A Speciation Study of Hexavalent Chromium on Filter Media

Moven Mututuvari
High Purity Standards
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Outline

- **Introduction**
- **Objectives**
- **Experimental Design**
- **Results**
- **Conclusions and Future Research**

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Health Effects of Chromium Species

Cr(III) + Cr(VI)

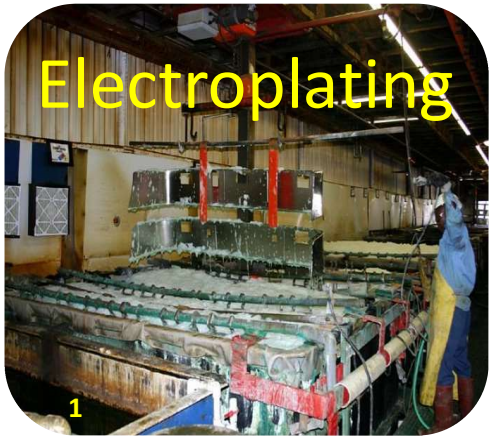
Cr(III) – essential micronutrient

- Glucose and protein metabolism

Cr(VI) – carcinogenic

- Lung cancer
- Chronic bronchitis

Sources of Cr(VI) Generation



[1]Photo courtesy of 10-4 Magazine
[2]Photo courtesy of Lincoln Electric
[3]Photo courtesy of Sigma-Aldrich
[4]Photo from Wikipedia

Cr(VI) Occupational Exposure Limits

National Institute for Occupational Safety and Health (NIOSH)

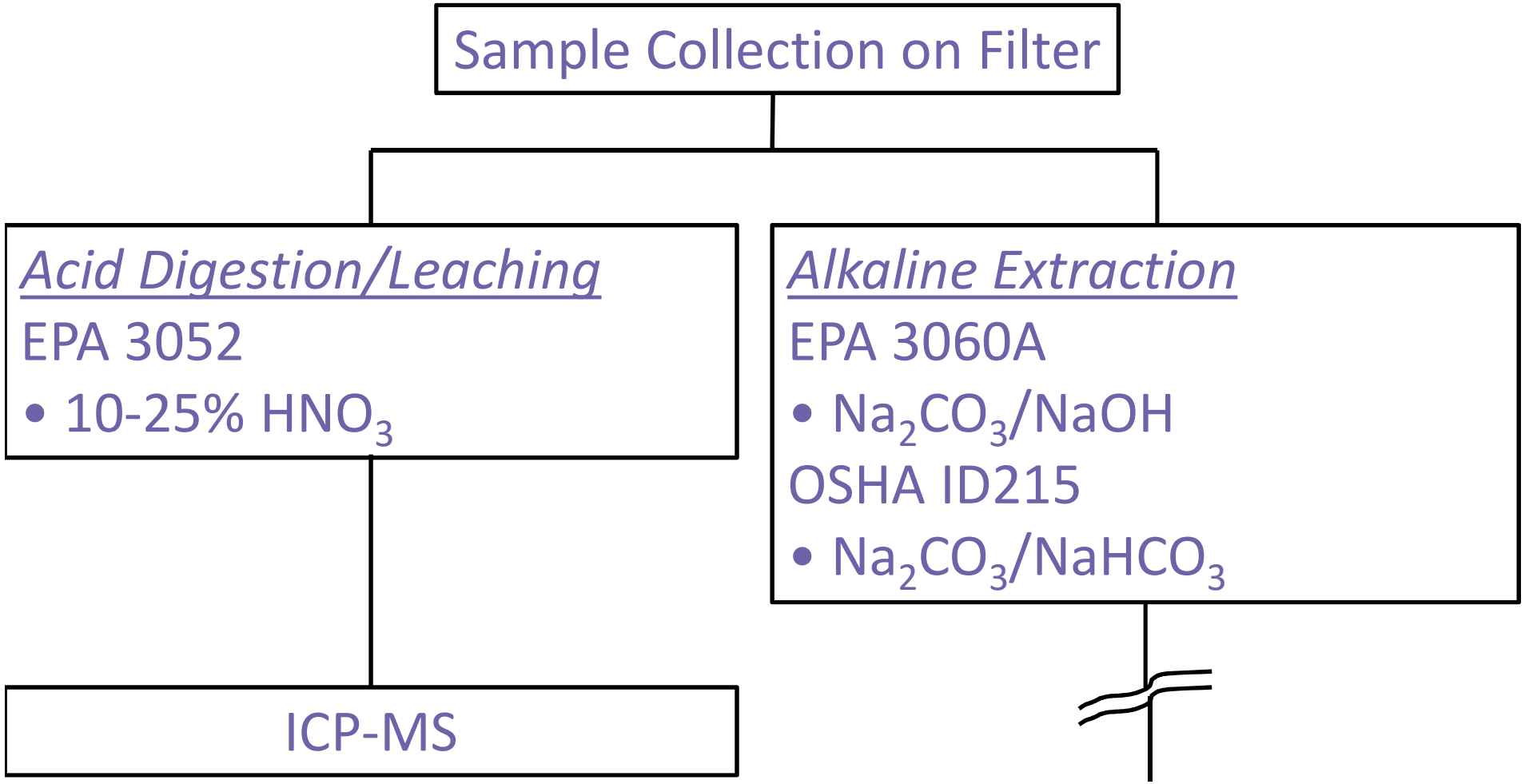
- Recommended Exposure Limit: 0.2 µg Cr(VI)/m^3 of air

Occupational Safety and Health Administration (OSHA)

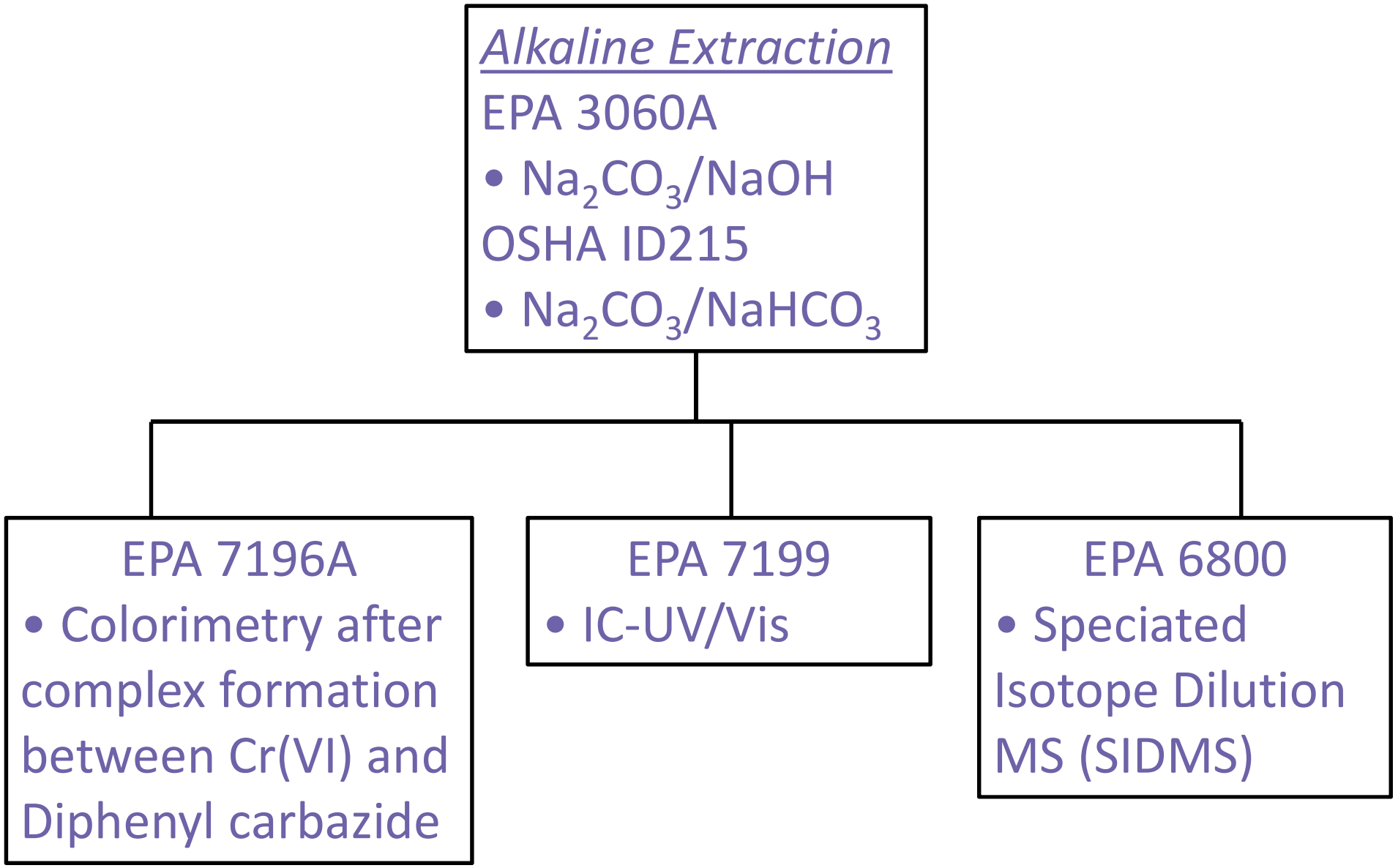
- Permissible Exposure Limit: 5µg Cr(VI)/m^3 of air
- OSHA limit is legally binding

NIOSH [2013]. [https://www.cdc.gov/niosh/docs/2013-128/pdfs/2013_128.pdf]. (*accessed July 28, 2016*).

Analytical Processes



Analytical Process ctd…



Challenges

- Contamination of filters with residual Cr.
- Efficiency of extraction solution.
- Storage stability.
- Interconversion of Cr(VI) and Cr(III) species.

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Objectives

- To evaluate the methods of cleaning filters to remove residual chromium
- To apply IC/ICP-MS to study speciation and stability of Cr on filter media
- To develop a Certified Reference Material (CRM) filter containing trace levels of Cr(VI)

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Experimental Design

- Determine background Cr contamination on filters.
- Evaluate 2 cleaning protocols used to remove background Cr from filters
- Apply EPA 7199 or modified OSHA ID 215 method to study Cr(VI) stability on filter media
- Apply IDMS from EPA Method 6800 to determine total Cr in spiked filters

Assessment of Cr Contamination of Filters

- Followed EPA method 3052 with slight modifications
  - Digestion/Extraction reagent: 10 mL of 10% or 25% HNO_3
  - Multiple filters of different media were digested using a Milestone Ethos Up microwave
    - Ramp to 130°C in 5 minutes, then ramp to 220°C in 20 minutes. Keep temperature at 220°C for an additional 20 minutes
    - Cooling time: 20 minutes
    - Microwave power: 1800 W

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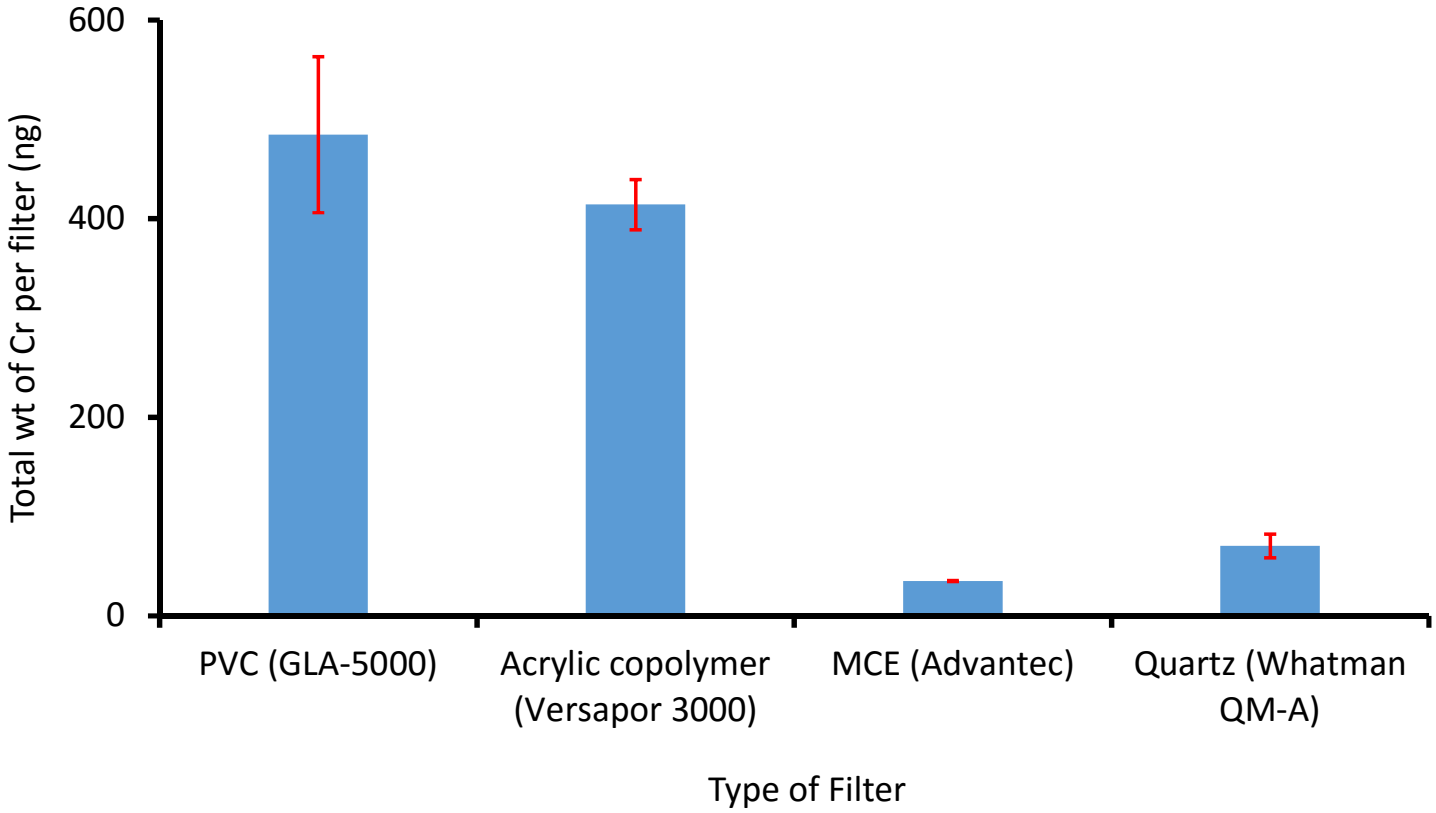
Trace Level of Chromium on Filters



Acrylic and PVC filters contain high levels of Cr

- Need to clean filters

Evaluating Cleaning Protocols

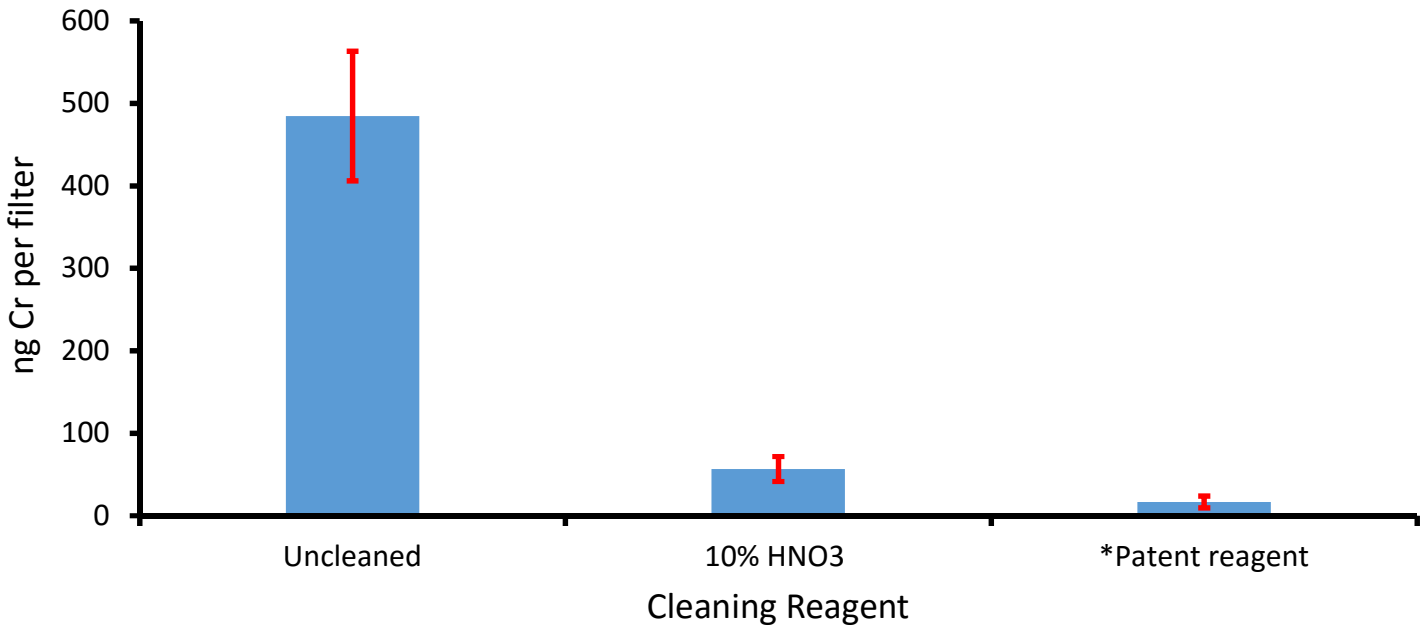
[1]*Protocol #1*: Soak filters in reagent per U.S. Patent 8,415,452

Protocol #2: Soak filters in 10% HNO_3

- Digest multiple filters using a Milestone Ethos Up microwave

[1]Rubenstein, M. Hexavalent chromium and total chromium removal from polyvinylchloride (PVC) polymers. *U.S. Patent 8,415,452*, April 9, **2013**.

Results of Cleaning PVC Filters



- Patent reagent more effective than HNO_3

*Rubenstein, M. Hexavalent chromium and total chromium removal from polyvinylchloride (PVC) polymers. *U.S. Patent 8,415,452*, April 9, **2013**.

Spiking Cr(VI) and Cr(III) onto Treated Filters

Filter being spiked with Cr solution

Dry filters and package under Nitrogen

Filters packaged and ready for storage

IC-UV Vis for Cr(VI) Determination

Extract Cr(VI) using a $Na_2CO_3/NaHCO_3$ solution

↓

Analyze by IC using the following conditions:

Instrument: Thermo Scientific Dionex 3000 System

Guard Column: Dionex IonPac AG7 Guard 2x50 mm

Analytical Column: Dionex IonPac AS7 2x250 mm

Eluent: 250 mM $(NH_4)_2SO_4$ + 100 mM NH_4OH

Eluent flow: 0.36 mL/min; Injection vol: 1000 µL

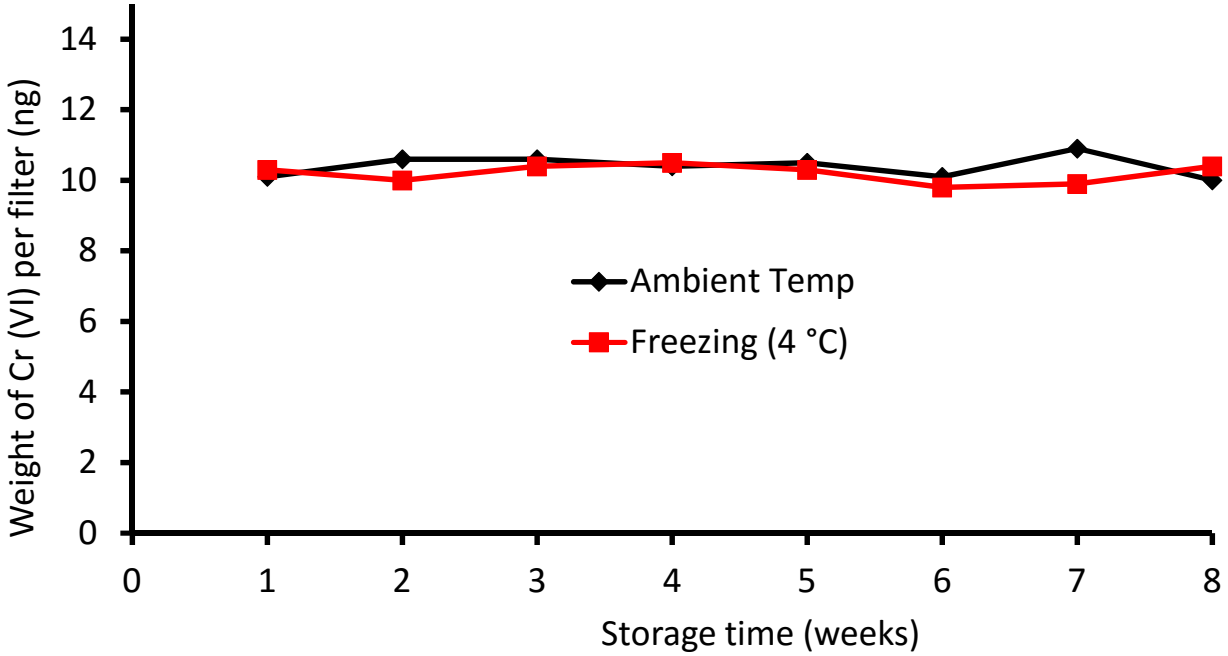
Temperature: 30 °C; Backpressure 1700-2000 psi

Post Column Reagent: 2 mM diphenylcarbazide in 10% methanol and 1 N H_2SO_4

Detection: UV Visible 540 nm

Run time: 10 min

Stability of Cr(VI) on PVC Filters



- *Note: 10.0 ng Cr(VI) was spiked on each filter*
- Cr(VI) stable for at least 8 weeks at both storage temperatures
- Samples were analyzed by IC-UV

[1]Isotope Dilution Mass Spectrometry (IDMS)

- Used to determine total concentration of Cr species in sample
- A known amount of enriched isotope $^{53}Cr(VI)$ or $^{50}Cr(III)$ is spiked into the sample and allowed to equilibrate
- Sample analyzed by ICP-MS
- Unaffected by partial loss of analyte after equilibration of sample and spike

[1]US Environmental Protection Agency, Method 6800 Update V, *Elemmental and molecular speciated isotope dilution mass spectrometry*, US Government Printing Office, Washington, DC, **2015**

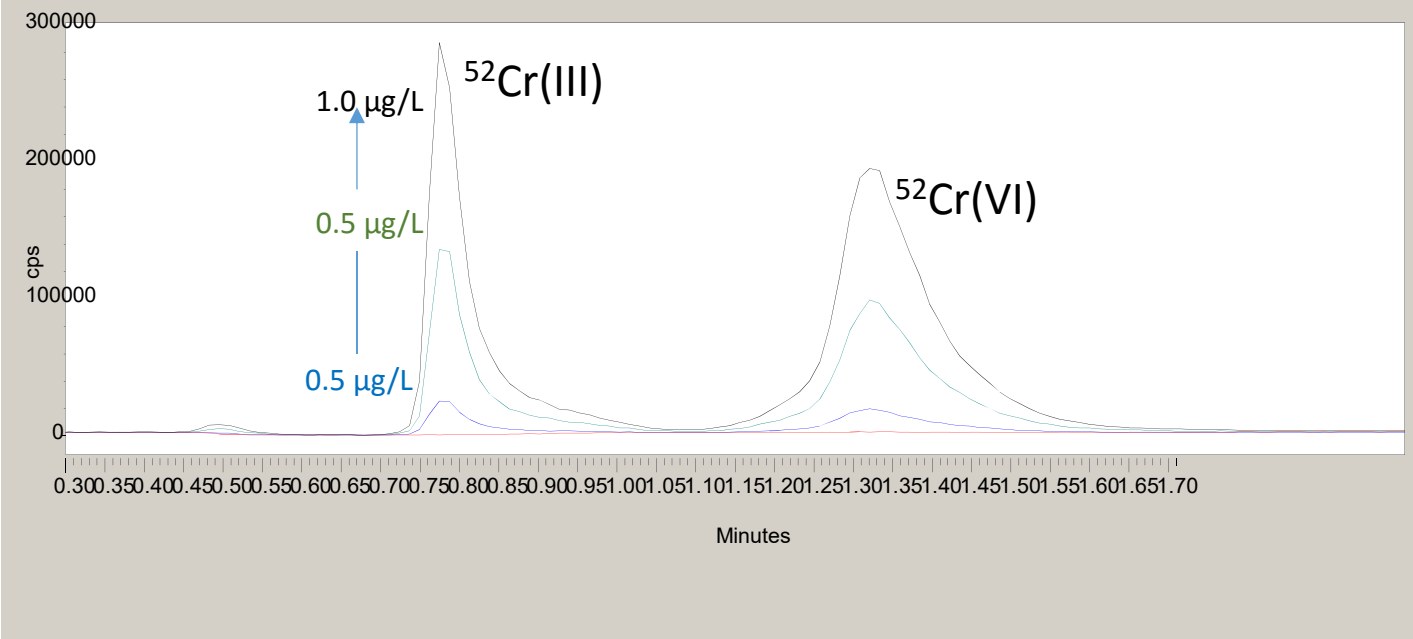
IDMS Results

Filter ID	Description	Cr-total (µg per filter)	Total Cr found (µg per filter)[a]
1600633	MCE filter, Blank	0	0.042±0.008
1600620	MCE filter, $^{nat}Cr(III)$	0.1	0.14±0.05
1600622	MCE filter, $^{nat}Cr(VI)$	0.1	0.12±0.01
1600623	MCE filter, $^{nat}Cr(VI)+^{nat}Cr(III)$	0.2	0.215±0.006

[a]n=4, 95% confidence interval

- Consistent recoveries.
- Filters still contained residual Cr that was probably not removed during the cleaning of filters.

IC-ICPMS: Preliminary Results



Dionex ICS 3000

IC Column: Dionex IonPac AG7

Mobile Phase: 0.2 mM HNO_3

Injection volume: 125 µL

Perkin Elmer NexIon 350D

DRC Gas flow: 0.7 ml/min NH_3

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Conclusions

- Filters, especially PVC-based ones, are contaminated with Cr, thus they require cleaning before use
- Cr(VI) remained stable for at least 8 weeks on PVC filter media under both ambient and refrigeration temperature conditions.
- IDMS was successfully applied to determine total chromium spiked on MCE filters.

Future Research

- Finish optimization of IC-ICPMS analysis
- Apply Speciated Isotope Dilution MS to study the stability of Cr(VI) on a variety of filter media.
- Develop a Certified Reference Material for trace levels of Cr(VI) on filter media

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Conclusions

- Filters require cleaning before use to remove residual Cr
- Cr(VI) remained stable for at least 8 weeks on PVC filter media under both ambient and refrigeration temperature conditions.
- IDMS was successfully used to determine total chromium spiked on MCE filters.