Radiation Damage of Redox-Sensitive Transition Metal Ions

Tsu-Chien Weng, **James E. Penner-Hahn**, Wen-Yuan Hsieh, and Vincent L. Pecoraro,
University of Michigan, Ann Arbor, Michigan USA
Ke Zhang, IIT / BioCAT, Argonne, Illinois USA

A limitation of x-ray spectroscopy, particularly as practiced at 3rd-generation sources, is sensitivity to x-ray photoreduction. This can seriously compromise measurements, even when made at cryogenic temperatures, and is particularly serious when one needs to make temperature dependent measurements, including measurements at room temperature. The latter are critical for correlating the structure and reactivity of biological metal sites. The focused beam and rapid scanning capabilities of the BioCAT beamline were used to investigate the rate of x-ray induced photoreduction and to develop strategies that will permit the measurement of x-ray spectra for radiation sensitive samples at room temperature. X-ray absorption spectra for solutions of Mn(III)(Salpn)(acac) were measured as fluorescence excitation data, using a rapid-scanning monochromator that permits scans to be completed in a few seconds. The incident beam was focused to a height of ca. 100 um, and samples were flowed through an x-ray transparent capillary at flow rates of 0.05 - 6.4 uL/s, corresponding to exposure times as short 14 ms. The rate of conversion from Mn(III) to Mn(II) was determined as a function of: solvent, dose-rate, added radical scavengers (nitrate, benzophenone); and added cryo-protectant (glycerol). This approach shows promise for permitting room temperature EXAFS of radiation sensitive samples.