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

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- This project will evaluate two analytical methods for measurement Cr(VI) in ambient air
  - IC-UV method
    - developed by ERG,
    - approved by USEPA,
    - currently used in NATTS
  - IC-ICPMS method
    - developed by EOHSI
    - used in UCAMPP
    - currently in second half of 2 year project "Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air".

And two sampling trains

- EPA approved method (NATTS)
  - Currently used in NATTS
    - developed by ERG

- Developed by NYS (Dirk Felton) & Clarkson U (Phil Hopke) (NYS)

Overview of Presentation

- Questions
- Who is going to do what
- Overview of IC-UV and IC-ICPMS Analytical Methods
- Cleaning and pretreatment of filters
- Spiking of filters for analytical module
- Overview of sampling trains
- Field sampling design

Do both sampling trains collect the same particles?

How many filters are needed?

# of samples/duplicates/field blanks for field module

Impact of passive sampling

How to clean all the Cr out of filters before pretreatment

- Clarkson U (Phil Hopke)
  - Build 4 samplers (1 filter each)
  - IC-ICPMS and IC-UV method
- ERG, Inc (Julie Swift)
  - Supply 2 NATTS samplers (2 filters each)
  - IC-UV method
- EOSHI (Zhi-Hua (Tina) Fan)
  - prepare, spike and ship filters
  - field sampling and ship filters
  - IC-ICPMS and IC-UV method

EOHSI Method

- Extraction w/ 5 mL HNO3, pH=4, sonicated 40 min @ 60℃
- Injection of 100 µL of solution into ion chromatograph for separation Cr(VI) and Cr(III)
- Detection with VG Elemental Plasma Quad 3 ICPMS. Dwell time 300 ms
- 6 pt calibration curve, 0.5,1,2,5,10, 25 ng/mL

Previously determined **MDL for Cr(VI) = 0.16 ng/m^3**

The MDL is expected to be improved by reducing the Cr(VI) filter background with acid wash.

Some potential +/-'s with EOHSI Method

- Ability to see Cr(III) so know if on cleaned filter
- Monitor conversion
  - It is hoped that a conversion correction factor can be deduced empirically and applied across the board.
- Expensive
- Recovery based on isotope spiked filter and isotope spiked NIST dust
- To date, conversion does not mass balance
  - Interconversion of Cr(III) to Cr(VI) ranged from 1-12% for blanks, 9-36% NIST
  - Cr(VI) to Cr(III) was 0-6% blanks, 0-18% for NIST

EPA Approved NATTS Method IC-UV

-Extracted 1 hr by sonicating filter and 10 mL 20 nM $NaHCO_3$ solution in DI water

-Anion exchange column derivitized by 1,5-diphenylcarbazide

-UV/VIS detection at 530 nm

MDL = 0.0065 ng/m^3

Some potential +/-’s with EPA approved NATTS method

- Lower cost than EOSHI method
- Can’t see Cr(III) so don’t know if still some on cleaned filter
- Can’t monitor conversion
- Recovery is based on filter spiked with Cr(VI) solution. May not be representative of Cr(VI) in ambient air PM

Filter pretreatment (both methods)

  - For this project, all cellulose filters are to be bought at the same time to reduce batch differences
- Soak filters in 10% (v/v) nitric acid solution overnight
- Rinse filters with DI until pH=5-6
- Dry in nitrogen environment
- Pretreat the cleaned filters with 10 g/L $NaHCO_3$ solution by soaking the filters overnight
- Dry the filters in the nitrogen environment

- Store the pre-treated filters at -15℃ until use
- After spiking / sampling, filters stored in Petri dishes in dedicated freezer at -15℃

- 10% of cleaned and pretreated filters will be checked to make sure all filter contamination has been removed.

New Cleaning Procedures

- The current cleaning procedures are sufficient to remove Cr(VI) but not Cr(III).
- New cleaning protocols will be evaluated, such as:
  - soak the filter in the nitric acid solution and then sonicate the filter in a hot water bath (60℃)
  - After cleaning with nitric acid, then try strong basic solution
  - Any ideas?

Analytical Module

- Evaluate the 2 analytical methods
  - All filters prepared at EOHSI and sent to ERG and Clarkson

Spiking of Filters

- 10 filters + 2 blanks per condition
  - Known conc Cr(VI) solution
  - NIST 1648 dust where total Cr is known but not Cr(VI)/Cr(III) ratio
  - Stable isotope solution USEPA method 6800
  - NIST 1648 dust with known Cr(VI) solution
  - NIST 1648 dust with stable isotope
  - NIST 1648 dust, stable isotope and Cr(VI) solution

Spiking of filters

- All will be spiked by same person
- Recorded in lab notebook and not shared with analytical person
- Dedicated syringes (the plunger is Teflon-coated) for each type of solution.
- Spiking with solution at 10x greater concentration than dust so that is what we'll base recovery on

- since small amount of solution (50 µL) used to spike, it is expected that filter will sorb entire solution
- spike high level of Cr(VI) isotope to make sure it can be detected, even if it decays to certain degree.
- 1 high concentration of Cr(VI) solution
- Stored in freezer till shipped on dry ice.
- When filters to be shipped are placed on dry ice, the filters that stay at EOSHI will also be put on dry ice until filters are received at other laboratories and frozen.

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

- Filters will be weighed prior to spiking
- ~ 5 µg of UPM will be ground into filter using glass stirring rod
- Shake filters to remove any loose material
- Weigh filters
- Fold and place into glass vials
- Overnight shipping on dry ice w/thermometer
- Samples at EOHSI also put on dry ice until samples received by ERG and Clarkson

- Interconversion can occur during shipping, extraction and analysis
- This will be assessed with filters spiked with isotope solution by IC/ICPMS methods.
- Spike before shipping
  - assume conversion of Cr(VI)/Cr(III) is the same in all filters for each method (IC-UV & IC-ICPMS)
    - IC/ICPMS can detect both Cr(VI) and Cr(III)

- The shipping vials will be used as the extraction vials so no transfer and potential loss of sample will not occur

- Analytical precision and bias should be within 20% or 10 more filters sent out for analysis.

- Replicate injections will be done on all filters for both methods

Statistical Analyses

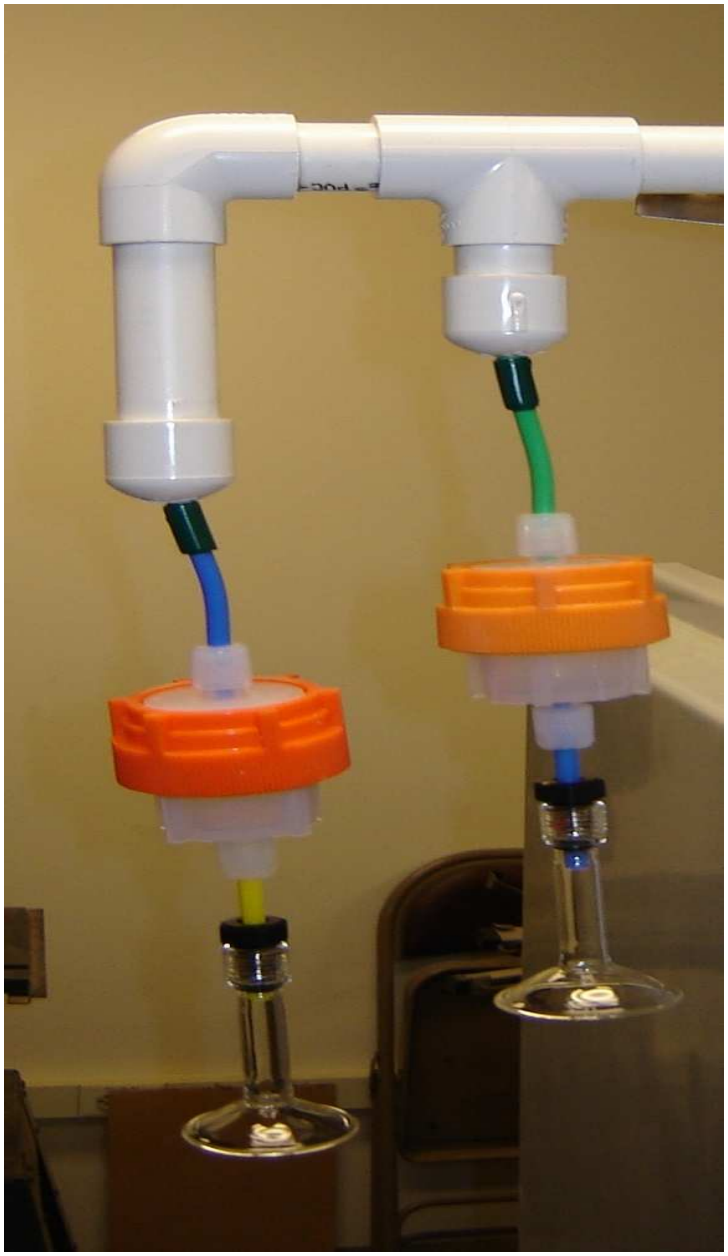
- ANOVA when 3 labs do same method, for same filter spiking condition
- t-test when 2 labs do same method for same filter spiking condition
- Or nonparametric methods if need be
- Difficult to predict if this will provide useful statistics

- EPA approved NATTS sampler
  - Collects TSP
  - Pick up filters next day unless ambient temperature is ≤59℉, than filters can stay in field for up to 3 days
  - Currently being modified to relax p/u restrictions

NATTS Sampler

- ~15 L/min for a total of 21.6 m^3 for a 24 hour period.
- Filter holders are SKC Product Code: 225-1712.
- They are built for 47 mm filters, with 1/4" ferrule nuts and wrench set.
- http://www.skcshopping.com/ProductDetails.asp?ProductCode=225-1712

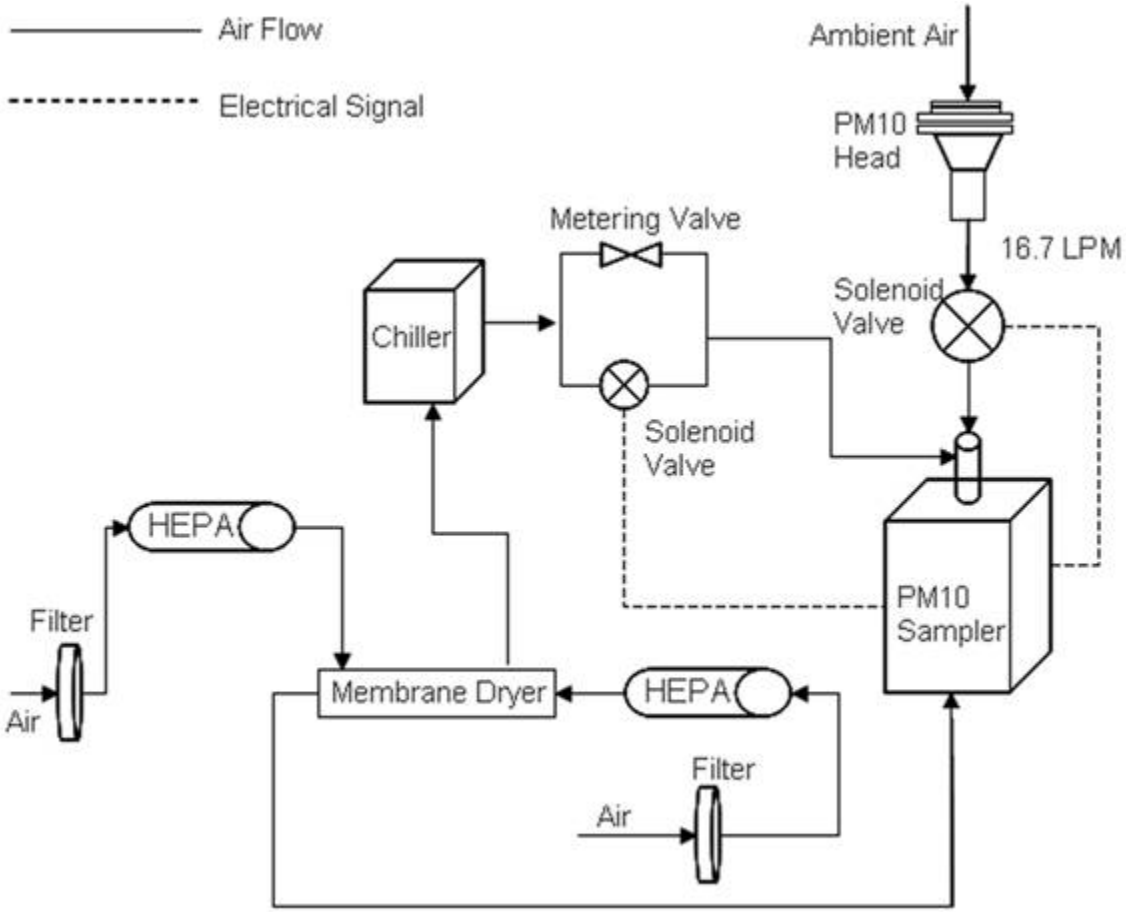

ERG



NYS/Clarkson Sampler

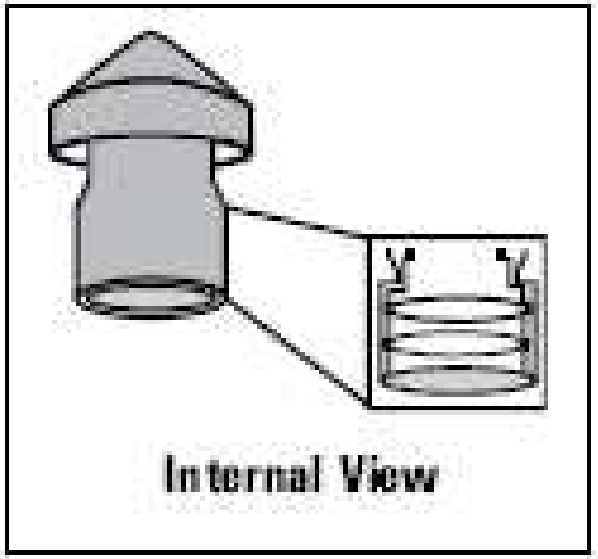
- Developed from PM_{10} FRM to preserve Cr(VI) during sampling (will change head to collect TSP)
- Allow filter to remain in sampler for up to three days to accommodate routine sampling schedules
- Reduce humidity (goal is 20% below ambient) and temperature (goal is 10% below ambient) during sampling

NYS/Clarkson Sampling System



NYS/Clarkson sampler Inlet

- Sampling flow rate 16.7 LPM
- URG-2000-30DG TSP sampling head
  - Teflon® Coated Aluminum
  - 1.25” ID with O-Rings
  - Fits Thermo’s TEOM and Partisol
  - Used as Inlet Cover on Custom Manifolds
  - Fits any Beta Gauge with a 1.246” OD Inlet Tube
  - Dimensions: 2 ½” OD x 2 5/8” Height
  - Weight 0.3 Lbs


Internal View

TSP collection assessment

- In order to determine if both samplers are collecting the same TSP
- Collocate
  - 4 NYS samplers- 4 filters
  - 2 NATTS samplers- 4 filters

Assessment of TSP

- Mass concentration for 2 (??) days of sampling providing 8 filters/sampler type
- Particle size distribution for 1 (??) day of sampling providing 4 filters/sampler type
  - Automated electron microscopy??
  - Morphology and elements (~$750/filter)??
  - Metal Analysis??

Field Sampling Module

- Purpose: to evaluate NYS and NATTS 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 Cr6 and better precision of duplicates.

Field Evaluation

- In order to get enough samples for field module, we need to be able to collect samples 2x's/week (p/u and set up same day)
- NJDEP is currently looking for suitable site (access on weekends required)
- Met station will be set up at site (if one is not already there)

Field Sampling

- Two dual channel NATTS samplers & four single channel NYS samplers will be collocated & sample midnight to midnight.

  – Pick up 2 filters/sampler type next day and leave other 2 in field until 3rd day after sampling to replicate routine monitoring.

- 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 

- All filters spiked before sampling to examine effect of natural environment, shipping, extraction, analyses on interconversion.

- Field blanks collected to duplicate filters left in field

- All labs will get duplicates for each sampling method and analytical method

Field sample matrix

Please See Handout

10 sample days will provide 1set duplicates/ analytical method/sampling train/pickup day and 1 set of FB/ analytical method/sampling train/pickup day

If repeated 4 times, 4 sets duplicates /analytical method/sampling train/pickup day and 4 sets of FB/ analytical method/sampling train/pickup day

day	NATTS	NATTS	NATTS	NATTS	NYS	NYS	NYS	NYS
1	IC-UV p/u day 1	IC-UV p/u day 3	IC-UV p/u day 1	IC-UV p/u day 3	IC-UV p/u day 1	IIC-UV p/u day 3	IC-UV p/u day 1	IC-UV p/u day 3
2	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3
3	IC-UV p/u day 1	IC-UV p/u day 3	IC-UV p/u day 1 FB	IC-UV p/u day 3 FB	IC-UV p/u day 1	IIC-UV p/u day 3	IC-UV p/u day 1 FB	IC-UV p/u day 3 FB
4	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3	IC-ICPMS p/u day 1 FB	IC-ICPMS p/u day 3 FB	IC-ICPMS p/u day 1	IC-ICPMS p/u day 3	IC-ICPMS p/u day 1 FB	IC-ICPMS p/u day 3 FB

- 8 filters/ analytical method/sampling train/p/u day
- 4 FB/analytical method/sampling train/p/u day

Blanks ???

- lab blanks – dealt with in analytical module
- 2 trip blanks ???necessary??
- 4 field blanks/sampling method/analytical method

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