

Chemical State Analysis with the **QuantumLeap-V210™** X-ray Spectroscopy System

The QuantumLeap-V210™ is the first vacuum laboratory x-ray absorption spectroscopy (XAS) system, enabling electronic structure analysis such as chemical state and bond lengths for elements ranging from low atomic numbers (e.g., sulfur) to transition metals.

This white paper will review the principles of XAS and the Sigray QuantumLeap-V210™'s design innovations



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The Physics: What is XAS? X-ray absorption spectroscopy (XAS) is a powerful chemical state analysis technique used for research in a broad range of disciplines. 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 (energy that corresponds to the energy required to eject an electron from an electron shell) of an element of interest (e.g. Fe). Small changes in how x-rays are absorbed near an atom's absorption edge correspond to the state of the electrons.

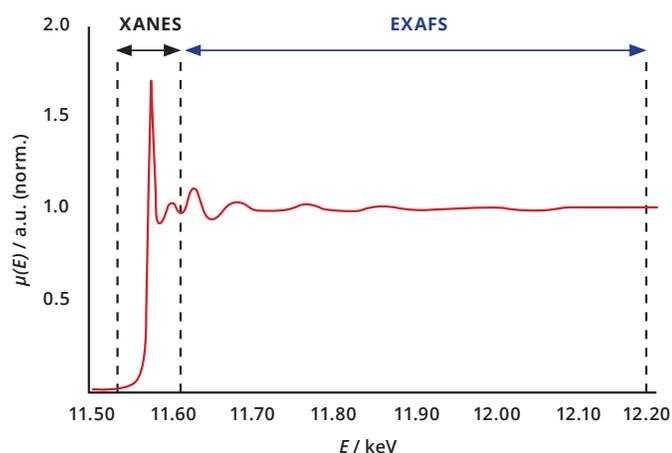


Figure 1: The two regimes of XAS: XANES and EXAFS. The XANES regime features sharp peaks, while the EXAFS region features gentle oscillations.

XAS is comprised of two regions (Fig. 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.

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

QuantumLeap-V210 Laboratory XAS

The QuantumLeap-V210™ system is a patented laboratory XAS system offering synchrotron-like performance. Unlike the QuantumLeap-H2000, the V210 is specialized for low atomic number analysis and micro-XAS. Key features include:

- **Wide energy coverage:** 1.7 - 10 keV due to a vacuum enclosure, enabling coverage of elements such as P and S that are inaccessible for many synchrotron beamlines due to ambient operation
- **Sub-eV energy resolution of <0.7 eV**
- The ability to perform **micro-XANES** mapping at 100 μm
- Recipe acquisition for unsupervised overnight runs
- Patented **acquisition approach** to optimize XAS spectra at highest throughput

The system's performance is the culmination of several major design innovations, including:

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 patented 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 and intense features (see Fig. 1); while
- EXAFS requires **lower energy resolution (e.g. <10 eV) but high x-ray flux** because of the small amplitudes of EXAFS signals.

In light of this difference, the QuantumLeap-V210 switches between two geometries to optimize the acquisition of XANES and EXAFS signals.

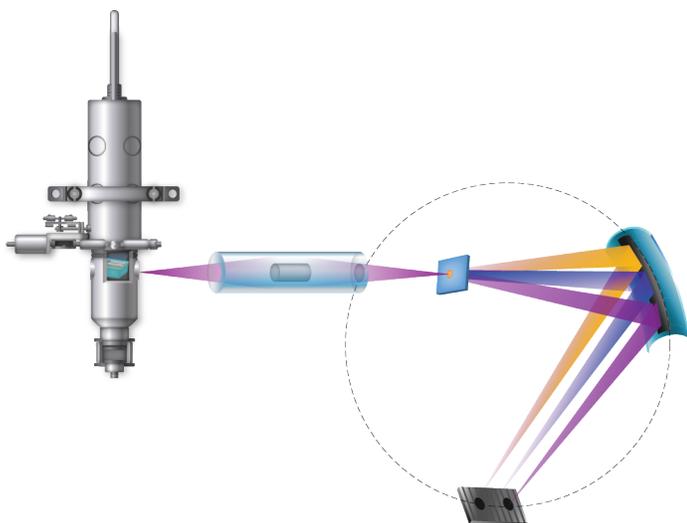


Figure 2A: QuantumLeap-V210 XANES Geometry: The system is in an off-Rowland geometry. In this geometry, sample is placed *within* (rather than *on*) the Rowland circle to enable simultaneous detection of multiple wavelengths.

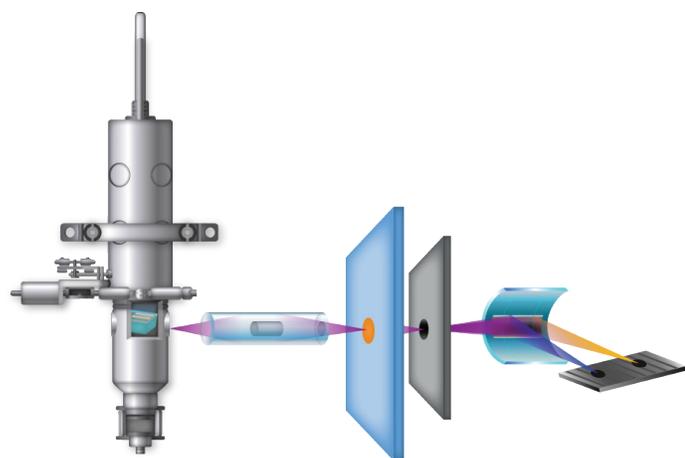


Figure 2B: QuantumLeap-V210 EXAFS Geometry: In this von Hamos geometry, a mosaic crystal allows high throughput detection of a wide energy spectrum simultaneously.

For **XANES measurements**, the system uses an off-Rowland circle geometry in which the sample is placed *within* the Rowland circle for simultaneous XANES spectra acquisition (Fig. 2A). In this patented method of acquisition, Sigray's patented x-ray source generates a high brightness beam of polychromatic (multi-energy) x-rays that is focused by an x-ray optic. Because the sample is not precisely on the Rowland circle but instead inside the circle, the downstream

single Johansson crystal will diffract a bandpass of wavelengths to spatially separate regions of a pixelated detector. The intensity measured by each detector columns corresponds to a given wavelength. In this way, the entire XANES spectrum is acquired in a single shot.

For **EXAFS measurements**, the system switches over to a von Hamos geometry, in which a mosaic curved crystal is used. Unlike the single crystal used in the XANES acquisition, mosaic crystals comprise small crystallites that are oriented slightly differently from one another. In this way, a broader spectrum is diffracted onto the detector. This method provides optimum collection efficiency and large spectral coverage (e.g., up to 1 keV) at sufficiently good energy resolution (5-10 eV). In this way, the high photon flux required for EXAFS is achieved.

Note that both acquisition processes in QuantumLeap-V210 are **dispersive acquisition processes** and different than scanning systems. In scanning systems (of which Sigray's other model of QuantumLeap-H2000 is one), a crystal is employed upstream of the sample to monochromatize the x-ray beam to a single energy. The crystal is then rotated to select different wavelengths, allowing "stepping" of the energies used to acquire the spectrum. Multiple steps are used to acquire what the QuantumLeap-V210 acquires in a single shot.

After both XANES and EXAFS data are acquired, the data is combined through software to provide the appropriate overlay, normalization, correlation, and stitching for refined XAS analysis.

XANES: Johansson Single Crystal Analyzers

Number of Crystals	4
Crystal Types	Ge (111), Ge (220), Ge (400), Quartz (10-10) Others on request

Table 1: Crystals used for XANES acquisition mode

von Hamos Mosaic Crystal Analyzer

Number of Crystals	1
Crystal Types	HAPG/HOPG (002)

Table 2: Crystals used for EXAFS acquisition

2. Novel X-ray Optics

A major distinguishing feature in QuantumLeap-V210 is its use of x-ray optics. These x-ray optics provide not only focusing down to 50-100 μm spot sizes for micro-XAS mapping, but also provide an additional benefit in enabling the system to operate at maximum efficiency because they remove the problem of higher order contamination.

In conventional laboratory XAS systems based on scanning geometries, a fundamental problem is that of **higher order harmonic contamination**. This arises because the crystal that monochromatizes the beam before the sample will also diffract integer multiples of the x-ray energy of interest; for example, if 2 keV is of interest, 4 keV (twice the energy) and 6 keV (three times the energy) will also be diffracted. The allowance of these higher order harmonics can severely reduce contrast and signal-to-noise ratios, 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.

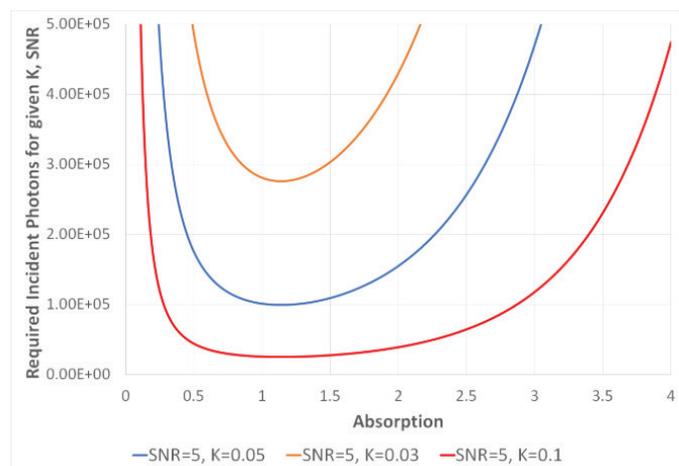


Figure 3: If the apparent absorption decreases because of higher background from higher order contamination, exponentially more incident photons are required; otherwise, there is a reduction in contrast for the same # of photons. Curves shown for signal-to-noise ratio (SNR) of 5 and contrasts of 3%,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

This higher order contamination problem is why traditional scanning 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 is 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). Thus, higher order harmonics are naturally removed from the spectrum. In this way, the source can be operated at maximum efficiency by operating at higher electron beam voltages without being concerned about producing higher order harmonics.

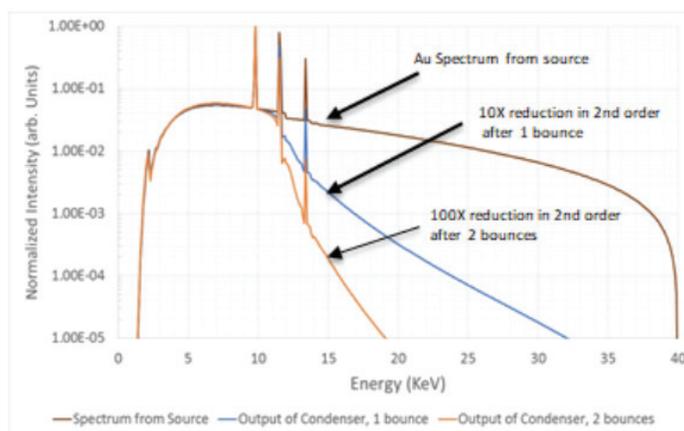


Figure 4: Sigray's optic inherently filters out higher energy x-rays because of the optic's double paraboloidal shape. The double-reflection (two-bounce) geometry removes ~100X of higher energy x-rays of the example source spectrum from an Au source.

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

A third innovation in QuantumLeap-V210 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 because of aberrations. To compensate for the source aberrations, these conventional systems must therefore be operated using crystals at high index reflection orders (high Bragg angles). This is not desirable because acquiring at high Bragg angles significantly reduces the integrated reflectivity of the crystal and therefore drastically restricts the acquisition speed.

3.2 Multiple Target Design

Another key design feature in QuantumLeap-V210's patented source design is that it features multiple target materials in the same source body. Each source target produces a different spectrum. This is to ensure the absence of characteristic x-ray lines that would otherwise contaminate the signal, thus ensuring a smooth spectrum for acquiring a full range of elements across the periodic table without restriction.

3.3 Microstructured Design with Diamond

The x-ray source target also features thermal strategies in which the 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 maximizing system throughput.

Patented 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 *Max power obtained only at high voltages
Number of Target Materials	2 for XAS 3 for calibration
Target Materials	Main: W, Mo Calibration: Fe, Cu, Cr

Table 4: Specifications for x-ray source

4) High DQE Direct Detection CCD Detector

A final innovation in QuantumLeap-V210's design is its incorporation of an advanced, high detection quantum efficiency (DQE) direct detection CCD with high resolution and multi-frame readout capabilities. This detector is spatially resolving, unlike silicon drift detectors used in conventional laboratory XAS systems. Since QuantumLeap-V210's acquisition approaches (outlined in section 1) enable diffracting narrow spectral ranges of x-rays into different positions along the detector, this pixelated detector is then used to "image" intensities along each column of the detector. Each column corresponds to an x-ray energy. In this way, parallel detection of a spectral range of x-ray energies can be acquired without the need to move components during measurement.

Window-Free X-ray Detector	
Detector Type	Direct Detection CCD (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 source

Summary

Sigray QuantumLeap-V210™ combines recent advances in key x-ray components (x-ray source, crystals, and detector) with patented innovations in parallel acquisition methods to maximize throughput and performance, including achieving sub-eV resolution. The system is uniquely capable of acquiring down to x-ray energies of 1.7 keV, enabling elements such as P and S, and for micro-XAS mapping at spatial resolutions ranging from 50-100 μm .



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