Determination of Hexavalent Chromium in Soil by HPLC/ICP-MS

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A global manufacturer of single and multielement standards for the calibration of analytical instruments.

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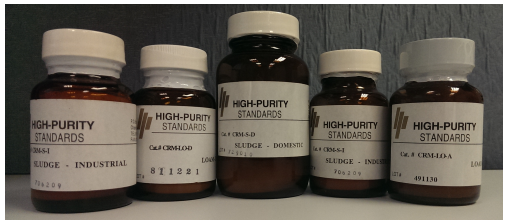
ABSTRACT

Chromium primarily exists as either trivalent or hexavalent forms. Cr^{+3} is a vital nutrient and Cr^{+6} is a toxin. As a result of the Cr^{+3} / Cr^{+6} differences, a total chromium analysis cannot provide a complete toxicity assessment.

Hexavalent chromium is used in a number of industrial processes (e.g., steel production, chrome plating, and metal working) and is categorized as known a carcinogen. These anthropogenic sources expose individuals to hexavalent chromium by breathing contaminated air, ingesting or inhaling contaminated soils or by drinking contaminated water. It is important to monitor and determine the environmental impact of the industries' generation of hexavalent chromium in the environment to assess pollution and prevent health hazards.

There is a need for environmental certified reference materials for the study of hexavalent chromium. High-Purity Standards has developed certified reference materials within the scope of ISO 17025 for hexavalent chromium in soil and sludge. The soil/sludge certified reference materials were manufactured by spiking and homogenizing the soil with hexavalent chromium salts. Varying levels of salts were spiked to represent samples that could be found in a contaminated environment.

The chromium species were separated isocratically using HPLC ion-pair chromatography. An isocratic separation was accomplished using tetrabutlyammonium hydroxide (TBAH) as the mobile phase. Dynamic reaction cell ICP-MS was the detection method. To account for the interconversion of Cr^{+3} and Cr^{+6}, a chromium speciation kit from Applied Isotope Technologies, Inc. was employed.



Certified Reference Material Preparation

Loam and Sludge Standards
- Loam obtained from Shelby County, Kentucky
- Industrial Sludge obtained from Charleston, South Carolina
- CRMs were dried by air and infrared lamps
- Milled and sieved to a particle size of ~149 µm
- Spiked with potassium dichromate and lead chromate

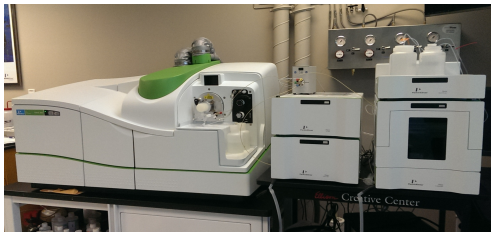
Homogeneity
- Homogenized in a polyethylene mixing drum
- Analyzed between and within sample bottle to insure proper mixing
- Defined at a relative standard deviation percentage of less than 3%

Total Digestion EPA Method 3052
- 9 mL HNO_3, 3 mL HCl, 3 mL HF
- 5.5 minutes temperature rise to 180 ± 5°C, hold for 9.5 minutes

Alkaline Digestion EPA Method 3060A
- 2.5 grams of sample
- Digestion solution: 0.28M Na_2CO_3/0.5M NaOH
- Buffer solution: 0.5M K_2HPO_4/0.5M KH_2PO_4, pH=7
- Heat at 90-95ºC for ~60 minutes with stirring
- Cool, filter and adjust pH to 7.5 using 5.0M HNO_3

INSTRUMENTATION

PerkinElmer HPLC/ICP-MS



HPLC operating parameters	
HPLC Instrument	PerkinElmer HPLC Flexar Series, autosampler, quaternary pump, vacuum degassing
HPLC Software	Chromera
Mobile Phase	1 mM TBAH + 0.6 mM EDTA (potassium salt) 5% methanol
Column	3x3 CR C8
pH	6.9 (adjusted with 5.0 M HNO3)
Injection volume	50 µL
Flow rate	1.5 mL/min
Analysis Time	3 minutes

ICP-MS operating parameters	
ICP-MS Instrument	PerkinElmer NexIon 300d
Nebulizer	Meinhard Quartz
Spray Chamber	Quartz Cyclonic
RF Power	1600 W
Plasma Flow - Argon	16 L/min
Nebulizer Flow - Argon	0.98 L/min
Dwell time	500 ms
Injection volume	50 µL
DRC reaction gas	NH_3
DRC gas flow	0.57 mL/min
RP_q	0.7
Analyte	$^{52}Cr+$

Chromium Speciated Analysis Software, Applied Technologies Inc.

(A) How much sample did you double spike?	no	g
(B) How much $^{50}Cr(III)$ did you spike?	0.0593	g
(C) How much $^{53}Cr(VI)$ did you spike?	0.0824	g
(D) What is the concentration of $^{50}Cr(III)$ spike?	10.00	µg/g
(E) What is the concentration of $^{53}Cr(VI)$ spike?	10.00	µg/g

Step 1
- Obtain AIT speciation standard
- Spike known quantities
- Enter data into software

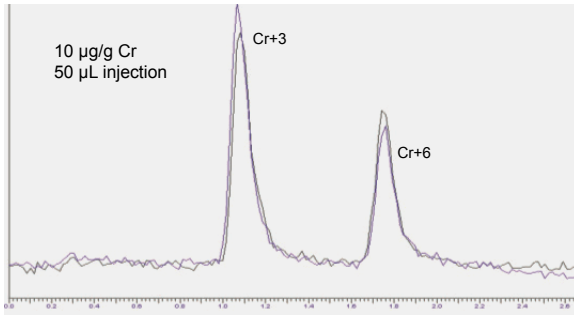
Step 2
- Ratios of analytical data

Replicate	Cr(III) $^{50}Cr/^{52}Cr$	Cr(III) $^{53}Cr/^{52}Cr$	Cr(VI) $^{50}Cr/^{52}Cr$	Cr(VI) $^{53}Cr/^{52}Cr$
1	12.1302	0.6836	0.2363	10.0245
2	11.5622	0.5874	0.2277	9.6211
3	11.5888	0.5622	0.2305	9.7391
4	11.6702	0.5567	0.2310	10.1802

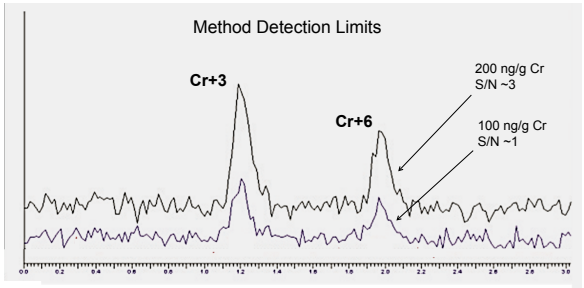
	Deconvoluted Concentration		Interconversion (%)	
Replicate	Cr(III) (mg/g)	Cr(VI) (mg/g)	Cr(III) to Cr(VI)	Cr(VI) to Cr(III)
1	0.039	0.0288	2.36%	3.81%
2	0.042	0.0326	2.35%	3.33%
3	0.042	0.0314	2.37%	3.15%
4	0.042	0.0274	2.28%	3.09%

Step 3
- Software calculates concentration and interconversion percentage
- Make correction(s) for interconversion

RESULTS



1000 µg/g hexavalent chromium standards were prepared. Standards of varying concentrations were made with dilution of the mobile phase. Separation of species occurs as Cr+3 complexes with EDTA and Cr+6 interacts with the TBAH, allowing for the separation on the C8 column. Adjustment of the methanol percentage assists in the elution of Cr+3 and Cr+6 species from the column .



CONCLUSION

This study was specifically aimed to develop a certified reference material (CRM) that can be used in the determination of hexavalent chromium in environmental matrices. High-Purity Standards developed CRMs to provide accurate determination of toxic metals by analytical methods.

The digested soil samples were separated and analyzed by HPLC/DRC-ICP-MS. The precision (% RSD) and bias obtained for the samples were each calculated to be ≤ 1% for 3 replicates. The analytical limits of detection were calculated at ~ 200 ng/g, which is more than sufficient in determining toxic levels of hexavalent chromium contamination in soil.

To account for interconversion between the Cr^{+3} and Cr^{+6} species, standards and software developed by AIT were used. Samples were also analyzed soon after preparation to minimize interconversion.

High Purity Standards manufactures products within the scope of ISO 9001:2008, ISO 17025:2005 and ISO 34:2009.

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