

QuantumLeap-H2000™ Lab Fluorescence XAS

For samples with low concentrations and heavy matrices

Traditional laboratory systems are not equipped to measure fluorescence mode XAS (f-XAS), an important technique for analyzing elements with concentrations below 5% or thick samples. In this white paper, we discuss how Sigray QuantumLeap H2000 is designed to enable f-XAS for elements at concentrations as low as 0.1wt%. We also demonstrate the system's f-XAS capabilities on challenging battery and catalyst samples that other systems cannot analyze using transmission XAS.

This white paper describes the capabilities of the QuantumLeap-H2000™, the only f-XAS system on the market.



5750 Imhoff Drive, Suite I
Concord, CA 94520 USA
P: +1-925-446-4183
www.sigray.com
info@sigray.com

Laboratory Fluorescence Mode XAS For Challenging Samples with Low Concentrations or Heavy Matrices

Authors: Dr. Yiyao Tian, Sylvia Lewis | Sigray, Inc.

Background: X-ray Absorption Spectroscopy (XAS) can be collected in either transmission or fluorescence mode. As a rule of thumb, transmission mode is recommended for elements above 5wt% in samples that can be prepared as thin (transmissive) samples. Alternatively, fluorescence mode is preferred for low concentration elements, thick samples, those with absorbing matrices, or those mounted on thick substrates. Furthermore, fluorescence mode XAS signals are not superimposed on a large background, leading to superior Signal-to-Noise Ratio (SNR) when compared to transmission mode [1].

Applications in which fluorescence XAS is preferred include:

- **Batteries:** *In-operando* studies [2] and realistic battery samples (e.g., modified coin cells and pouch cells) [2] often require fluorescence mode XAS.
- **Heterogeneous Catalysts:** Catalysts are often supported with materials such as activated carbon. Such supports maximize the catalytic surface area and minimize the amount of catalysts required [3]. Due to their low concentrations, supported catalysts usually necessitate fluorescence XAS.

Novel Approach: Sigray QuantumLeap™

QuantumLeap™ is the **only fluorescence mode laboratory XAS system on the market**, enabled and protected by US patents 11,215,572 and 11,428,651. With its ability to analyze concentrations as low as 0.1 to 0.5wt% at good SNR, it is the only laboratory system of its kind. Unlike other XAS designs, QuantumLeap-H2000 employs a high brightness x-ray source in combination with Johansson crystals, resulting in a small spot size on the sample that can be efficiently collected by an SDD detector (see Fig. 1, right). In comparison, other XAS systems have a far larger (>20X) spot size (Fig. 1, left) due to the use of high power x-ray sources in combination with spherically bent Johann crystals. The larger spot of traditional lab XAS systems results in low detection efficiency, and they are able to collect only a fraction (e.g. 5%) of the solid angle that Sigray's QuantumLeap achieves. This leads to impractically long f-XAS acquisition times and is why thus far, f-XAS has largely not been possible with conventional lab XAS.

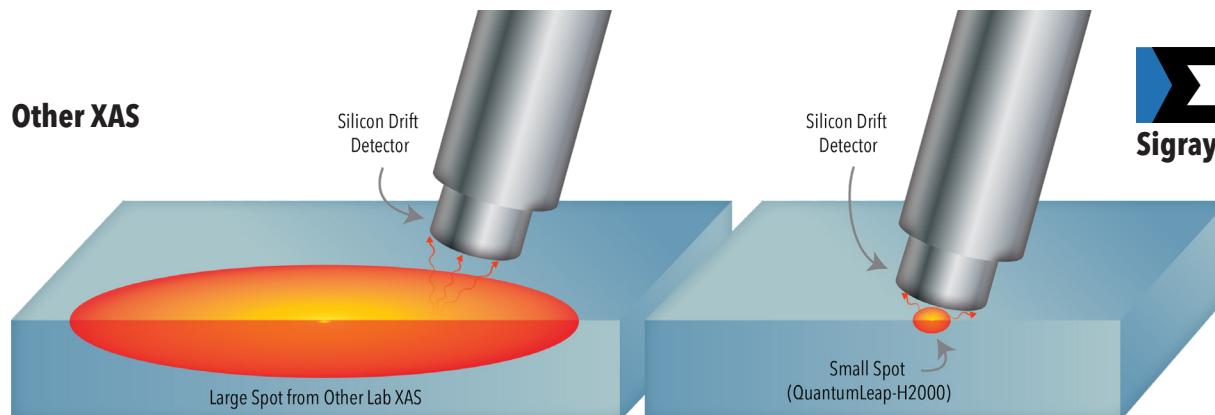


Figure 1 - How Sigray Uniquely Enables Fluorescence XAS: Laboratory XAS designs rely on a high power x-ray source coupled to a Johann spherical crystal. This results in a large spot size on the sample (left). The QuantumLeap's patented design results in a small spot size on the sample, with comparable flux within the smaller spot size in comparison to other lab XAS designs. Thus the fluorescence collected by a detector (example: 50mm diameter SDD) is far greater for the Sigray QuantumLeap, enabling f-XAS at practical throughputs.

Experiments and Results

In this report, we utilized the Sigray QuantumLeap™ to analyze five difficult applications that could not be resolved using transmission mode XAS. These samples included battery materials with heavy matrices and catalysts containing low concentrations of elements of interest.

Method: QuantumLeap Scan Set-up

The intuitive interface of the QuantumLeap™ software was used to select the element and absorption edges of interest from the periodic table of elements. The system then automatically chose the parameters and crystals that were necessary for the best data quality. These included the energy range, step sizes, and acquisition time of each spectrum. The XAS data was then processed and analyzed with the Athena program of the IFEFFIT package [4].

Application #1: Mn in Ni-Dominant NMC Battery

A cylindrically curved Johansson crystal Ge (331) was utilized to acquire f-XAS mode spectra at a rate of 24 hours per spectrum for a pair of charged and discharged NMC battery samples. Due to the combination of low concentration of Mn (2%) and the high Ni content in the samples, they had not been previously successfully analyzed using transmission XAS.

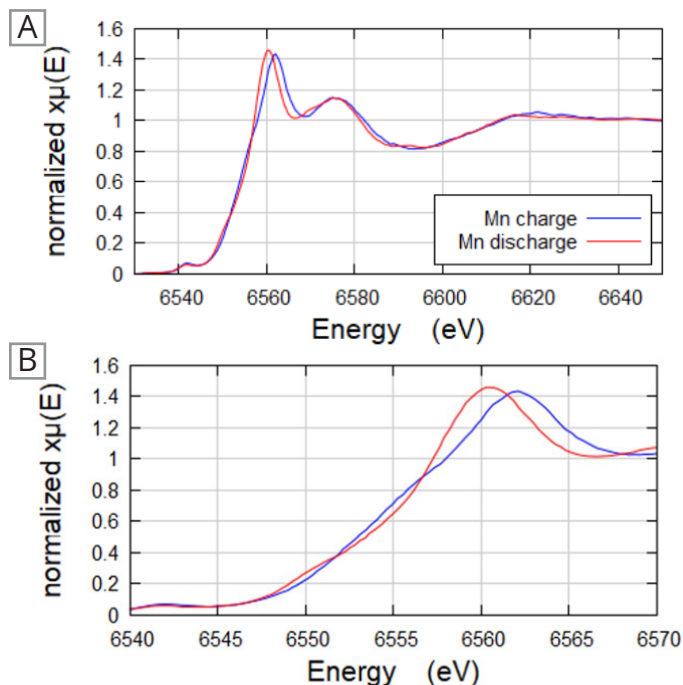


Figure 2 - Mn K-edge XANES of charged and discharged NMC samples. Bottom figure shows an expanded XANES region.

As can be seen in Fig. 2, the edge energy (as defined by the maximum of the first derivative of the absorption curve) is shifted towards a lower energy by 2 eV for the discharged sample, indicating that Mn has been reduced. Additionally, the pre-edge peak, edge slope, and white line positions of the two NMC samples display distinct differences.

Application #2: Co in Ni-Dominant NMC Battery

The Co K-edge in the charged and discharged NMC battery samples were also analyzed. Like Mn, the Co concentration (~3-5wt%) was too low for transmission geometry XAS.

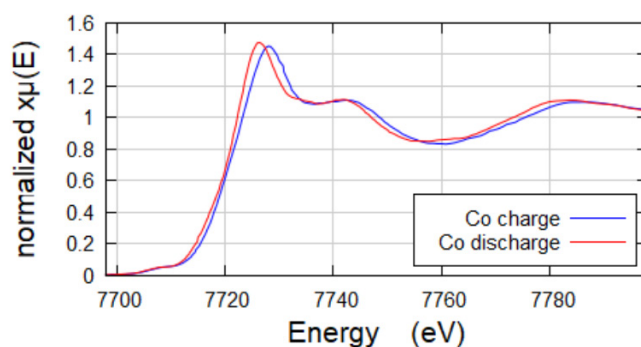


Figure 3 - Co K-edge XANES of charged and discharged samples.

Co spectra were collected using a cylindrically curved Johansson crystal Ge (331) at ~18 hours per sample. As shown in Fig. 3, the edge energy of the XANES region is shifted towards lower energy by 2eV for the discharged sample, indicating that the Co in the discharged sample is reduced.

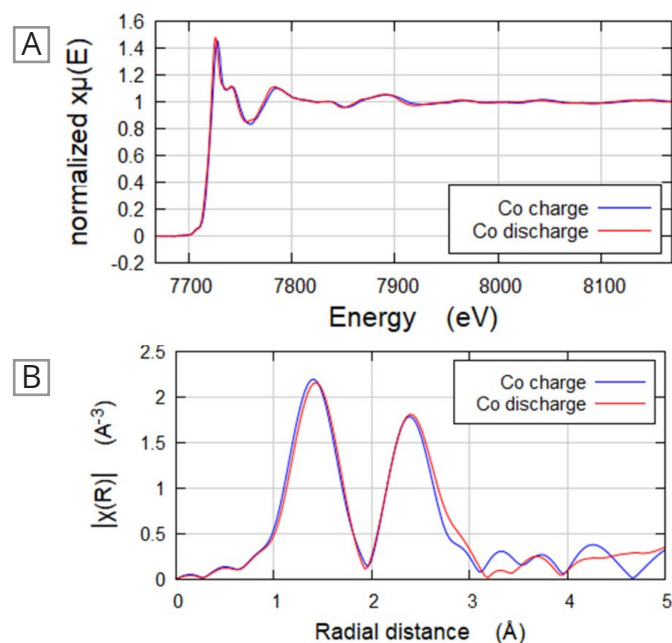


Figure 4 - Co K-edge EXAFS of charged and discharged samples.

We analyzed the Co EXAFS region (Fig. 4A) using Athena. Fig. 4B shows the results, with the first peak corresponding to the Co-O bond and the second peak corresponding to Co-metal bonds. Notably, Fig. 4B indicates that the bonds of the discharged sample are slightly longer than those of the charged sample.

Application #3: Pt/W Catalyst

A catalyst sample with 1% Pt and 0.5% W was measured with f-XAS using a cylindrically curved Johansson Si crystal (440) to acquire the L3 absorption edge for both elements. The W spectrum (Fig. 5) was measured over a 48-hour period, while the Pt spectrum (Fig. 6) was completed in a 24-hour timeframe.

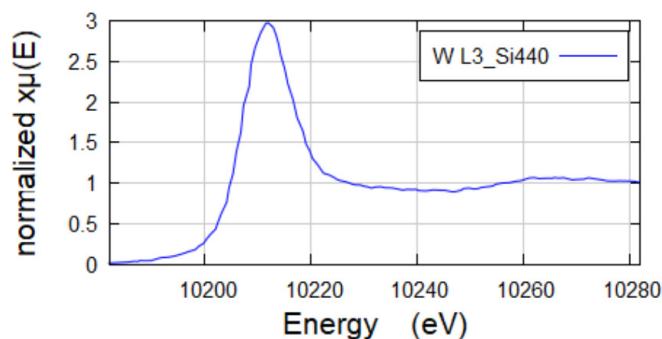


Figure 5 - W L3-edge XANES of a PtW catalyst with 0.5wt% Tungsten

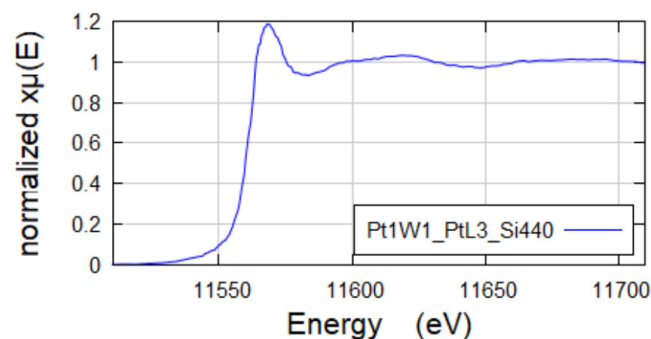


Figure 6 - Pt L3-edge XANES of a PtW catalyst with 1 wt% Platinum

References

1. S Calvin. XAFS for Everyone 2013
2. P Ghigna and E Quartarone 2021 J. Phys. Energy 3 032006
3. G Busca 2014 Advances in Catalysts
4. B Ravel and M Newville 2005 J Synch Rad 12

REF20230111

Application #4: Pt/Sn Catalysts with 0.5wt% Pt

Spectra of four catalyst samples (Fig. 7), each containing 0.5 wt% Pt, were collected using a cylindrically curved Si Johansson crystal (311) at 24 hours per sample. Of the four samples, Pt3 showed the highest white line intensity, indicating that it was the most oxidized sample among the lot.

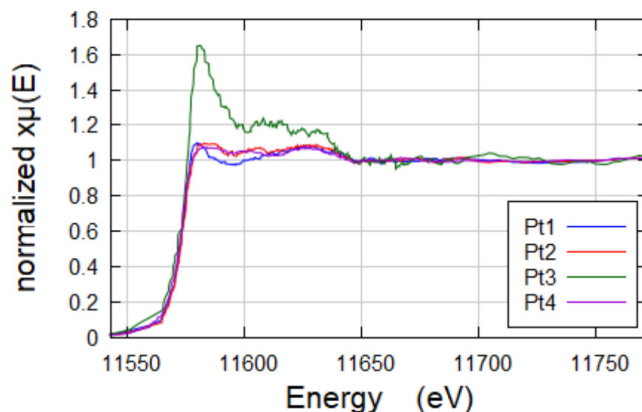


Figure 7 - Pt L3-edge XANES of PtSn catalysts with 0.5wt% Platinum

Application #5: Pd Catalysts at 0.5 and 2wt% Pd

Spectra of catalysts having varying Pd concentrations (0.5wt% and 2wt%) were measured using a cylindrically curved Si Johansson crystal (311) at 24 hours per sample. The white line position, width, and intensity changed for all four samples, however the absorption edge energy remained constant.

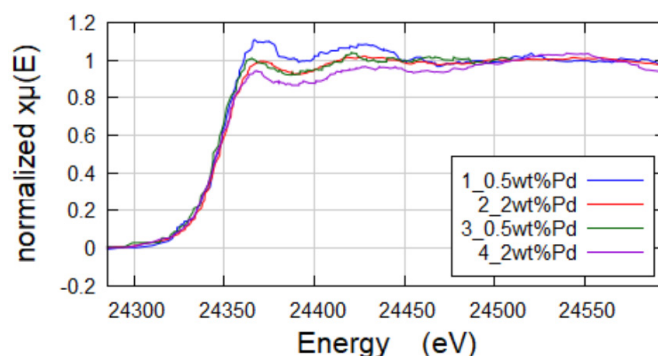


Figure 8 - Pd K-edge XANES of Pd catalysts w/0.5-2wt% Pd

Summary

We have demonstrated how Sigray QuantumLeap's fluorescence mode XAS produces high quality XAS spectra for samples that would be otherwise be impossible with transmission XAS, including samples with highly absorbing matrices and low concentration (0.5wt%) samples.