

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.



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

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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 battery samples (e.g., pouch cells and low weight percent Co NMC formulations) [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 synchrotron-quality **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.

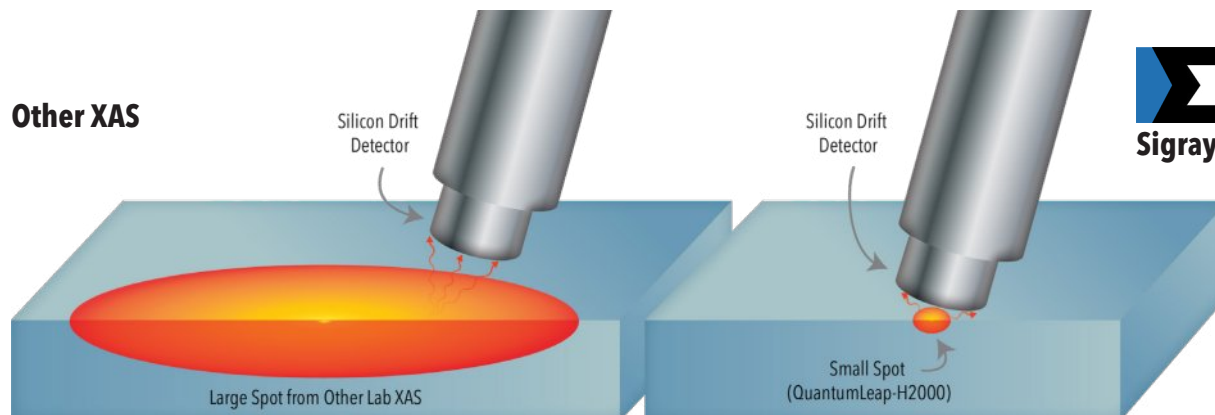


Figure 1 - How Sigray Uniquely Enables Fluorescence XAS: Laboratory XAS designs rely on a high power x-ray source coupled to a Johann spherical crystal. This results in a large spot size on the sample (left). The QuantumLeap's patented design results in a small spot size on the sample, with comparable 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 several 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.

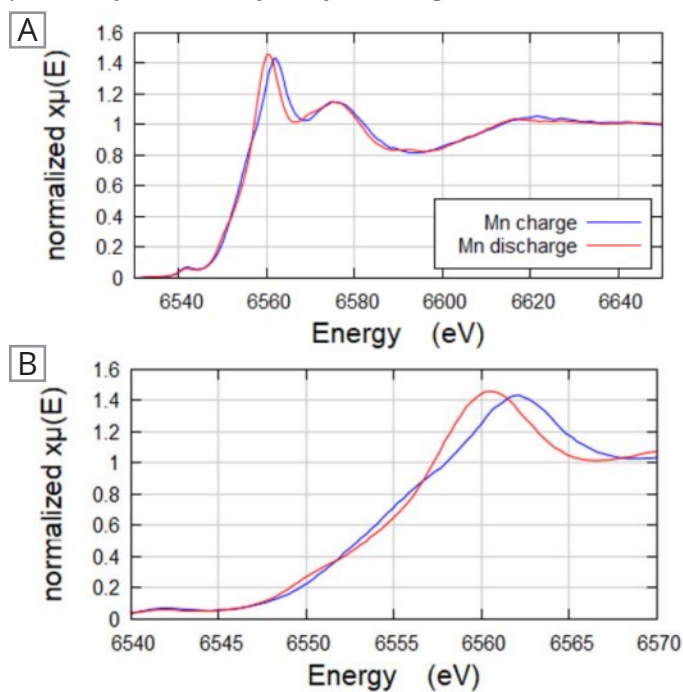


Figure 2 - Mn K-edge XANES of charged and discharged NMC samples. Bottom figure shows an expanded XANES region.

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.

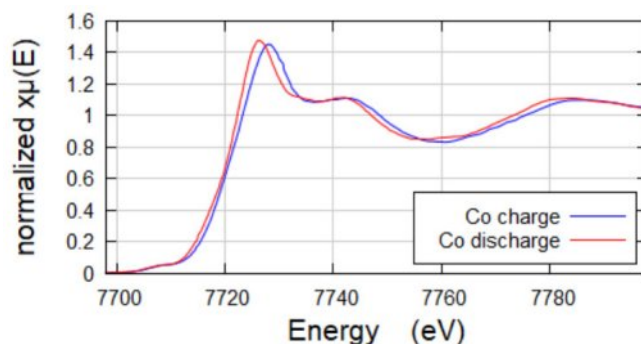


Figure 3 - Co K-edge XANES of charged and discharged samples.

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.

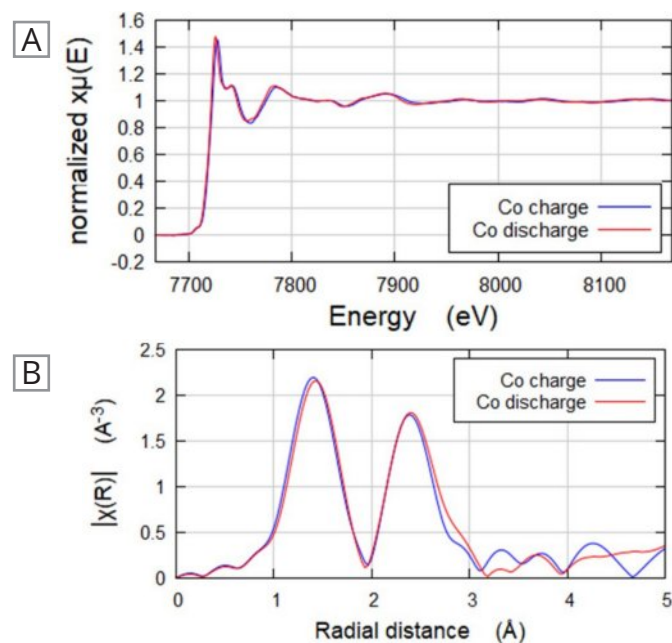


Figure 4 - Co K-edge EXAFS of charged and discharged samples.

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: 1% Pt/y-Al₂O₃ Sample

A powdered catalyst sample with <1% Pt was acquired with QuantumLeap in f-XAS mode. Pt L3 spectra (Fig. 5) was collected until $k=15 \text{ \AA}$ and then subsequently analyzed (Fig. 6).

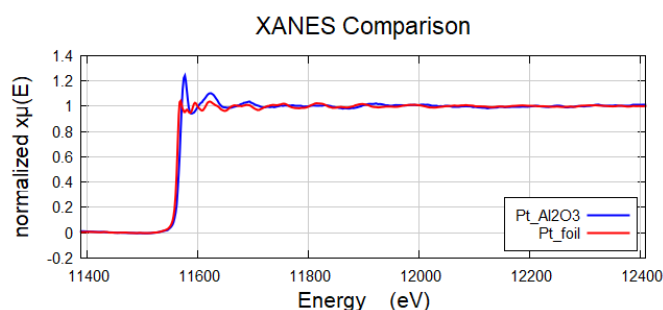


Figure 5 - Pt L3-edge XAS acquired in f-XAS mode of a 1% Pt/y-Al₂O₃ catalyst (blue) and a reference Pt foil (red)

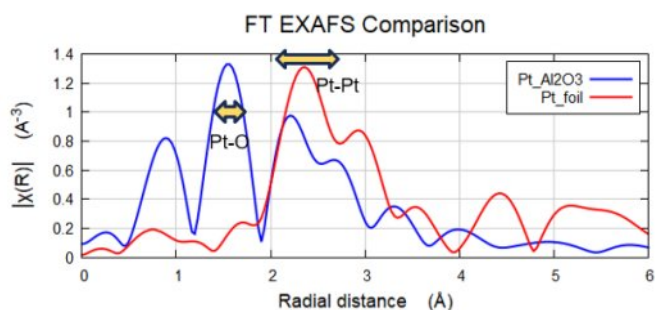


Figure 6 - Athena analysis of Fig. 5 spectra, showing Pt-O bonds (~1.8 Å, non phase-shifted) and Pt-Pt bonds (2.4 and 2.8 Å).

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

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Application #4: V Catalysts with 5% V

Spectra of 5% Vanadium catalysts were acquired in fluorescence XAS mode on QuantumLeap until $k=15 \text{ \AA}$. XANES (Fig. 7) shows a strong pre-edge that corresponds to a VO₂ tetrahedral system. EXAFS analysis (Fig. 8) indicates an average coordination of a CN of approximately 4, indicating a tetrahedral geometry.

Figure 7 - XANES comparison, indicating a tetrahedral VO₂ system

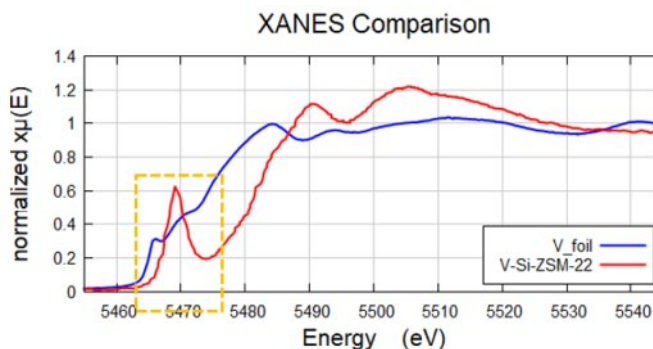
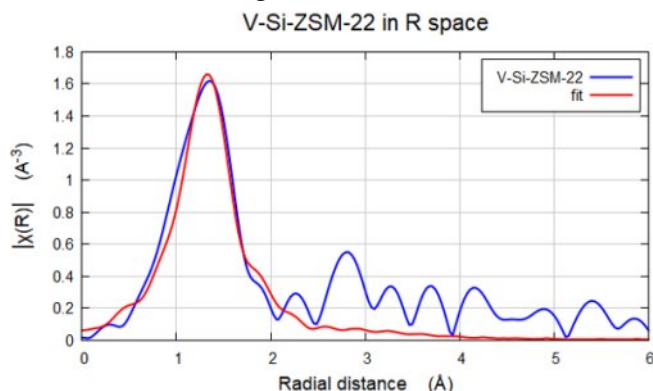


Figure 8 - EXAFS fit to first shell V-O, showing coordination number and a bond length of 1.73 Å.



Path	N (CN)*	R (Å)	DW (σ²)	E	R-Factor
V-O	4.11	1.73	0.00766	11.173	0.0249

Summary

We have demonstrated how Sigray QuantumLeap's fluorescence mode XAS produces high quality XANES and EXAFS spectra for samples that would be otherwise be impossible with transmission XAS, including challenging battery and catalyst samples.