Chemical Shift Measurements for Elemental Oxidation State Determination using a Cryogen-Free Microcalorimeter X-Ray Spectrometer

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Cryogenic microcalorimeter X-ray detectors based on superconducting transition edge sensors (TES) offer up to a roughly 60-fold improvement in energy resolution as compared with conventional detectors for energy-dispersive spectrometry. The best energy resolutions demonstrated to date are 0.72 eV full width at half maximum (FWHM) at 1.5 keV (Al-Kα) and 1.6 eV FWHM at 5.9 keV (Mn-Kα). The energy resolution of state-of-the-art microcalorimeter detectors rivals the resolution of spectrometers for wavelength-dispersive spectrometry (WDS), yet microcalorimeters offer all the advantages of EDS detectors - ease of use, long-term stability, and the ability to quickly provide qualitative as well as quantitative chemical analysis. We report the measurement of XRF peak shifts associated with the uranium Mα line at 3.171 keV and the iron Lα and Lβ lines at 707 and 717 eV that are indicative of the oxidation state of the uranium and iron. The oxidation state of an element defines the chemistry and molecular bonding of that element. A high resolution microcalorimeter mounted on a scanning electron microscope has provided a transformative approach to oxidation state measurements. The microcalorimeter detector with a resolution of 5-7 eV was used to detect the X-ray fluorescence emission of the different specimens using an electron beam at 7 kV and ~55 μA. This excitation was sufficient to generate Mα XRF emission from the uranium specimens with oxidation states of 0, +4 and +6. The peak fit shift measured for the 0 and +4 oxidation states was ~1 eV and for the 0 and +6 oxidation states ~4 eV. Two iron compounds, ammonium iron citrate and iron nitrate were measured. While both iron atoms are in the +3 oxidation state, the peak positions and shapes of the peaks are different. The iron results suggest not only a measure of the oxidation state, but a measure of the coordination environment of the iron. Due to the complex nature of the iron L spectra, more sophisticated modeling of the peak fits will be needed to fully understand the scientific basis for peak positions and shapes. Additional peak shifts of the nitrogen in the ammonium and nitrate moieties were also measured, indicating the different chemical environments. These results demonstrate the feasibility of oxidation state measurements using microcalorimeter detectors in an SEM.

Figure 1. Overlay of Fe Lα and Lβ peaks around 700 eV for two different iron compounds in +3 oxidation state.