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

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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\(^\circ\) 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 MgCl₂ causes immediate precipitation of Mg(OH)₂/MgCO₃.
  - Zatka (1985, Am. Ind. Hyg. Assoc. J.) found suppression of Cr(III) oxidation is sensitive to MgCl₂ 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 HNO₃ required for neutralization can overfill 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
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

1. Moon et al. (2008) *STOTEN*
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

<table>
<thead>
<tr>
<th>Method</th>
<th>7196A(^{1}) colorimetric</th>
<th>6800(^{1}) isotope dilution</th>
<th>XANES(^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median Cr(VI) Concentration (mg kg(^{-1}))</td>
<td>365</td>
<td>551</td>
<td>3000-3400</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>74</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

1. NIST Certificate revised 13 Sept 2013
2. Mahlerbe et al. 2011 ES&T
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

- NJ COPR 2B – did not pass through 2 mm sieve
- NJ COPR 2B – passed through 2 mm sieve
- NJ COPR 2B – 2 mm sieve and shatterboxed + micronized 10 minutes with methanol
- NIST 2701 as Delivered
Effect of Micronization on Particle Size of NIST 2701

Volume Percent

Particle Size (μm)

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

USGS
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

USGS
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

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromite</td>
<td>(Fe,Mg)Cr$_2$O$_4$</td>
<td>Major host of Cr(III)</td>
</tr>
<tr>
<td>Brownmillerite</td>
<td>Ca$_2$(Fe, Al)$_2$O$_5$</td>
<td>Can host Cr(III) [Cr(VI)?]</td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
<td></td>
</tr>
<tr>
<td>Larnite</td>
<td>Ca$_2$SiO$_4$</td>
<td></td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>Calcite/Aragonite</td>
<td>CaCO$_3$</td>
<td></td>
</tr>
<tr>
<td>Calcium silicate hydrate</td>
<td>CaH$_2$SiO$_4$</td>
<td></td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>Ca$_3$Al$_2$((Si/H$_4$)O$_4$)$_3$</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Hydrocalumite</td>
<td>Ca$_4$Al$<em>2$(OH)$</em>{12}$(OH)$_2$ • 6H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>Mg$_6$Al$_2$(CO$<em>3$)(OH)$</em>{16}$ • 4H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Ca$_6$Al$<em>2$(OH)$</em>{12}$(SO$_4$)$_3$ • 26H$_2$O</td>
<td>Can host Cr(VI)</td>
</tr>
</tbody>
</table>

Geelhoed et al. (2002) GCA
Hillier et al. (2003) STOTEN
Mahlerbe et al. (2011) ES&T
Effect of Extraction on COPR Mineralogy (XRD)

Chromite: FeCr$_2$O$_4$
Quartz: $\text{NaAlSi}_3\text{O}_8$
Albite: $\text{NaAlSi}_3\text{O}_8$
Mullite: $2\text{Al}_2\text{O}_3\text{SiO}_2$
Periclase: MgO
Brownmillerite: $\text{Ca}_2(\text{Fe,Al})_2\text{O}_5$
Calcite: $\text{CaCO}_3$
Layered Double Hydroxides: $\text{Ca}_2(\text{Fe,Al})_2\text{O}_5$

**As Delivered**

- Not Extracted
- 0.25 Hours
- 2.25 Hours
- 48 Hours

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

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

\[ \text{net signal} \times \text{slope (RF)} = \sim 1300 \text{ to } 1600 \text{ mg kg}^{-1} \text{ Cr(VI)} \]
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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