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ADVANCES IN DETECTION OF HEXAVALENT CHROMIUM

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Outline

- Why is this still an emerging contaminant?
- Historic methods for measuring Cr(VI) still in use today
- “Recent” technology advances
- Comparative data
- Q&A



Chromium

22nd Most Abundant Element



	VB 6	VIB 7	VIIB 8
23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845
41 Nb niobium 92.906	42 Mo molybdenum 95.94	43 Tc technetium 98	44 Ru ruthenium 101.07

Common
valence states
are
+3 and +6

Chromium

Essential nutrient in the trivalent form

- 50 – 200 $\mu\text{g}/\text{day}$ *

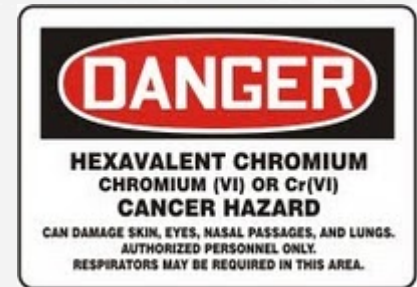
Required for sugar and fat metabolism

*Anderson RA, "Chromium as an Essential Nutrient,"
Regulatory Toxicology and Pharmacology, 1997
Aug;26(1 Pt 2):S35-41



Cr(VI) is Another Matter

- The health effects associated with Cr(VI) have been known for decades through inhalation
 - Known to cause cancer
 - Targets respiratory system, kidneys, liver, skin and eyes
- Estimated that 558,000 workers exposed continually in US alone – *OSHA website**
- DoD policy - minimize hexavalent chromium (an anti-corrosive) in items acquired by DoD (deliverables and construction material), due to the serious human health and environmental risks related to its use



*<https://www.osha.gov/SLTC/hexavalentchromium/>

Why Is This Still an EC?

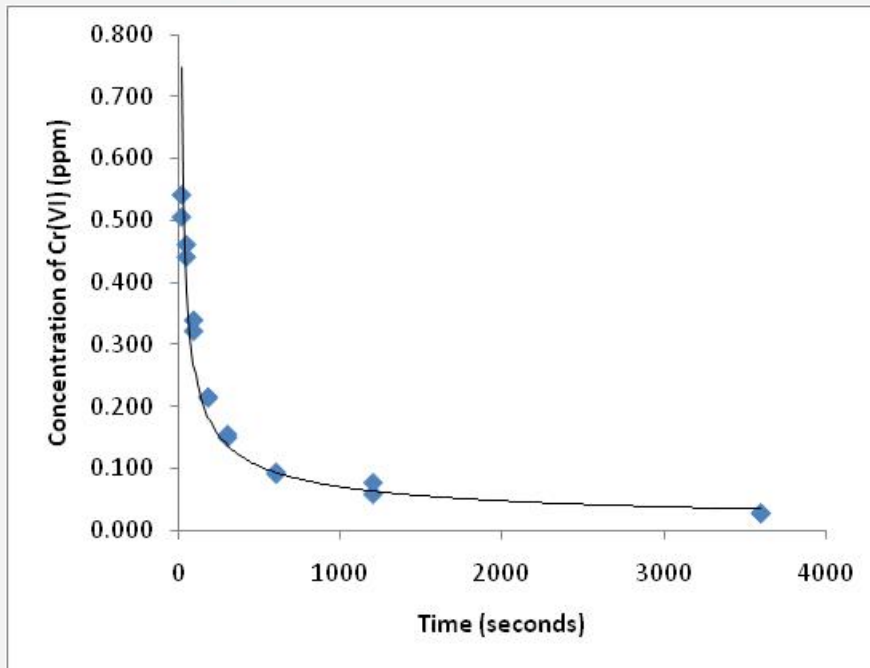
- The health effects associated with Cr(VI) are less clear with ingestion
- Currently under review by EPA
 - DHHS NTP Toxicological report in 2008
 - IRIS Report for public comment in 2010
- NJDEP – used 2008 NTP report to develop suggested risk-based soil remediation cleanup criterion of 1 ppm
- CA SWRCB – 10 ppb MCL and 0.02 ppb PHG in DW



Why Is This Still an EC?

Fate of Cr(VI) After Ingestion

Human Gastric Fluid (diluted 10x)



Spiked with 1 ppm Cr(VI) at $t = 0$

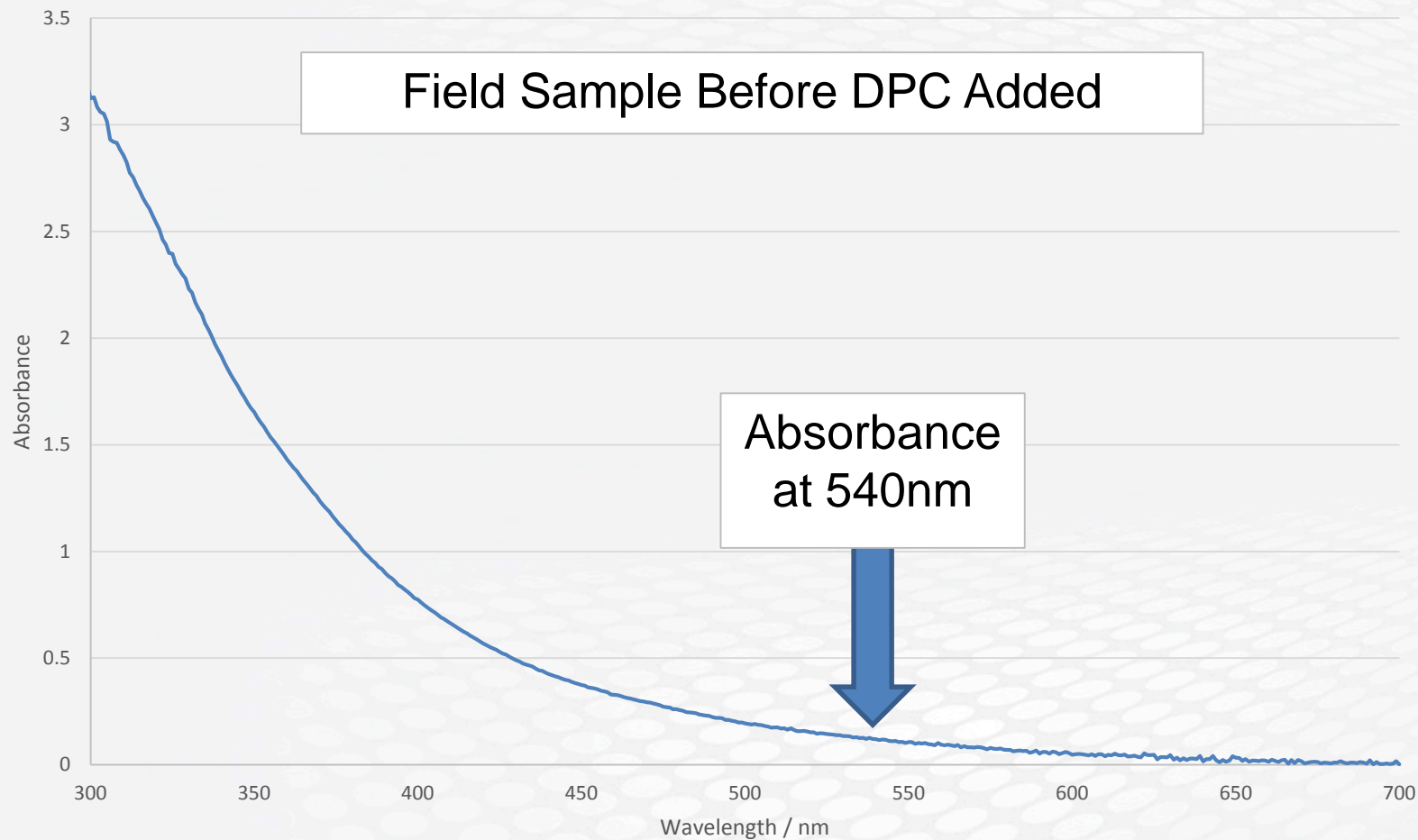
At each time point, an aliquot is collected and spiked with enriched Cr(III) and Cr(VI) standards

Kirman, C., Su, M., Hays, S., Gurleyuk, H., Gerads, R., De Flora, S., Parker, W., Lin, S., Haws, L., Harris, M., Proctor, D. 2016. Reduction of hexavalent chromium by fasted and fed human gastric fluid. II. Ex vivo gastric reduction modeling. *Toxicology and Applied Pharmacology*, 306: 120-133.

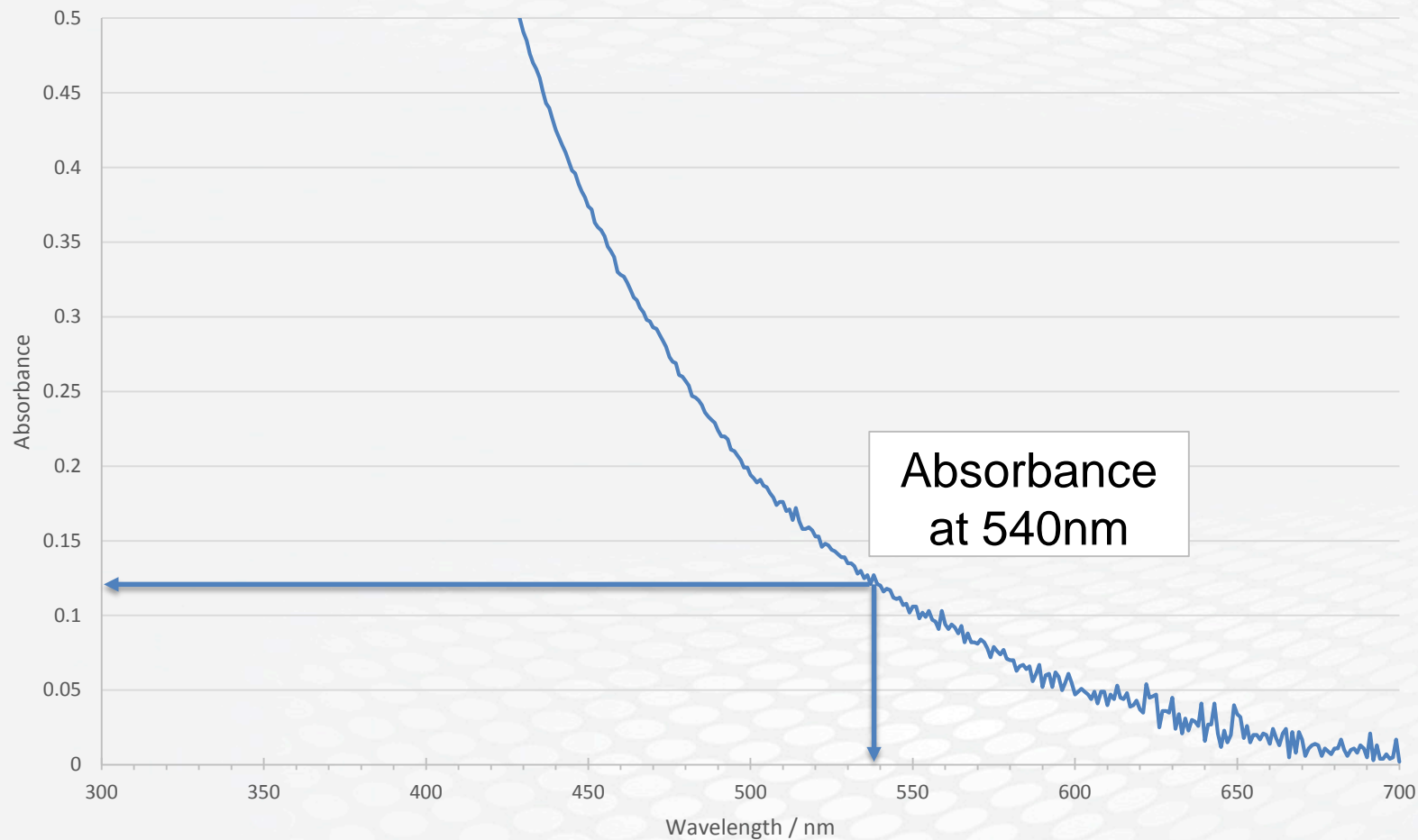
Analytical Methods for Cr(VI) Analysis

- EPA Method 7196: UV-Vis Colorimetry
 - Colorimetric method that is prone to interferences/false positives caused by Mo, V, Hg, MnO_4^- , turbidity, organic matter, etc.
- EPA Method 218.6 / 218.7 / 7199: Ion Chromatography/UV-Vis Colorimetry
 - Ion chromatography is used to separate Cr(VI), and detection is achieved by a post column reaction with diphenylcarbazide (DPC)

Background by Colorimetry



Background by Colorimetry



Background by Colorimetry

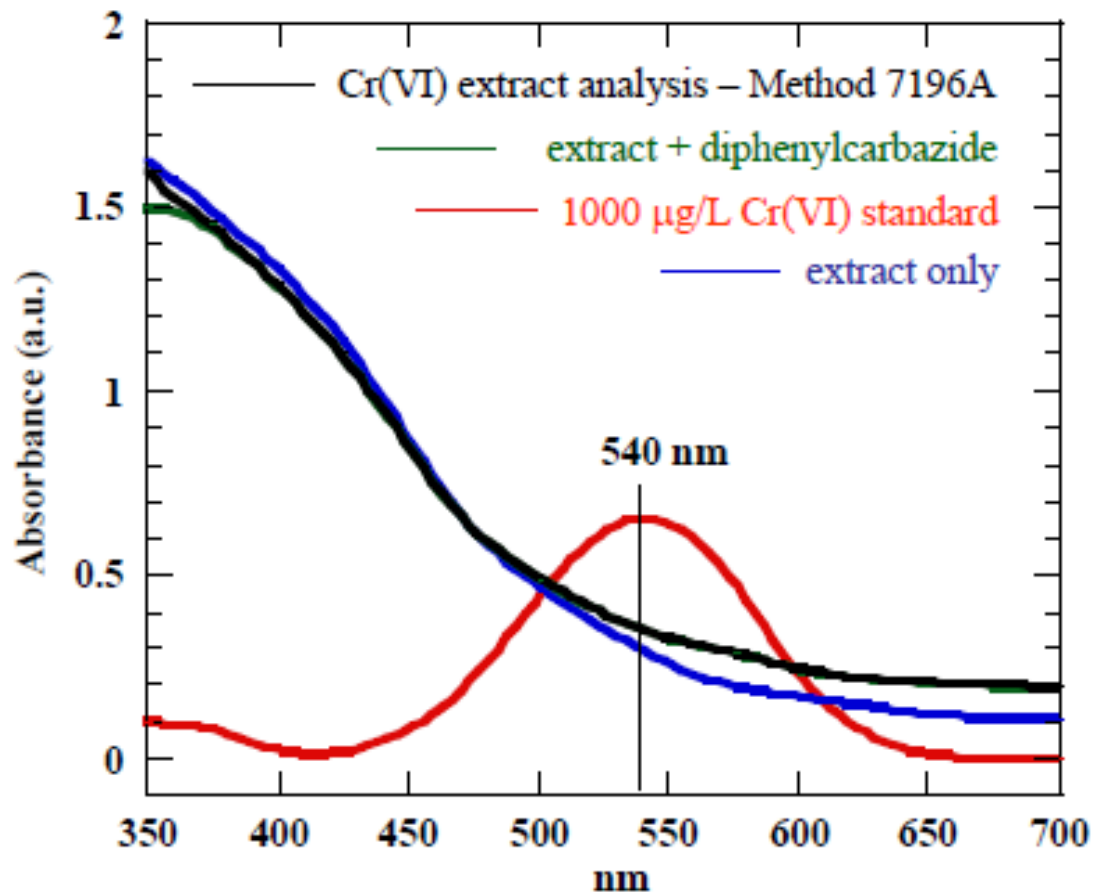


Figure 3-1. UV/Vis spectra of (a) Cr(VI) 1000 mg/L standard, (b) Bedford-6 Cr(VI) extract solution, (c) Bedford-6 Cr(VI) extract solution and diphenylcarbazide, and (d) Bedford-6 extract solution prepared as prescribed by SW-846 Method 7196A.

“Recent” Technology Advances

Determination of chromium(III) and chromium(VI) using suppressed ion chromatography inductively coupled plasma mass spectrometry†

JAAS

FULL PAPER

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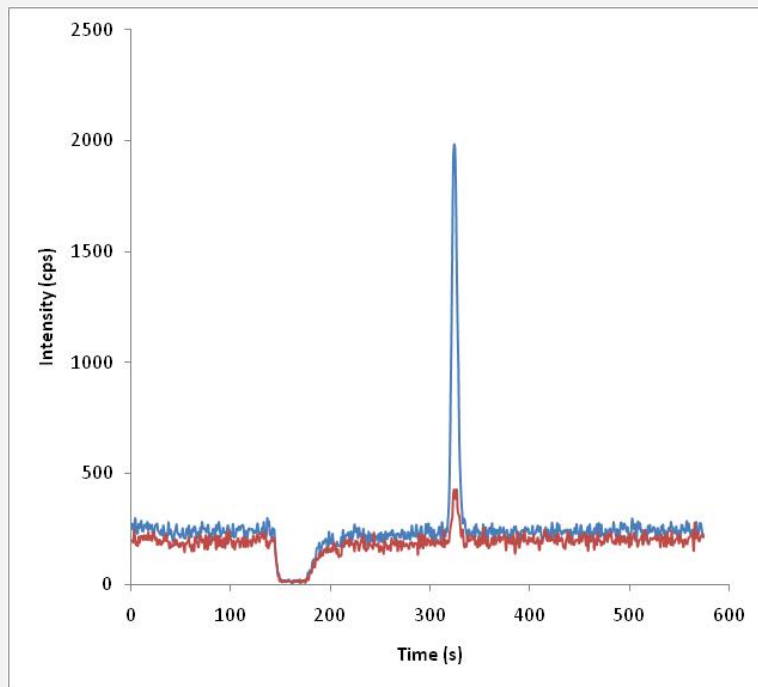
Table 1 Comparison of detection limits for chromium speciation analyses by LC-ICP-MS (not corrected for injection volume)

Technique	Detection limit/ng L ⁻¹		Ref.
	Cr(III)	Cr(VI)	
IC-ICP-MS	400	1000	11
IC-HHPN-ICP-MS	100	200	12
IC-ICP-MS	300	500	13
IC-ICP-MS	330	440	16
HPLC-DIN-ICP-MS	60	100	17
IPC-ICP-MS	300	300	25
IC-ICP-MS	5	12	This work

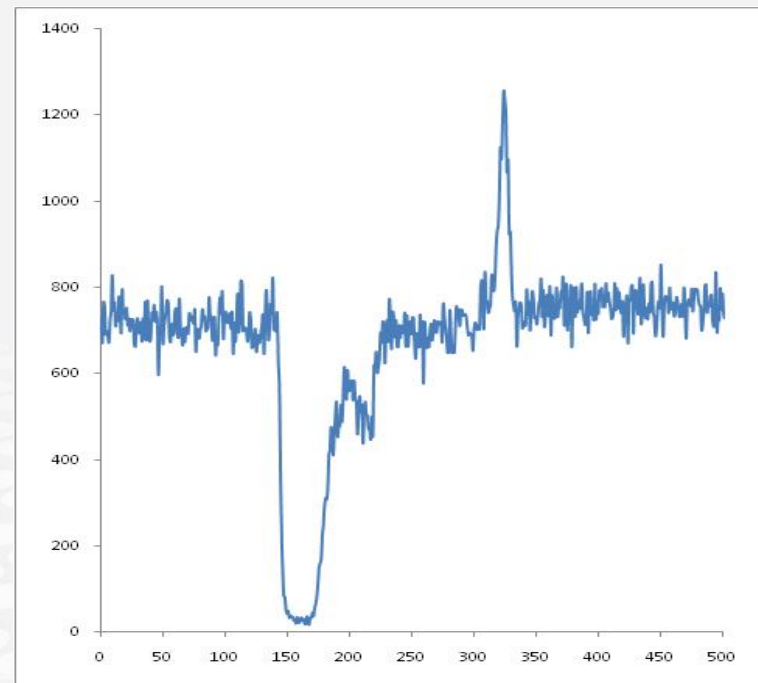
Providing less than 10 ng/L (ppt) detection limits for the last 16 years utilizing ion chromatography coupled to an ICP-MS

Cr(VI) by IC-ICP-MS

10 ng/L Cr(VI) Standard
vs. Blank



Groundwater Sample
Containing 3.6 ng/L
Cr(VI)



Analytical Methods for Cr(VI) Analysis

- Solid samples require an alkaline extraction of Cr(VI)
 - EPA Method 3060a - solubilizes adsorbed and precipitated forms of Cr(VI) compounds
 - The method allows for analysis of the extracts by IC-ICP-MS

Reporting Limits		
3060a/7196 (UV-Vis)	3060a/7199 (IC/UV-Vis)	3060a/7199mod (IC-ICP-MS)
4 mg/kg	0.4 mg/kg	0.01 mg/kg

Comparison of Colorimetry to IC-ICP-MS

	IC-ICP-MS		
Sample ID	Cr(VI), ppm	QC Spike, ppm	QC Spike % Rec
BLK1	0.014		
BLK2	0.009		
BLK3	0.008		
BLK4	0.007		
Cr(III) BS	0.053	20.00	0.3%
Cr(VI) BS	22.07	20.00	110.4%
PbCrO4 BS	644.5	637.2	101.1%
NIST 2701 CRM	514.1	551.2	93.3%
1702018-09	0.357		
DUP	0.326		
Cr(III) MS	0.601	25.26	1.0%
Cr(III) MSD	0.579	25.53	0.9%
Cr(VI) MS	27.33	25.31	106.6%
Cr(VI) MSD	27.70	25.46	107.4%
PbCrO4 MS	624.6	787.0	79.3%
PbCrO4 MSD	688.0	798.3	86.1%

Comparison of Colorimetry to IC-ICP-MS

	Colorimetry			IC-ICP-MS	
Sample ID	Turbidity Blank Absorbance	Absorbance (with DPC)	Cr(VI), ppm	Cr(VI), ppm	Ratio (Color / IC-ICP-MS)
1702018-01	0.056	0.067	0.381	0.092	4.1
1702018-02	0.001	0.012	0.304	0.199	1.5
1702018-03	0.007	0.016	0.233	0.157	1.5
1702018-04	0.003	0.011	0.218	0.068	3.2
1702018-05	0.000	0.010	0.251	0.066	3.8
1702018-06	0.003	0.013	0.249	0.137	1.8
1702018-07	0.001	0.014	0.326	0.319	1.0
1702018-08	0.001	0.011	0.252	0.066	3.8
1702018-09	0.003	0.010	0.206	0.072	2.9

Comparison of Colorimetry to IC-ICP-MS



Almost all 3060a extracts come out colored.
A turbidity blank should be analyzed for every sample.

Comparison of Colorimetry to IC-ICP-MS

- Oxidation and/or reduction can happen concurrently
- Quality control samples can help us understand redox reactions
- Utilize Cr(III), Cr(VI), and PbCrO_4 spikes

mg/kg	3060a/7196	3060A/IC-ICP-MS	Bias Ratio
Client1-Sample1	23.04	0.331	70
Client2-Sample1	11.66	0.005	2248
Client2-Sample2	4.49	0.039	116
Client3-Sample1	2.57	0.326	8
Client3-Sample2	2.33	0.360	6

Speciated Isotope Dilution Mass Spectrometry (SIDMS)

- Produces legally defensible data by correcting for oxidation and reduction that may happen during sample preparation.
- Traditional speciation methods attempt to hold each species static while making the measurements.
- In SIDMS, each species is “labeled” with a different isotope-enriched spike in the corresponding species form.
- Thus, the interconversions that occur after spiking are traceable and can be corrected for.

Speciated Isotope Dilution Mass Spectrometry (SIDMS)

- Requires license from patentholder to use the SIDMS method (difficult to get)
- Isotopically enriched Cr(III) and Cr(VI) standards
 - $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$
 - EXPENSIVE!!! ~ \$4,000,000 per gram
- IC method that can separate Cr(III) and Cr(VI)
- ICP-MS that can accurately monitor all 3 Cr isotopes (m/z 50, 52, 53)
 - CRC, DRC, QQQ, or HR-ICP-MS

What Does It All Mean?

- Evidence shows Cr(VI) should be evaluated and not just total Cr
- Cr(VI) by colorimetry is prone to interferences
- IC/UV-Vis is better but still reliant on reaction chemistry
- IC-ICP-MS provides best data quality
- SIDMS would be great but not readily available due to patent limitations and high standard costs

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