

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

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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

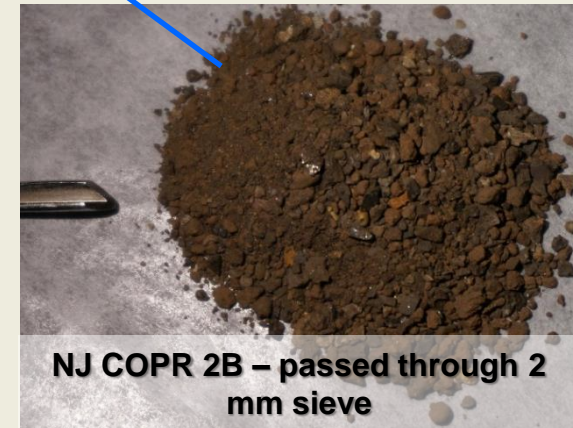
- Sample homogeneity critical to accurate and reproducible results!
- Good recoveries on homogeneous SRM materials not indicative of typical sample recoveries unless samples are similar in particle size, etc. to SRM(s)
- SRM Preparation
 - Air Drying
 - Mechanical disaggregation (ceramic)
 - 2 mm sieve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



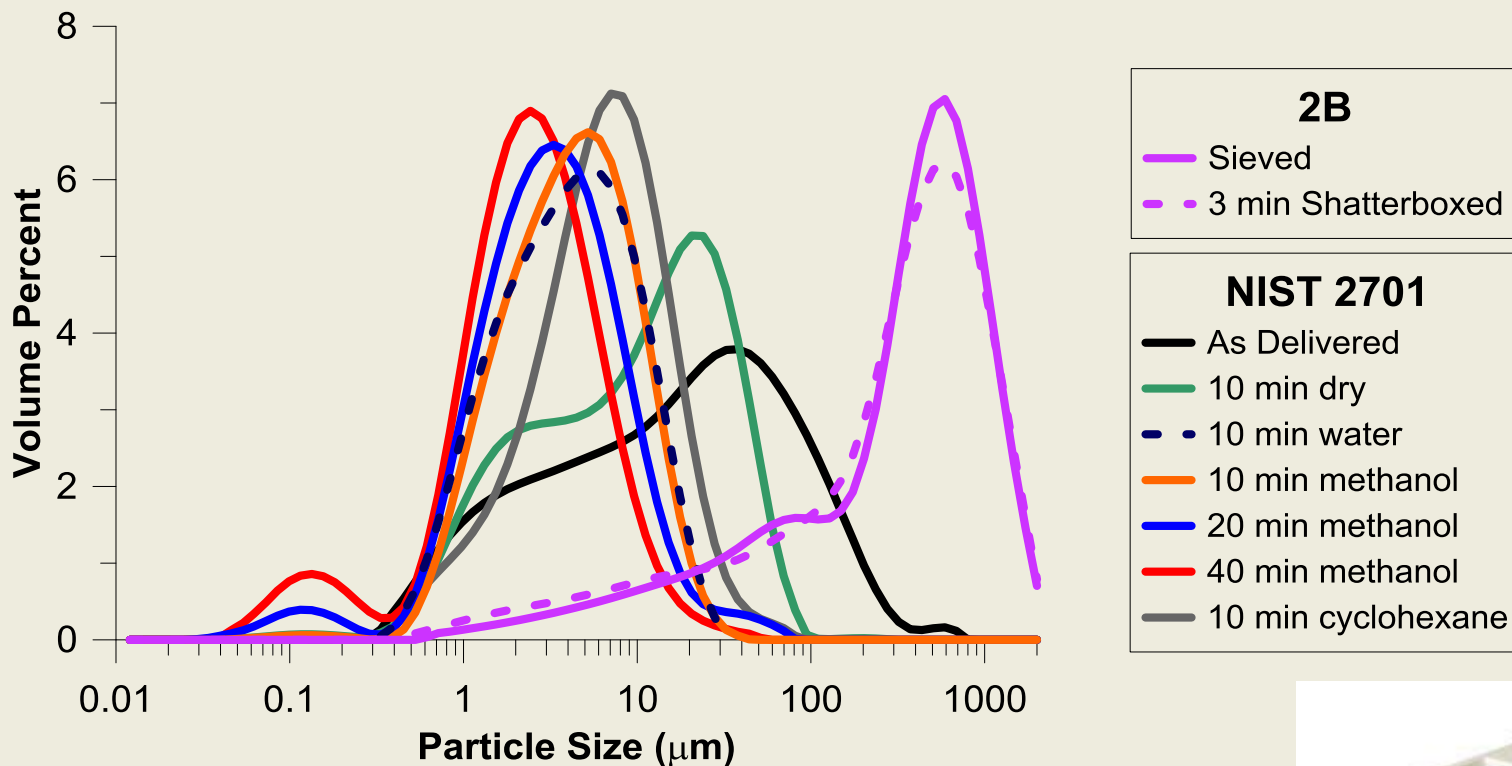
Considerations for Sample Preparation

- 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

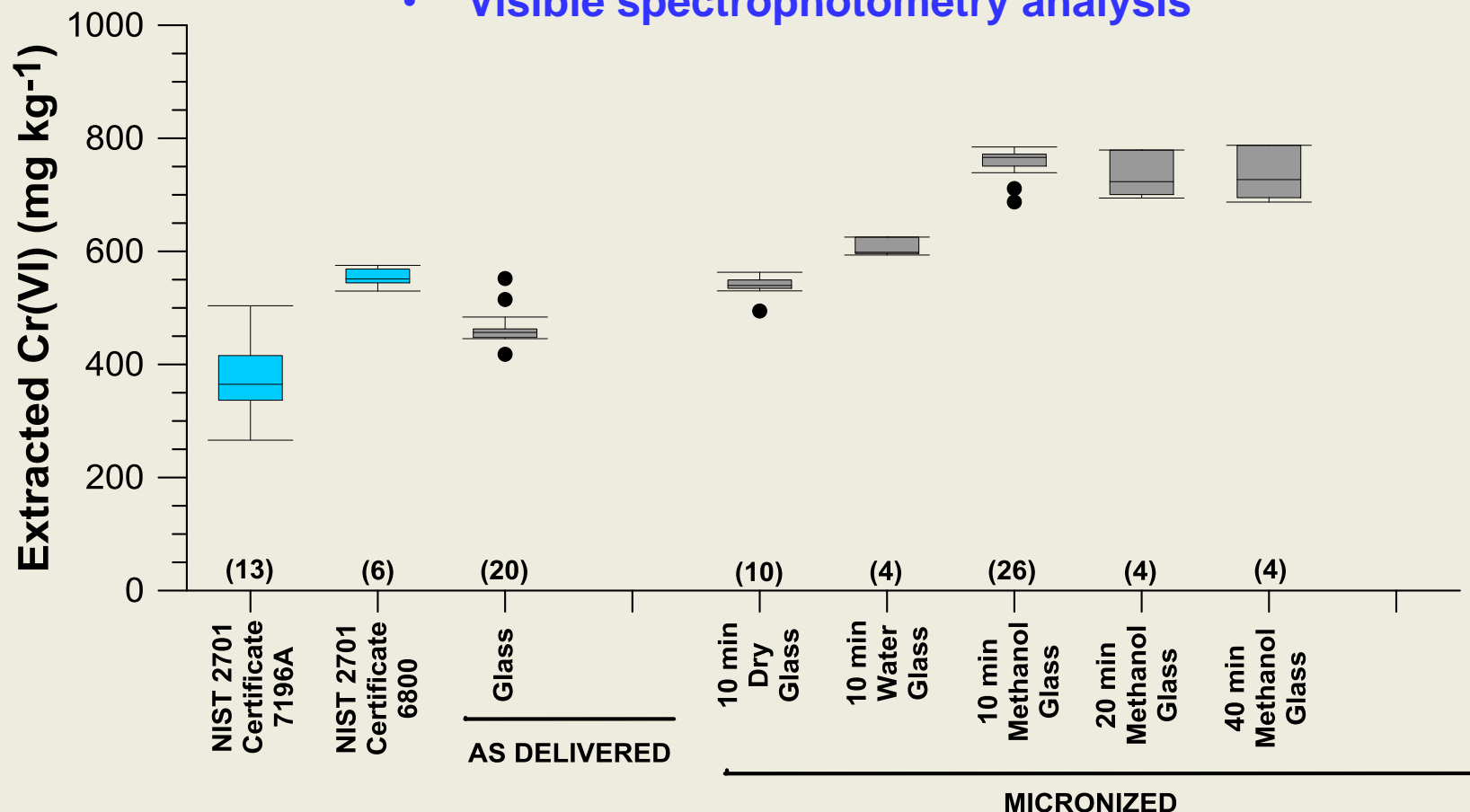


Effect of Micronization on Particle Size of NIST 2701



Effect of Micronization on Cr(VI) extraction

- 2.25 hour extraction time
- Visible spectrophotometry analysis



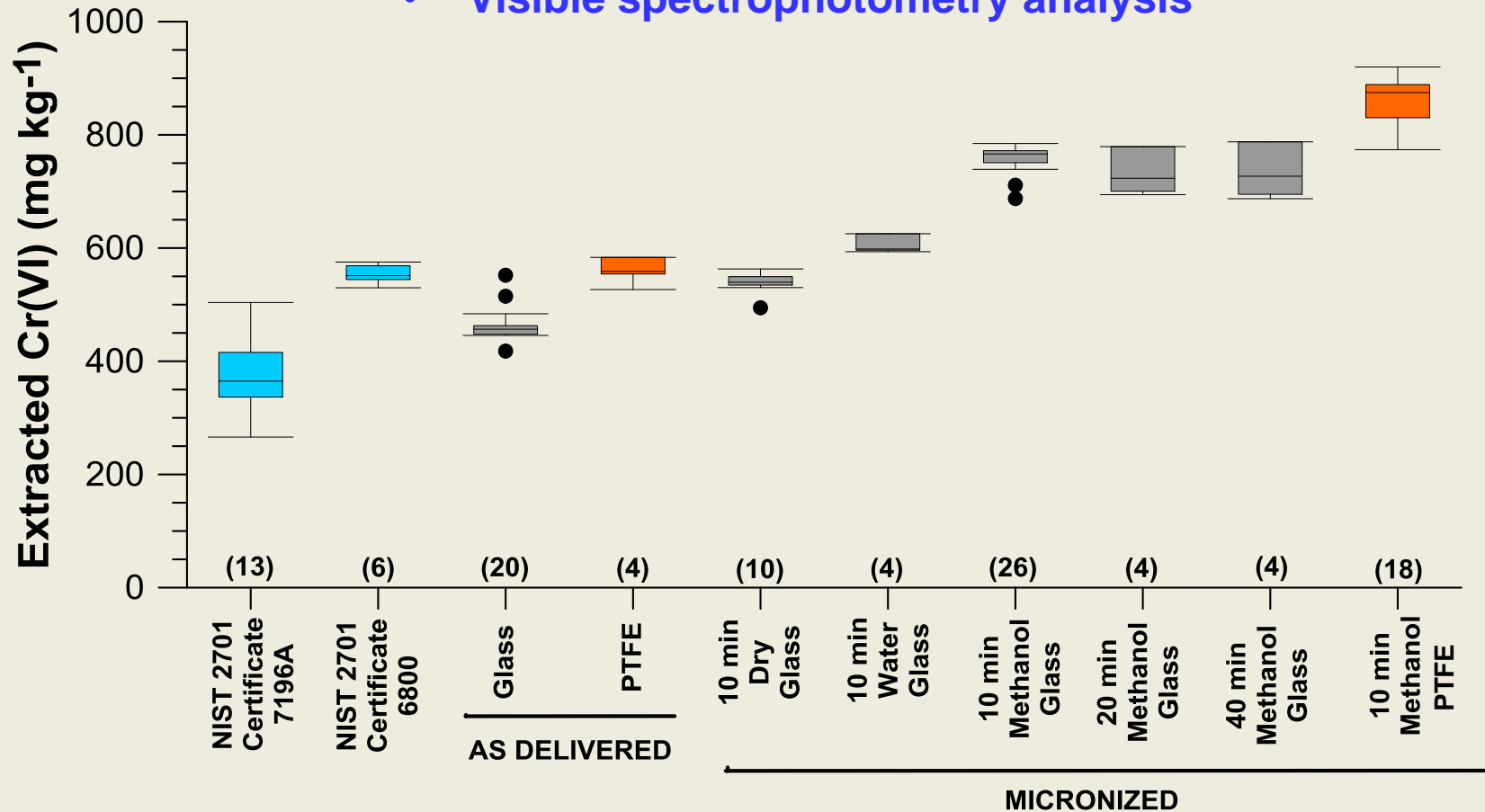
Vessel and Agitation Type

- 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

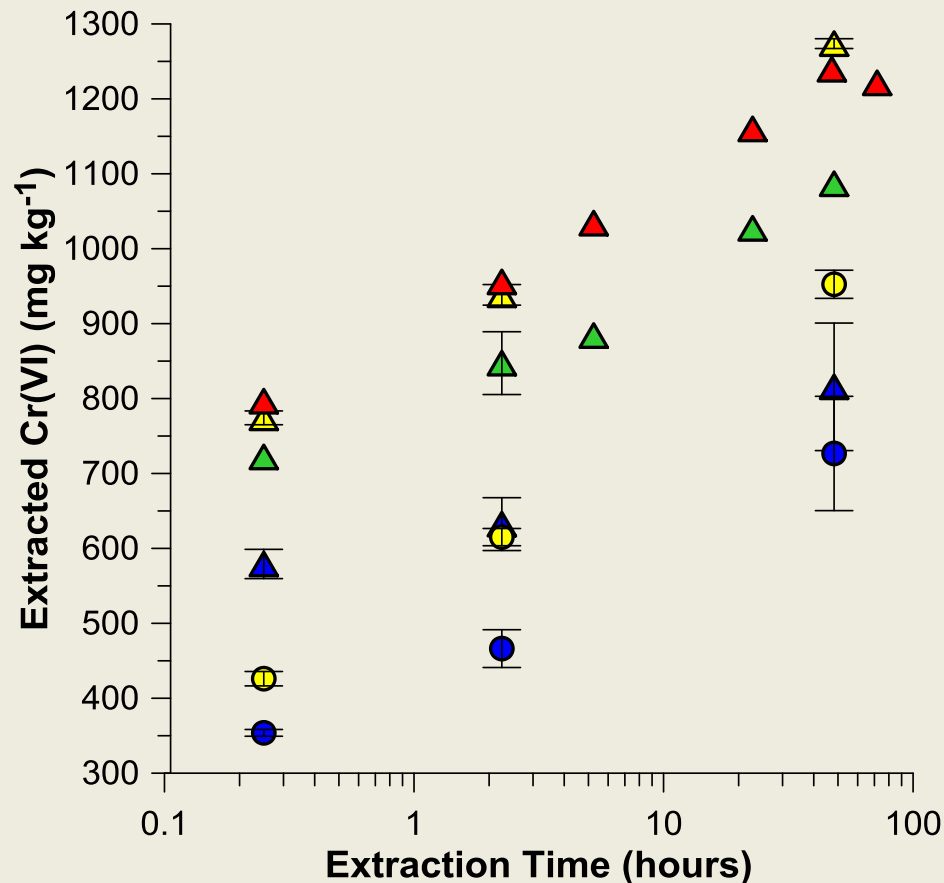


Effect of Vessel Type on Cr(VI) Extraction

- 2.25 hour extraction time
- Visible spectrophotometry analysis

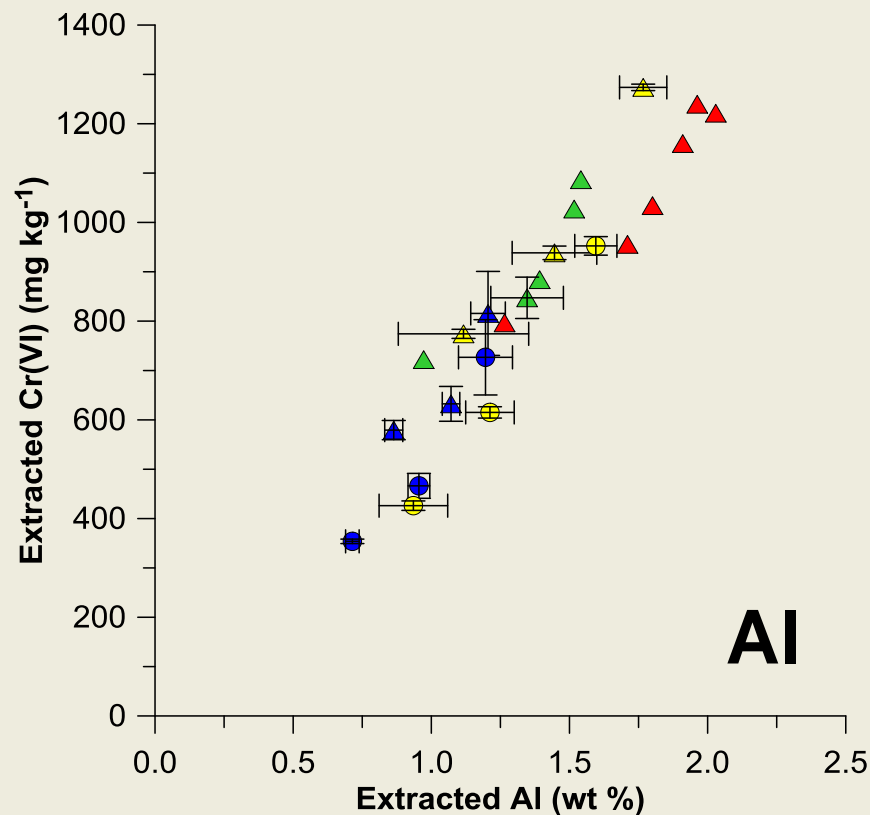
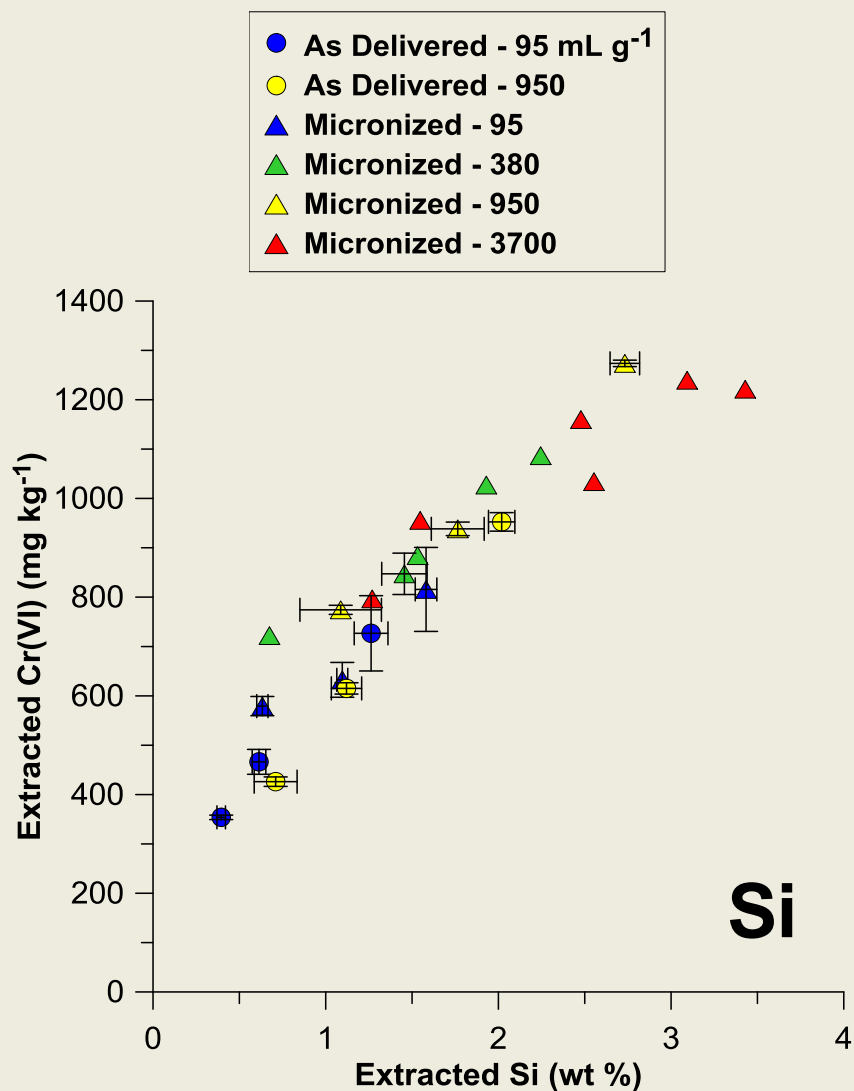


Effect of Liquid to Solid Ratio and Extraction Time



- 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	$\text{Ca}_3\text{Al}_2((\text{Si/H}_4)\text{O}_4)_3$	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)

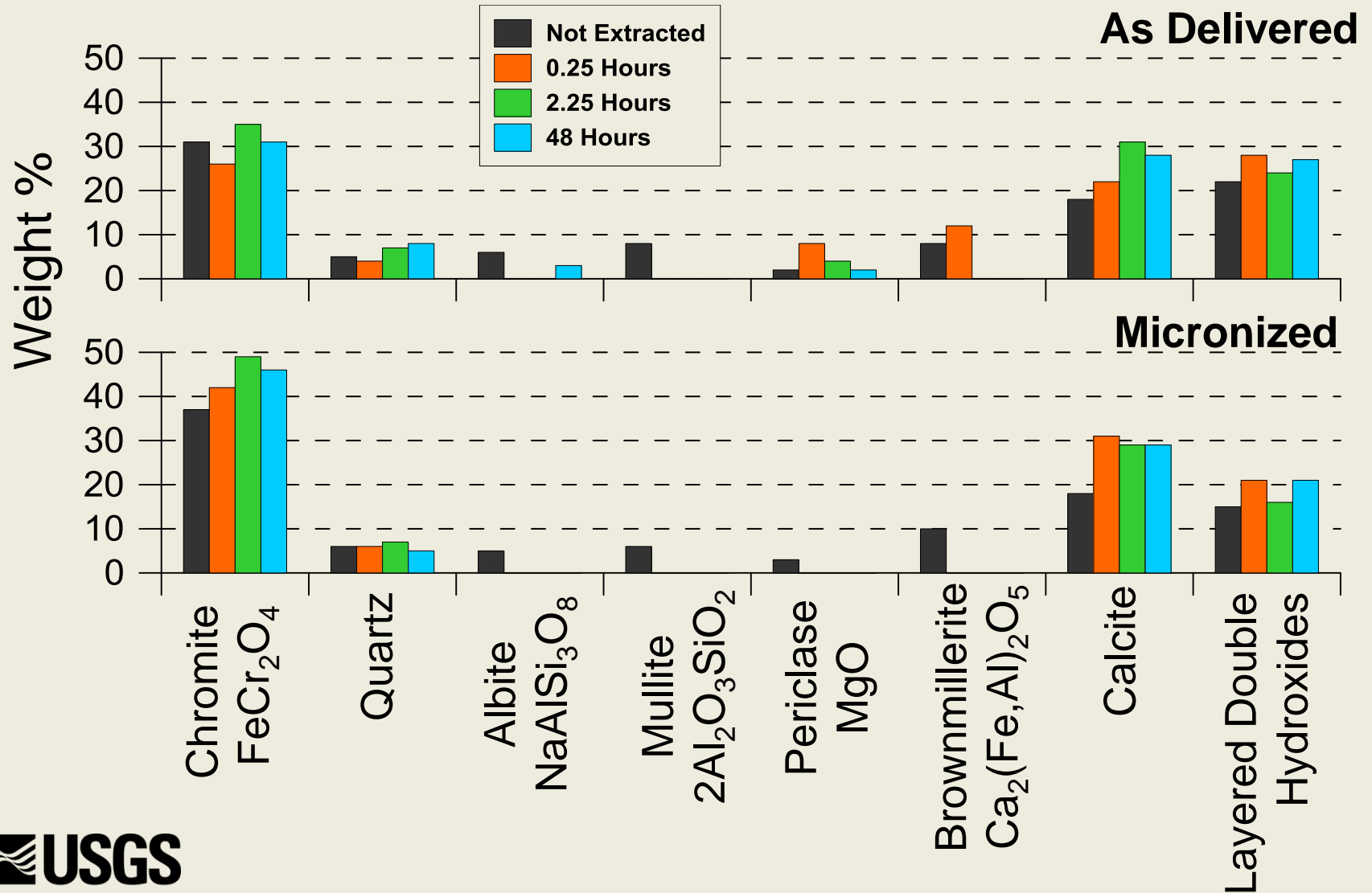
Geelhoed et al. (2002) *GCA*

Hillier et al. (2003) *STOTEN*

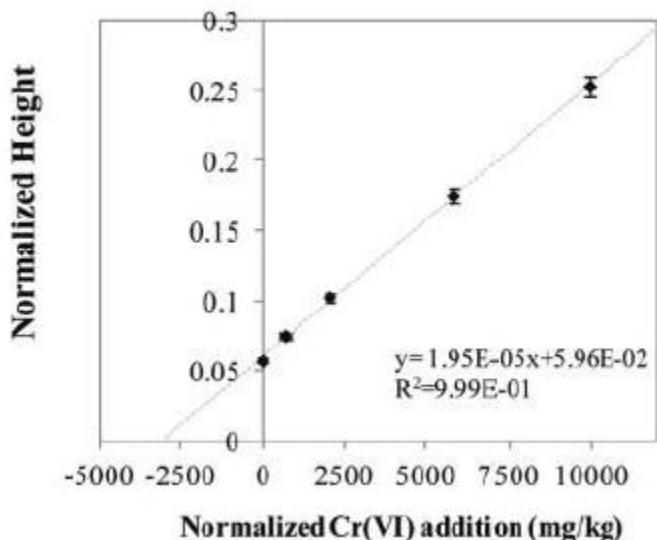
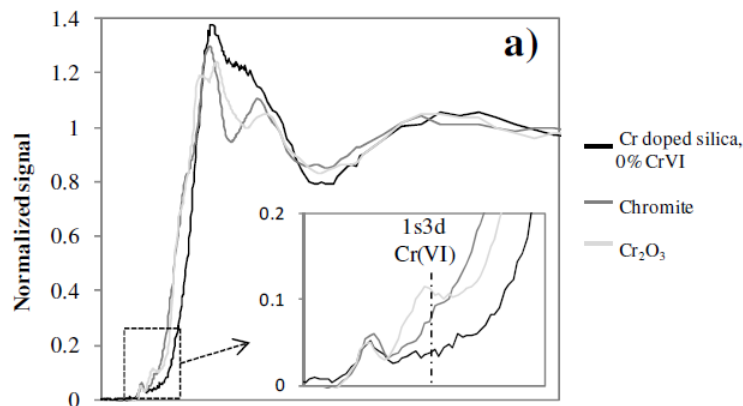
Mahlerbe et al. (2011) *ES&T*



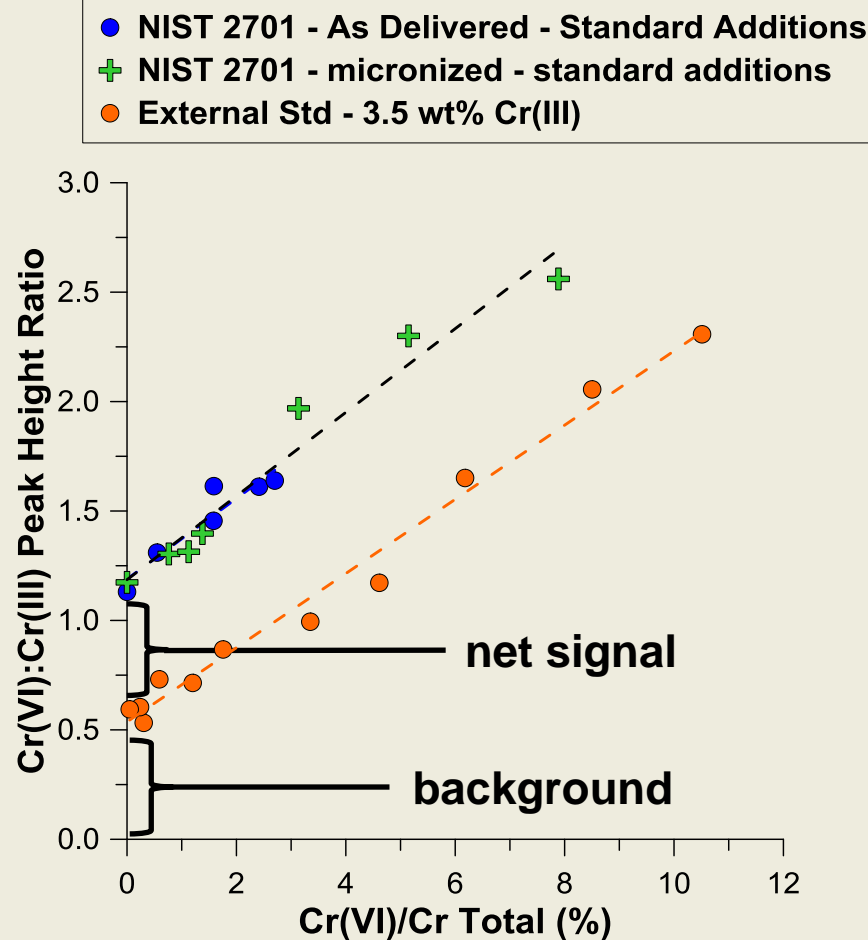
Effect of Extraction on COPR Mineralogy (XRD)



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



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



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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