# Chemical State Analysis with the **QuantumLeap** X-ray Spectroscopy System

Author: Dr. Srivatsan Seshadri | Sigray, Inc.

## Background

X-ray absorption spectroscopy (XAS) is a powerful chemical state analysis technique use for research in a broad range of disciplines, particularly in the development of advanced materials for catalysis, batteries, and semiconductor devices. This technique involves measuring the transmission of x-rays as a function of incrementing x-ray energy in small steps at energies close to the absorption edge (binding energy) of an element of interest (e.g. Fe).

XAS is comprised of two regions (Fig. 1):

1. X-ray absorption near edge structure (**XANES**/NEXAFS): Comprising x-ray energies nearest to the absorption edge (~100 eV around the edge), this region exhibits sharp resonance peaks. Generally, the region is sensitive to local atomic states such as oxidation states and symmetry.

2. Extended fine structure (**EXAFS**): features that appear after the XANES region and up to 1000 eV or greater than the absorption edge. These features appear as gentle oscillations in the measured signal, and is caused by the multiple scattering of the ejected electron by surrounding atoms. EXAFS measurements can be used to infer neighboring atom information, including bond lengths and chemical coordination environments.

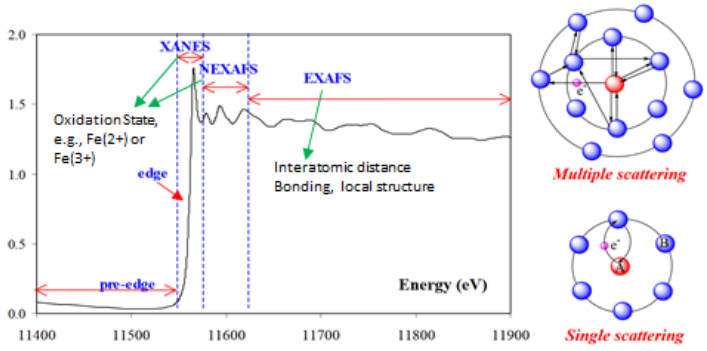


**Figure 1:** The two regimes of XAS: XANES/NEXAFS and EXAFS. The XANES regime features sharp peaks, while the EXAFS region features gentle oscillations.

## Challenges to XAS

Although laboratory approaches to XAS have been designed, most research is primarily performed at synchrotron facilities. These multi-hundred-million-dollar centers provide high intensity beams of x-rays for acquiring XAS data within reasonable acquisition times. However, access to these facilities is challenging to obtain and typically introduces delays in research of several months to a year.

## Sigray QuantumLeap XAS Solution

The QuantumLeap is the first laboratory XAS offering synchrotron-like performance.

Key capabilities include:

- Both XAS Modes: XANES with sub-eV resolution and high throughput EXAFS
- Wide energy coverage: 2.1 - 12 keV
- Energy resolution of <0.5 eV
- High throughput of seconds to minutes for the complete XAS spectrum

To achieve this, the system features incorporates several major design innovations:

1. Patent-pending approach to acquisition with **parallel detection spectrometer**, making use of modern crystal and detector technology

2. Novel **x-ray optics** that remove higher order harmonics for improved acquisition speed

3. Patented **high brightness x-ray source** that enables use of high efficiency, low diffraction orders of the crystal analyzers

4. High DQE direct detection detector

### *1) Innovative Approach to Acquisition*

The QuantumLeap is based on a patent-pending acquisition method that optimizes collection efficiency and is based on the realization that XANES and EXAFS regimes have opposing requirements:

- XANES requires **high resolution** (e.g. <1 eV) but not as much flux (due to the sharp features, see Fig. 1); while
- EXAFS requires lower energy resolution (e.g. <10 eV) but **high x-ray flux** because of the

minute scale of EXAFS signals; such oscillations of absorption are a very small fraction of total absorption and thus to detect them accurately, a large number of photons are required - for example, ~$10^6$ photons per point is required for accuracy of <0.1%

The QuantumLeap acquires XAS information by using a flexible geometry that changes based on the regime of interest (XANES vs EXAFS, as shown in Figures 2A and 2B).

## QuantumLeap XANES Geometry

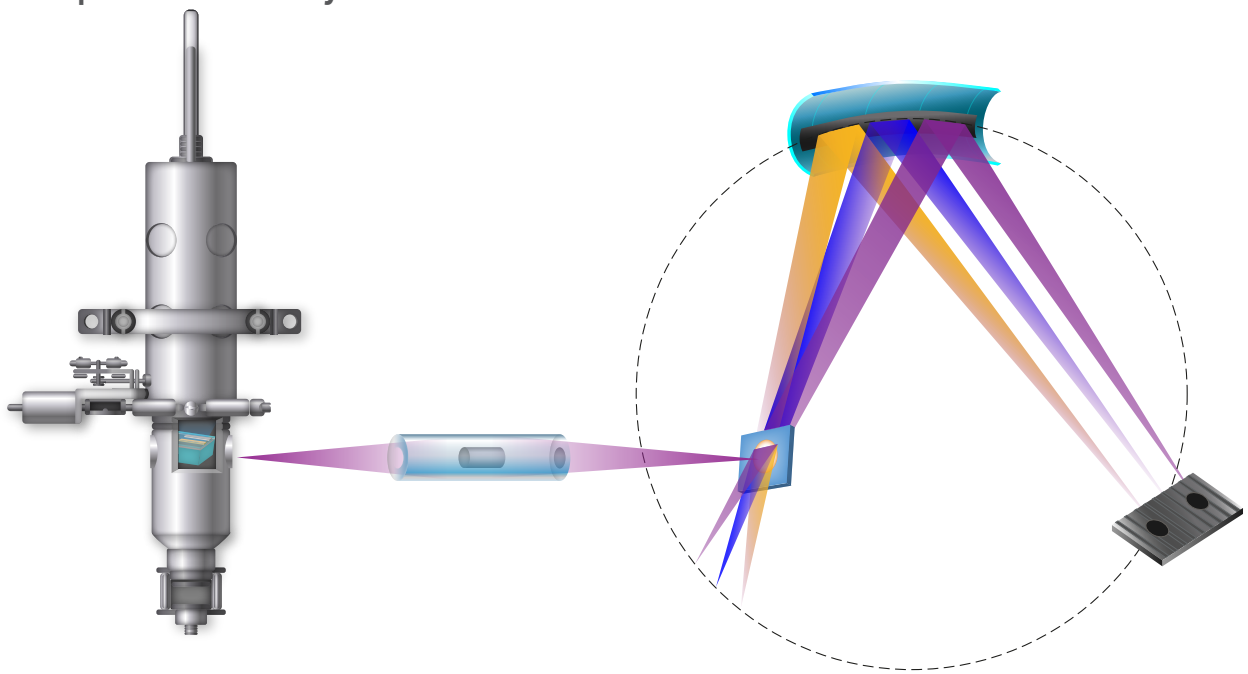

**Figure 2A (above):** QuantumLeap's XANES off-Rowland geometry: Sample is placed within the Rowland circle to enable simultaneous detection of multiple wavelengths (rather than a single-energy low throughput approach); by using Johanson crystals coupled with a high resolution CCD, the energy resolution is <0.5 eV.

## QuantumLeap EXAFS Geometry

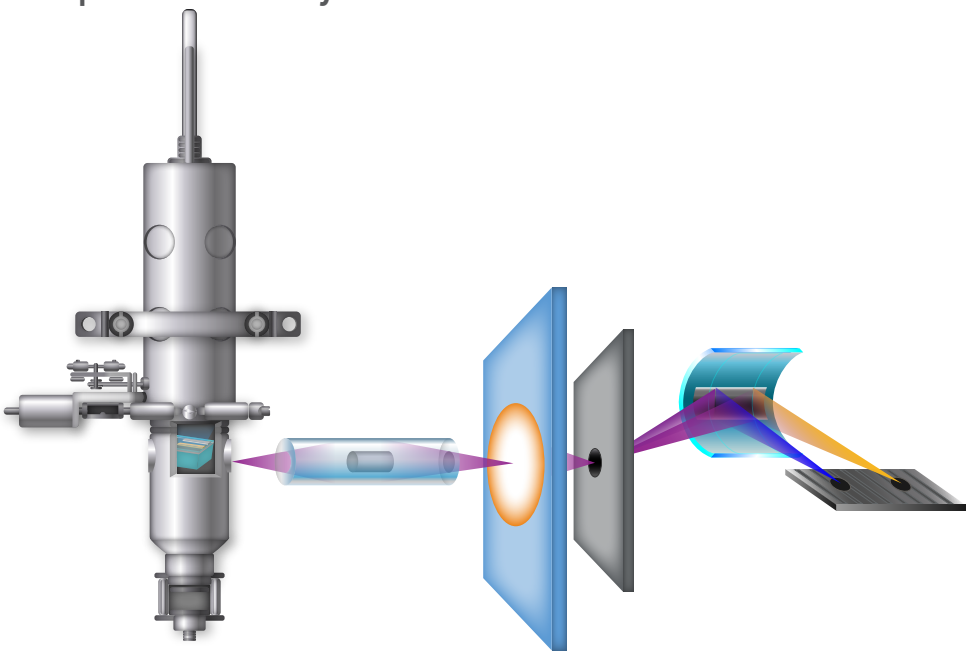

**Figure 2B (left):** QuantumLeap's EXAFS geometry: von Hamos geometry is a high throughput approach that detects a wide energy spectrum simultaneously using a mosaic crystal.

For **XANES measurements**, the system achieves high throughput through an off-Rowland circle geometry in which the sample is placed within the Rowland circle for simultaneous XANES spectra acquisition (without single-energy stepping). Johannson crystals are employed to achieve high resolution stemming from their excellent focusing of x-rays in the dispersion plane (minimization of focusing errors) and because of the wide energy range of the crystals, which reduce the number required.

For **EXAFS measurements**, the system switches over to a von Hamos geometry, in which a mosaic curved crystal is used to optimize collection efficiency and achieve large spectral coverage (up to 1 keV) and sufficient energy resolution (<10 eV) with high throughput. The von Hamos geometry offers further advantages in simple construction, ease of alignment, stability and reproducibility.

Sigray's patent-pending approach uses the data from the two geometries, effectively combining the high resolution XANES data obtained using a Johansson crystal with the high throughput EXAFS data obtained using a mosaic crystal. Software then provides the appropriate overlay, normalization, correlation and stitching to produce refined XAS analysis. Both geometries make use of major advances in crystal analyzer fabrication technology that have only developed in the past years, including high quality cylindrically bent Johansson crystals and curved mosaic von Hamos crystals. This approach greatly simplifies the number of crystals required; e.g. for the energy range of 2.1 - 12 keV, the QuantumLeap only requires 4 crystals (vs. 10 Johann crystals).

| Johansson Single Crystal Analyzers | |
|---|---|
| Number of Crystals | 3 |
| Crystal Types | Ge (111), Ge (220), Ge (400)<br>Others on request |

**Table 1:** Specifications for XANES: Johansson crystal analyzers

| von Hamos Mosaic Crystal Analyzer | |
|---|---|
| Number of Crystals | 1 |
| Crystal Types | HAPG/HOPG (002) |

**Table 2:** Specifications for EXAFS: von Hamos crystal analyzer

### *2) Novel X-ray Optics*

In conventional laboratory XAS, higher order harmonic contamination (integer multiples of the x-ray energy of interest will also be diffracted by the crystal because they satisfy the Bragg condition) is a major problem because it reduces contrast and signal-to-noise ratio, thus limiting throughput.

An example is shown in Figure 3 in which the required number of photons for a given contrast (K) and signal to noise ratio (SNR) is plotted as a function of absorption of the sample for three different contrasts: 3%, 5% and 10%. Higher order contamination background will reduce the apparent absorption value (X-axis), requiring more photons for the desired contrast and signal-to-noise.

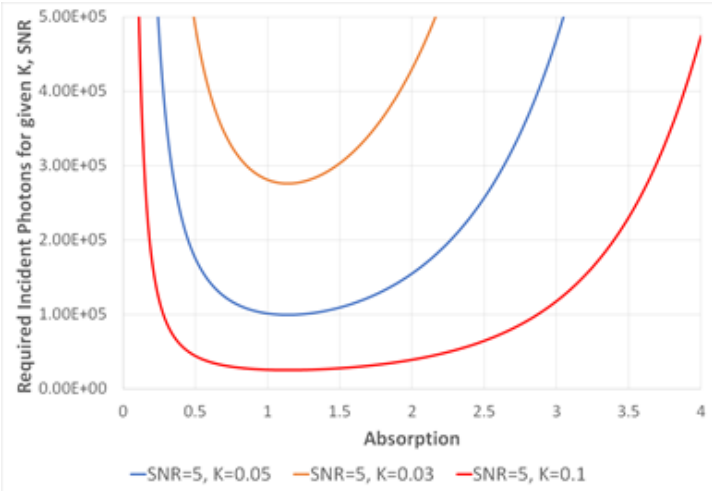


**Figure 3:** If the apparent absorption decreases because of higher background from higher order contamination, exponentially more incident photons are required (or there is a reduction in contrast for the same # of photons). Curves shown for signal-to-noise ratio of 5 and contrasts of 3%, 5%, and 10%.

This higher order contamination problem is why traditional laboratory-based systems have always operated with x-ray sources at electron beam accelerating voltages of just below 2X the energy of interest, thus preventing the higher order x-ray energy from being produced in the first place. However, the use of lower energy electrons are less efficient at producing x-rays (x-ray production is approximately proportional to incident voltage) and thus this is a major limiter to throughput.

Sigray's novel double paraboloidal optic inherently has a cut-off energy above which higher energy x-rays are substantially removed (Figure 4). This optic therefore uniquely allows maximum source efficiency by operating at higher electron beam voltages.

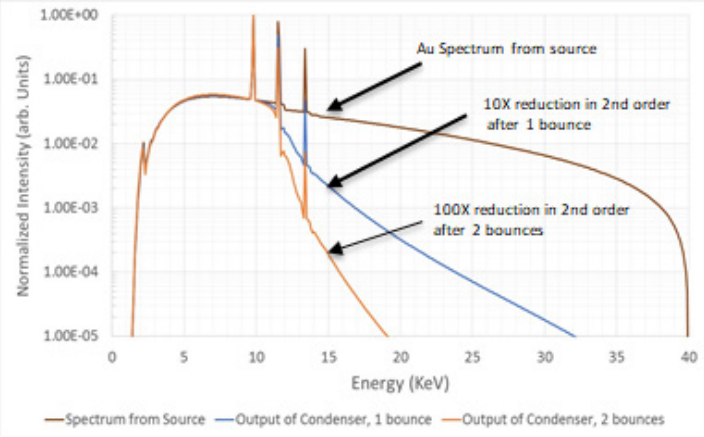


**Figure 4:** Sigray's optic inherently filters out higher energy x-rays because of the optic's double paraboloidal shape. The double-reflection (two-bounce) geometry removes ~100X of higher energy x-rays of the example source spectrum from an Au source.

In addition, the optic enables micro-XANES at 100 µm for analysis of inhomogeneous samples. The working distances of the optics provides the space for *in-situ* and *in-operando* experiments.

| Double Paraboloidal X-ray Condenser Optics | |
|---|---|
| Number of Optics | 4 |
| Reflection Efficiency (%) | >70 |
| Coating on Reflecting Surface | Pt |
| Point Spread Function FWHM | ~5 µm |

**Table 3:** Specifications for x-ray optics

## *3) Patented Ultrahigh Brightness X-ray Source*

The final innovation is Sigray's patented ultrahigh brightness, microfocus source. Advantages of using the source are detailed in the following sub-sections.

### 3.1 Small Spot Size

Conventional approaches to laboratory XAS have used various high-power sources such as rotating anode types (up to 15 kW) to maximize flux. However, the spot size of these sources are typically too large and limit the energy resolution of the system at the low index (preferred) reflection orders of the crystal analyzers. As a result, for XANES, which requires high energy resolution, the crystals must be used at high index reflection orders; however, these only using high index reflection orders significantly reduce the integrated reflectivity of the crystal and therefore the throughput of the system.

### 3.2 Multiple Target Design

Sigray's x-ray source features selectable choices of different x-ray target materials, thus providing optimal spectra to study a broad range of elements.

### 3.3 Microstructured Design with Diamond

The x-ray source target also features an innovative design in which microstructured target materials are in thermal contact with a diamond substrate and liquid cooled. The rapid thermal dissipation enables higher power loading on the source (limited by anode melting), thus providing high brightness and system throughput.

| Ultrahigh Brightness Microfocus Source | |
|---|---|
| Source Type | Reflection |
| Nominal X-ray Take-off Angle | 6 - 12° |
| Maximum Voltage (kV) | 50 kV |
| Maximum Power (W) | 300* W<br>*Max power obtained only at high voltages |
| Number of Target Materials | 3 |
| Target Materials | W, Mo, Cr*<br>*Other materials on request |

**Table 4:** Specifications for x-ray source

## *4) High DQE Direct Detection CCD Detector*

The QuantumLeap uses an advanced high detection quantum efficiency (DQE) direct detection CCD with high resolution and multiframe readout capabilities. This detector enables parallel detection of a spectral range of x-ray energies without need to move components during measurement.

| Window-Free X-ray Detector | |
|---|---|
| Detector Type | Direct Detection CCD<br>(back-illuminated, deep depletion with anti-fringing and low dark current) |
| Digitization | 16-bit |
| Pixel Size | 13 µm |
| Readout Noise | 9 e at 2 MHz |
| Linearity | > 99% |
| Cooling | - 80 °C |

**Table 5:** Specifications for x-ray detector

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