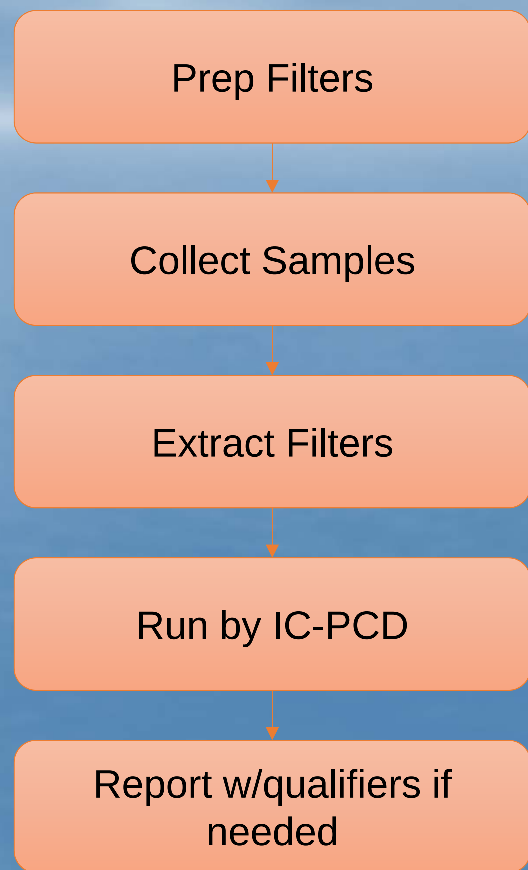
HEXAVALENT CHROMIUM IN AMBIENT AIR

A Practical Guide to:

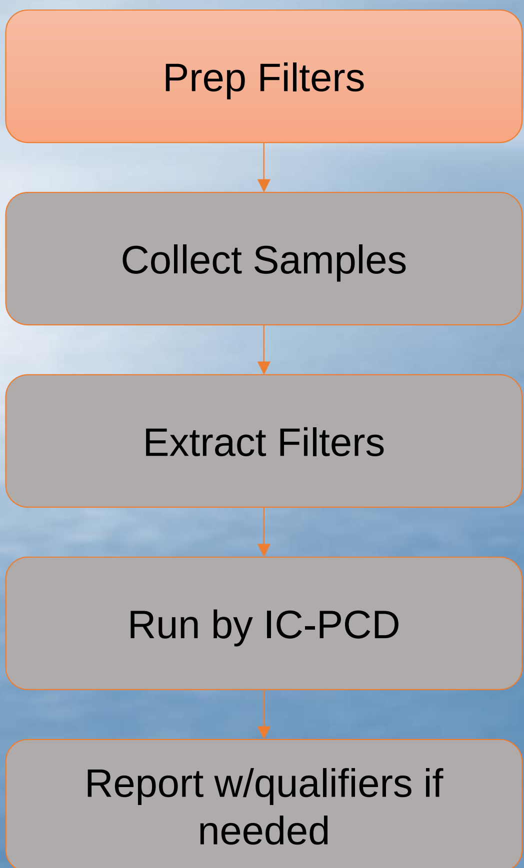
ASTM D7614-12: *Determination of Total Suspended Particulate (TSP)* ***Hexavalent Chromium in Ambient Air*** *Analyzed by Ion Chromatography (IC) and Spectrophotometric Measurements*

Sheri Heldstab
CHESTER LabNet

ASTM METHOD FLOW CHART



FILTER CLEANING & IMPREGNATION



1. Filter type: Acid Hardened Cellulose. 47 mm Whatman Grade 541 or Ahlstrom Grade 55 (37 mm by custom order only)

2. Filter Cleaning & Impregnation:

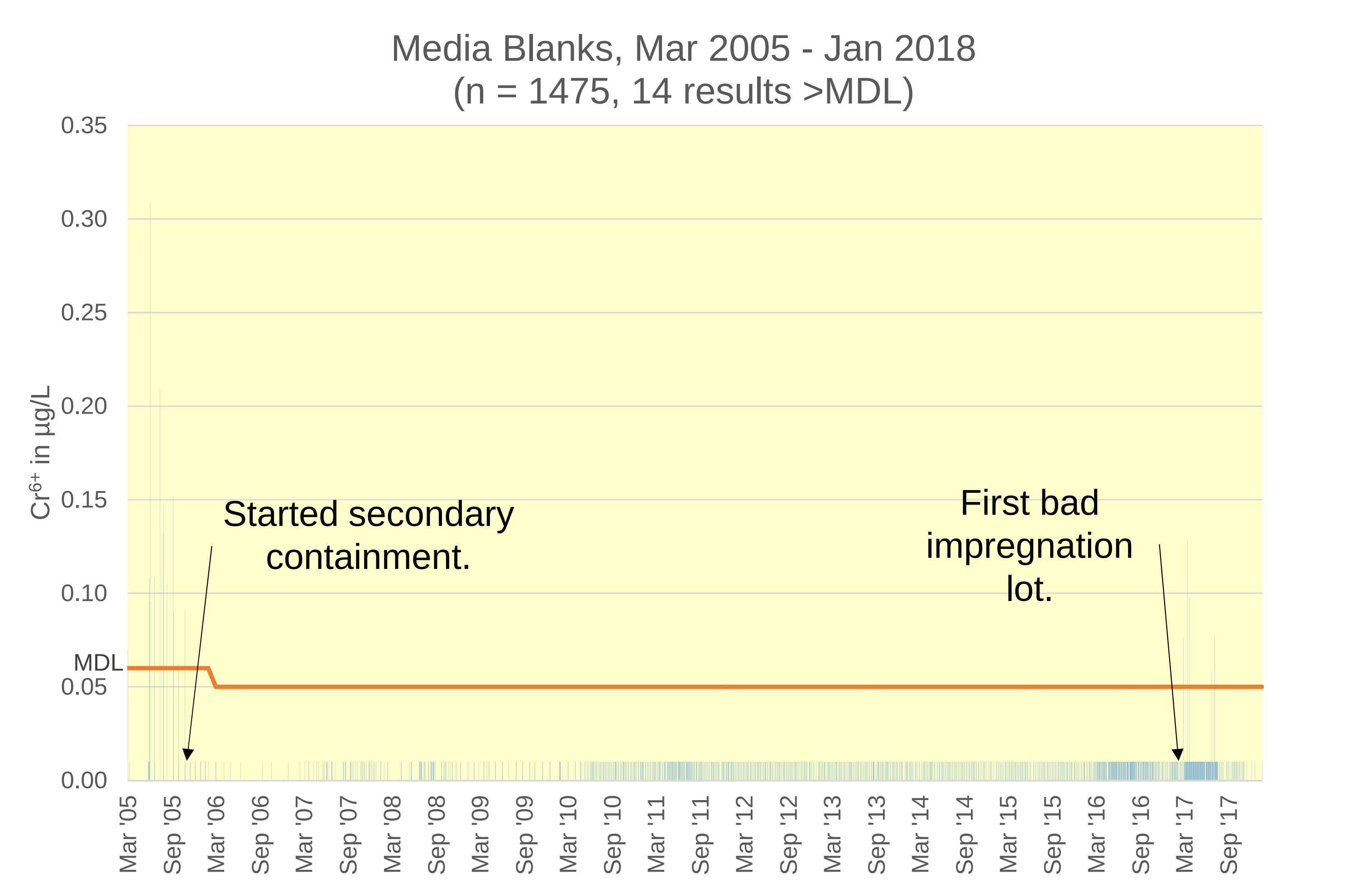
   A. Need clean area, does not have to be glove box.
   B. If using clean filters, do not need to follow cleaning protocol as described in method.
   C. Recommend at least one round of cleaning with extraction solution to oxidize any Cr^{3+} to Cr^{6+}.

3. Impregnate with 120 mM $NaHCO_3$. Dry in clean environment on non-metallic surface w/good airflow.

4. Impregnation Lot Check - prescreen at least 10% before using.

5. **<u>Store frozen in well sequestered container(s).</u>**

MEDIA BLANKS



CASSETTE TYPES

Prep Filters

Collect Samples

Extract Filters

Run by IC-PCD

Report w/qualifiers if needed

1. Cassette type: Federal Reference Method (FRM or $PM_{2.5}$) or PTFE as described in ASTM method.

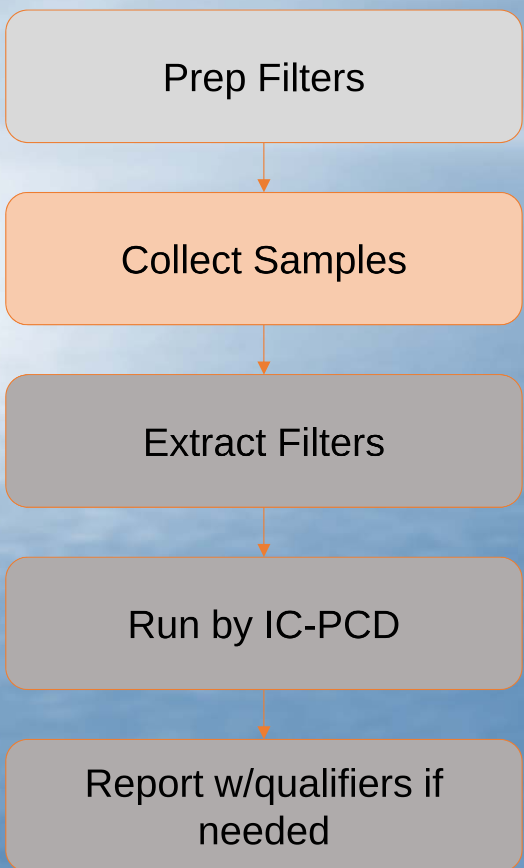
- FRM Pro's: Easy to load, easy to ship, no glass to break, familiarity
- FRM Con's: Easy to lose deposit esp. larger particles, metal support screens

- Teflon Pro's: difficult to contaminate, don't lose particulate.
- Teflon Con's: loading difficult, requires glass funnels (breakage), static will trap fine PM on inside of cassettes, ~$100/cassette

2. Both require shipping "frozen"

3. Both need secondary container, FRM needs tertiary container.

SAMPLE COLLECTION & SHIPMENT



1. Freeze cassettes/filters until sampling.

2. Freeze immediately after sampling.

    A. “After sampling” means when sampler turns off.
    B. EPA 3-day or 6-day sampling schedule = lost sleep.

2. Ship frozen:

    A. Blue ice not ideal as it likely won’t stay <0 °C
    B. Dry ice will survive overnight shipping at <0 °C, however, is HazMat
    C. Any possible shipping delays, keep in freezer until overnight delivery is more realistic.
    D. Helpful Hint: use cooler boxes instead of plastic coolers. They’re better insulators and cheaper to ship.

SAMPLE RECEIPT AND UNLOADING

- Prep Filters
- Collect Samples
- **Extract Filters**
- Run by IC-PCD
- Report w/qualifiers if needed

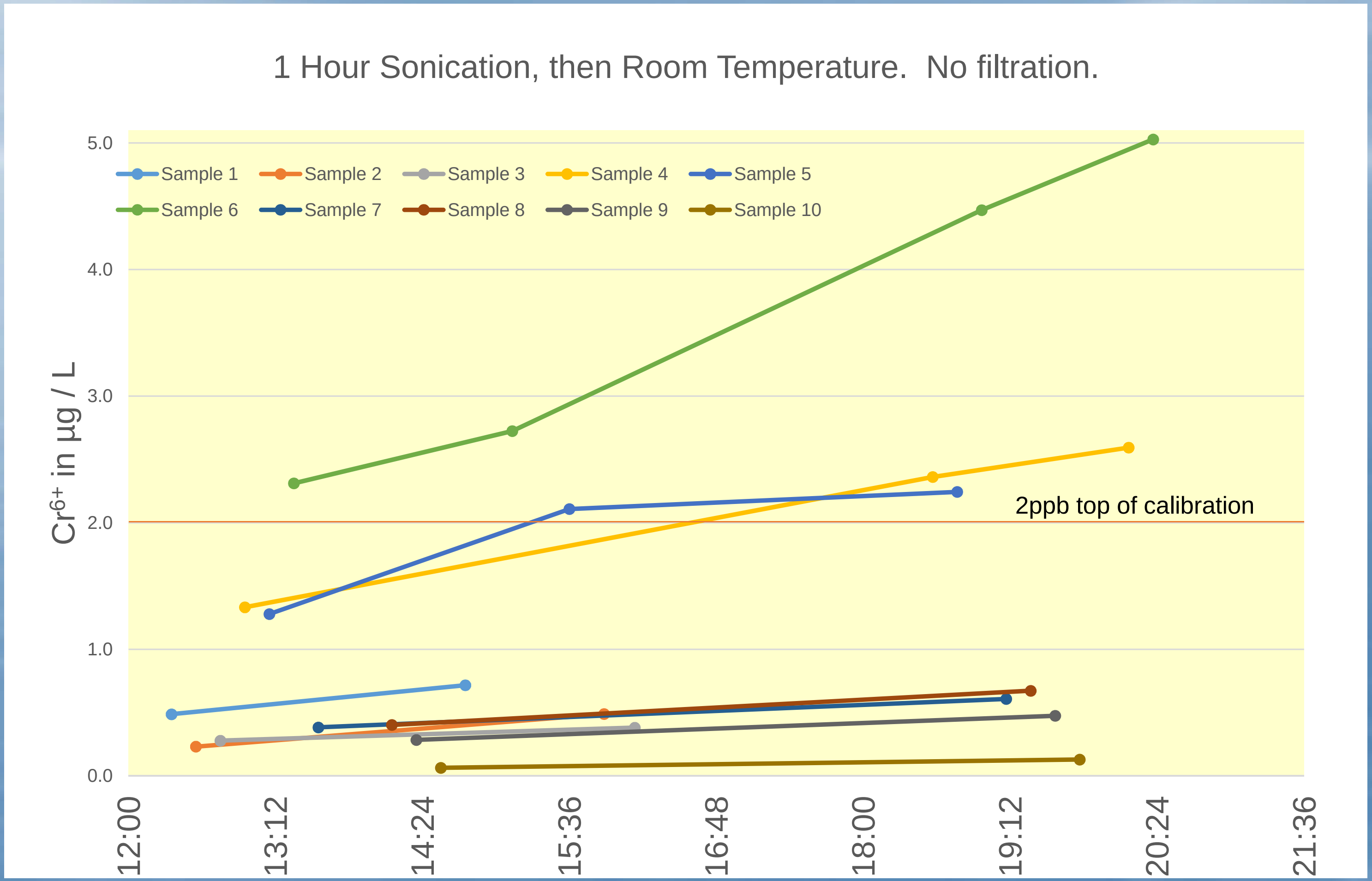
1. Upon receipt, record temperature of container using IR thermometer.
2. Unload Cassettes:
   A. Unload in same location as loading took place.
   B. Put filter directly into extraction vessel and cap tightly
   C. Store in freezer until ready to extract.
3. Nitrile and Latex gloves react with DPC. Use PVC gloves if using gloves. Recommend using plastic forceps instead.

FILTER EXTRACTION

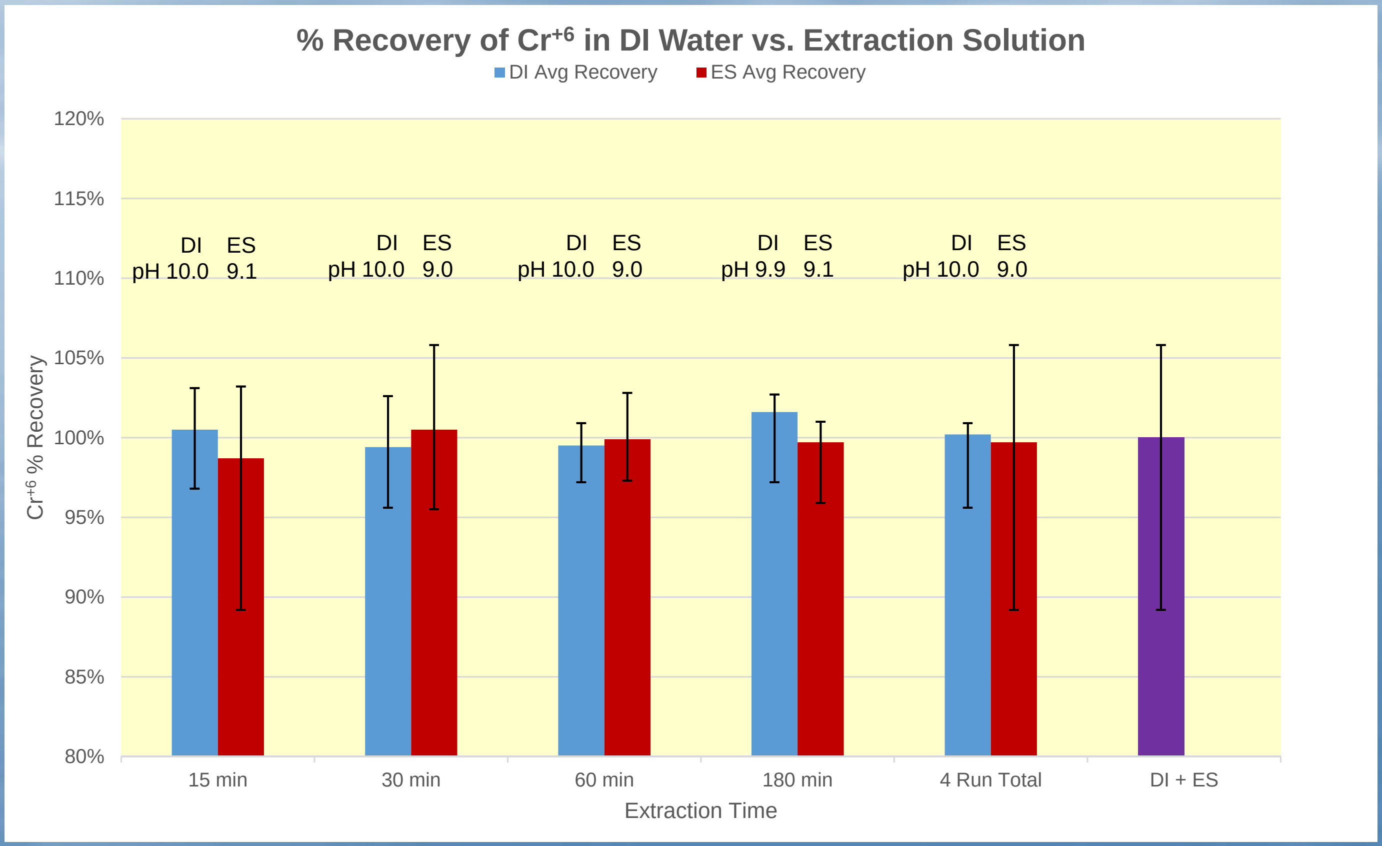
- Prep Filters
- Collect Samples
- **Extract Filters**
- Run by IC-PCD
- Report w/qualifiers if needed

ASTM D7614-12	Yeah, but…
"add 10 mL [extraction solution]."	10 mL volume is just barely enough to run one sample injection and one replicate injection. If dilutions or reruns necessary, there's no extract remaining.
"Place…in the ultrasonicator for one hour. … Place 5 mL extract into a 5-mL disposable autosampler vial." (11.4.3)	Note that there is no filtration step in here. (Filter through 0.2 µm Acrodisc immediately after sonication)

Cr^{3+} TO Cr^{6+} CONVERSION OVER TIME

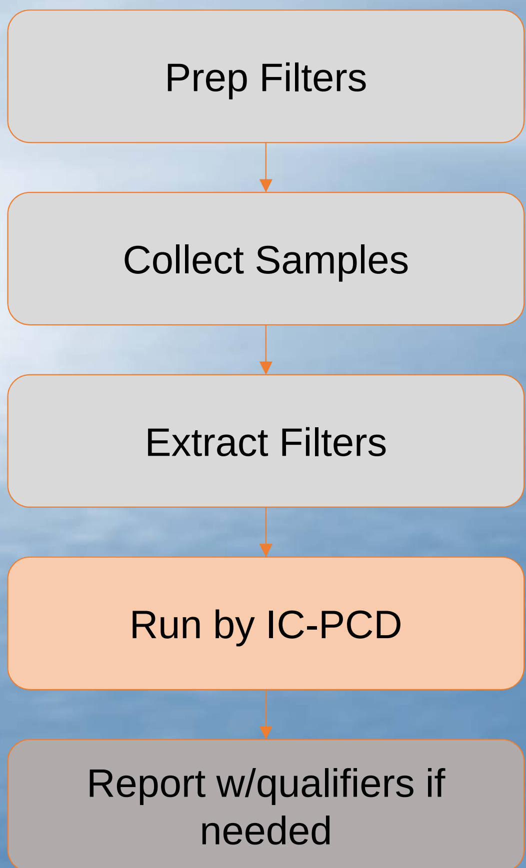


Cr^{3+} TO Cr^{6+} CONVERSION OVER TIME



Chester LabNet results from February, 2018.

ERRORS TO BE AWARE OF



- Eluent recipe: incorrect, need 13 mL NH_4OH (not 7 mL)
- Impregnation recipe: correct recipe, nominal value is 0.12 M (not 1.2 M)

Not really errors, but:

- Prescreen filters upon receipt.
- Prescreen impregnation solution prior to use.

INSTRUMENTATION

Prep Filters

Collect Samples

Extract Filters

Run by IC-PCD

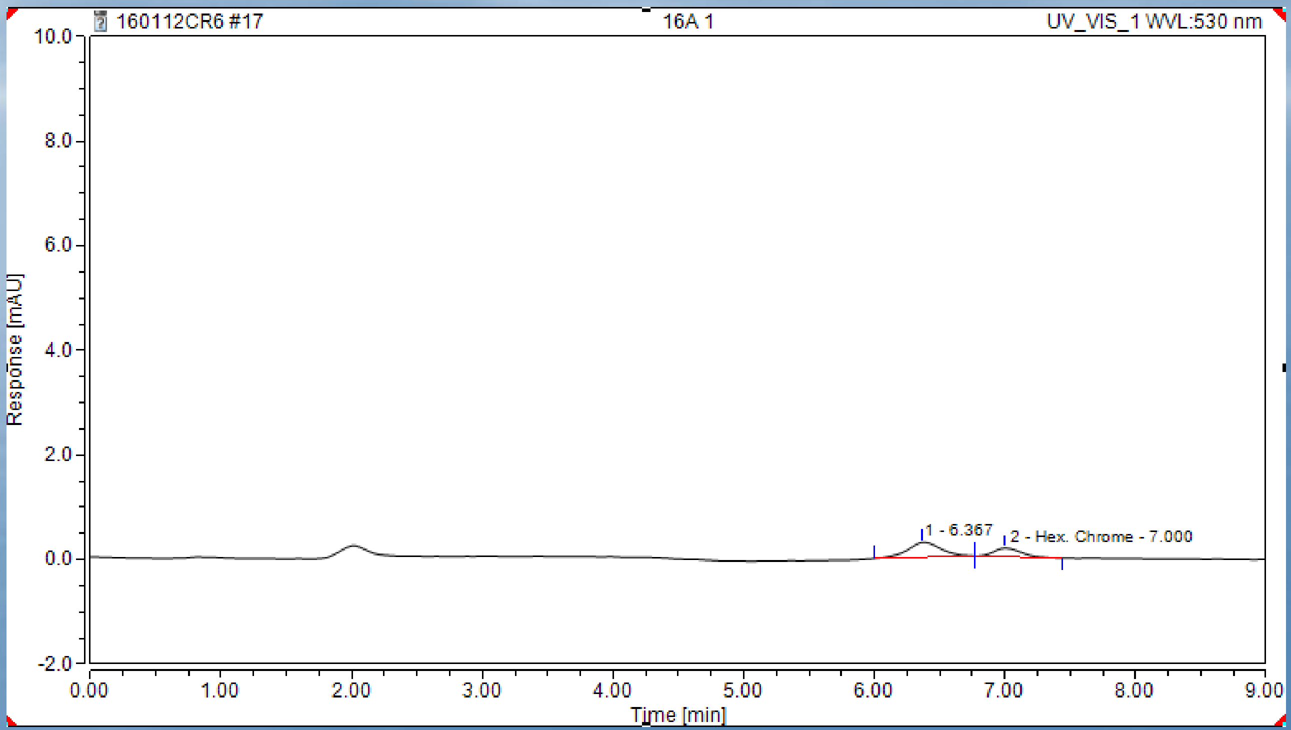
Report w/qualifiers if needed

ASTM Method is Prescriptive (and vague)

What you actually need:

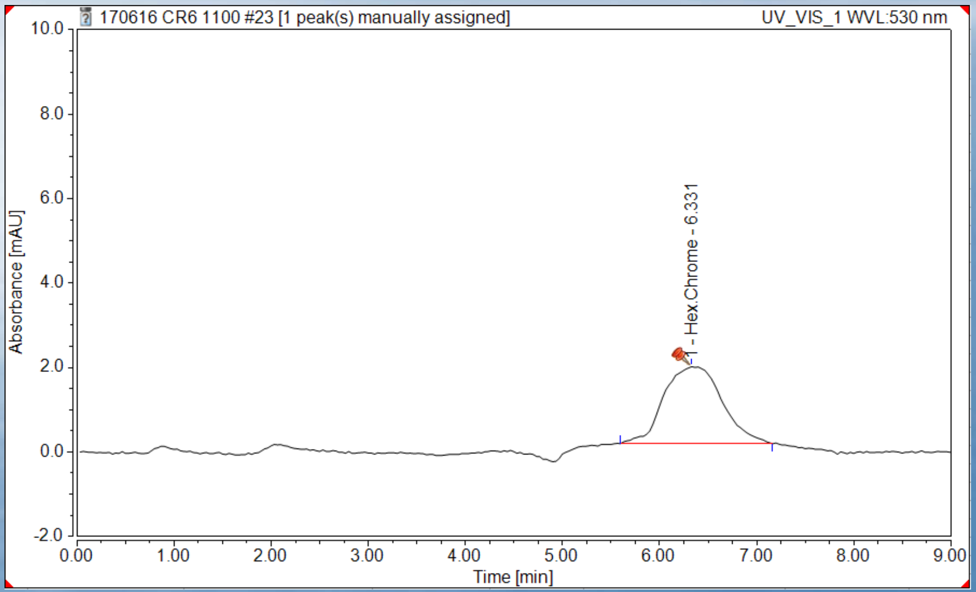
1. Eluent Pump
2. Colorimetric Pump (older pneumatic systems will work)
3. Guard and Separatory Columns
4. Mixing coil
5. 1 mL sample loop (really)
6. UV/Vis detector @ 530 nm
7. Waste container with conc H_2SO_4 (not in method)

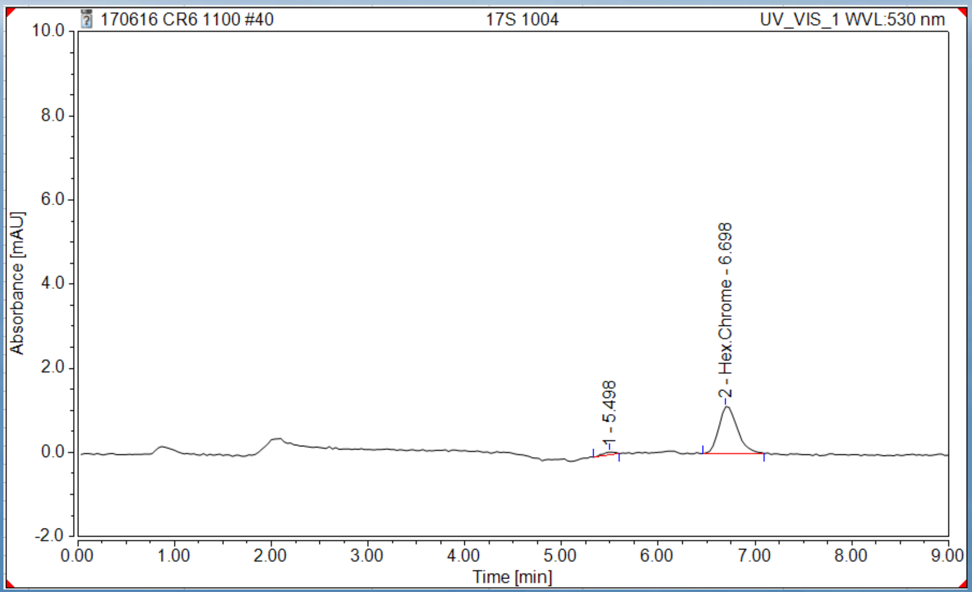
CHROMATOGRAPHIC INTERPRETATION



Pristine Ambient Air Sample

CHROMATOGRAPHIC INTERPRETATION





Unknown

5x dilution of same sample

CHROMATOGRAPHIC INTERPRETATION

- Prep Filters
- Collect Samples
- Extract Filters
- Run by IC-PCD
- Report w/qualifiers if needed

What is ***that***?!

1. Fe^{3+} - elutes off immediately prior to Cr^{6+}. Common in natural and pristine air sheds. Typically larger in urban airsheds. Very common in industrial airsheds. Cr^{6+} often riding on the Fe^{3+} tail.

2. Ti^{4+} - elutes off several minutes before Cr^{6+}. Common in industrial airsheds containing aerospace industries.

3. V^{5+} - elutes off between Ti^{4+} and Fe^{3+}. Common in industrial airsheds with ore refining or high purity metal production.

4. Mo^{6+} - elutes off around the same time as Ti^{4+}. Common in some industrial airsheds with ink, dye and certain lubricant production.

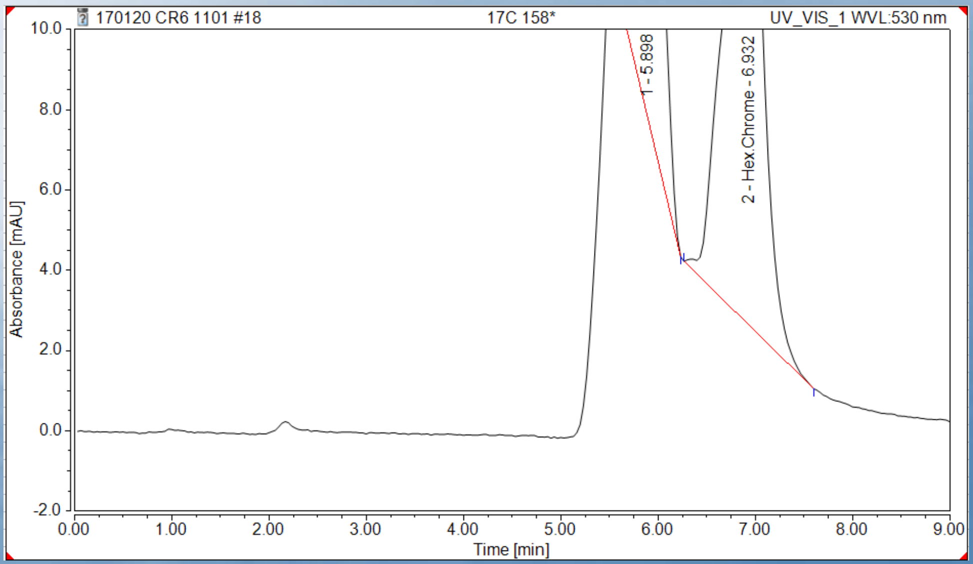
CHROMATOGRAPHIC INTERPRETATION

- Prep Filters
- Collect Samples
- Extract Filters
- Run by IC-PCD
- Report w/qualifiers if needed

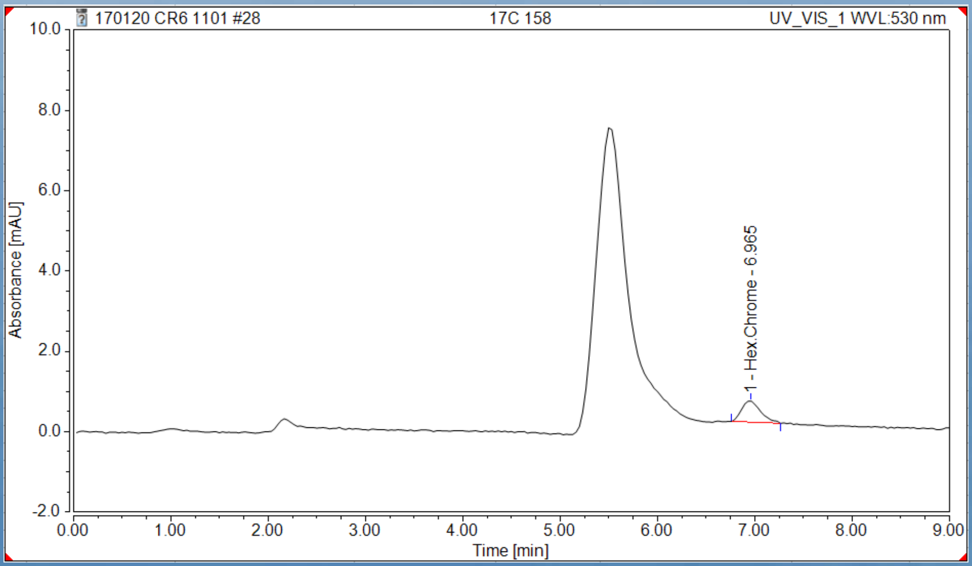
And what do I do with it?!

1. "The solution to pollution is dilution."
2. No way to remove these without affecting the Cr^{6+} concentrations.
3. Document, document, document!
4. Ensure all of the above is clearly annotated in final report to client.

CHROMATOGRAPHIC INTERPRETATION

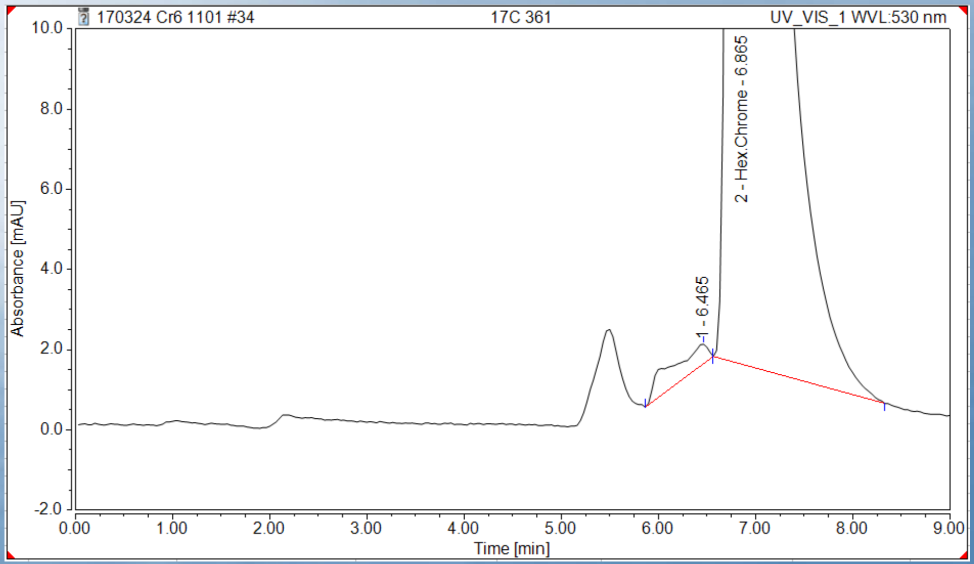


High Ti^{4+} with high Cr^{6+}

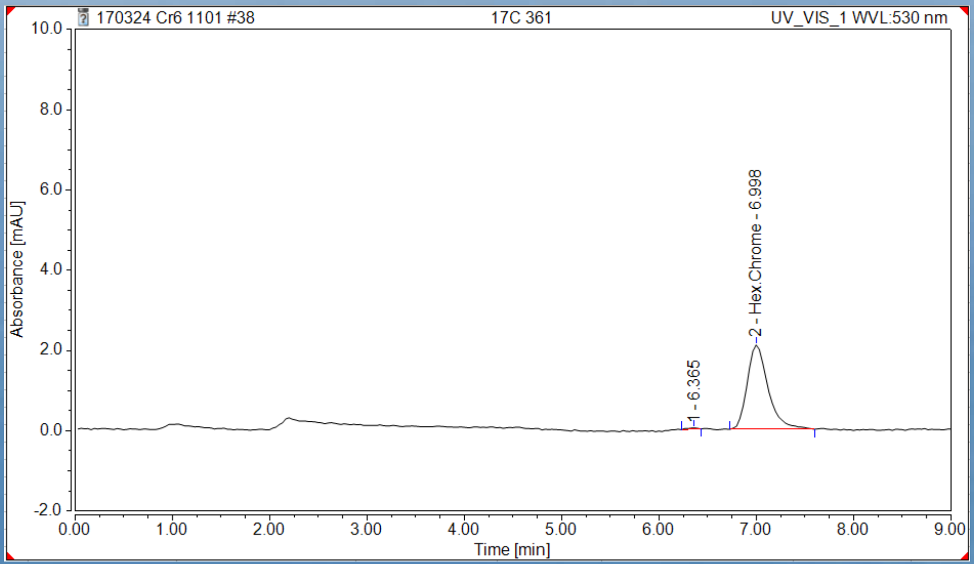


10x dilution of same sample

CHROMATOGRAPHIC INTERPRETATION



High Cr^{6+} + Ti^{4+} + Fe^{3+} + (maybe) V^{5+}



200x dilution of same sample

DATA INTERPRETATION

Is it really Cr^{6+} in my airshed?

1. Pristine ambient – “It depends”
   A. Fe^{2+} in air may be converting Cr^{6+} to Cr^{3+}, so low bias possible given crustal availability of Fe^{2+} but…
   B. Cr^{3+} may be converted to Cr^{6+} by atmospheric oxygen (ozone).

2. Urban ambient – “It depends”
   A. SO_x or NO_x fumes create an acidic airshed that may convert Cr^{6+} to Cr^{3+}, but…
   B. O_3 (Ozone) converts Cr^{3+} to Cr^{6+}, and
   C. Sulfides and various microorganisms can convert Cr^{6+} to Cr^{3+}, and
   D. Mn can convert Cr^{3+} to Cr^{6+},
   E. And more!!

DATA INTERPRETATION

Gah! What do I tell my client?

No financially feasible way to know for certain which valence state the Chromium was in prior to pulling through the filter and extracting.

Then "Be Prepared!" Know your potential sources. Think outside the process and/or airshed being monitored. Understand the three conditional states that the Cr^{6+} is brought through during sampling and analysis.

Airshed → particle + gas → particle + particle → aqueous extract + Cr species

CONCLUSIONS

1. Ambient air samples provide unique and difficult sampling and data interpretation challenges.

2. The laboratories are challenged with detection limits so low that creating clean impregnated filters is difficult.

3. The field engineers are challenged with the monumental task of attempting to determine what is contained within the airshed that may be falsely increasing the observed concentration of Cr^{6+}.

4. No financially or technologically feasible way to determine, *in situ,* the starting valence state of the observed Cr^{6+}.

CONTACT INFO & APPRECIATION

Sheri Heldstab

QA Officer & Technical Director

Chester LabNet

12242 SW Garden Pl. Tigard, OR 97223

sheldstab@chesterlab.net   (503) 624-2183

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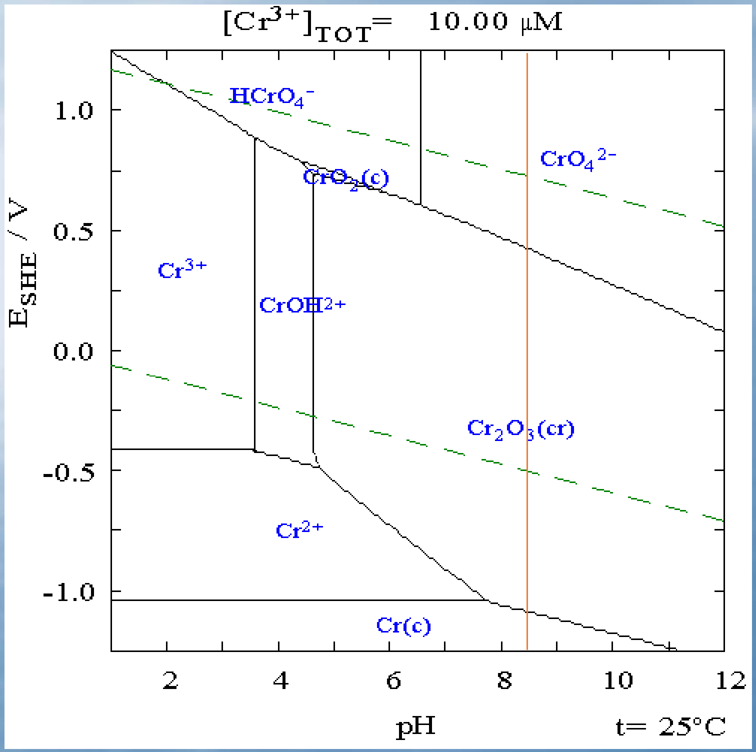
Karen O'Fearna, Tai Wu, Dr. Greg Fowler, professor emeritus at Oregon Health Science University, and Dr. Pat Gower (retired) for editorial contributions.

BONUS MATERIAL

Photograph of Cr^{6+} sampler using Teflon cassettes and glass funnel:

POURBAIX DIAGRAM OF CHROMIUM



Chromium Pourbaix Diagram in Water

By volume, dry air contains ~78% nitrogen and ~21% oxygen. PO_2 ~0.2 bar at sea level.

pH 8.5 – 9 Cr^{6+} most stable

pH <8 Cr^{6+} converts to Cr^{3+}

pH >10 Cr^{3+} converts to Cr^{6+}

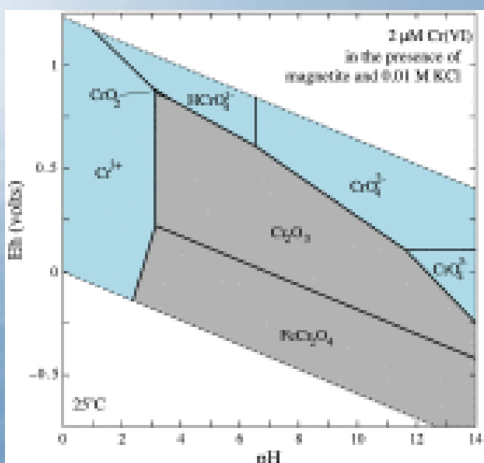
Under normal atmospheric pressures, with pure Cr^{3+} and Cr^{6+} standards, pH is the most likely contributor to conversion.

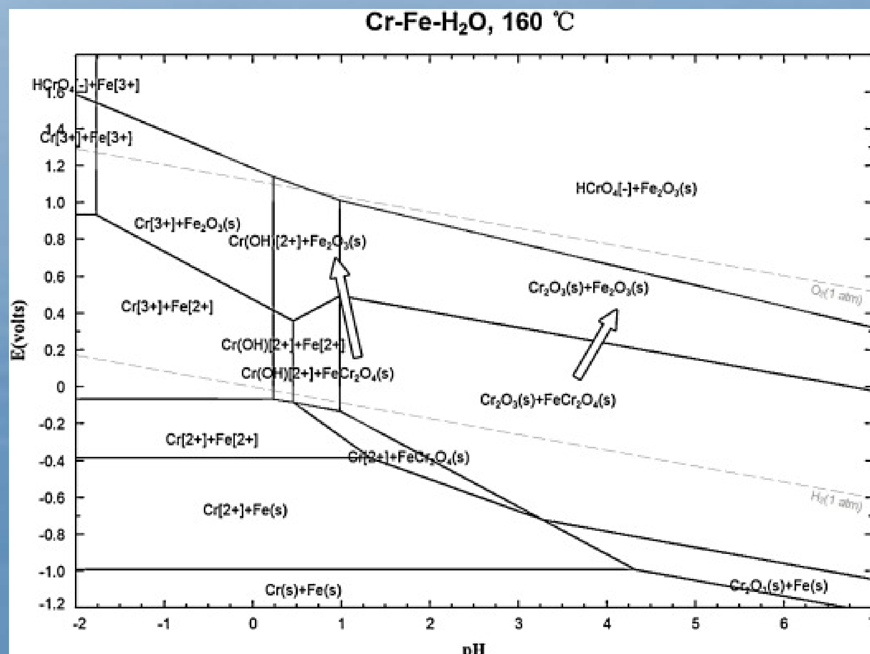
eH: other reducers or oxidizers present in the particulate or gaseous fraction, the conversion could go either way.

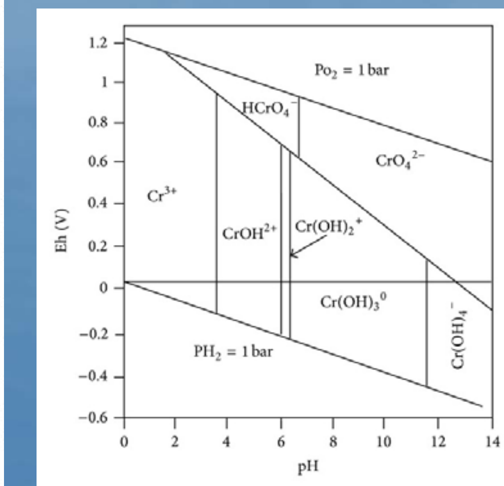
Pourbaix Diagram from: https://en.wikipedia.org/wiki/File:Chromium_in_water_pourbiax_diagram.png

POURBAIX DIAGRAMS UNDER VARIOUS CONDITIONS

Left to Right: Cr in 0.01M KCl with Magnetite (Fe_3O_4), Cr at 160° C w/Fe^{2+}, Cr in saline-sodic soils







RECOMMENDED QC SAMPLES

1. Prep Filters
2. Collect Samples
3. Extract Filters
4. Run by IC-PCD
5. Report w/qualifiers if needed

Recommended Preparation QC Samples (2016 TNI compliant)

- Method Blank - no filter
- Sample Media Blank - filter that has never left lab
- Low Level LCS (DL studies and bottom of curve check)
- LCS
- LCS-Duplicate

Recommended Analytical QC Samples (2016 TNI compliant)

- 6 point Cal Curve plus blank
- ICV
- ICB
- Replicate
- Post Extraction Spike
- CCV
- CCB

CREDITS & CITATIONS

Photograph of FRM Cassettes: Human Nature Art (Will Mahoney-Watson)

Photograph of Teflon Cassette: Savillex corporation (https://www.savillex.com/en/product/filtration-assemblies/47-mm-single-stage-filter-assembly-14-x-14-pfa-clamp--401-21-47-10-21-2?pageid=19)

Photograph of Cr^{6+} sampler in field: Oregon Department of Environmental Quality

Collection and Analysis of Hexavalent Chromium in Ambient Air (2007): https://www3.epa.gov/ttnamti1/files/ambient/airtox/hexavalent-chromium-paper-06.pdf

ERG's Final Report to EPA on method development (2005): https://www3.epa.gov/ttnamti1/files/ambient/airtox/hexchrommethod.pdf

Method Development Studies for Hexavalent Chromium in Ambient Air Samples (2012): https://www3.epa.gov/ttnamti1/files/2012conference/3BSwift.pdf

South Coast Air Quality Management District SOP: http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1469/scaqmd-hexavalent-chromium-draft-sop.pdf

The Fate of Hexavalent Chromium in the Atmosphere. P.M. Grohse, W.F Gutknecht, L. Hodson, B.M. Wilson. Prepared for California Air Resources Board [CARB], October, 1988.

Interconversion of Chromium Species During Air Sampling: Effects of O3, NO2, SO2, Particle Matrices, Temperature, and Humidity. Lihui Huang, Zhihua (Tina) Fan, Chang Ho Yu, Philip K. Hopke, Paul J. Lioy, Brian T. Buckley, Lin Lin, and Yingjun Ma. *Environ. Sci. Technol., 2013, 47 (9), pp 4408–4415*

BONUS READING

Determination of hexavalent chromium in ambient air: A story of method induced Cr(III) oxidation: https://www.sciencedirect.com/science/article/pii/S1352231011006558

PVC filter cleaning & Cr^{6+} stability: http://apps.nelac-institute.org/nemc/2016/docs/presentations/Wed-Air%20Methods%20&%20Monitoring%20-%20Session%202-16.1-Mututuvari.pdf

Interconversion of Chromium Species During Air Sampling: Effects of O3, NO2, SO2, Particle Matrices, Temperature, and Humidity: https://pubs.acs.org/doi/ipdf/10.1021/es3046247

The reactions of diphenylcarbazide and diphenylcarbazone with cations Part IV. Cations of Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn And Pb: https://www.researchgate.net/publication/244096508_The_reactions_of_diphenylcarbazide_and_diphenylcarbazone_with_cations_Part_IV_Cations_of_Mn_Fe_Co_Ni_Cu_Zn_Cd_Sn_And_Pb

Influence of pH on hexavalent chromium reduction by Fe(II) and sulfide compounds: https://www.ncbi.nlm.nih.gov/pubmed/26114267

A cleaner method for preparation of chromium oxide from chromite: https://www.sciencedirect.com/science/article/pii/S0957582016302166

Removal of Hexavalent Chromium from Wastewaters by Bone Charcoal: Dahbi, S & Azzi, Mohammed & Guardia, Miguel. (1999). Removal of Hexavalent Chromium from Wastewaters by Bone Charcoal. Fresenius Journal of Analytical Chemistry. 363. 404-407. https://www.researchgate.net/publication/227166566_Removal_of_Hexavalent_Chromium_from_Wastewaters_by_Bone_Charcoal