

Analytical Considerations of Hexavalent Chromium

Kristie Armstrong, Ph.D.
Chemistry Laboratory Manager
Scientific Analytical Institute



Valence States of Chromium

- Multiple Valence States
 - +2 → CrCl_2
 - +3 → Cr_2O_3 (chromium (III) oxide)
 - +6 → K_2CrO_4 (chromate); $\text{K}_2\text{Cr}_2\text{O}_7$ (dichromate)
 - Rarely +1, +4, +5
- Cr(III) is the most stable
- Cr(VI) is the most toxic



Sample Stability

- Redox between valence states occurs readily
- Avoid oxidation or reduction of the contaminant
 - Oxidation of Cr(III) overestimates Cr(VI) exposure
 - Acid digestion of filter media for ICP or AA analysis
 - Reduction of Cr(VI) underestimates Cr(VI) exposure
 - Organics present in filters (MCE) or backup pads



Formation of Cr(VI)

- Acid mists
 - Chromic acid used in plating or corrosion conversion process
 - Generated by the bursting of small bubbles of gases during electrolysis
- Fumes
 - Stainless steel (13-26% chromium)
 - Cr(III) oxide
 - welding or other hot work activities
 - Oxidation of Cr(III) to Cr(VI)



Formation of Cr(VI)

- Chromate coatings
 - Used for their anti-corrosive properties
 - Chromate pigments
 - zinc chromate
 - strontium chromate
 - calcium chromate (rare)
 - lead chromate
 - Paint aerosols
 - Application of chromate coatings
 - Dried paint solids
 - sanding, abrading or other mechanical removal of chromate coatings



Sample Stability

- Stability of Cr(VI) compound must be considered
 - How fast does it need to get to the lab?
 - Welding samples – ship to lab within 24 hours; analyzed within 8 days of collection (due to interferences with Fe(II))
 - Chromium plating samples
 - PVC filter - stabilize in buffer solution within 24 hours (in lab); analyze within 2 weeks
 - NaOHqz (NaOH coated quartz fiber filters) – no special treatment after sampling; excellent storage stability



Sample Stability

- Stability of Cr(VI) compound must be considered
 - Will the analytical method sufficiently extract Cr(VI) from the sampling media?
 - Soluble or insoluble Cr(VI)
 - OSHA ID-215 addresses both
 - Spray paint aerosols require extra extraction step
 - Clearly indicate operation sampled on the COC



Airborne Cr(VI) Analytical Methods

Method	Technique	LOD $\mu\text{g/sample}$	Comment
NIOSH 7300	ICP	0.02	total Cr
NIOSH 7024	AAF	0.06	total Cr
NIOSH 7703	Ultrasonic extraction; SPE (UV/Vis, field portable)	0.08	sufficient for field method
NIOSH 7600	UV/Vis	0.05	no separation step
NIOSH 7605	IC (UV/Vis, post-column derivative)	0.02	possible interference by Fe(II)
OSHA ID-215	IC (UV/Vis, post-column derivative)	0.01	precipitation step reduces Cr(III) oxidation



Cr(VI) Dust Analytical Methods

Method	Collection Method	Technique/Comments
OSHA W-4001	PVC or NaOHqz filter (used as a wipe)	IC - Follow OSHA ID-215 for sample analysis; specific to Cr(VI)
NIOSH 9102	Wash 'n Dri or ASTM equivalent	ICP - total Cr; long digestion process; negative matrix effects
ASTM D6966	Ghost Wipe	Used for various metals (Pb) but can be applied to Cr(VI)
NIOSH 9101	Settled dust scooped into sample vial	Qualitative or semi-quantitative



Biomarkers

- Current research for reliable quantifiable biomarkers for Cr(VI) occupational exposure
 - Exposure levels
 - Effects of exposure
- Cr(VI) reduced to Cr(III) *in vivo*
 - Most are total chromium levels
 - Cr(VI)-specific biomarkers are needed
 - Urine, whole blood, plasma, and blood cells can be monitored



Biomarkers of Exposure

- Urinary Cr
 - Creatinine used as BEI
 - Total Cr monitored
 - Dependent of exposure
 - Cr levels measured before and after work shift
- Blood Cr
 - Cr(VI) can pass cell membrane while Cr(III) cannot
 - Allows direct monitoring of Cr(VI)
 - Sampling independent of time of exposure
 - 120 day life span of the cell
 - Kinetics of Cr(VI) uptake can be studied
 - Requires sensitive techniques
 - Electrochemistry-based sensors



Biomarkers of Effect

- Renal Biomarkers
 - Increased *N*-acetyl- β -glucosaminidase (NAG) levels in urine indicate early effects of Cr(VI) exposure
- Genotoxic Biomarkers
 - Increased DNA strand breaks in Cr(VI)-exposed workers



Conclusions

- Chromium exists ubiquitously in multiple valence states, Cr(VI) being of most concern
- Cr(VI) results from chrome-plating, welding, and chrome-based coatings techniques
- Sampling considerations maintain integrity of the sample
 - Know sampling technique best suited for occupational exposure as well as analytical technique to be used
- Future of Cr(VI) monitoring in biomarkers



Thank You!!

