

Evaluation of Hexavalent Chromium Extraction from Solids Using XANES and XRD

J. Malherbe^{1,2}, P.E. Stutzman³, W.C. Davis², J.R. Sieber², R.P. Watson², S.E. Long², M.P. Isaure¹, F. Séby⁴, P. Rodriguez-Gonzalez⁵, C. Maurizio⁶, N. Unceta⁷, O.F.X. Donard¹

¹ Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, IPREM, UMR CNRS 5254, Université de Pau et des Pays de l'Adour, Hélio parc Pau-Pyrénées, 2, ave. Pierre Angot, 64053 Pau Cedex 9, France

² Analytical Chemistry Division, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, Maryland 20899 USA

³ Materials and Construction Research Division, Engineering Laboratory, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, Maryland 20899 USA

⁴ Ultra Traces Analyses Aquitaine, Hélio parc Pau-Pyrénées, 2, avenue Pierre Angot, 64053 Pau Cedex 9, France

⁵ Universidad Oviedo, Departamento de Química Física y Analítica, c/ Julián Clavería, 8. E-33006, Oviedo, Spain

⁶ European Synchrotron Radiation Facility, BM 08 GILDA, 6, Rue Jules Horowitz B.P.220 F-38043 Grenoble, France

⁷ Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country, Vitoria-Gasteiz, Spain

Chromium is widely used in the chemical industry for applications such as metal plating, catalysts, colorants, and leather tanning. As a result, different species of Cr may be incorporated into consumer products (electronics, plastics, etc.) and may be released into the environment (soil, surface and ground waters). As such, Cr species may be converted to bio-available forms. Chromium can exist in oxidation states from 0 to +6; however, only trivalent (Cr(III)) and hexavalent (Cr(VI)) forms are stable enough to occur in the environment. Cr(III) is considered an essential micronutrient in the human diet and is widely used as a nutritional supplement for humans and animals. In contrast, Cr(VI) is much more toxic than Cr(III) for both acute and chronic exposures, and its compounds are regulated in a number of jurisdictions.

Most analyses of Cr(VI) in soils and solid wastes are performed using an extraction procedure (for example, alkaline NaOH/Na₂CO₃ digestion) followed by one or more of the existing determinative methods: derivatization and UV absorption; chromatography, derivatization and UV absorption; and speciated isotope dilution inductively coupled plasma mass spectrometry (SID-ICPMS). Recently, improvements in accuracy have been introduced by the SID-ICPMS method because inter-conversion of chromium species during extraction and analysis is monitored and corrected. Although work has been done to improve detection, nothing has been done to evaluate the quality of the extraction step since the study by James, published in 1995 [1]. The ideal extraction will break down all materials in a matrix and dissolve Cr(VI) without converting Cr to other oxidation states.

The completeness of extraction of Cr(VI) from the solid to the liquid phase is a crucial factor for accurate quantification. Using synchrotron-based X-ray Absorption Near Edge Structure spectroscopy (XANES) in fluorescence mode, the extraction yield of the alkaline NaOH/Na₂CO₃ approach was determined for three different matrices: loamy soil, paint sludge, and NIST SRM 2701 Hexavalent Chromium in Contaminated Soil. Extraction effectiveness was found to be related to matrix mineral composition determined using X-ray diffraction. Identified Cr-containing mineral phases included chromite (FeCr₂O₄), magnesiochromite (MgCr₂O₄), Cr-substituted hydrocalumite (Ca₂(Al,Fe)(OH)₇·3H₂O), and Cr-substituted hydrogarnet (Ca₃(Al,Fe)₂(OH)₁₂). SRM 2701 showed the lowest extraction effectiveness, and it contains all four minerals; whereas the other two materials do not.

[1] James, B., Petura, J., Vitale, R., and Mussoline, G., *Hexavalent chromium extraction from soils: a comparison of five methods*, Environ. Sci. Technol. 1995, pp 2377-2381.