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Cr(VI) Measurements: Feasibility, Fate, and Stability

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Recent Issues Concerning Cr(VI) Measurement

- State of California proposal for Cr(VI) regulatory limit from 0.05 µg/L to 0.02 µg/L in drinking water
  - Requires MDLs in 0.002 – 0.004 µg/L
- Recent study finds Cr(VI) in numerous municipal water sources
- No recent studies on Cr(VI) stability
  - Particularly in “naturally occurring matrices”

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Analytical Method†

- HPLC – reversed phase, ion-pairing
  - Column: Brownlee C8
    - Column Oven 35 ºC
  - Mobile Phase:
    - 2mM tetrabutylammonium hydroxide (TBAOH) + 0.5mM K_2EDTA, pH = 7.4 – 7.6
      - EDTA converts Cr(III) to anionic EDTA-Cr(III)
    - 5% MeOH added on-line
  - Autosampler 10 ºC
  - Samples: Diluted minimally 1:1 in mobile-phase, 50 µL injection
- DRC-ICP-MS
  - Reaction gas: N_2 or NH_3
  - Sample Introduction:
    - Baffled quartz cyclonic spray chamber
    - Meinhard TQ-30-A3 nebulizer

The use of company, trade, and/or product names is for identification purposes only and does not imply endorsement by the United States Government.

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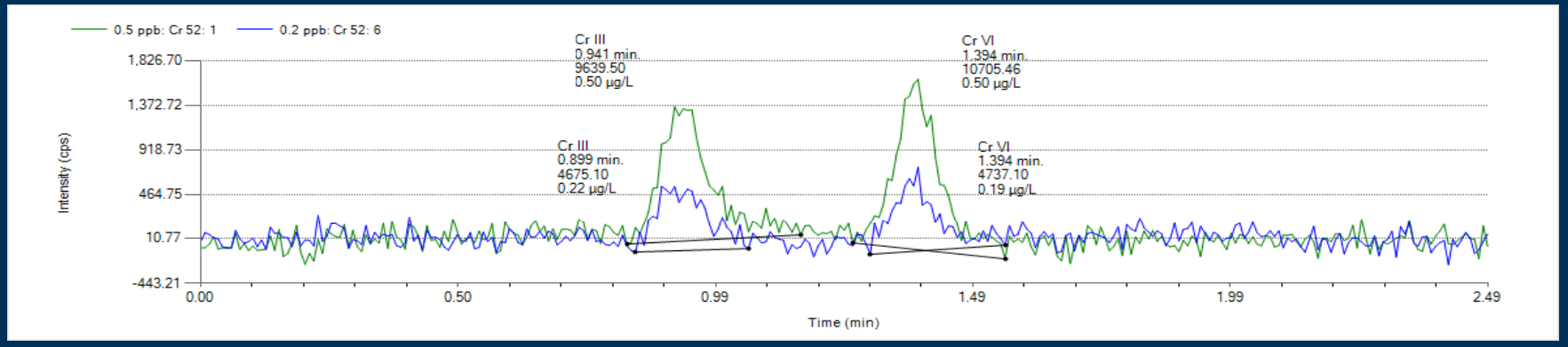
† Complete description in J. Anal. At. Spectrom., 2007, 22, 1051-1060
* Stated column working range to pH=7; however, have run up to pH=8 without significant column life issues

Analytical Figures of Merit:

Parameter	NH_3 Reaction Gas Flow 0.75, RPq=0.65		N_2 Reaction Gas Flow 1.0, RPq=0.50	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Instrument Detection Limit (IDL), µg/L	0.09	0.06	0.1	0.1
Practical Quantitation Limit (PQL), µg/L	0.2	0.2	0.2	0.2



Chromatogram showing low calibration standard at 0.5 µg/L and standard at PQL of 0.2 µg/L
Using 50 µL injection volume

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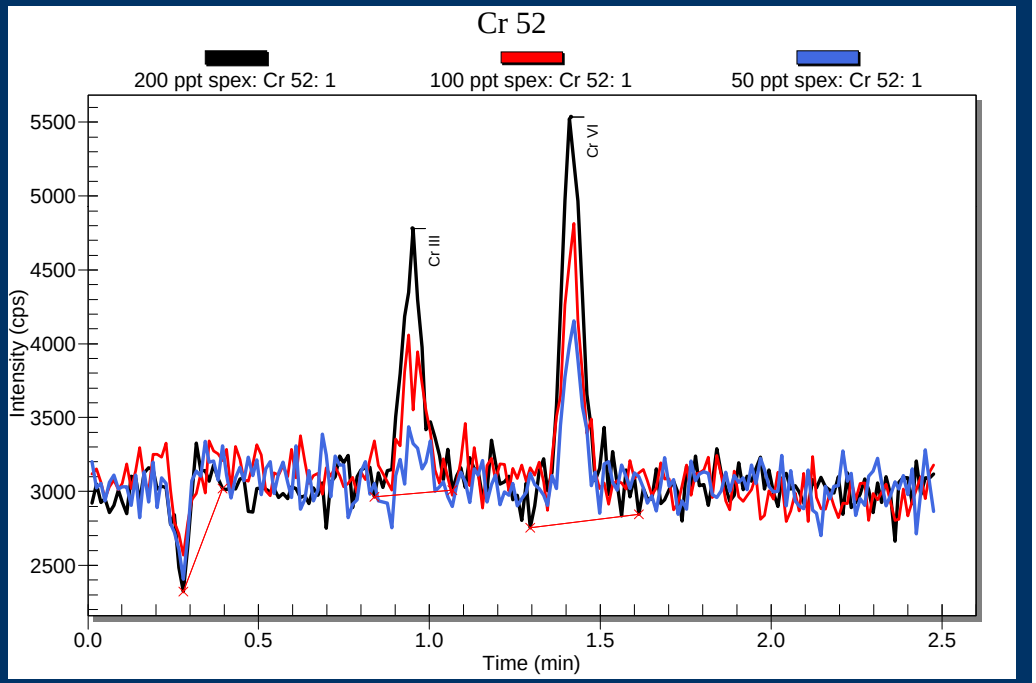
Method Modifications to Improve IDLs

- Use NH_3 Reaction Gas
- Investigate use of larger injection volume
- Careful optimization of instrument parameters



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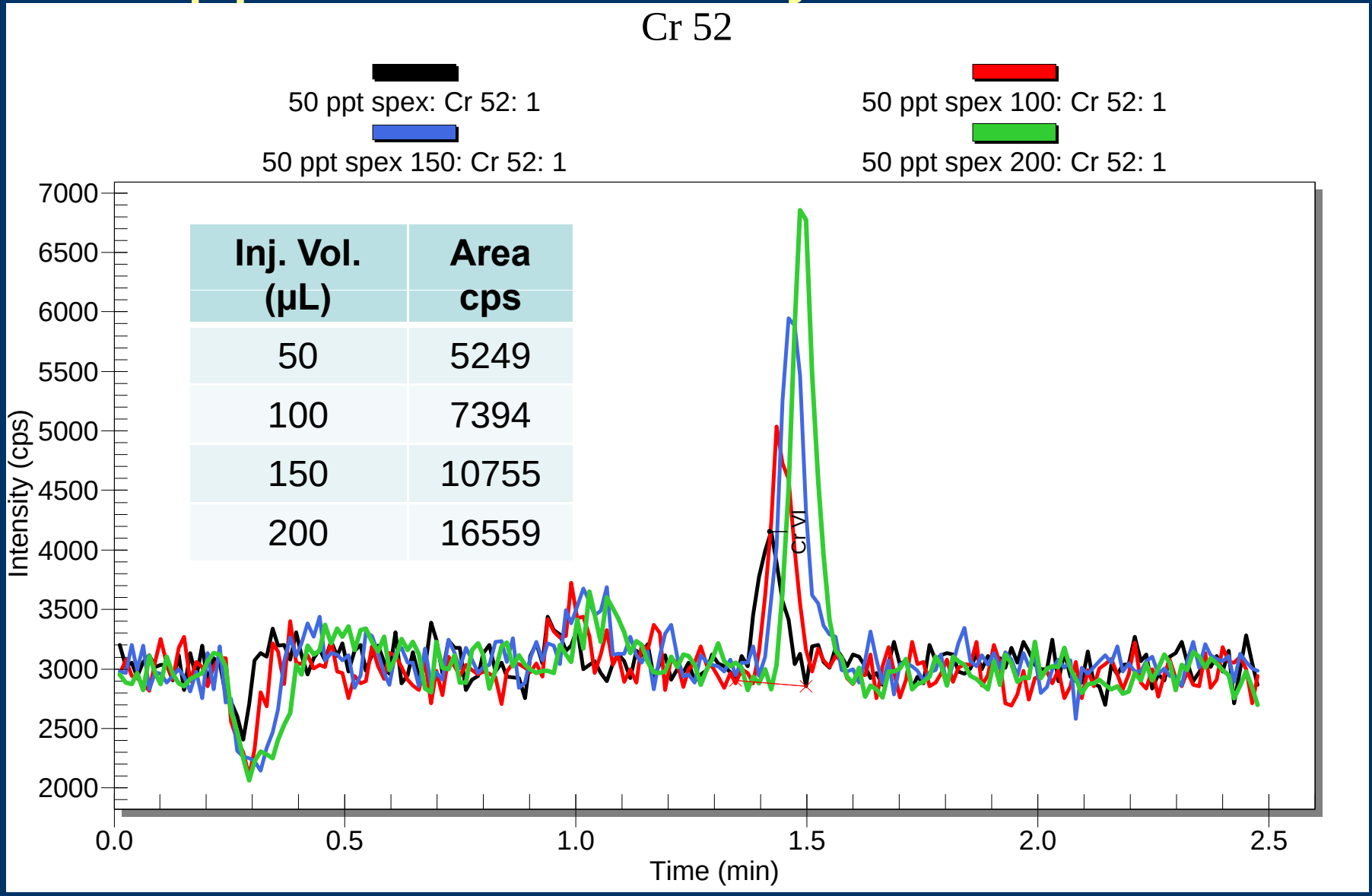
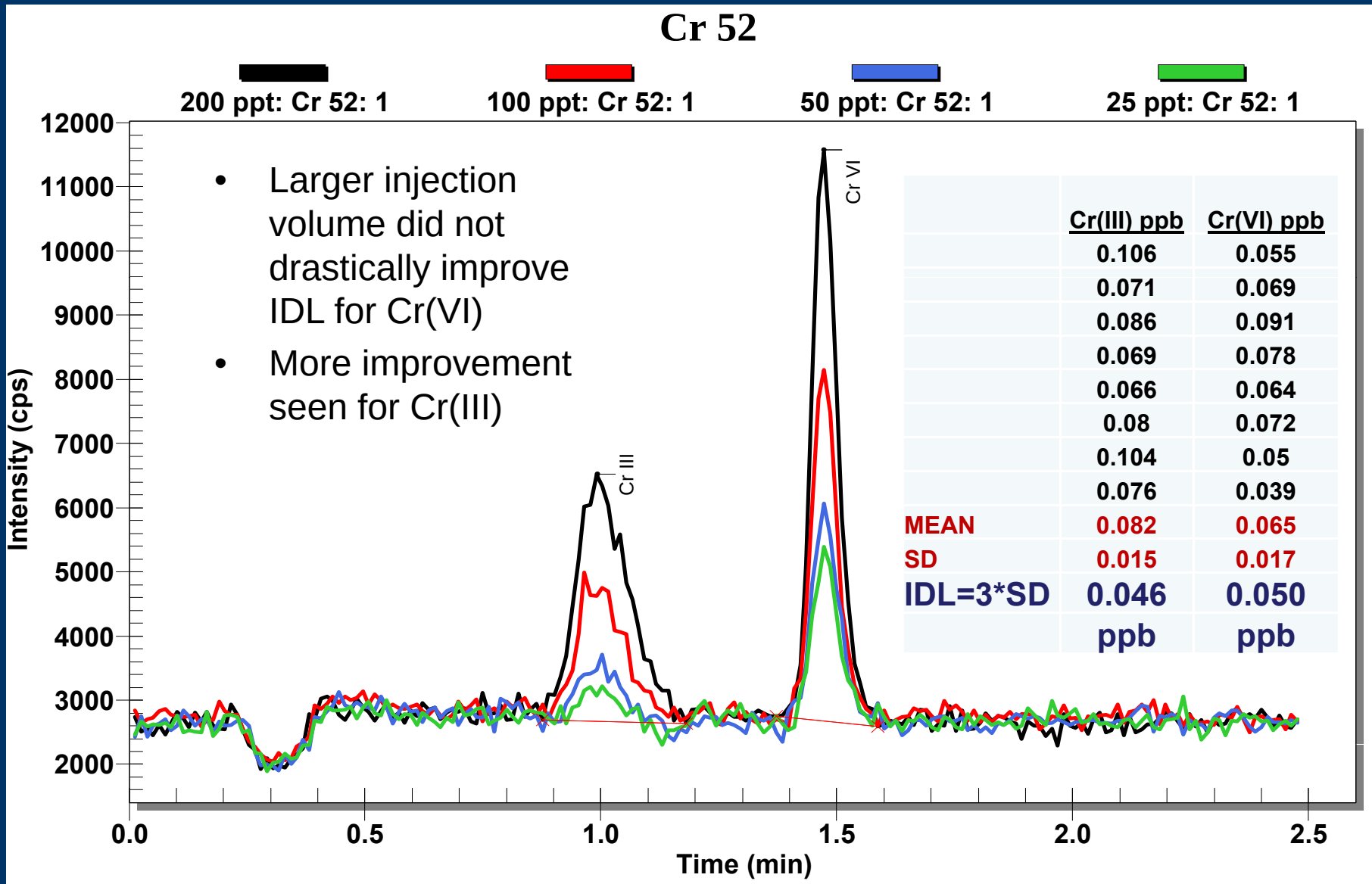
50 ppt at different injection volumes



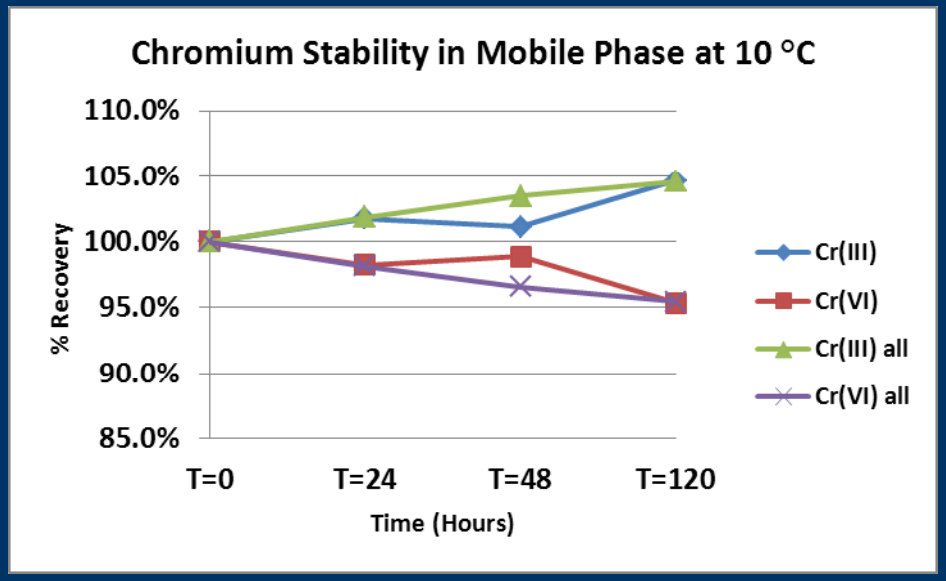
Inj. Vol. (µL)	Area cps
50	5249
100	7394
150	10755
200	16559

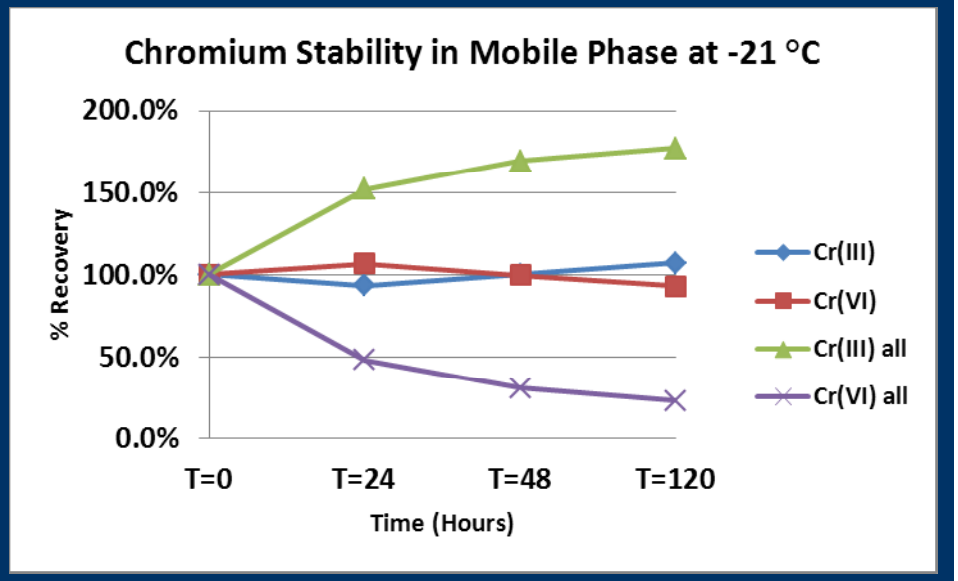
IDL Determination – 200µL injections



Stability of Cr(III) and Cr(VI)

- Cr(VI) standards stable in mobile phase at 10 °C
- Storage at -21 °C detrimental if other species are present
  - As(III), As(V), Se(IV), Se(VI)
  - Reduction of Cr(VI) to Cr(III)





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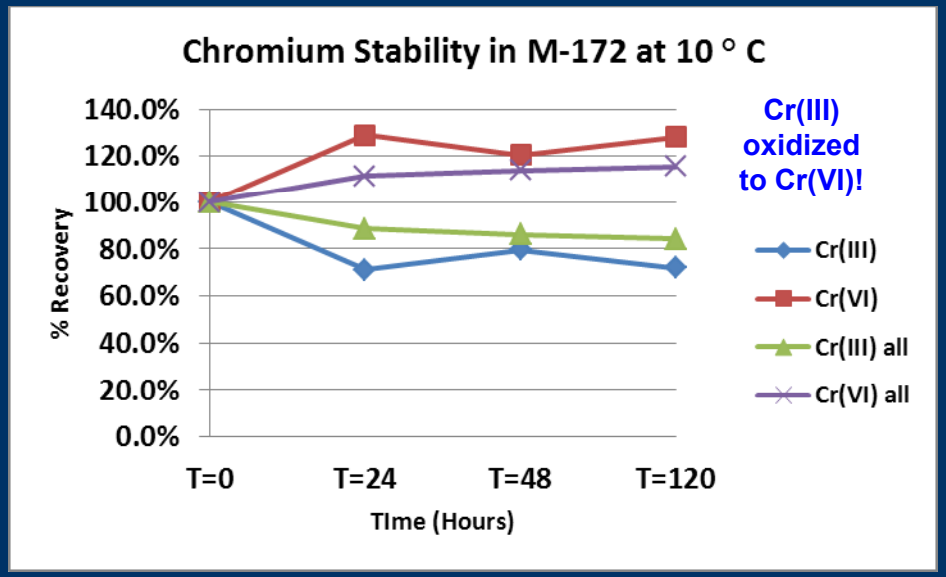
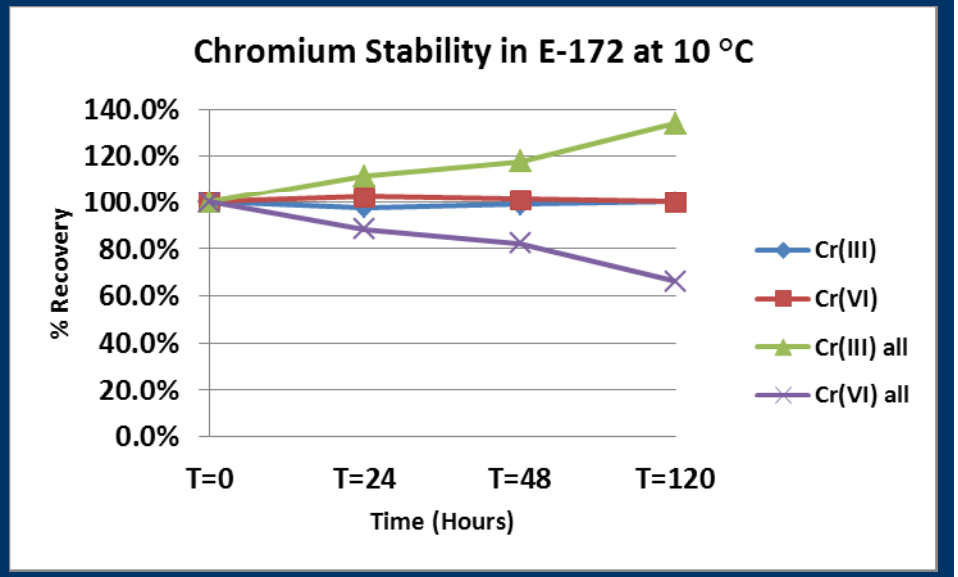
Stability of Cr(III) and Cr(VI)

- Standards spiked into USGS reference water M-172 showed varying stability
  - Elapsed time in hours from t=0 to t=120
  - M-172 preserved with NaOCl – causes oxidation of Cr(VI)!
- Addition of 10 mM K_2EDTA preservative (E-172) showed limited improvement if As and Se species present
  - Eliminates oxidation of Cr(III) to Cr(VI)
  - More info in Analytical & Bioanalytical Chemistry, in press
    - http://dx.doi.org/10.1007/s00216-011-5275-x





In Vitro Bioaccessibility Methods - Cr(VI) Stability in the Human Body

- Ingestion Pathway
  - Simulated gastric leach fluid (based on Drexler and Brattin, 2007)
    - pH 1-2 glycine/HCl solution to simulate stomach environment
    - 1 part solid sample to 100 parts leachate fluid, placed in orbital shaker incubator at 37 ºC for 1 hour, filtered and analyzed for pH and metals
  - Simulated intestinal fluid (modified from Basta, 2007)
    - Gastric leach fluid titrated to a pH of 5.5 ± 0.1 with Na_2CO_3 prior to addition of porcine pancreatin and bile
- Inhalation Pathway
  - Simulated lung fluid (SLF) (based on Mattson, 1994)
    - Simple proxy for a near neutral pH solution encountered along an inhalation pathway
    - 1 part solid sample to 100 parts SLF for 24 hours at 37 ºC

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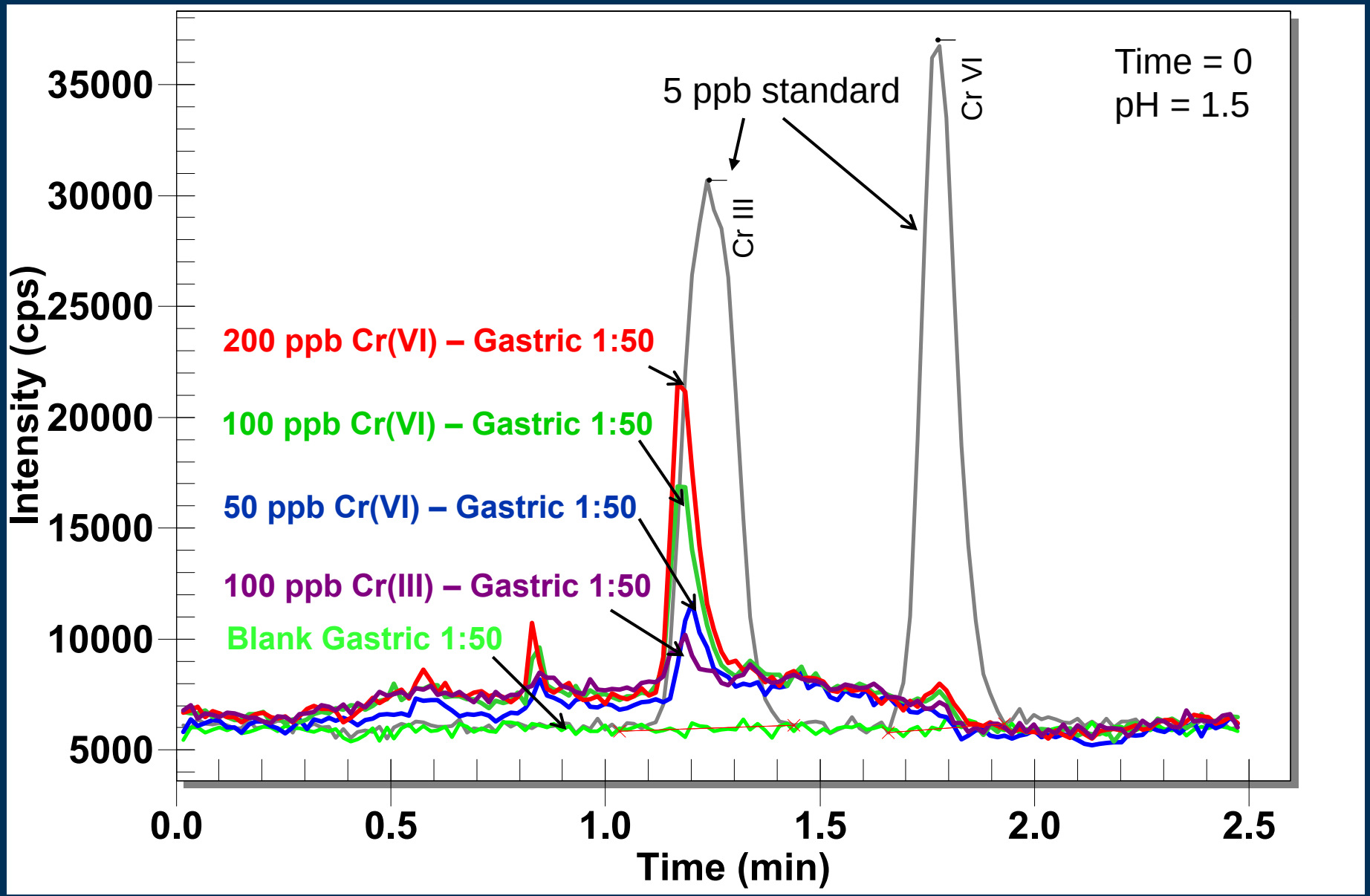
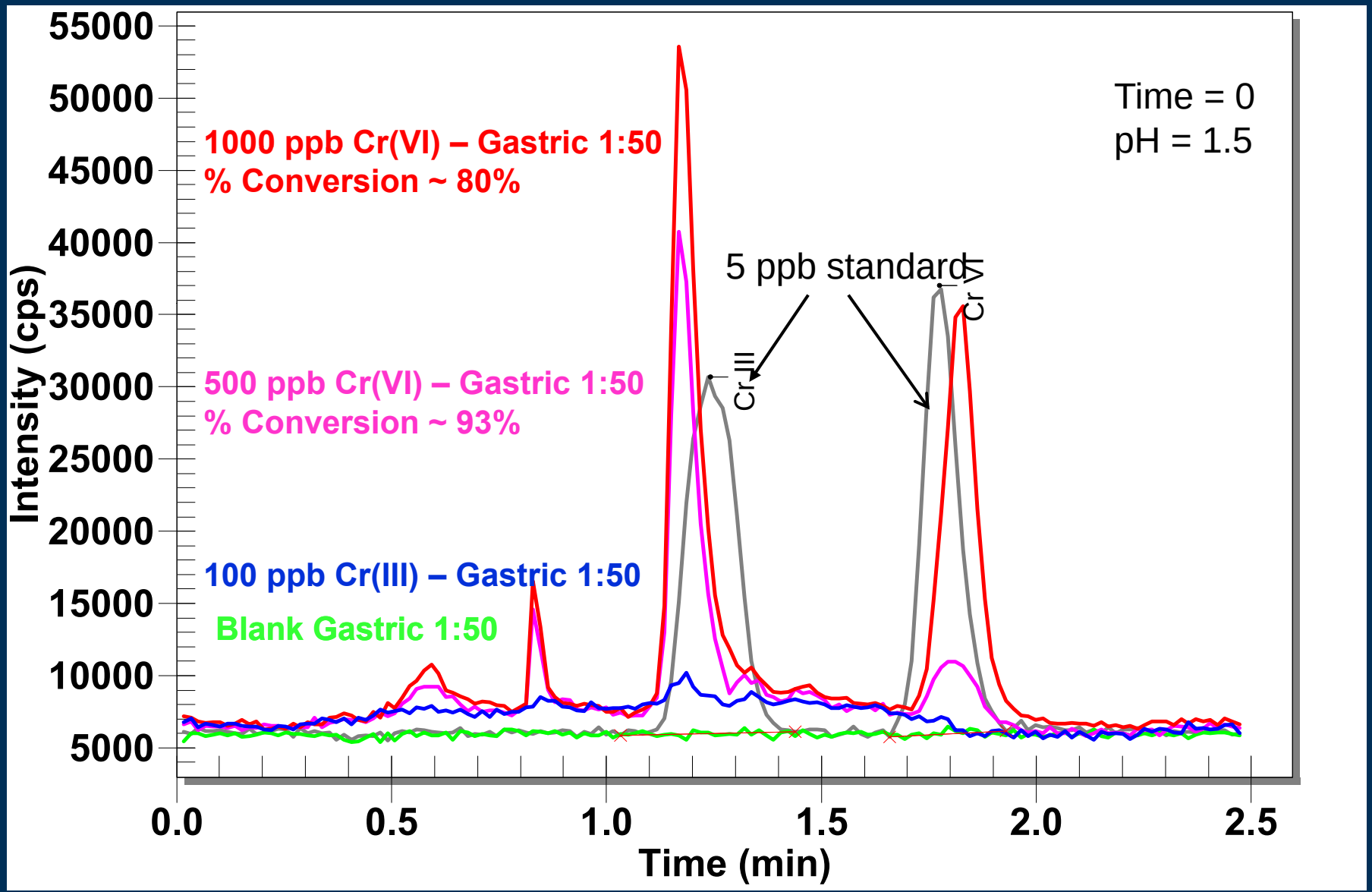
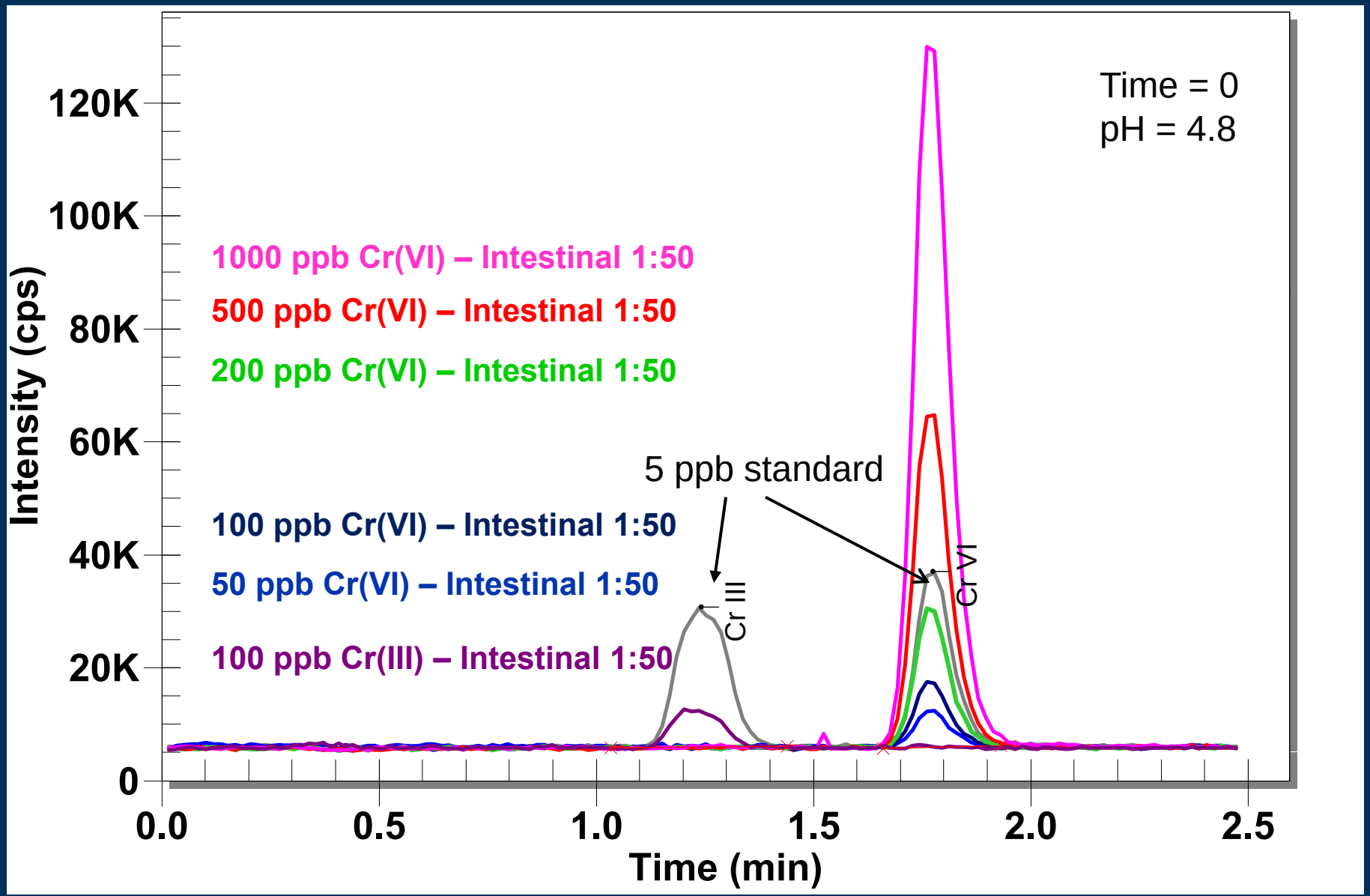
Gastric Fluid: Converts Cr(VI) to Cr(III) ≤ 200 ppb



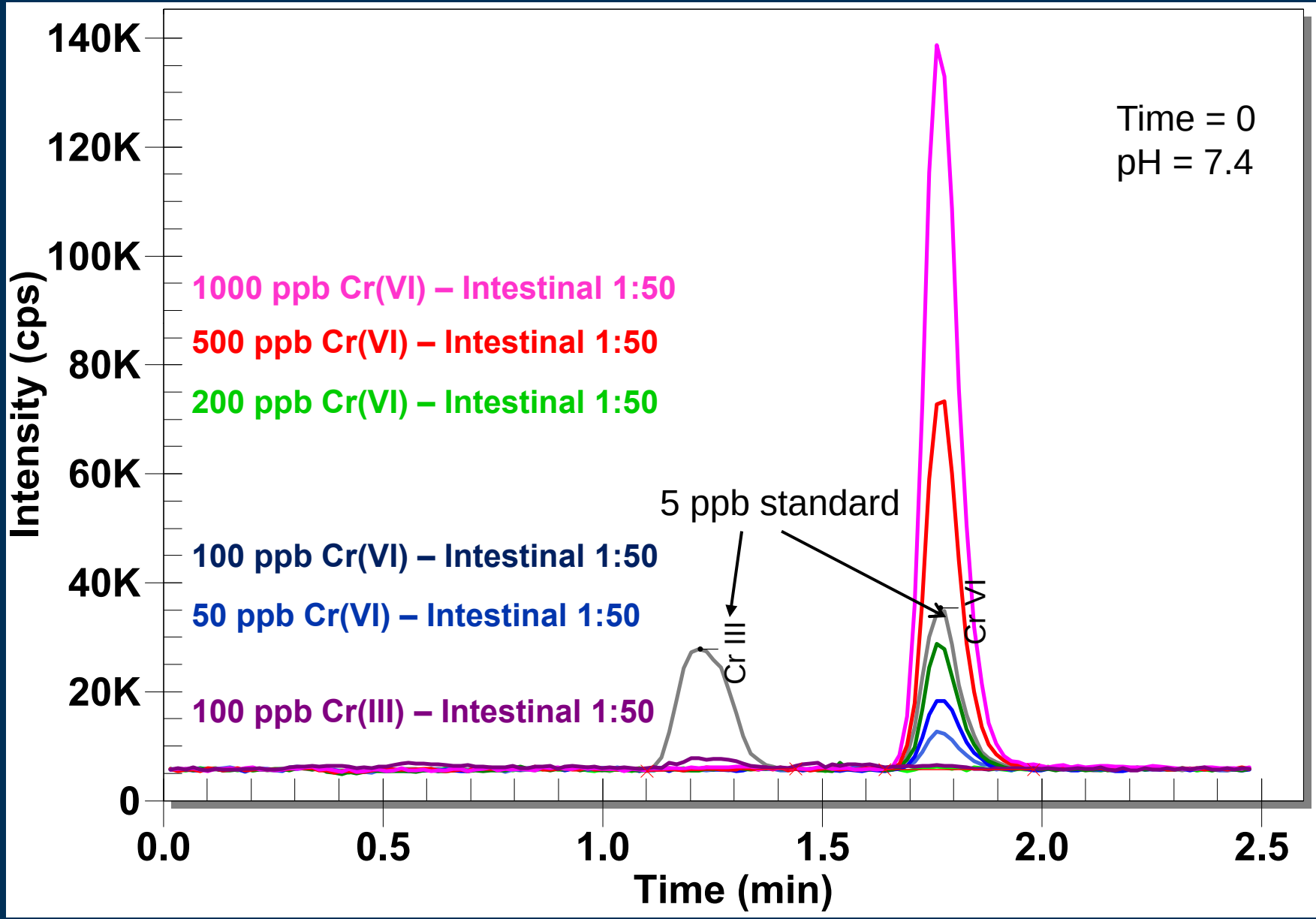
Gastric: Partial conversion to Cr(III) ≥ 500 ppb



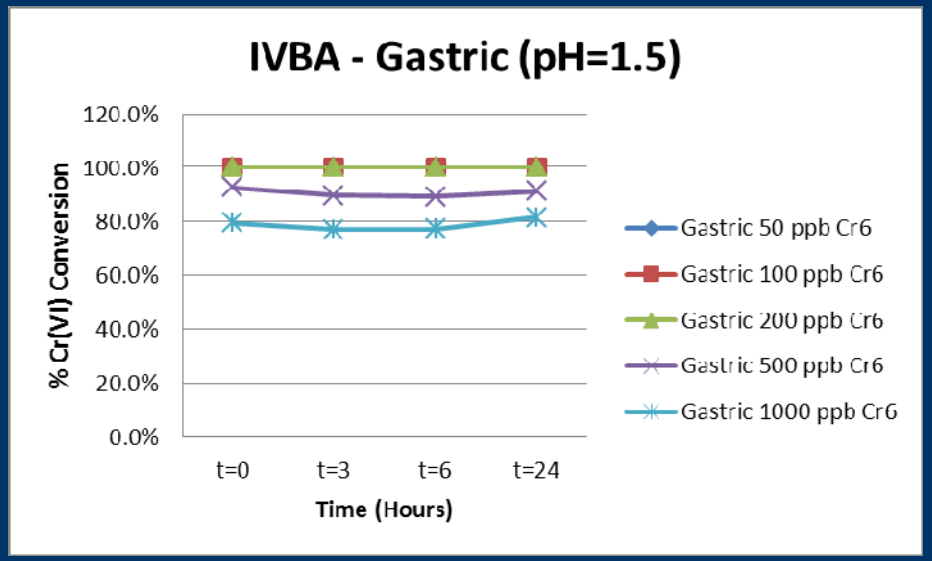
Intestinal: No immediate conversion

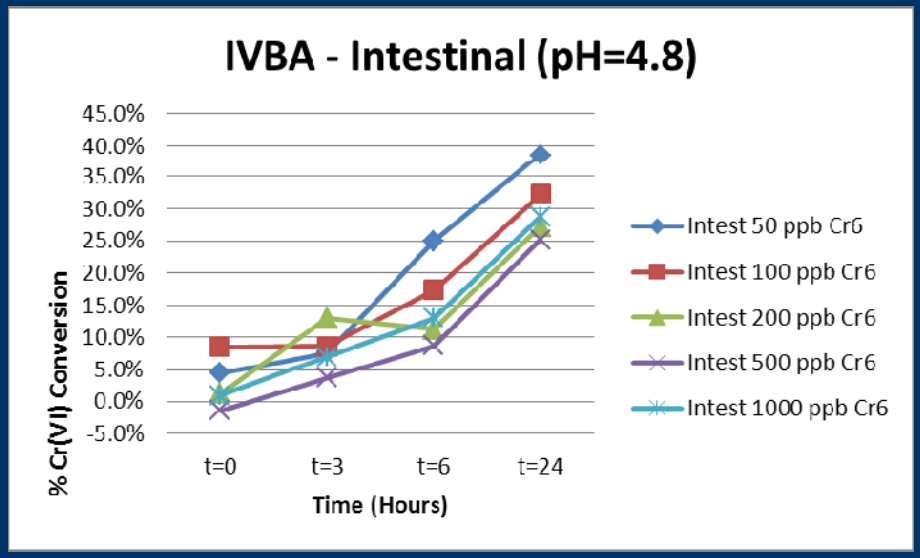


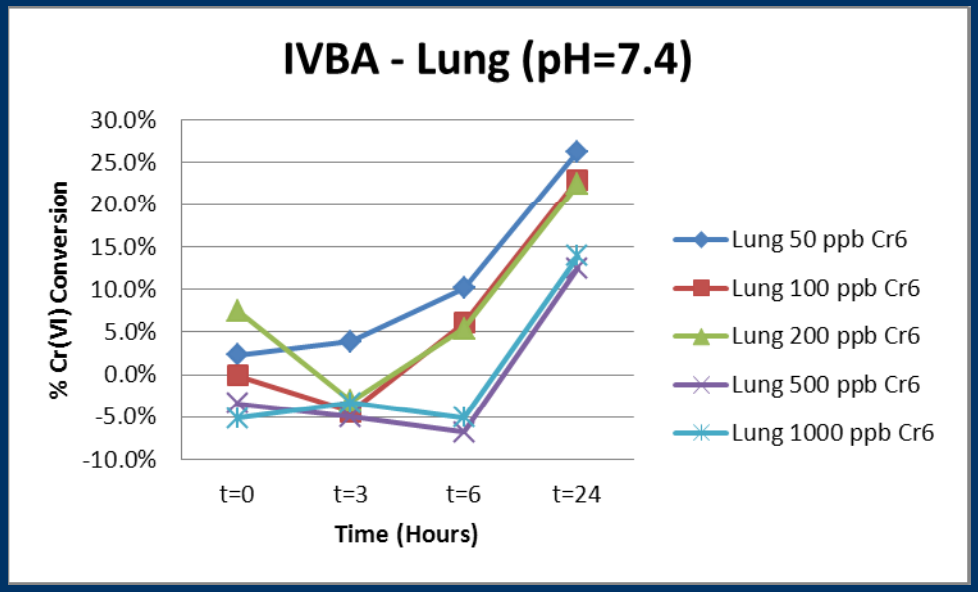
Lung Fluid: No immediate conversion



Cr(VI) Conversion vs. Time







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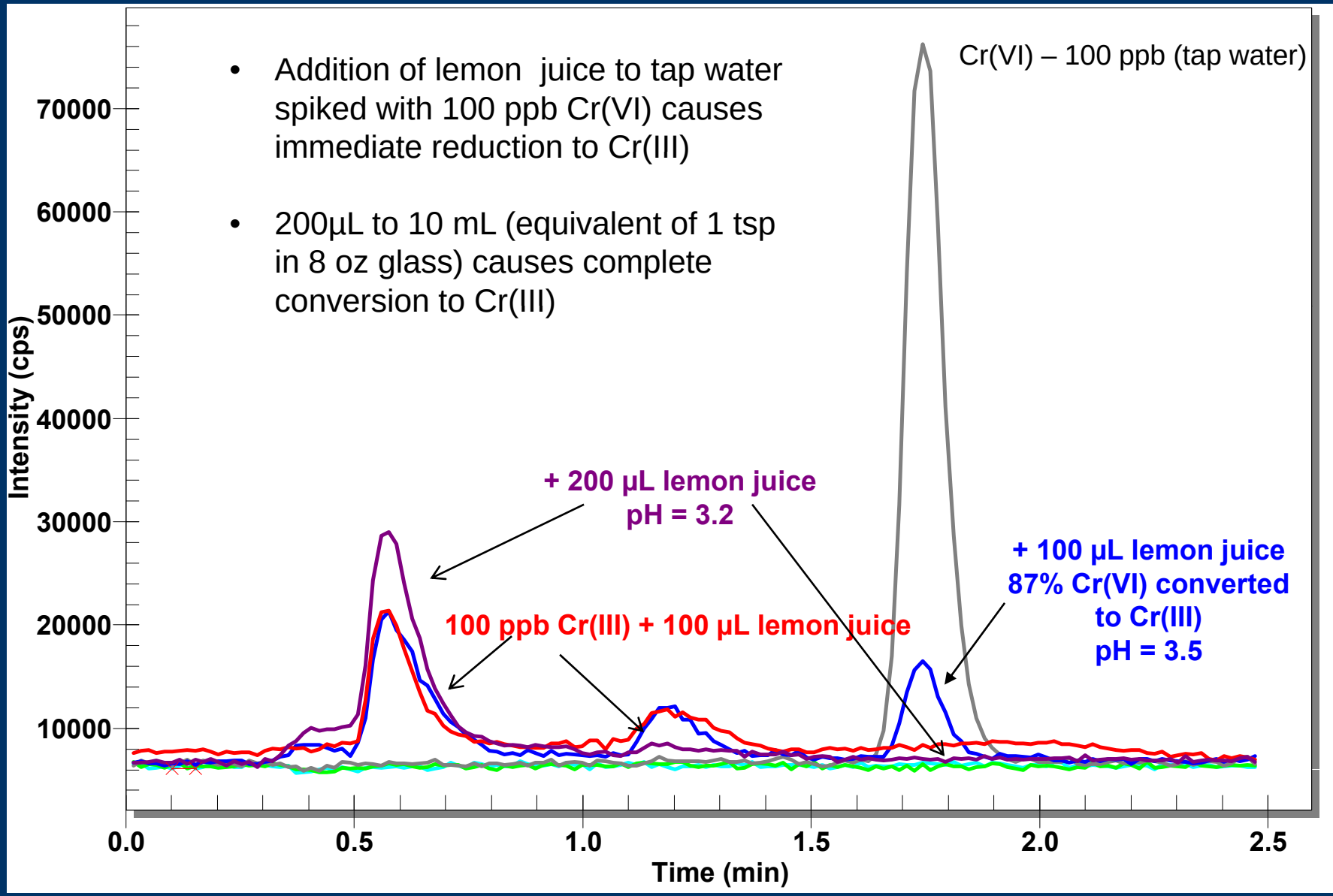
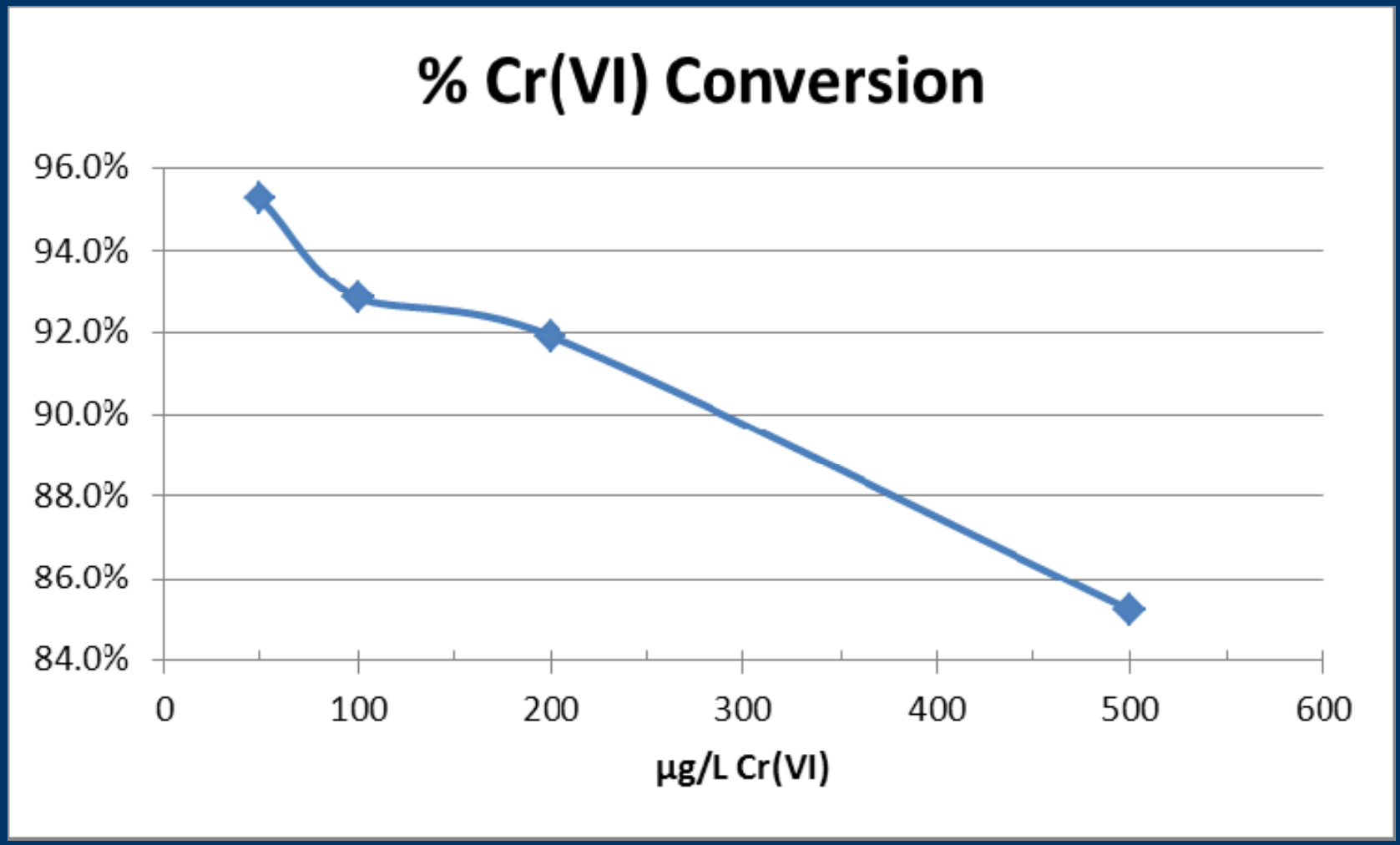
Removal of Cr(VI) in Tap Water

- Addition of lemon juice to tap water spiked with 100 ppb Cr(VI) causes immediate reduction to Cr(III)
- 200µL to 10 mL (equivalent of 1 tsp in 8 oz glass) causes complete conversion to Cr(III)



Lemon Juice Converts Cr(VI) to Cr(III)



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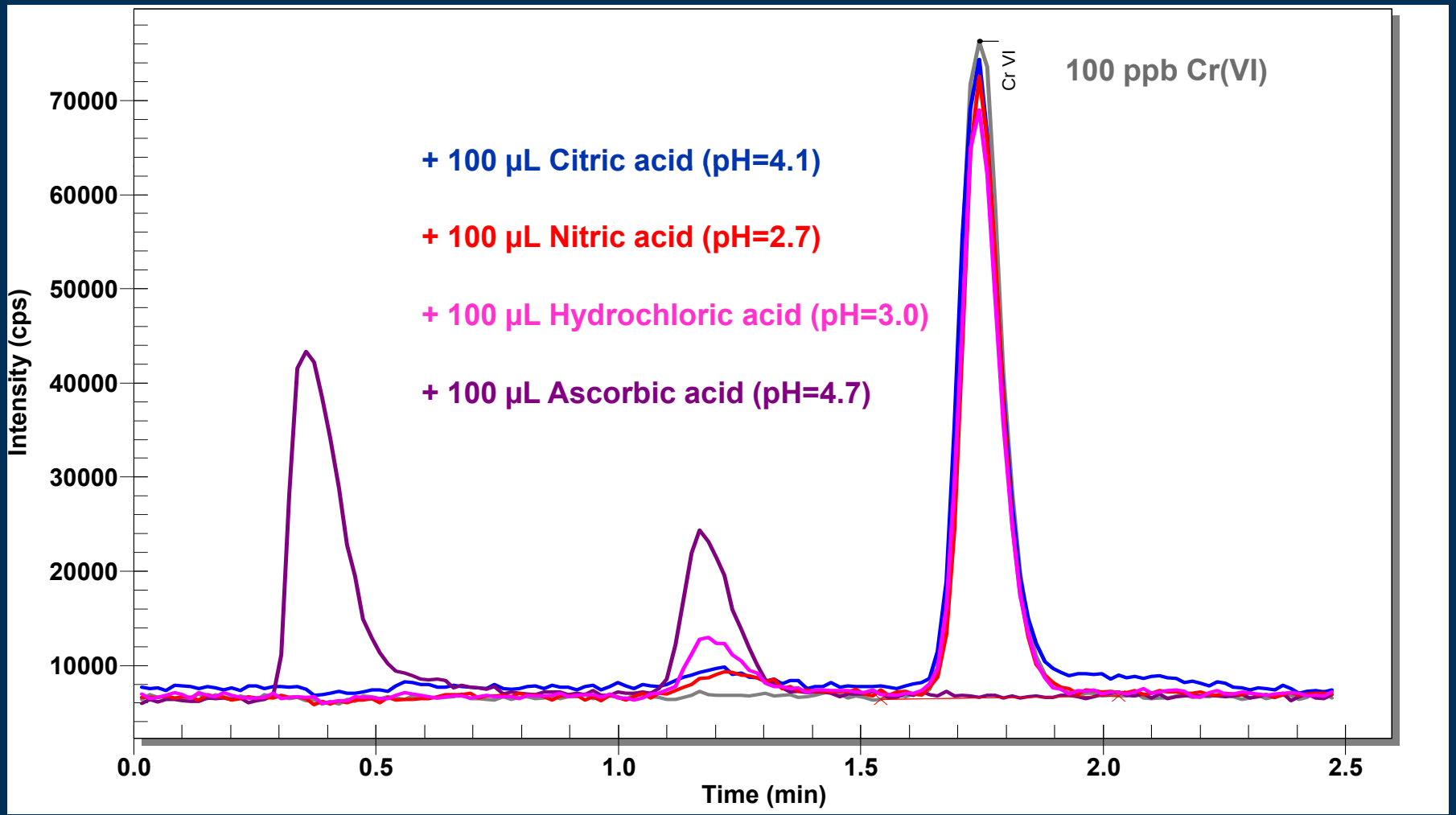
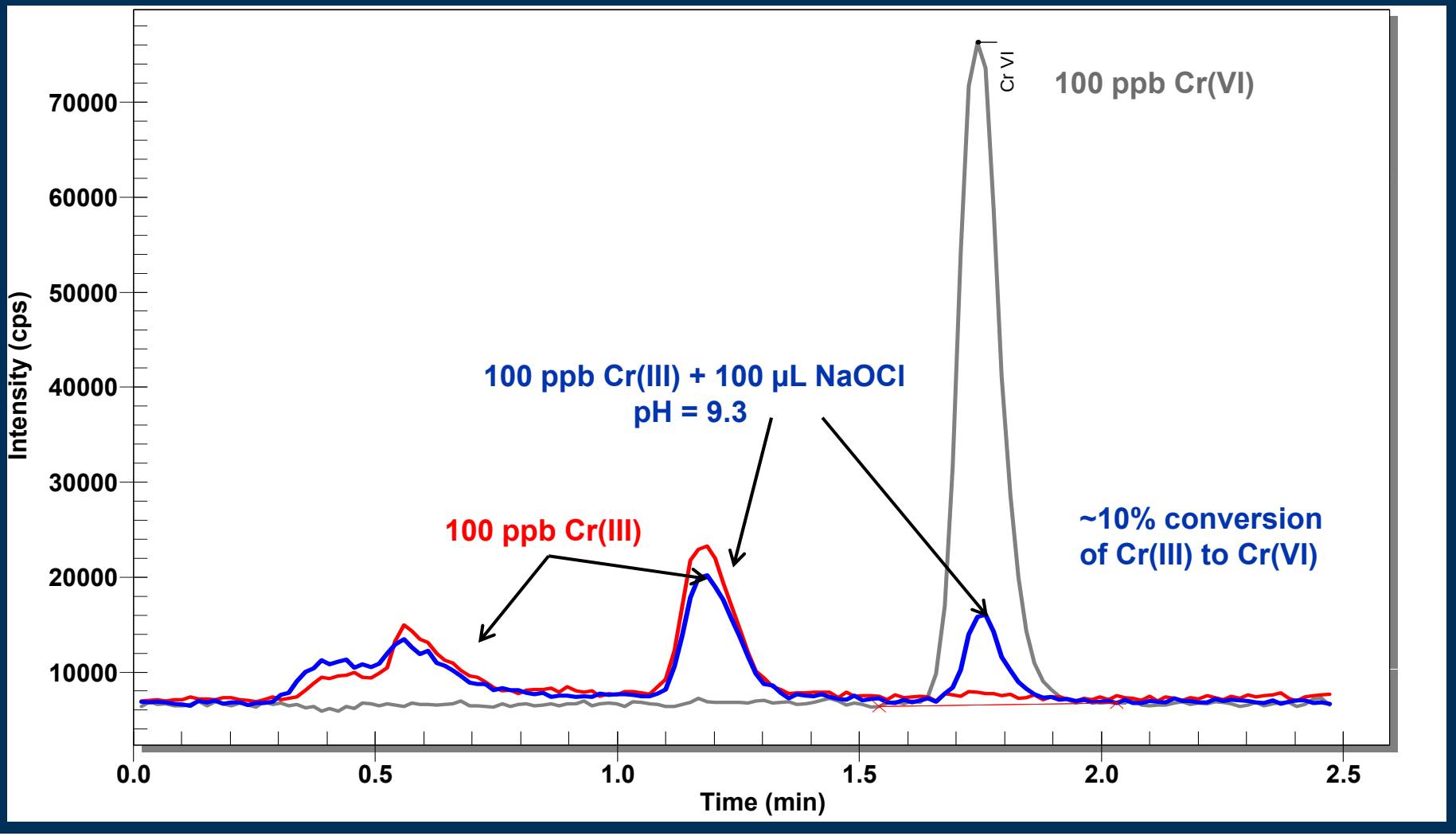
Effect of Acids on Cr(VI) Stability

- 100 ppb Cr(VI) in tap water
- Added 100 µL of 2% acid solution to 10 mL



NaOCl can cause oxidation of Cr(III)

- Added 100 µL 5% NaOCl to 100 ppb Cr(III) in tap water



Conclusions

- Larger injection volumes did not dramatically improve IDL for Cr(VI) in our method
- Studies on standards shows Cr(VI) stability highly variable and can be affected by other elements in the sample
  - Sample preservation and holding times need to address this
  - Stability studies with just Cr(VI) present may not be valid
- Studies done on effects of stomach acid on Cr(VI) show immediate conversion to Cr(III) up to 200 µg/L
  - Potential impact on Drinking Water limit for Cr(VI)
- Study shows addition of lemon juice or ascorbic acid can convert > 90% of Cr(VI) to Cr(III) "in the glass" for concentrations up to 200 µg/L Cr(VI)
- Addition of NaOCl can oxidize Cr(III) to Cr(VI)
  - Agrees with studies that water chlorination can oxidize Cr(III)

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