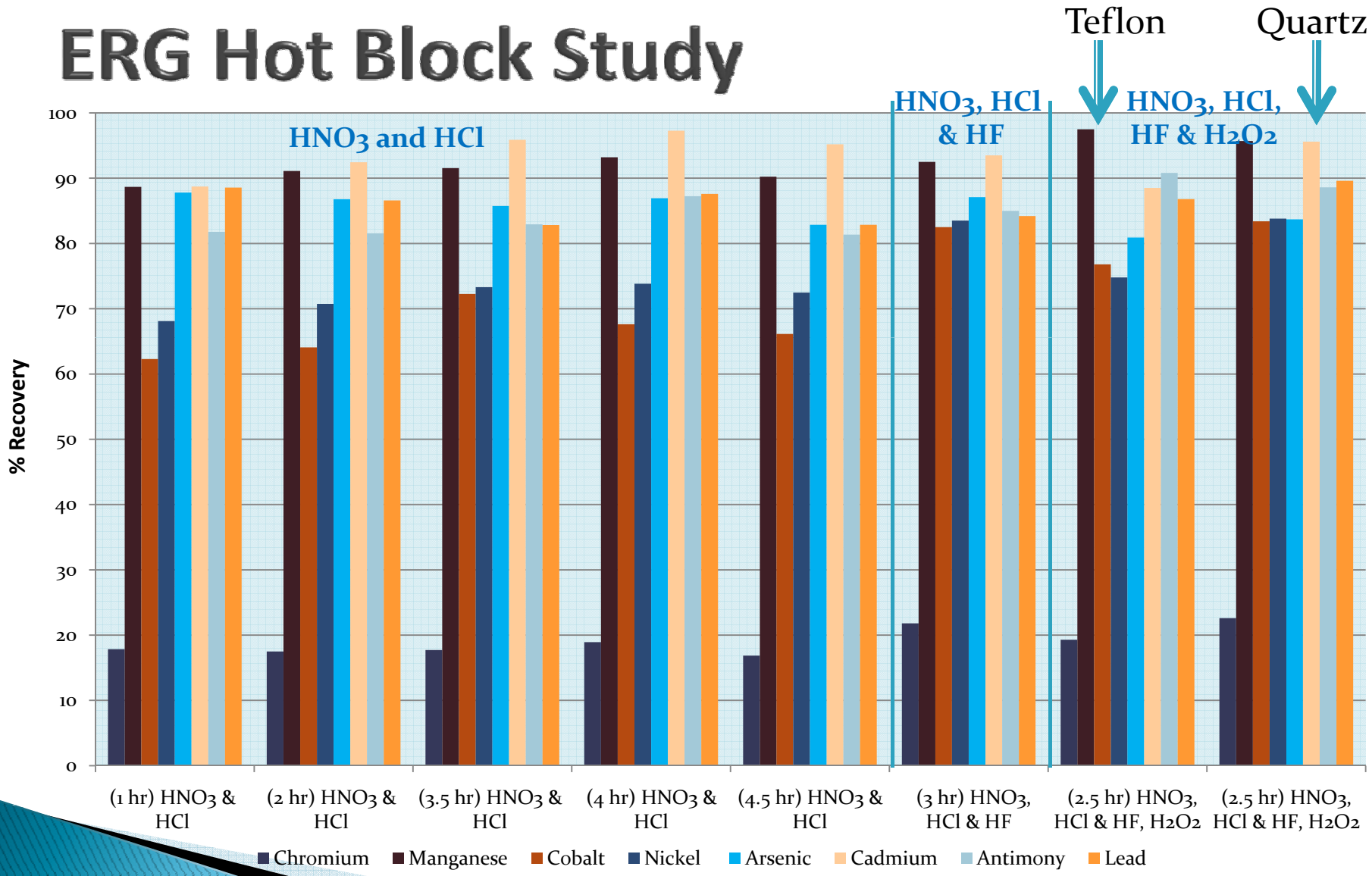
Compendium Method IO-3.5 Method Development

- 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 – HNO3 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



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

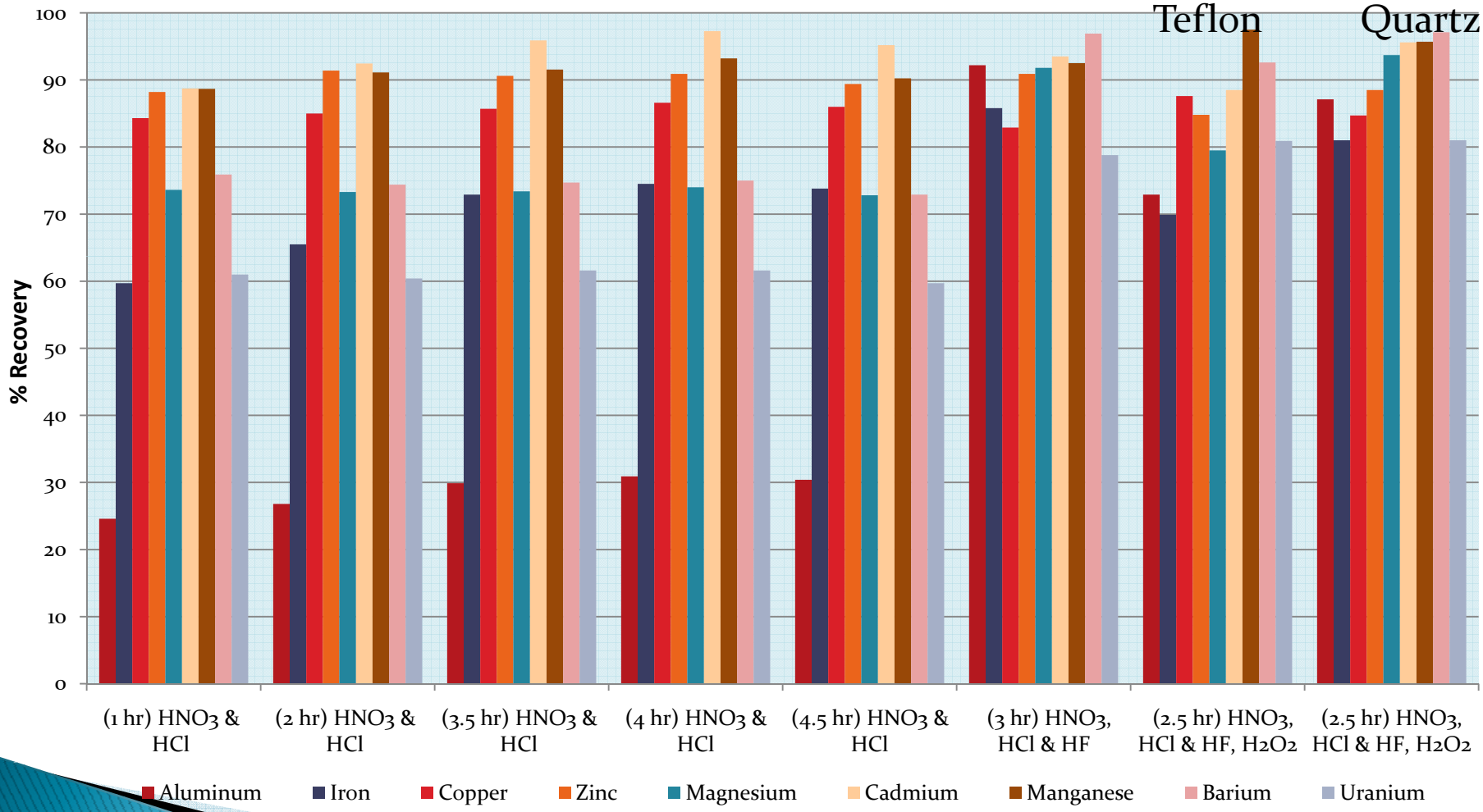
Difference between our method and others?

- 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:
    - HNO_3
    - HCl
    - HF
    - H_2O_2
  - 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)



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 (Cr^{6+})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)

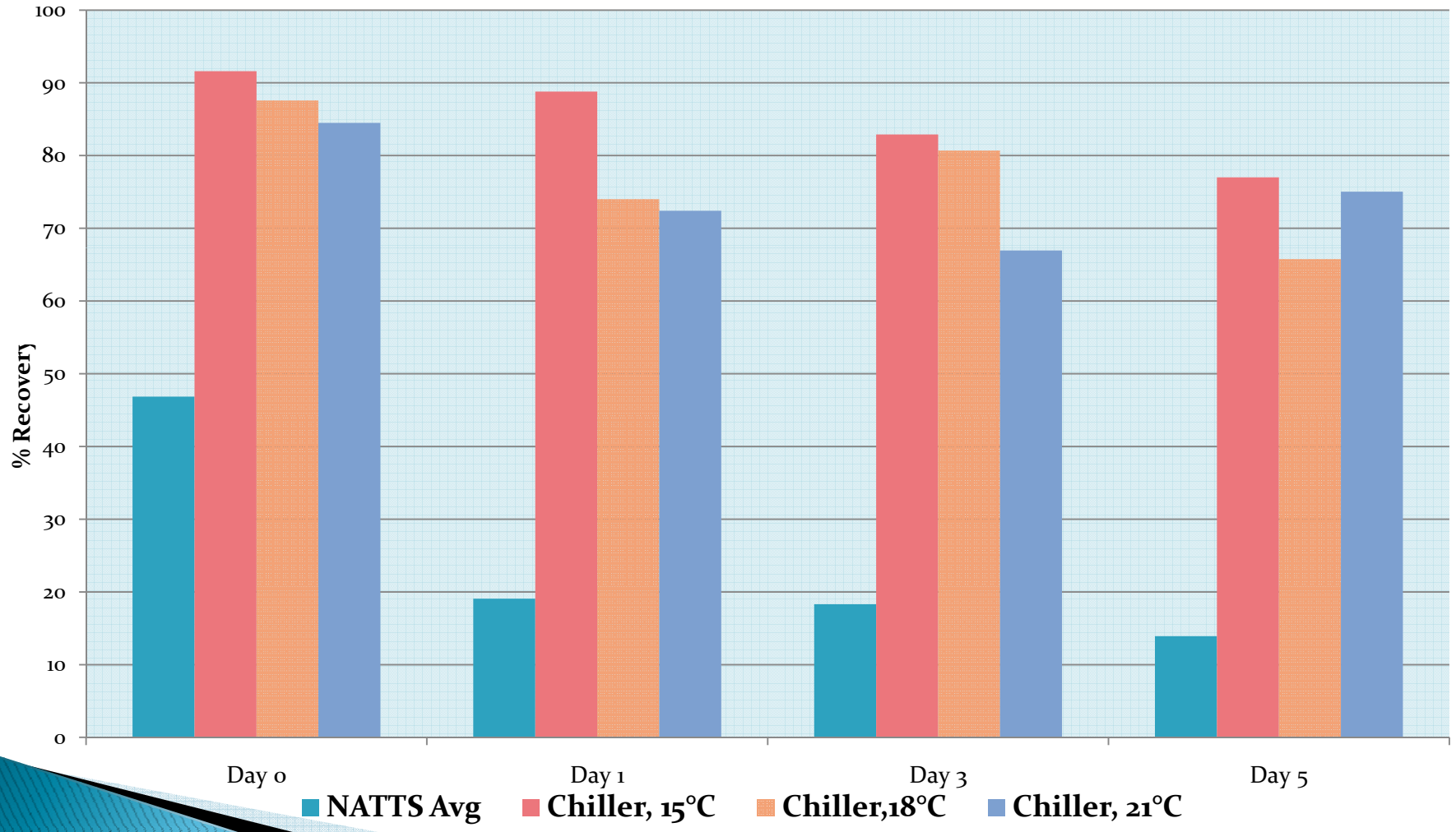
Hexavalent Chromium - Sampling

Currently collect samples at ambient conditions

- Filters are stored frozen before analysis
- More stable when stored at temperatures <15°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

DS



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DST6 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 hex chrom values open to criticism?
Donna Tedder, 3/31/2011

Hexavalent Chromium – Sample Prep

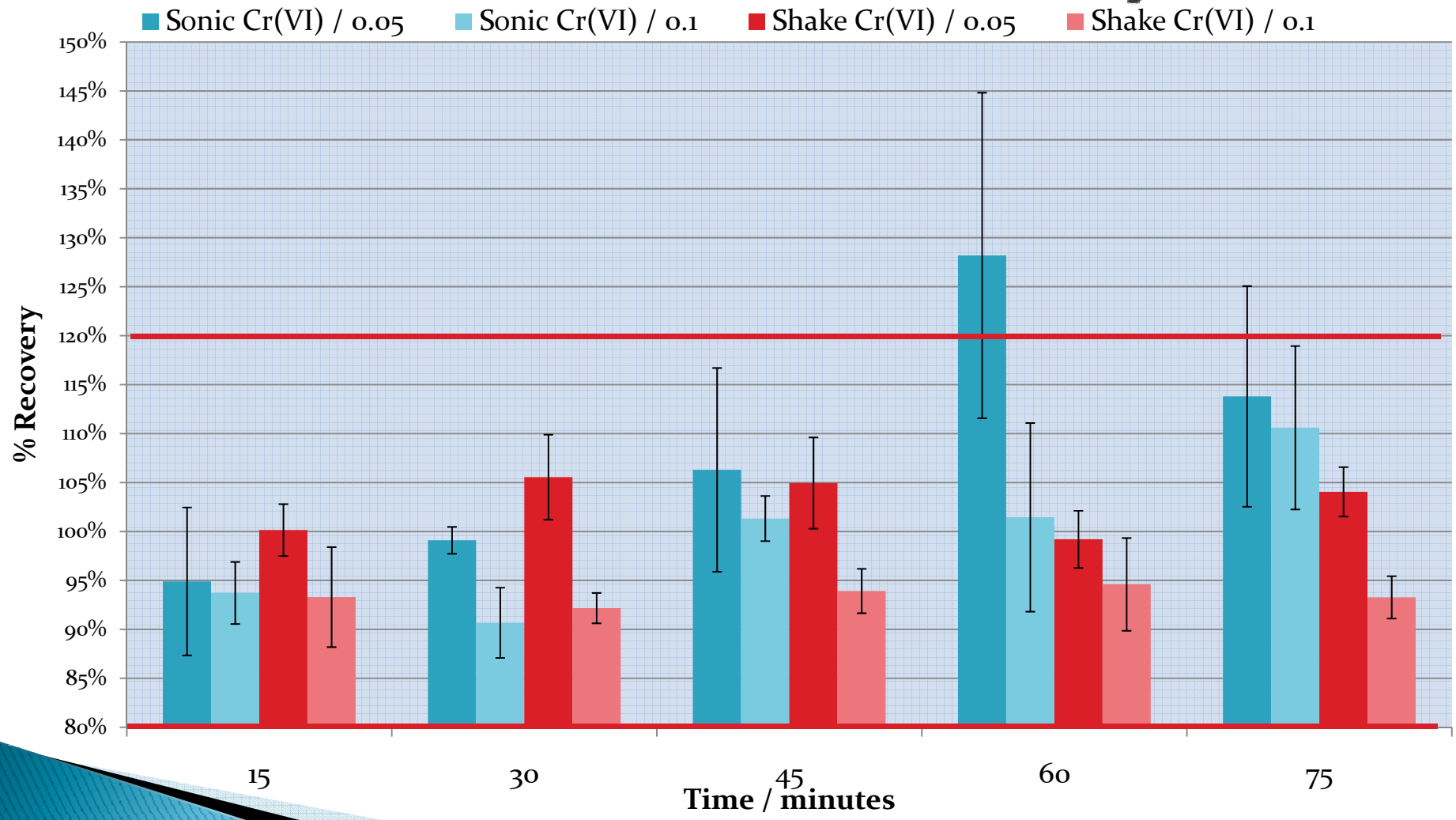
Currently prepare samples for analysis by sonicating filters in NaBicarb solution

- 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

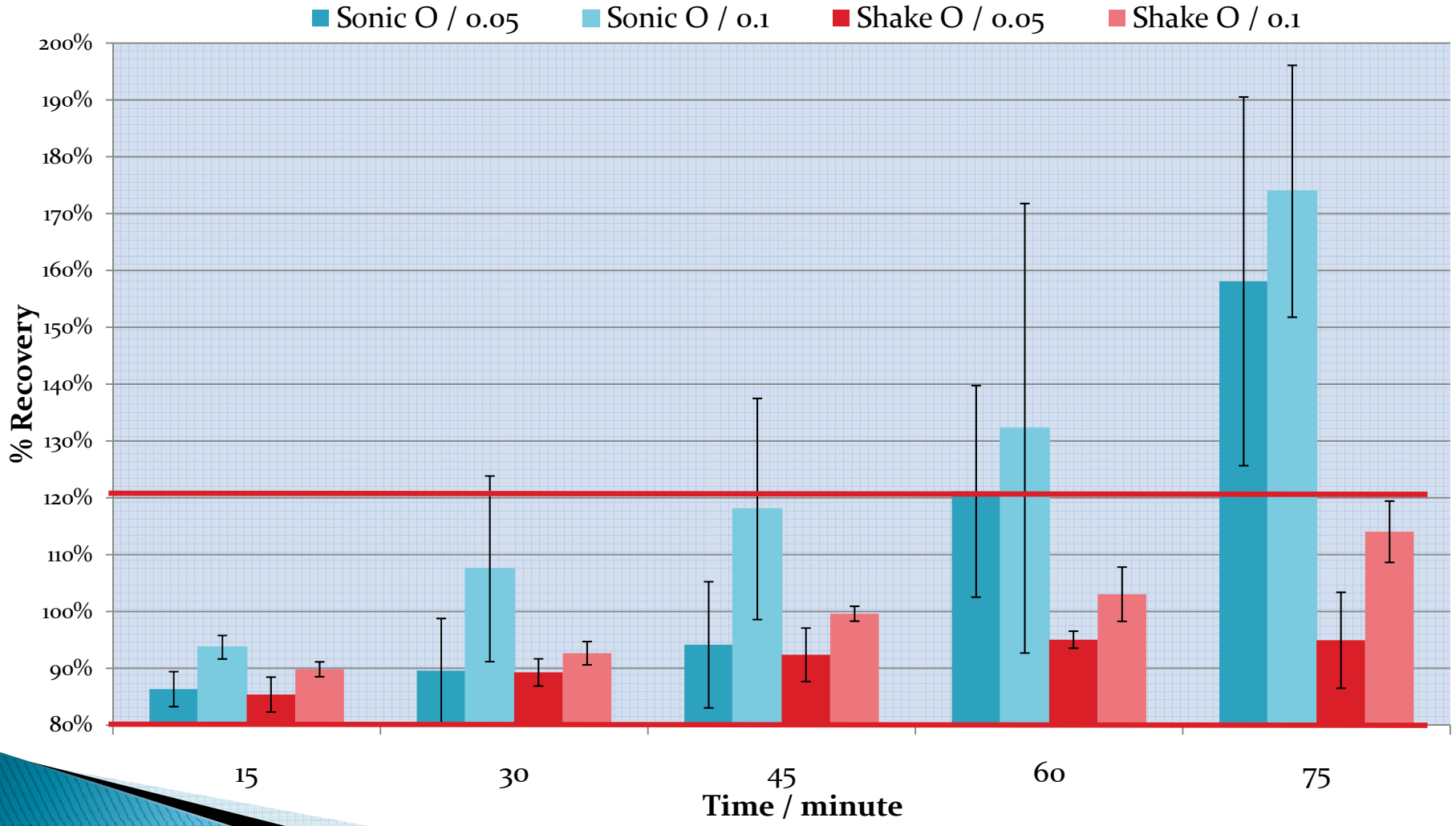
Hexavalent Chromium – Sample Prep

- 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

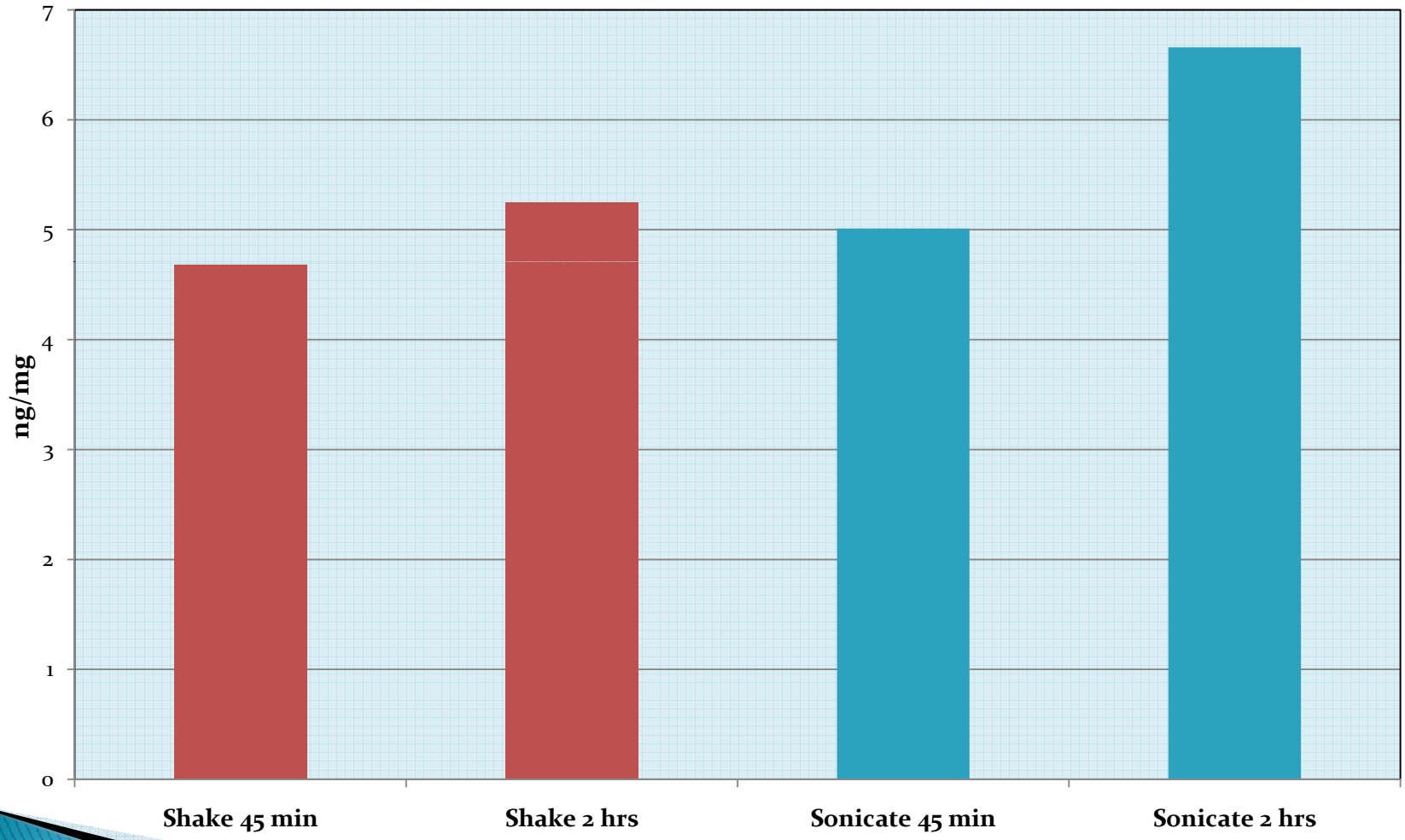
Hexavalent Chromium – Sonication vs. Shake – Cr^{6+} Only



Hexavalent Chromium – Sonication vs. Shake – Cr^{6+} & Cr^{3+}



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)

Acknowledgemnts

- US EPA
  - Mike Jones, OAQPS
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