

# An Analytical Comparison of Synchrotron XANES and Laboratory-based XES for the Determination of Hexavalent Chromium Fractions in Solid Matrices

Evan P. Jahrman<sup>1</sup> (\*), Gerald T. Seidler<sup>1</sup>, and John R. Sieber<sup>2</sup>

<sup>1</sup>Physics Department, University of Washington, Seattle, WA 98195-1560

<sup>2</sup>Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8391

(\*) ejahrman@uw.edu

Cr(VI) is a well-known human carcinogen with many water-soluble moieties. Its presence in both natural and man-made substances poses a risk to public health, especially when contamination of ground water is possible.<sup>1</sup> This has led to extensive regulation and monitoring of mine tailings and also has caused the European Union and other jurisdictions to include Cr(VI) in restriction of hazardous substances (RoHS) regulations for consumer products. However, for several important industrial and commercial purposes, analytical capability to characterize Cr(VI) is known to be insufficient for regulatory purposes. For example, advanced x-ray spectroscopies, particularly synchrotron-based x-ray absorption fine structure (XAFS) studies, have shown that species interconversion and under-extraction can be difficult to prevent in many existing liquid extraction protocols when applied to plastics, mining ores and tailings, and paint sludges.<sup>2-4</sup>

Here, we report that laboratory-based<sup>5</sup> x-ray emission spectroscopy (XES) resolves fine spectral differences between the Cr K $\alpha$  spectra of Cr(VI) and Cr(III) compounds.<sup>6</sup> Consequently, the concentration fraction of Cr(VI) in a material may be determined by fitting its K $\alpha$  XES spectrum to a linear combination of spectra from reference Cr(III) and Cr(VI) compounds. This procedure is used here, where we investigate several plastics that have been part of ongoing efforts by standards development organizations to create improved Cr(VI) testing protocols.

The Cr(VI)/Cr fractions determined via XES agreed well with the results of established XANES procedures performed at NSLS, including for a range of plastic matrices and for total chromium contents as dilute as 100 mg/kg. Moreover, the method produced quantitative results with typical uncertainties around a few percent. As an immediate application of this work, the measured Cr(VI) mass fraction can be assigned as a reference value for the new NIST Standard Reference Material 2859 Restricted Elements in Polyvinyl Chloride.

The present work provides a direct proof-of-principle for the use of benchtop XES as an alternative to liquid extraction methods for regulatory compliance testing of Cr(VI) content. This also gives a new direction for analytical application to mining ores and tailings, another arena where synchrotron beamtime may not be necessary and benchtop XES can play a role in environmental studies and regulatory compliance efforts.

1. R. Saha, et al., J Coord Chem **64** (10), 1782-1806 (2011).
2. J. Malherbe, et al., Environ Sci Technol **45** (24), 10492-10500 (2011).
3. J. Malherbe and F. Claverie, Anal Chim Acta **773**, 37-44 (2013).
4. C. Oze, et al., Intern Geology Rev **46**, 97-126 (2004).
5. G.T. Seidler, et al., Review of Scientific Instruments **85**, 113906 (2014).
6. E. Jahrman, G.T. Seidler, J. R. Sieber, *submitted*, Analytical Chemistry (2018).

This work was supported by the Joint Center for Energy Storage Research, The United States Department of Energy, and the United States National Institute of Standards and Technology.