



Modifications to EPA Method 3060A that improve the Cr(VI) extraction efficiency from chromium ore processing residue (COPR)-contaminated soils

Christopher T. Mills¹, Carleton R. Bern², Ruth E. Wolf³, Andrea L. Foster⁴, Jean M. Morrison¹, William M. Benzel⁵

- 1) U.S. Geological Survey, Crustal Geophysics and Geochemistry Science Center, MS964D, Denver Federal Center, Denver, CO 80225.
- 2) U.S. Geological Survey, Colorado Water Science Center, Denver Federal Center, Denver, CO 80225
- 3) Perkin Elmer, Inc., 75 Nicholson Lane, San Jose, CA 95132
- 4) U.S. Geological Survey, Geology, Minerals, Energy, and Geophysics Science Center, 345 Middlefield Road, Menlo Park, CA 94025.
- 5) U.S. Geological Survey, Central Mineral and Environmental Resources Science Center, Denver Federal Center, Denver, CO 80225



EPA Method 3060A

Revision 1, December 1996

Applicable to soils, sludges, sediments, and similar waste materials.

Method Requirements (as stated in method):

- Solubilize all forms of Cr(VI)
- No reduction of native Cr(VI) to Cr(III)
- No oxidation of native Cr(III) contained in the sample to Cr(VI)

Method Parameters:

- High pH (~13) and high carbonate
- Liquid:solid ratio = 20 mL g⁻¹
- Borosilicate glass or quartz extraction vessels
- Stir samples at 90-95° C for at least 1 hour – no prescribed time limit
- Adjust pH to 7.5 with nitric acid

Analysis

- 7196A Visible Spectrophotometry
- 7199 Ion Chromatography
- 6800 Speciated Isotope Dilution Mass Spectrometry

Issues with Method 3060A

- **Operationally difficult to perform**

- Sample collection/processing does not address heterogeneity or particle size.
- Addition of MgCl_2 causes immediate precipitation of $\text{Mg}(\text{OH})_2$ / MgCO_3 .
- Zatka (1985, Am. Ind. Hyg. Assoc. J.) found suppression of Cr(III) oxidation is sensitive to MgCl_2 being added before extraction solution. Order reversed in 3060A.
- Addition of phosphate interferes with speciation by HPLC-ICP-MS.
- Addition of phosphate as buffer results in the neutralization of 3% of hydroxide.
- Thorough rinsing of solids during filtration and volume of 5M HNO_3 required for neutralization can overflow the 100 mL volumetric flask.
- Large amounts of chromite/magnetite in COPR coats stir bars which interferes with their function and may affect extraction efficiency.

- **Incomplete Cr(VI) Extraction**

- Several studies show extraction of Cr(VI) from COPR-contaminated materials is not quantitative compared to X-ray absorption near edge structure (XANES) spectroscopy results
 - Dermatas, D.; Chrysochoou, M.; Moon, D. H.; Grubb, D. G.; Wazne, M.; Christodoulatos, C., Environ. Sci. Technol. 2006, 40 (18), 5786–5792.
 - Wazne, M.; Jagupilla, S. C.; Moon, D. H.; Jagupilla, S. C.; Christodoulatos, C.; Kim, M. G., J. Hazard. Mater. 2007, 143 (3), 620–628.
 - Malherbe, J.; Isaure, M. P.; Séby, F.; Watson, R. P.; Rodriguez-gonzalez, P.; Stutzman, P. E.; Davis, C. W. Maurizio, C.; Unceta, N.; Sieber, J. R.; Et al., Environ. Sci. Technol. 2011.
 - Yu, S.; Du, J.; Luo, T.; Huang, Y.; Jing, C., J. Hazard. Mater. 2012, 209–210, 250–255.

Approaches to Improve Method 3060A

- **Particle Size**
 - EPA 3060A does not specify sample prep
 - Others have found decreasing COPR particle size increases Cr(VI) extraction efficiency^{1,2}
 - We investigated the effect of micronizing to a fine particle size
- **Extraction Vessel**
 - High pH/high carbonate extraction fluid dissolved borosilicate glass
 - We compared glass with PTFE extraction vessels
- **Liquid to Solid Ratio**
 - 20 mL g⁻¹ ratio may prevent mineral dissolution or anion exchange
 - We tested ratios from 95 to 3700 mL g⁻¹
- **Extraction Time**
 - Dissolution of mineral phases and exchange processes may be kinetically limited
 - We investigated a range of extraction times from 0.25 to 72 hours

NIST SRM 2701 – Cr(VI) Reference Material

- Soil heavily contaminated with chromite ore processing residue (COPR)
- Collected from Liberty State Park, Jersey City, NJ
- Prepared by Steve Wilson (USGS), Ball mill ground
- Total Cr 4.26% (42,600 mg kg⁻¹), pH = 9.6

Method	7196A ¹ colorimetric	6800 ¹ isotope dilution	XANES ²
Median Cr(VI) Concentration (mg kg ⁻¹)	365	551	3000-3400
Standard Deviation	74	16	

Considerations for Sample Preparation

- Sample homogeneity critical to accurate and reproducible results!
- Good recoveries on homogeneous SRM materials not indicative of typical sample recoveries unless samples are similar in particle size, etc. to SRM(s)
- SRM Preparation
 - Air Drying
 - Mechanical disaggregation (ceramic)
 - 2 mm sieve
 - Fines ground in ball mill (ceramic/corundum) for 8 hours 25 lb at a time
 - Combined batches mixed in V-blender for 24 hours



Steve Wilson (USGS) preparing NIST 2701 material (May 2006)



NIST 2701 as Delivered

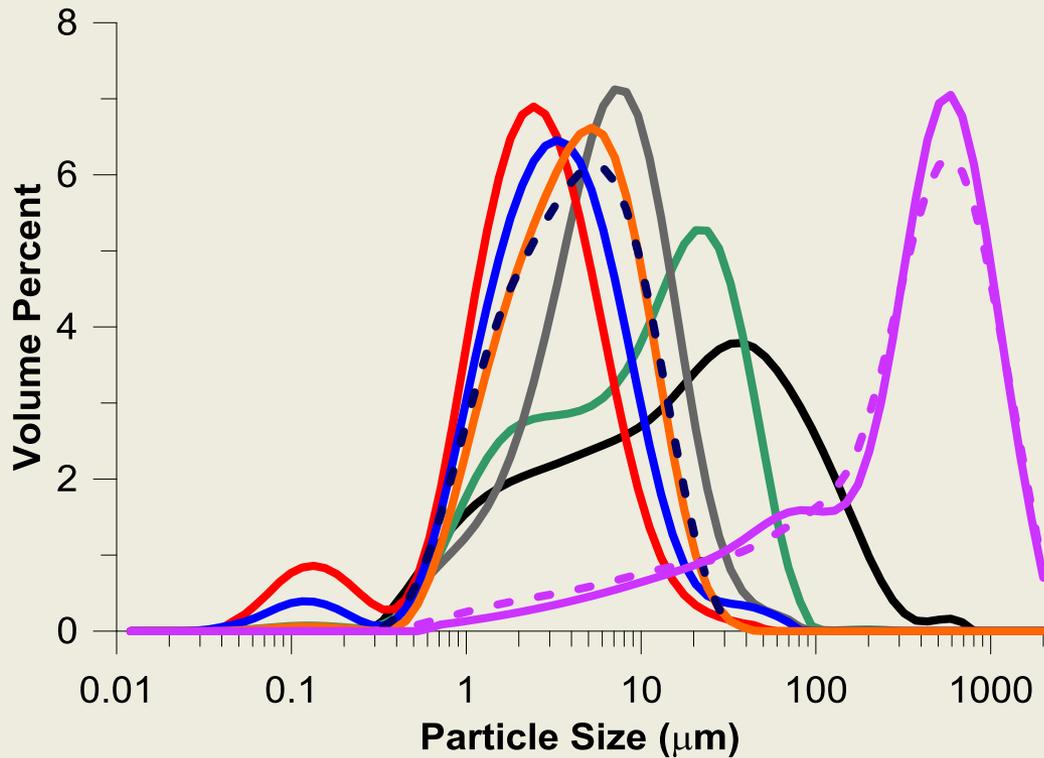
Considerations for Sample Preparation

- NJ COPR 2B
 - Soil collected same time as NIST 2701
 - Similar location
 - Not processed for SRM
 - Closer to a “real” sample
 - Used for some of our testing

Original Sample



Effect of Micronization on Particle Size of NIST 2701



2B

- Sieved
- 3 min Shatterboxed

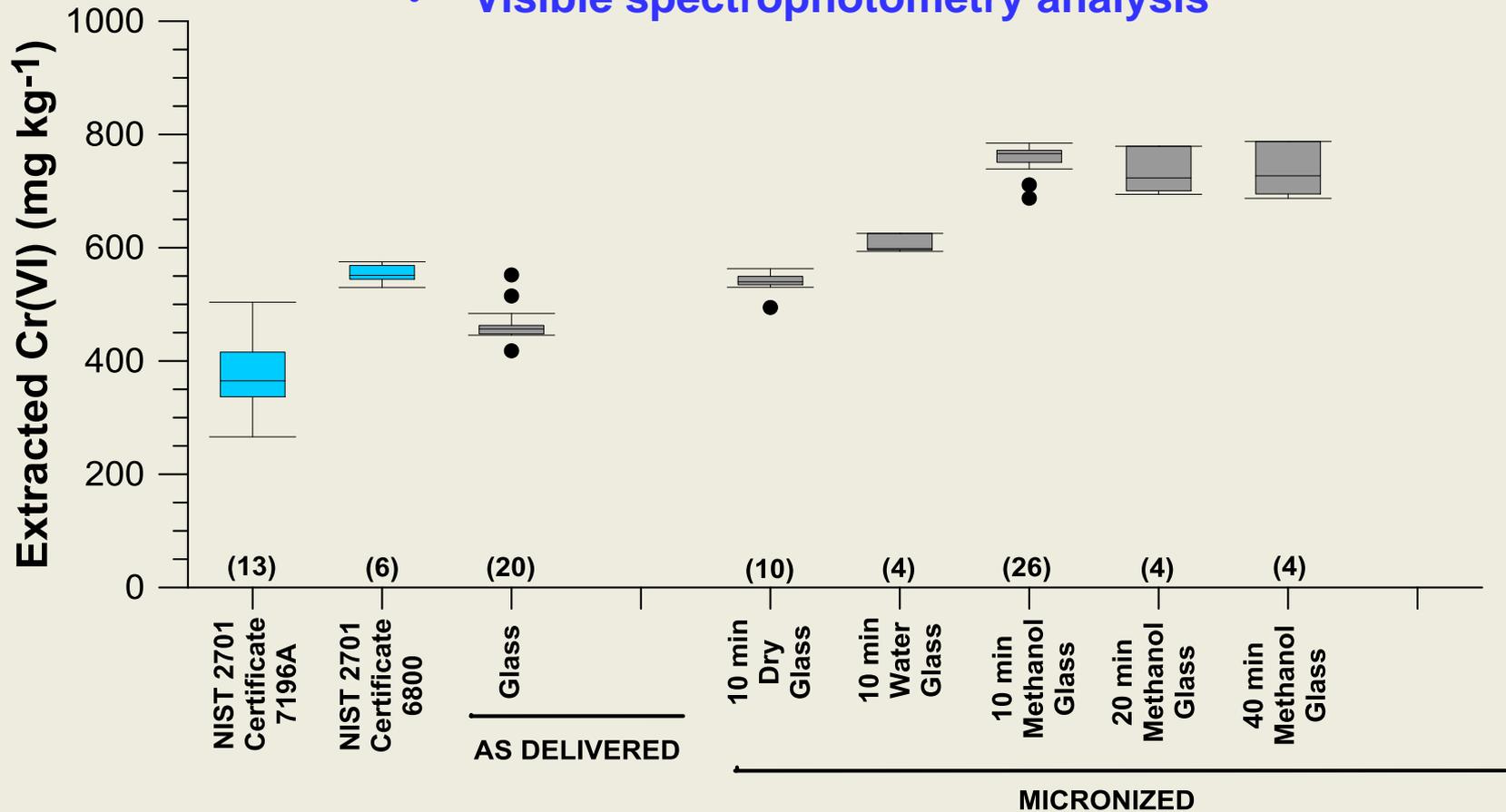
NIST 2701

- As Delivered
- 10 min dry
- 10 min water
- 10 min methanol
- 20 min methanol
- 40 min methanol
- 10 min cyclohexane



Effect of Micronization on Cr(VI) extraction

- 2.25 hour extraction time
- Visible spectrophotometry analysis



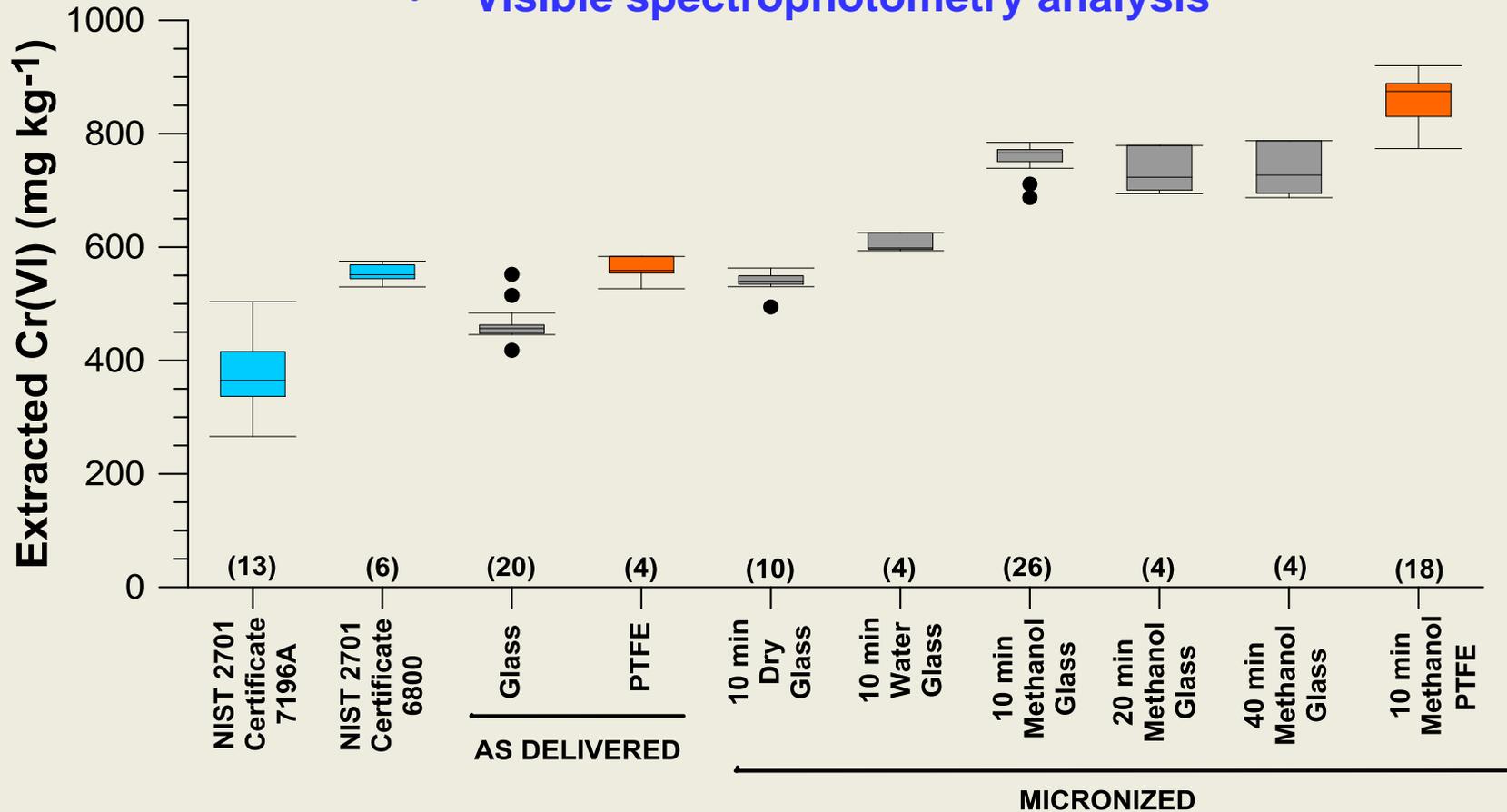
Vessel and Agitation Type

- Water bath shaker table
 - Easier to agitate and control temperature
 - Better temperature control
 - No stir bars
- Use of PTFE vessels
 - Do not dissolve in high pH/high carbonate like borosilicate glass
 - Less potential for contamination

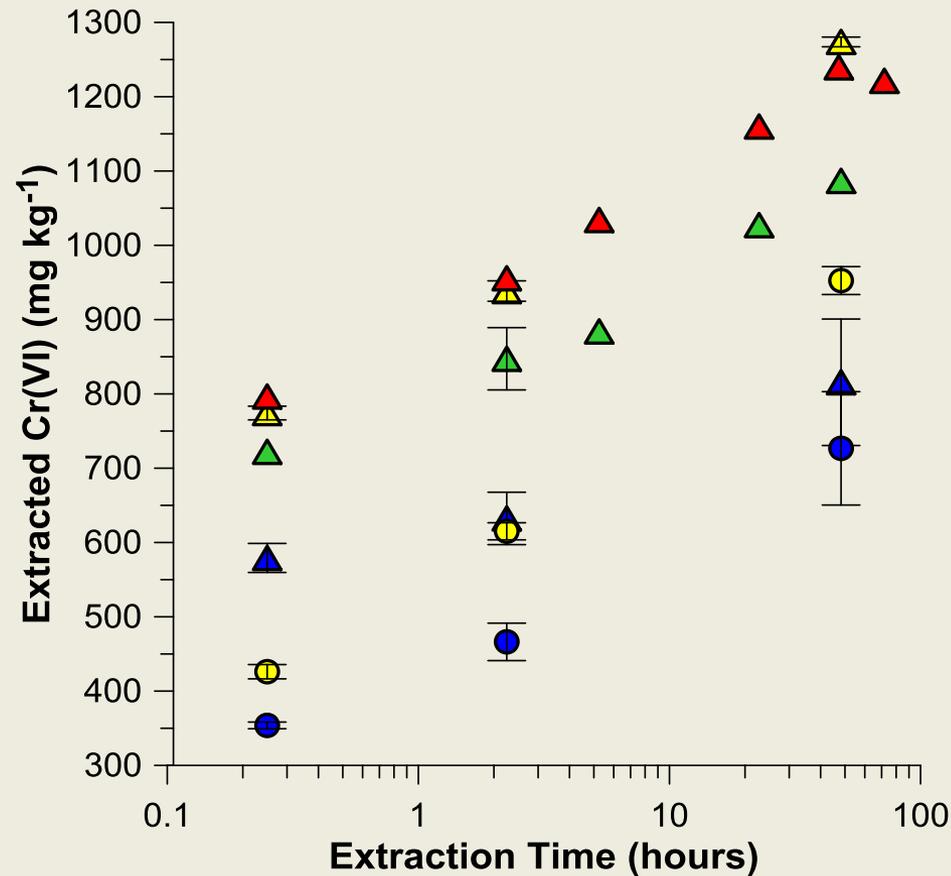


Effect of Vessel Type on Cr(VI) Extraction

- 2.25 hour extraction time
- Visible spectrophotometry analysis

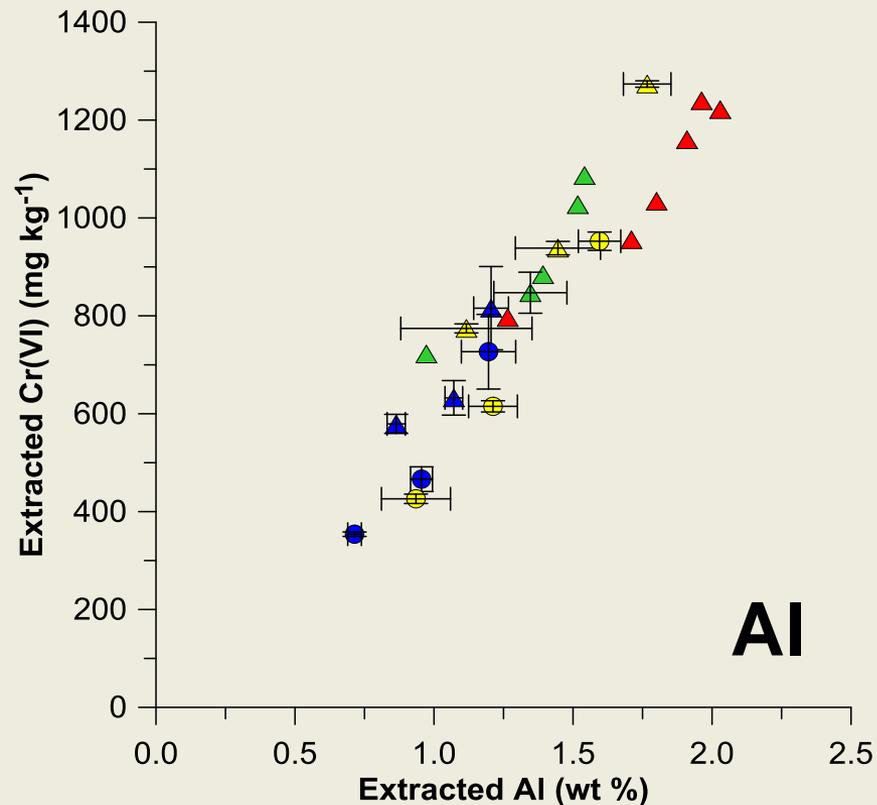
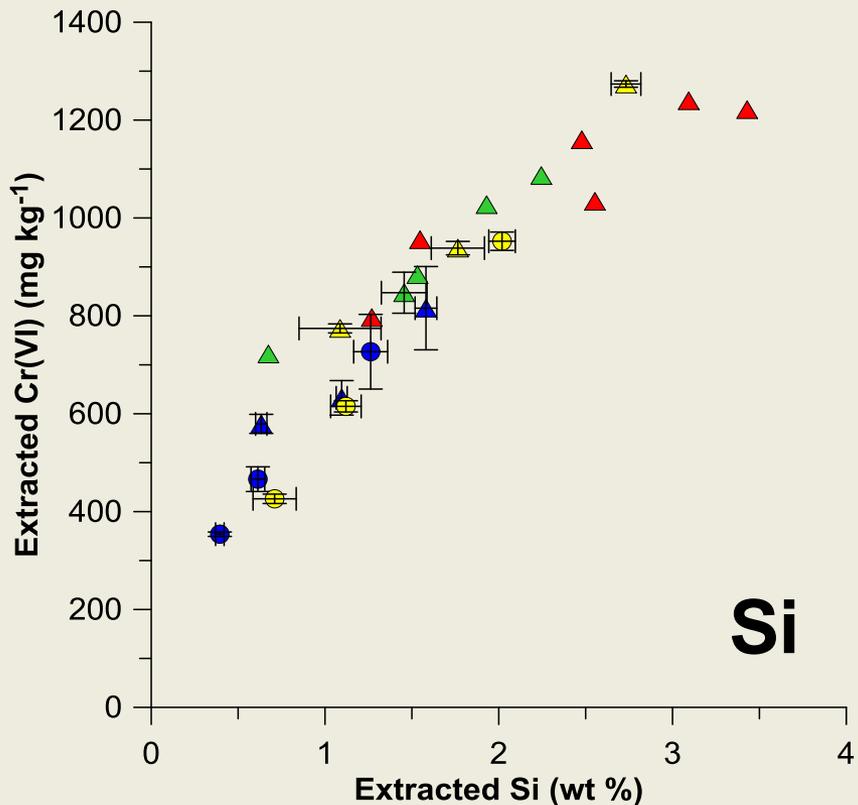


Effect of Liquid to Solid Ratio and Extraction Time



- All extractions in PTFE
- Micronized = 10 min MeOH
- Varied extraction time
- Varied liquid to solid ratio

Extracted Cr(VI), Al, and Si are Highly Correlated



Common Minerals in COPR

Chromite	$(\text{Fe,Mg})\text{Cr}_2\text{O}_4$	Major host of Cr(III)
Brownmillerite	$\text{Ca}_2(\text{Fe, Al})_2\text{O}_5$	Can host Cr(III) [Cr(VI)?]
Periclase	MgO	
Larnite	Ca_2SiO_4	
Brucite	$\text{Mg}(\text{OH})_2$	
Calcite/Aragonite	CaCO_3	
Calcium silicate hydrate	CaH_2SiO_4	
Hydrogarnet	$\text{Ca}_3\text{Al}_2((\text{Si}/\text{H}_4)\text{O}_4)_3$	Can host Cr(VI)
Hydrocalumite	$\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	Can host Cr(VI)
Hydrotalcite	$\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$	Can host Cr(VI)
Ettringite	$\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$	Can host Cr(VI)

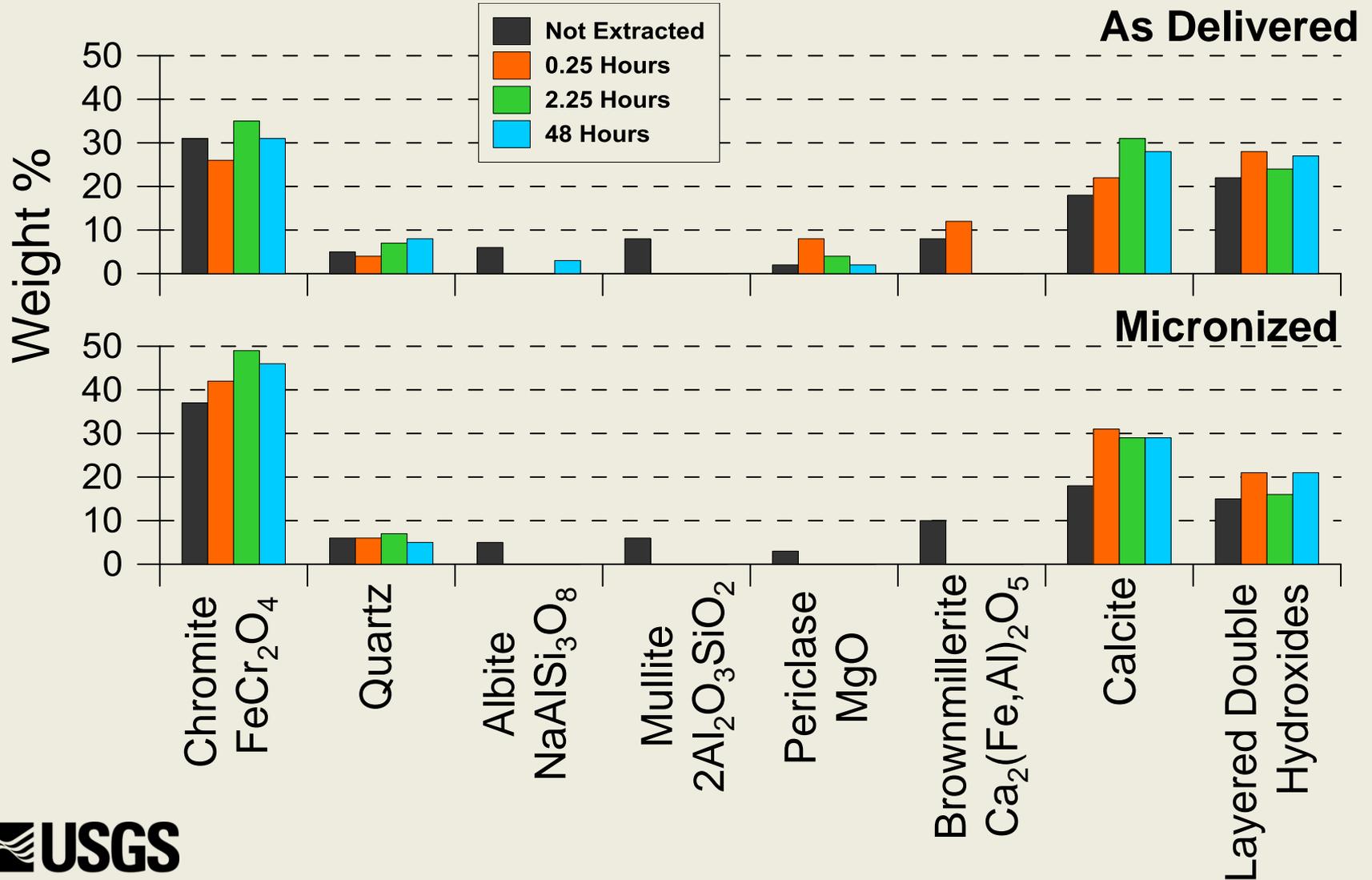
Geelhoed et al. (2002) *GCA*

Hillier et al. (2003) *STOTEN*

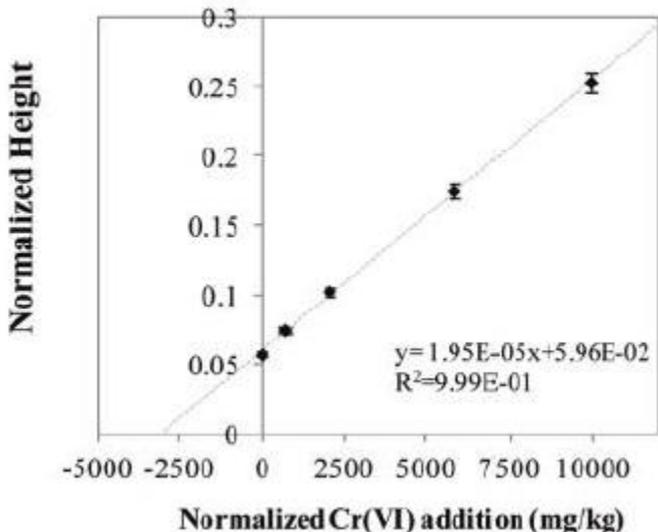
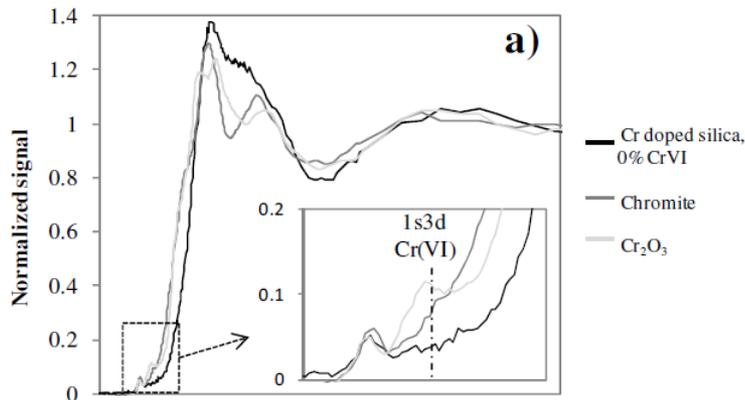
Mahlerbe et al. (2011) *ES&T*



Effect of Extraction on COPR Mineralogy (XRD)

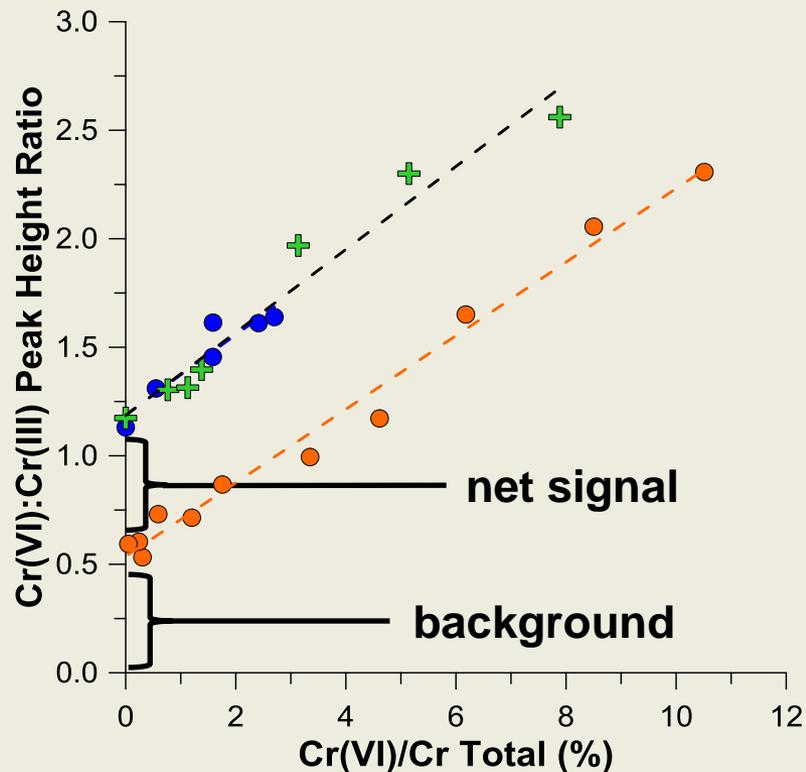


New estimate of Cr(VI) in NIST 2701 (XANES)



Mahlerbe et al. (2011) *ES&T*

- NIST 2701 - As Delivered - Standard Additions
- + NIST 2701 - micronized - standard additions
- External Std - 3.5 wt% Cr(III)



net signal x slope (RF) =
~1300 to 1600 mg kg⁻¹ Cr(VI)

Conclusions

- **Our XANES-based estimate for Cr(VI) in NIST 2701 is ~1300 to 1600 mg kg⁻¹**
- **Amount of Cr(VI) extracted from NIST 2701 varies greatly with extraction parameters**
- **We extracted a maximum of 1270 mg kg⁻¹ Cr(VI) but cannot rule out increased oxidation of Cr(III) during extraction**
 - **Colorimetric detection method (7196A)**
 - **Micronized sample**
 - **Liquid to solid ratio of ~1000 (50x that of prescribed ratio)**
 - **PTFE extraction flasks**
 - **Extraction time of 48 hours**
- **Layered double hydroxides – one of the main hosts of Cr(VI) in COPR**
 - **did not substantially dissolve or transform during the extraction**

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