Evaluation of Two Analytical Methods & Three Sampling Trains for the Measurement of Hexavalent Chromium in Ambient Air

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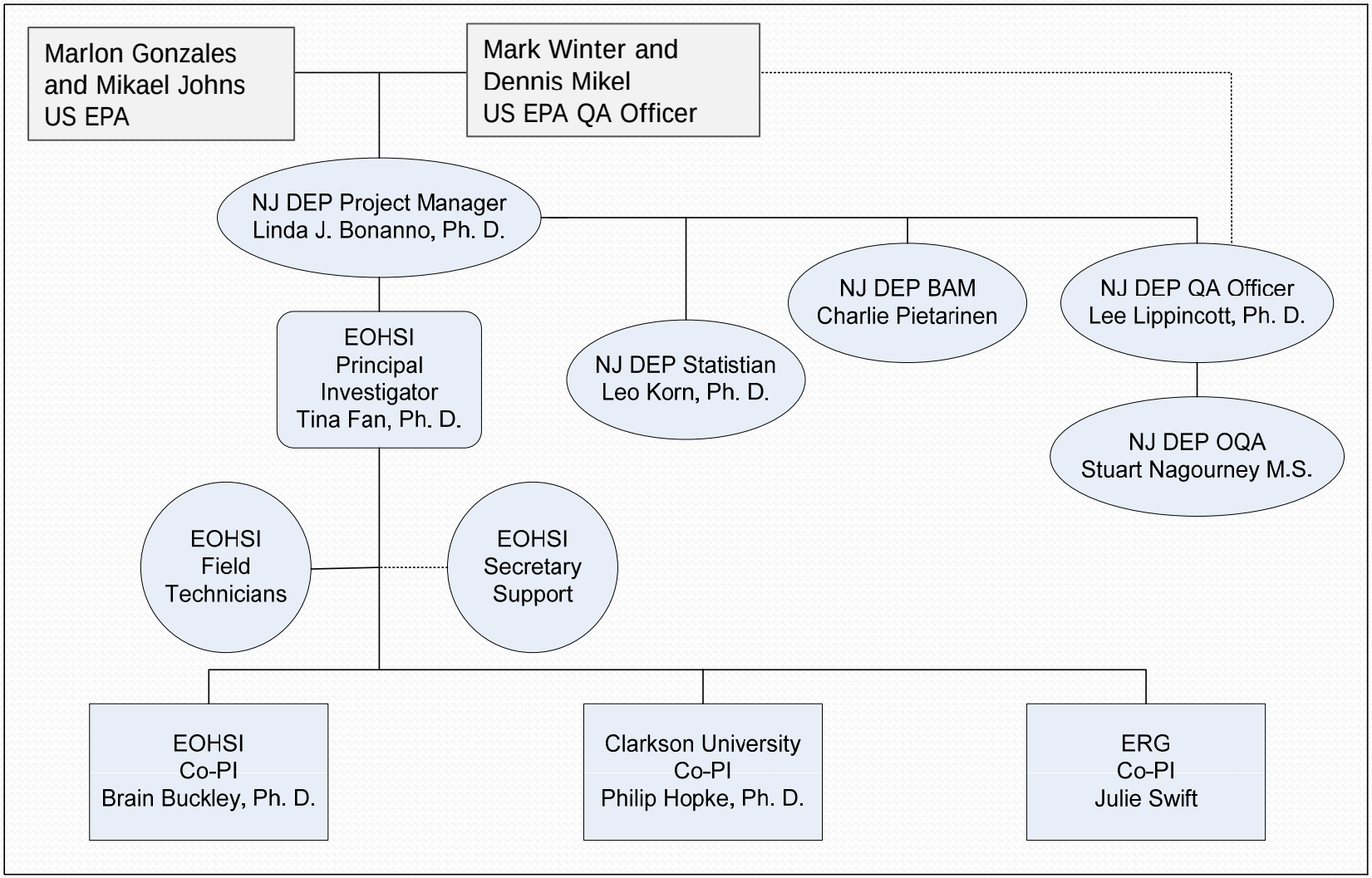
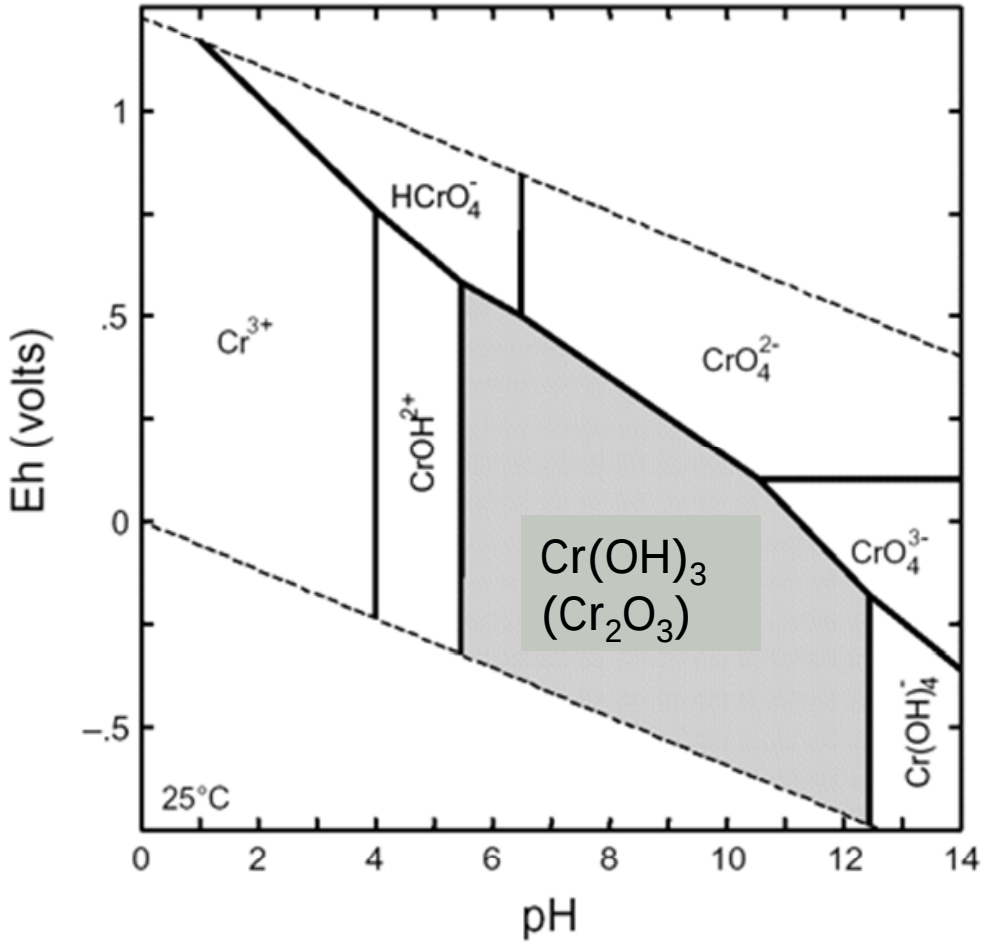
Project Management and Study Team



Background

- Hexavalent chromium [Cr(VI)] is recognized as a pulmonary carcinogen. Cr(VI) compounds have been enlisted as one of the 18 core HAPs by the USEPA.
- It is difficult to measure Cr(VI) because of its instability.
  - Cr(VI) $\leftrightarrow$ Cr(III)
- Cr(VI) is much more toxic and mobile than Cr(III). The interconversion can be affected by the particle matrix, e.g. pH, H_2S, transitional metals (Mn, Fe, etc.), organic acids, etc.

Eh-pH Diagram of Chromium (Ball, 1998)



Cr isotopes

^{50}Cr: ^{52}Cr: ^{53}Cr

4.35 : 83.79 : 9.50

Overview of Analysis Methods

- IC-UV method
  - developed by ERG
  - approved by USEPA
  - used for NATTS program

- IC-ICPMS method
  - developed by EOHSI
  - used in UCAMPP
  - "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air"
    - Evaluation of environmental factors on the measurements in controlled lab conditions

EOHSI Method IC-ICPMS

- Extraction filter samples w/ 5 mL HNO_3, pH=4, sonication for 40 min @ 60°C
- Injection of 400 µL of solution into IC for separation Cr(VI) and Cr(III)
- Detection with VG Elemental Plasma Quad 3 ICPMS. Dwell time 300 ms
- 6 pt calibration curve, 0.2, 0.5, 1, 2, 5, 10 ng/mL
- MDL = 0.075 ng/mL (equivalent to 0.0156 ng/m^3 for 24 m^3 < MRL(0.083 ng/m^3))

jls4

Slide 6

jls4 Is this the correct number now? In the last study you had 0.038 ng/mL ... x 5 mL / 21.6 m3 = 0.0088 ng/m3, correct?
Julie Swift, 3/23/2011

Potential +/-'s with EOHSI Method

Plus:

- Ability to detect isotopes of Cr(VI) and Cr(III) jls5
- Ability to determine potential conversion of Cr(VI) and Cr(III) for each sample
  - Conversion correction factor can be deduced empirically and applied across the board

Minus:

- Expensive
- Potential interference from Argon and other species
- To date, conversion does not mass balance
  - Cr(VI) to Cr(III) was 0-6% blanks, 0-18% for NIST
  - Cr(III) to Cr(VI) ranged from 1-12% for blanks, 9-36% NIST

Slide 7

jls5 CAN NOT SEE Cr(III). THIS STATEMENT SHOULD NOT BE INCLUDED
Julie Swift, 3/22/2011

EPA Approved NATTS Method (IC-UV)

- Extraction of filter for 1 hr by sonicating in 10 mL of 20 mM $NaHCO_3$ solution – during first part of study
  - During initial study, it was determined that there was potential conversion of Cr(III) to Cr(VI) during sonication. EPA Method has recently changed to *shaking* filters in 20 mM $NaHCO_3$ for 1 hour
- Anion exchange column derivatized by 1,5-diphenylcarbazide
- UV/VIS detection at 530 nm
- 6 pt calibration curve, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 ng/mL
- MDL from EPA laboratory Cr(VI) = 0.0027 ng/m^3

Potential +/-'s with EPA approved NATTS method

Plus

- Lower cost than IC-ICPMS method
- ~6 times more sensitive than IC-ICPMS method
- Precision and Accuracy tested and reported yearly (6 years of continuous data collected)
- Recovery is based on filter spiked with Cr(VI) solution, however uncertified NIST SRM has been tested with acceptable preliminary results (Detected 9.29 ng/mg, acceptable concentration range 9.0 – 14.0 ng/mg) jls7

Minus

- Cannot monitor conversion

Slide 9

jls7 Deleted comment about not being able to detect Cr(III) on filter. Filters were tested on ICPMS to determine if we were remoivng all of the Cr from the filters. We did not detect any Cr (total) in the acid washed filters. I do not think this is an accurate statement

Julie Swift, 3/23/2011

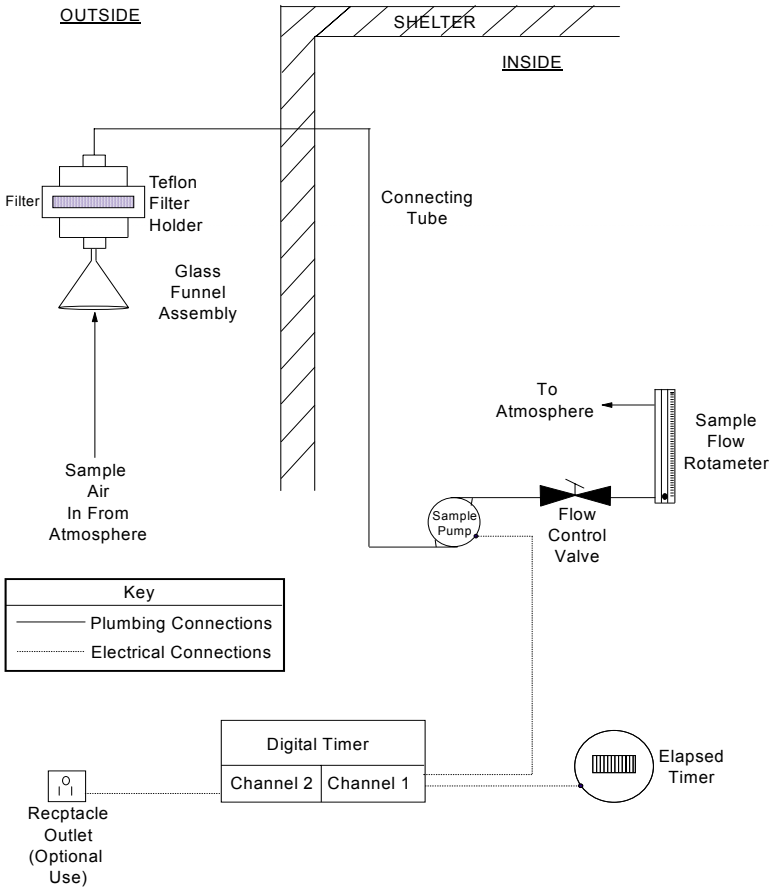
Overview of Samplers

- Three sampling trains
  - EPA approved method (NATTS)
    - Used in NATTS Program
    - Developed by ERG
  - ERG new prototype
    - Based on NATTS sampler - chilled sample holder
  - Developed by NYS (Dirk Felton) & Clarkson U (Phil Hopke)
    - Chills and dehumidifies sampling air stream

NATTS Sampler

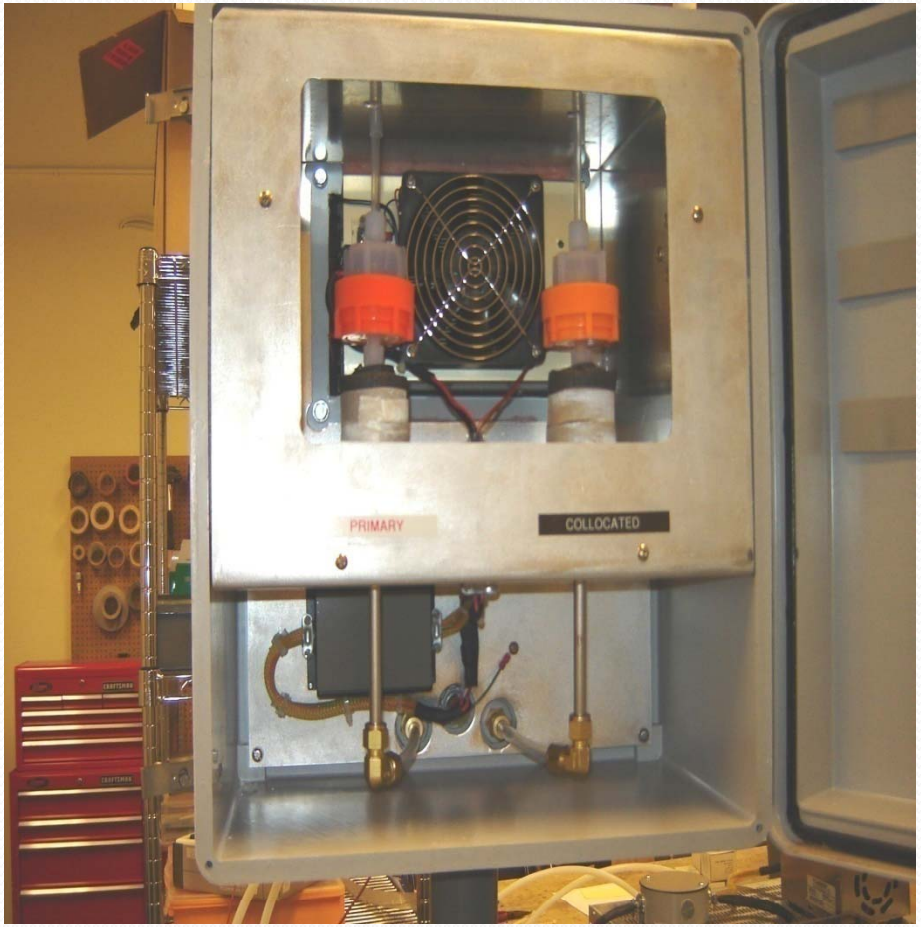
- EPA approved NATTS sampler
  - Collects TSP
  - Collect @15 L/min (total of 21.6 m^3) for a 24 hour period
  - 47 mm MCE filter
  - Pick up filters next day
    - If ambient temperature is ≤59°F, filters can stay in field for up to 3 days

NATTS Sampling System



ERG Prototype Sampler

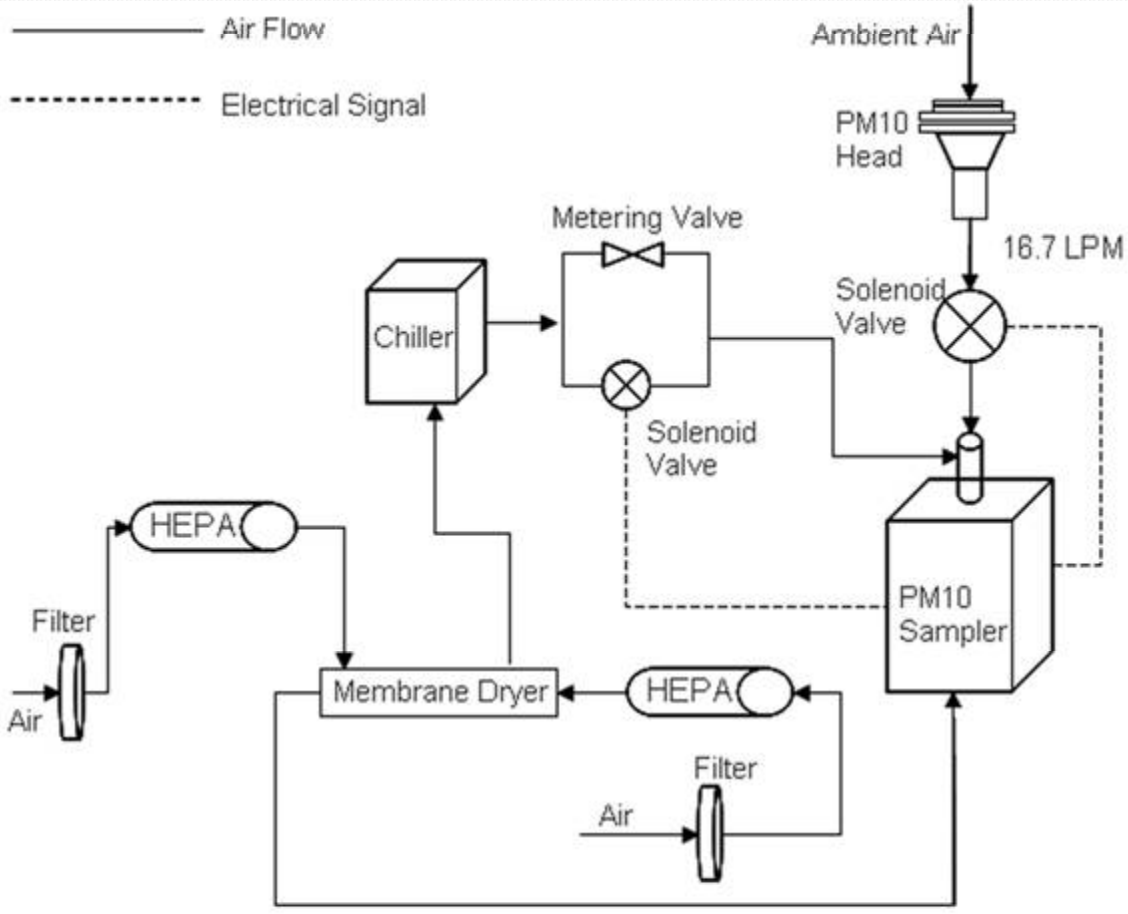
- Same design as NATTS sampling module
  - Collects TSP
  - Collocated sampler
  - ~15 L/min, 21.6 m^3 in 24 hours
- Differences:
  - Chilled filter housing with continuous temperature of 20°C until sample pick-up
  - Inverted filters
  - Pick up filters within 5 days after sampling



NYS/Clarkson Sampler

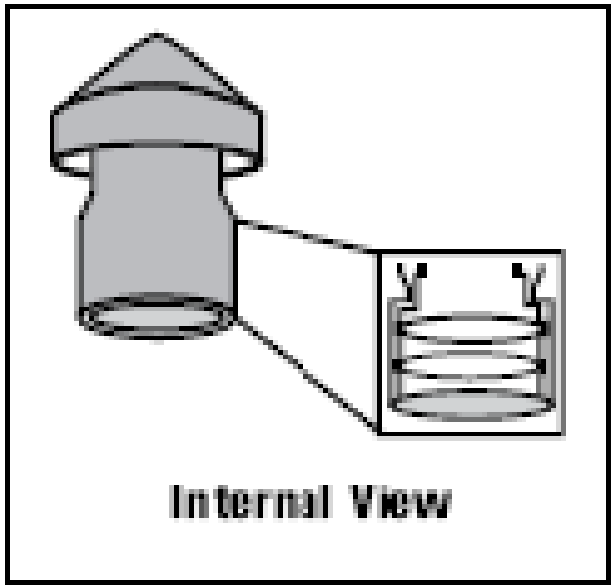
- Developed from PM_{10} FRM to preserve Cr(VI) during sampling (will change head to collect TSP)
- Allow filter to remain in sampler for up to three days to accommodate routine sampling schedules
- Reduce humidity (goal is 20% below ambient) and temperature (goal is 10% below ambient) during sampling

NYS/Clarkson Sampling System



NYS/Clarkson sampler Inlet

- Sampling flow rate 16.7 LPM
- URG-2000-30DG TSP sampling head



Objectives of the Study

- Analytical Module – evaluation of the two analysis methods
- Field Sampling Module – evaluation of the three sampling train and potential impact of environmental factors on the measurement of Cr(VI)

Analytical Module

Evaluate the 2 analytical methods

- All Cellulose filters are prepared at ERG. All MCE filters prepared at EOHSI. The filters are spiked at EOHSI and sent to ERG, Clarkson, and kept in-house.

Spiking of Filters (7 filters + 3 blanks per round)

Sample Type	Cr(VI) Standard	^{50}Cr(III) and ^{53}Cr(VI) Isotopes	NIST 1648a Particles
I	√		
II		√	
III			√
IV	√		√
V		√	√
VI	√	√	√

jls15

Slide 18

jls15 inserted table instead of text. it might be easier quickly to present this way
Julie Swift, 3/23/2011

Spiking of Filters

- High level isotope spike - make sure that Cr(VI) can be detected, even if it decays to certain degree. jls2
- Low level spike - make sure that the recovery of Cr(VI) agrees with real world samples jls9
- Store in freezer until shipped

Slide 19

jls2 This is an extremely large amount of spike to add to prepared filters, if the spike solution is not prepared in NaBicarb. It is possible that some conversion could take place on the cellulose filters because you are washing off the coating. We do our spikes with anything greater than 10 µL!
Julie Swift, 3/23/2011

jls9 This makes the whole study questionable, don't you think? What are we basing the study on if we decay before we start? This does not happen on the cellulose filters as shown in the first study (I don't think it happened for the IC-ICPMS, either). Maybe we need to delete the "even if it decays to a certain degree" part of the statement.
Julie Swift, 3/22/2011

Spiking Filters with NIST SRM 1648a Urban Particulate Matter (UPM)

- Filters will be weighed prior to spiking
- ~ 5 mg of UPM will be collected on a filter jls10
- Shake filters to remove any loose material
- Weigh filters
- Fold and place into polystyrene vials
- Ship overnight on dry ice w/thermometer jls3
- Put on dry ice at EOHSI on dry ice until samples are received by ERG and Clarkson

Slide 20

jls3 Removed "Glass vials"... are other labs using glass or the polystrene vials we use? Glass would contribute Cr background
Julie Swift, 3/22/2011

jls10 teflon? glass would contribute Cr
Julie Swift, 3/23/2011

Filter Spiking Overview, Cont

- Shipping vials for NIST spikes will be used as the extraction vials to prevent loss of sample
- Expected analytical precision and bias within 20%
  - If precision is not met, 10 more filters sent out for analysis
- Replicate analysis will be done on all filters analyzed by IC-UV and IC-ICPMS

Additional QA/QCs

- Spiked filters by the same person
- Recorded in lab notebook and not shared with analytical person
- Dedicated syringes (the plunger jls1 is Teflon-coated) for each type of solution.

jls8

Slide 22

jls1 A micropipette may work better than a syringe. They seem to be more accurate than the syringes are.
Julie Swift, 3/22/2011

jls8 I do not understand what we are trying to say here
Julie Swift, 3/22/2011

Wibby Audit Samples

Filter Type (N=1 for each type)	Clarkson		EOHSI		ERG	
	Measured Cr(VI)	Recovery or Conversion	Measured Cr(VI)	Recovery/ Conversion	Measured Cr(VI)	Recovery/ Conversion
IC-UV						
Complete blank	ND	NA	ND	NA	ND	NA
Acid blank	ND	NA	ND	NA	0.44 ng	NA
0.75 ng ^{nat}Cr(VI) spiked	0.76 ng	101%	0.75 ng	100%	0.83 ng	111%
8.0 ng ^{nat}Cr(III) spiked	2.00 ng	[a]25%	3.54 ng	[a]44%	0.93 ng	[a]12%
IC-ICPMS						
Complete blank	ND	NA	ND	NA	NA	NA
Acid blank	0.31 ng	NA	ND	NA	NA	NA
0.75 ng ^{nat}Cr(VI) spiked	0.12 ng	16%	0.92 ng	123%	NA	NA
8.0 ng ^{nat}Cr(III) spiked	0.06 ng	[a]0.8%	2.85 ng	[a]36%	NA	NA

Note: ERG analyzed samples by IC-UV method only

[a]Conversion from Cr(III) to Cr(VI)

Recovery and Conversion of Cr Species (IC-UV)

Filter Type	Clarkson		EOHSI		ERG	
	Measured Cr(VI)	Recovery or Conversion	Measured Cr(VI)	Recovery or Conversion	Measured Cr(VI)	Recovery or Conversion
Blank (N=3)	0.46 ng	NA	ND	NA	ND	NA
0.5 ng ^{nat}Cr(VI) spiked (N=5)	0.88 ng	175(17)%	0.72 ng	144(27)%	[a]0.31 ng	123(7)%
1.5 ng ^{nat}Cr(VI) spiked (N=7)	1.47 ng	98(26)%	1.45 ng	97(14)%	1.51 ng	101(5)%
1.66 ng ^{53}Cr(VI) + 11.0 ng ^{50}Cr(III) spiked (N=7)	3.28 ng	198(52)% [c]15(106)%	[b]8.35 ng	503(9)% [c]61(11)%	3.81 ng	229(43)% [c]20(76)%
10.0 ng ^{nat}Cr(III) spiked (N=7)	2.27 ng	[c]23(62%)	[b]6.03 ng	[c]60(23)%	0.64 ng	[c]6(43)%

Recovery/conversion percent represented as AVG(RSD) from 5~7 filters
[a]ERG spiked at 0.25 ng/filter
[b]Sonicated three times
[c]Conversion from Cr(III) to Cr(VI)

Recovery and Conversion of Cr Species (IC-ICPMS)

Filter Type	Clarkson			EOHSI		
	^{50}Cr(VI)	^{52}Cr(VI)	^{53}Cr(VI)	^{50}Cr(VI)	^{52}Cr(VI)	^{53}Cr(VI)
Blank (N=3)	NA	6.52 ng	NA	NA	0.50 ng	NA
1.5 ng ^{nat}Cr(VI) spiked (N=7)	NA	1.16 ng 77(63)%	NA	NA	2.20 ng [a]114(21)%	NA
1.66 ng ^{53}Cr(VI) + 11.0 ng ^{50}Cr(III) spiked (N=7)	1.29 ng [b]12(78)%	NA	1.91 ng 115(11)%	2.97 ng [b]27(32)%	NA	1.46 ng 88(1)%
10.0 ng ^{nat}Cr(III) spiked (N=7)	NA	1.28 ng [b]13(76)%	NA	NA	3.16 ng [b]32(21)%	NA

Note: ^{52}Cr(VI) represents the overall Cr(VI) in the sample; NA: not applicable
Recovery/conversion percent represented as AVG(RSD) from 7 filters
[a]FB subtracted
[b]Conversion from Cr(III) to Cr(VI)

Field Evaluation Module

- In order to determine if all samplers are collecting the same TSP
- Collocate at Elizabeth site, NJ
  - 4 NYS samplers- 4 filters
  - 2 NATTS samplers- 4 filters
  - 2 ERG protytype samplers- 4 filters

Field Evaluation Module-cont

- Purpose: to evaluate NYS, NATTS and ERG prototype samplers to preserve the integrity of Cr(VI) in the field under current NATTS protocol
  - If 1 sampler does better job of preservation, we would expect to see higher concentrations of Cr(VI) and better precision of duplicates.

jls13

Slide 27

jls13 Is this necessarily true? What if we are converting Cr(III) to Cr(VI)... then the Cr(VI) values will decrease, won't they? Larger concentrations cannot be the way to determine if the sampler is doing a good job at preserving the sample.

Interconversion between Cr(III) and Cr(VI) occurs and is not well understood yet. Precision and accuracy when a known concentration of Cr(VI) and Cr(III) is measured determines if the sampler is preserving the sample's original Cr(VI) and Cr(III) concentrations or ratio.
Julie Swift, 3/23/2011

Field Sampling, Cont

- All filters isotope spiked on MCE filters (IC-ICPMS analysis) before sampling to examine effect of natural environment, shipping, extraction, analyses on interconversion.
- Duplicate field blanks are left in field during sampling jls14
- All labs will get duplicates for each sampling and analytical method

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jls14 Did I interpret this statement correctly? It did not make sense so I revised it. It previously read "Field blanks collected to duplicate filters left in field"

Julie Swift, 3/23/2011

Field Sampling, Cont

- PM mass concentration for 3 days of sampling
- 3 days as pilot study so EOHSI can resolve any field sampling, COC, equipment issues etc

- 16 weeks summer, generally expect high ozone, high temp, high RH

- 16 weeks winter, generally expect low ozone, low temp, RH can be variable

Acknowledgements

- Team at the NJDEP
- Team at Clarkson, EOHSI, and ERG
- Dirk Felton, NYSDEC
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