Analysis of Hexavalent Chromium in Industrial Sludge

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INTRODUCTION

Chromium is a naturally occurring element present in water, rocks, soils, and in biological organisms. Even though, chromium exist in various oxidation states, the only biologically and environmentally stable forms are Cr3+, trivalent Cr(III) and Cr6+, hexavalent Cr(VI) chromium (Ducros, 1992). The presence of Cr(III) versus Cr(VI) is pH dependent, Cr(VI) exists under alkaline or neutral conditions and converts to Cr(III) in acidic environment (EPA, 1984). While Cr(III) is an essential nutrient for metabolism, Cr(VI) is toxic and a known carcinogen. Cr(VI) can be found in solution state, as chromate, CrO_4^{2-}, hydro chromate, $HCrO4^-$, dichromate, $Cr_2O_7^-$ or as water-soluble anion (Callahan et al., 1979). Potassium dichromate has been shown to increase the negative effects of Cr(VI) in organisms (Susa, 1994). Exposure to airborne or dissolved Cr(VI) by inhalation or ingestion of contaminated air, water, or soil, is a major concern for various industries, involving welding, electroplating, and chromate painting (ATSDR, 1993). Thus, it is crucial to monitor Cr(VI) levels to protect workers at various working environment. High-Purity Standards is developing reference materials for the analysis and quality control of Cr(VI) from various source materials for use in industrial hygiene and air monitoring applications.

OBJECTIVE

•To develop reference materials to detect Cr(VI) for industrial hygiene

• To analyze hexavalent chromium and total chromium in industrial sludge

MATERIALS

•Industrial sludge
•Industrial sludge spiked with Lead chromate (insoluble)
•Industrial sludge spiked with Cr(VI) from Potassium dichromate (soluble)

METHODS

For Total Cr:
Acid Digestion with $HClO_4$
For Leachable Cr:
EPA Method 3050B
Digest sample HNO_3/H_2O_2 and add HCl for ICP-OES
Digest sample with HNO_3/H_2O_2 without adding HCl for ICP-MS-DRC
For Cr(VI):
• EPA Method 3060A - Alkaline Digestion for Cr(VI)

Instrumentation:
•ICP-OES - Perkin Elmer Optima 8300
•ICP-MS - Perkin Elmer NexION 300D
•HPLC - Agilent Model 1100, Column – Ultra C8 5µm
•IC - Dionex Model DX-120, Column: Ion/Pac AG/AC23

Analysis Method:
Analysis of Cr via relevant instrumentation against appropriate standard solutions using comparison, bracketing and spiking method.

RESULTS

Chromium In Industrial Sludge			
Chromium	Concentration (µg/g)	Digestion Method	Analysis Method
Total Cr	117 ± 4	$HNO_3/HClO_4$ acid	ICP-OES / ICPMS
Leachable Cr	98.7 ± 3.2	EPA 3050 HNO_3/H_2O_2 digestion	ICP-OES / ICP-MS-DRC
Hexavalent Cr(VI)	(4-5)	EPA 3060A Alkaline Extraction	HPLC/IC/ICP-MS-DRC

Table. 1. Chromium concentrations resulted from different digestion methods by using comparison, bracketing and spiking method to analyze data. Hexavalent Cr(VI) data in parentheses provided for reference only.

Evaluation 3060A Extraction Method			
Sample ID	Spiked Component	Recovery (%)	Method
Digestion Method Blank			ICP-MS NexION DRC
Method Blank + Insoluble Cr(VI)	$PbCrO_4$	99	
Method Blank + Soluble Cr(VI)	$K_2Cr_2O_7$	98	
Industrial Sludge			
Industrial Sludge + Insoluble Cr(VI)	$PbCrO_4$	93	
Industrial Sludge + Soluble Cr(VI)	$K_2Cr_2O_7$	98	
Industrial Sludge + Insoluble Cr(VI)	$PbCrO_4$	108	IC
Industrial Sludge + Soluble Cr(VI)	$K_2Cr_2O_7$	99	

Table. 2. Samples obtained from digestion method EPA 3060A were analyzed by ICP-MS DRC and IC.

$$\text{Recovery}(\%) = 100 * \frac{C_T - C_S}{C_{Spiked}}$$

C_T – The readings from spiked sample concentration (or cps)
C_S – The readings from unknown concentration (or cps)
C_{Spiked} – The known concentration spiked in the sample

Evaluation Analytical Results		
Sample ID	Spiked Component	Recovery (%)
Digestion Method Blank		
Digestion Method Blank	$^{53}Cr(VI)$	98
Industrial Sludge		
Industrial Sludge	$^{53}Cr(VI)$	103
Industrial Sludge + Insoluble Cr(VI)		
Industrial Sludge + Insoluble Cr(VI)	$^{53}Cr(VI)$	101
Industrial Sludge + Soluble Cr(VI)		
Industrial Sludge + Soluble Cr(VI)	$^{53}Cr(VI)$	103

Table. 3. Samples obtained from digestion method EPA 3060A were spiked with AIT $^{53}Cr(VI)$ and analyzed by ICP-MS-DRC.

Calibrators: Based on digestion and analytical methods, appropriate Cr calibrators are prepared to match samples.

Calibrator Cr(VI) only: Calibration Standard - Source from AIT ($^{Nat}Cr(VI)$ and $^{53}Cr(VI)$, prepared intermediate solution (1µg/g in ~ 0.1% NH_4OH) from AIT standards by weight. Then weighed intermediate solution and diluted to volume before use.

Calibrators for ICPMS		
$^{Nat}Cr(VI)$	1, 5, 10	µg/L
$^{53}Cr(VI)$	1, 5, 10	µg/L

CONCLUSION

• Hexavalent chromium can be quantitatively extracted and measured in natural and simulated reference materials. High-Purity Standards will next apply these to a variety of filter media to determine the impact of the filter media to the viability and stability of Cr(VI) reference material for use in industrial hygiene applications.

• Further testing will include analysis of various environmental and industrial samples using HPLC/ICP-MS.

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