White Paper

Chemical State Analysis with the QuantumLeap-H2000™ X-ray Spectroscopy System

The QuantumLeap-H2000™ is the first laboratory system capable of achieving synchrotron-grade performance x-ray absorption spectroscopy (XAS) in both transmission and fluorescence modes to provide access to chemical state and electronic structure information.

This white paper will review the principles of XAS and the Sigray QuantumLeap-H2000™'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.

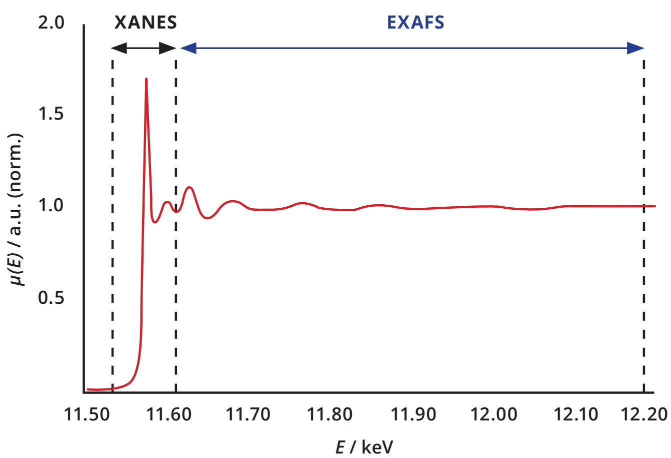

Figure 1: The two regimes of XAS: XANES and EXAFS. The XANES regime features sharp peaks, while the EXAFS region features gentle oscillations.

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.

As can be seen in Fig. 1, the XANES region requires the highest energy resolution (it features sharp structures) while the EXAFS region generally requires lower energy resolution over a larger extended bandwidth of generally 500eV to 1 keV. The best energy resolution required therefore corresponds to the XANES regime, where it is usually set to half of the radiative line width (caused by core-hole lifetime broadening). Energy resolution beyond what is necessary (e.g. 0.1 eV when 1 eV is needed) will result in throughput loss without any gain in signal quality. Table 1 lists the energy resolution required for example characteristic x-ray energies.

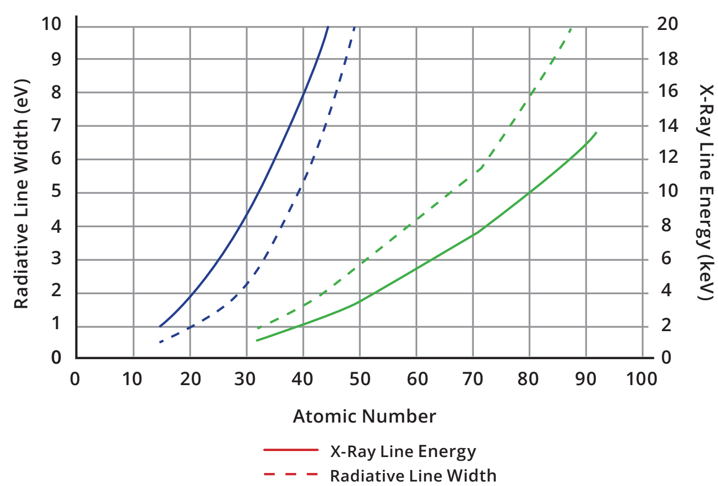

Figure 2: Radiative line widths due to core hole broadening and characteristic x-ray energy as a function of atomic number. Note that for 2 keV (e.g. K-line of sulfur), around 0.5 eV is required. For 8 keV (e.g. copper), the highest energy resolution required is 2 eV.

Table 1: Energy resolution required is based on ~1/2 the radiative line width.

X-Ray Energy (keV)	Resolution Req'd (eV)
2	0.5
4	1
6	1.5
8	2
11.7	2.5
17.4	4

Breakthrough Laboratory System Design

The QuantumLeap-H2000™ Hybrid system is the product of several patented innovations, both in x-ray component technology and system design, including:

1) Novel design enabling acquisition at **low Bragg angles** (e.g. 15 to 30 degrees) through use of a Johansson crystal in combination with a photon counting detector (patented method)
2) **A patented x-ray source** with outstanding brightness and a multi-target design for ideal spectral output
3) Secondary **silicon drift detector (SDD)** for fluorescence mode XAS

The combination of the patented concepts results in breakthrough performance achieving up to E/ΔE energy resolution of 6000 to 7000.

1) Novel Design for Low Bragg Angle Acquisition

The Bragg angle is the angle at which x-rays of specific wavelengths are incident upon and reflected by a crystal analyzer (see Fig. 1). The angle follows the well-known Bragg: Equation: $n\lambda = 2d\sin\theta_B$, in which n is an integer multiple, λ is the x-ray wavelength of interest, d is the d-spacing of the crystal lattice planes of the crystal analyzer, and θ_B is the Bragg angle.

Operating at **low Bragg angles** (15 to 55°) for XAS is **highly advantageous**. High Bragg angles (>60°) result in numerous complications, including low throughput, stringent requirements for sample uniformity, and the need to manually change multiple crystals for a single acquisition. As a result, nearly all synchrotron XAS beamlines are designed for operating at low Bragg angles.

However, modern laboratory systems primarily operate at non-optimal **high Bragg angles** (near-backscatter). This is due to a combination of two system limiters:

Limiter #1 of Conventional Lab XAS - Detector and crystal

Because laboratory x-ray sources produce polychromatic x-rays, laboratory XAS systems use silicon drift detectors (SDDs) to reject certain x-ray energies known as harmonic contamination. To focus onto the small footprint of an SDD placed, these systems use a crystal geometry known as spherically bent crystal analyzers (SBCAs). SBCAs are bent in both directions, providing point-to-point focusing to allow utilizing a SDD. However, to achieve bi-directional focusing, the SBCA curvature is currently limited to Johann (see Fig. 6), giving an associated Johann focusing error (Fig. 3) that is approximated by: $\varepsilon = 1/2\,(w/2R)^2 \cot\theta_B$, in which w is the crystal size, R is the Rowland circle diameter, and θ_B is the Bragg angle. Due to focusing error, SBCAs operate at high Bragg angles of 75° to near backscattered (90°) for high energy resolution.

Limiter #2 of Conventional Lab XAS - Source broadening

Laboratory systems generally use high powered, large spot sized x-ray sources to provide sufficient x-ray flux. The large size of the x-ray source spot results in source broadening errors at low Bragg angles (Fig. 4). This contribution of source size is described by the differential Bragg equation: $\Delta E = E\cot\theta_B\,\Delta\theta$, in which E is energy and is the Δθ source angular width as seen by the crystal.

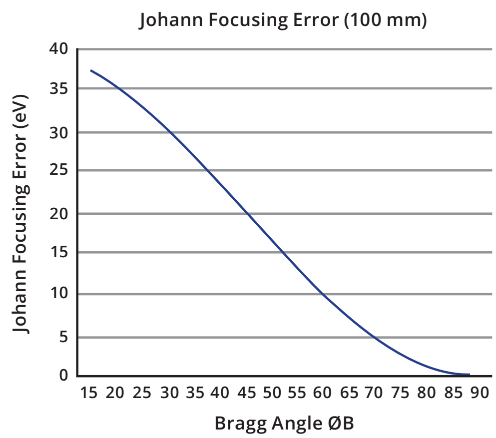

Figure 3: *Johann Focusing Error for conventional XAS using 100mm SBCA assuming operation energy at 8 keV and keeping the source size contribution fixed by assuming a source-crystal distance of 500mm. As can be seen, the Johann error becomes severe at low Bragg angles of 20-50 degrees. Energy resolution of better than 2 eV (required for 8 keV, see Table 1) thus requires large Bragg angles of ~77 degrees or more.*

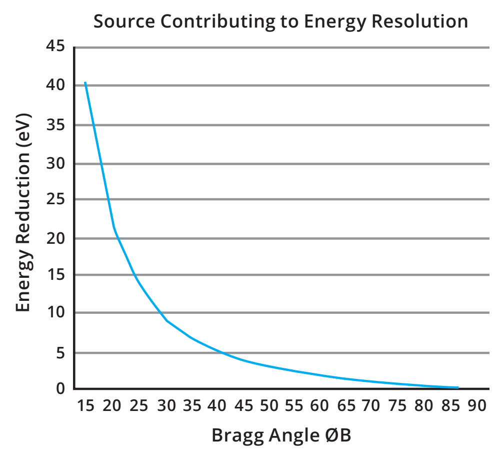

Figure 4: *Source contribution to energy resolution for a conventional XAS system using a 400 um spot and 500mm Rowland circle diameter at 8 keV. Angular contribution is the spot size divided by the distance from the source to crystal, which is equivalent to $2R\sin\theta_B$. Achieving 2 eV resolution (required for 8 keV) can only be achieved at Bragg angles of 73 degrees and above.*

The Johann error from the crystal (Fig. 3) and the source broadening (Fig. 4) forces conventional laboratory approaches to operate only at suboptimal **high Bragg angles**. Furthermore, the SBCA must be of a high Miller index crystal type (Fig. 5). The higher the Miller index, the narrower the Darwin width becomes and the more the crystal acts as a spectral filter, reducing flux. Because **Darwin width is proportional to throughput** (e.g. a 1 eV Darwin width will provide 10X the throughput of a narrower 0.1 eV Darwin width), it is better to use crystals with Darwin widths that match the energy resolution ***needed*** (Table 1). Darwin widths that are too narrow will only limit throughput, without improving the signal. As shown in Fig. 5, higher Bragg angle typically significantly limits crystal selections to those with poor efficiency (very narrow Darwin widths).

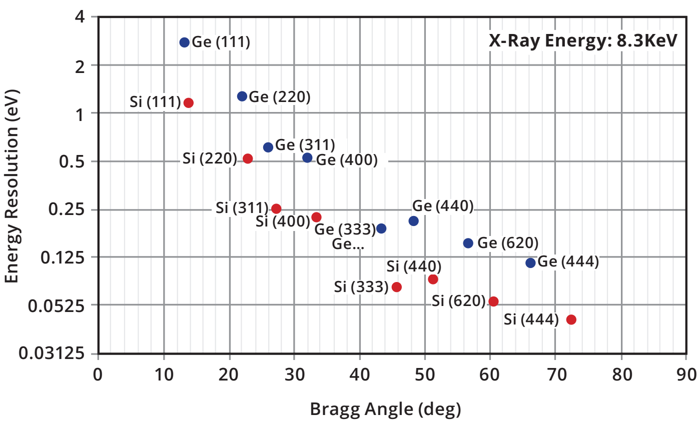

Figure 5: *Crystals and their Darwin widths as a function of Bragg angle at 8.3 keV. As shown by the red lines, operating at 70 degrees and above limits the crystal selection to Si (444) with a <0.06 eV Darwin width. Because XANES measurements at 8 keV require 2 eV energy resolution (see Fig. 1), the Darwin width of the Si (444) crystal is too small, resulting in effectively a 33X loss in throughput.*

The QuantumLeap-H2000™ has made **significant system design improvements** over conventional laboratory systems which remove the constraints enumerated above that necessitate high Bragg angle operation. Its patented design includes the following major improvements:

Improvement #1 for Low Bragg Operation - Detector & Crystal: A novel pixelated photon counting detector is used in place of an SDD. Such detectors have only been recently commercialized and they provide ~keV level energy discrimination. By using the energy thresholding capabilities, x-ray energies corresponding to harmonic contamination can be removed without needing an SDD. Due to its large footprint, QuantumLeap's photon counting detector can efficiently capture x-rays focused from a cylindrically bent Johansson crystal (point-to-line focus) instead of a spherically bent crystal (SBCA). The crystal, as shown in Fig. 6, provides superior focusing and does not suffer Johann focusing errors.

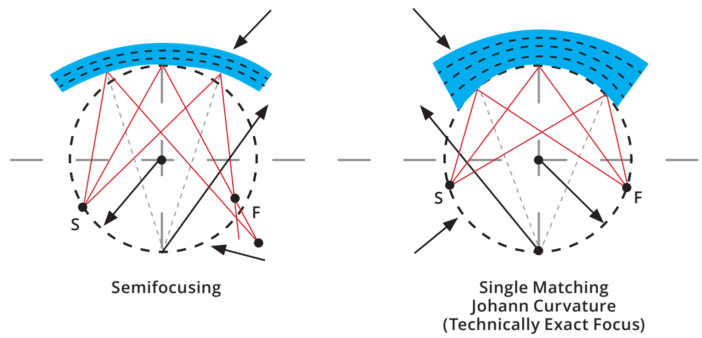

Figure 6: *Johann (left) and Johansson curvature (right). The surface of a Johann crystal does not completely match the Rowland circle and therefore causes the Johann focusing error. Johansson crystals do not suffer such aberrations but are challenging to make.*

Additional advantages of QuantumLeap's detector are that it offers far higher count rates (>10^8 ph/s) than the SDDs used in conventional laboratory XAS systems (5×10^5 ph/s). The spatially resolving capabilities also enable unique advantages, such as segmenting out specific regions of crystals for the highest quality data and acquiring multiple samples simultaneously.

Improvement #2 for Low Bragg Operation - Source-side: QuantumLeap uses a novel, high brightness x-ray source that has a small focal spot in the tangential direction, as will be described in the next section. The size in the critical tangential direction enables high energy resolution even at low Bragg angles (Fig. 7).

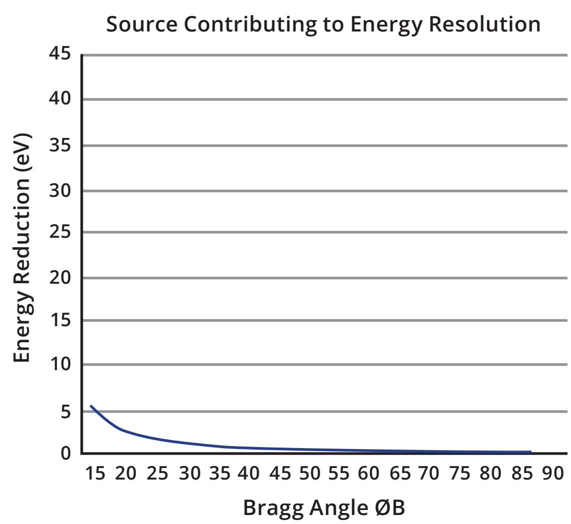

Figure 7: *Source broadening in the Sigray QuantumLeap-H2000™ is minimal, even at low Bragg angles.*

Thus the design of QuantumLeap-H2000™ (fig. 8B) enables operation at **low Bragg angles (e.g. 15 degrees)**. This provides significant advantages, including:

- Optimized throughput of **5X for XANES** and **20X for EXAFS** over conventional designs.
- Only 3-4 crystal analyzers are needed to cover the **energy range of 4.5 to 20 keV** (in comparison, for high Bragg angle operation, multiple crystals may be required for a ***single*** 1 keV XAS spectrum). The small number enables the system to include all crystals on a software selectable robotic stage.
- Constant spot profile. At the high Bragg angles used by conventional laboratory XAS systems, there is a well-known issue that the spot size changes significantly for every crystal rotation which places restrictions on sample uniformity (making sample preparation challenging).
- Flux for operation in **fluorescence-mode.**

2) Patented x-ray source with substantially higher brightness and novel multi-target design

As mentioned in the previous section, a key enabling factor for the performance of QuantumLeap-H2000 is Sigray's patented ultrahigh brightness, microfocus source. The brightness of the x-ray source is achieved through a novel target comprising multiple metals in thermal contact with a diamond substrate and cooled by high heat capacitance fluids. The diamond and fluid cooling provide rapid thermal dissipation so that higher currents of electron beams can be loaded onto the source for intense x-ray output.

Another critical benefit of the source design is its incorporation of **multiple x-ray target materials**, which enables customizability of the primary target material for applications of interest and allows for internal calibration targets within the x-ray source. Spectral lines of different metals within the source are used for automated calibration and are only required once upon system set-up, in contrast to the time-consuming manual foil calibrations required by other laboratory XAS systems.

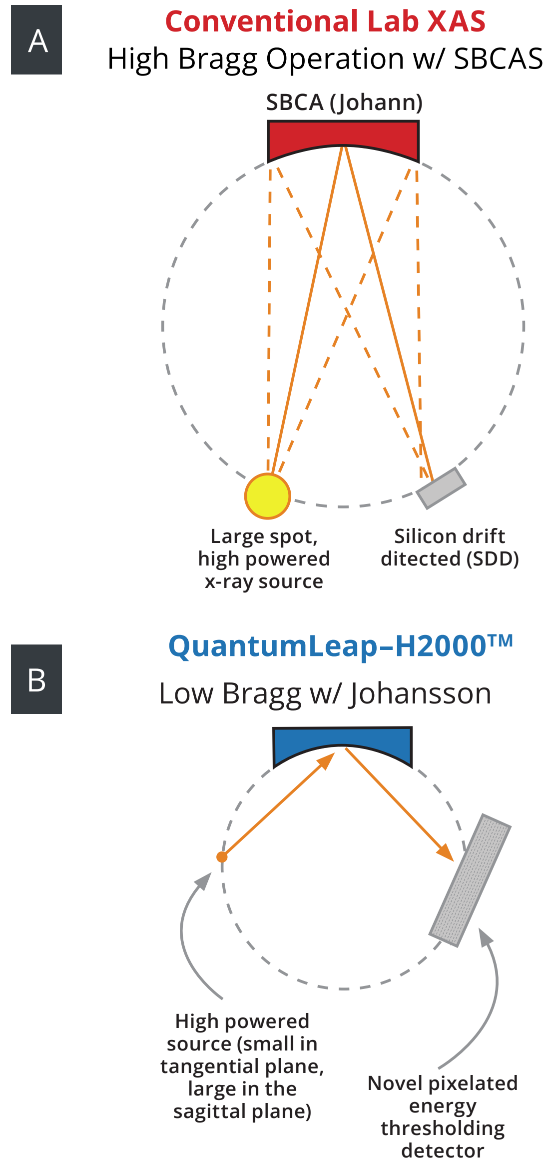

Figure 8: Comparison of Geometries

a) Schematic of a conventional laboratory XAS system shown on the top. Such systems use large spot sized, high powered x-ray sources, a Johann spherically bent crystal analyzer (SBCA), and a silicon drift detector; such designs operate at high Bragg angles on a large Rowland circle.
b) Sigray QuantumLeap-H2000™ uses a high powered x-ray source that has a small dimension along the tangential direction and large dimension in the sagittal direction (which in this illustration, is into the paper). The combination of this source, Johansson crystals, and a novel pixelated energy thresholding detector, enables advantageous operation at low Bragg angles.

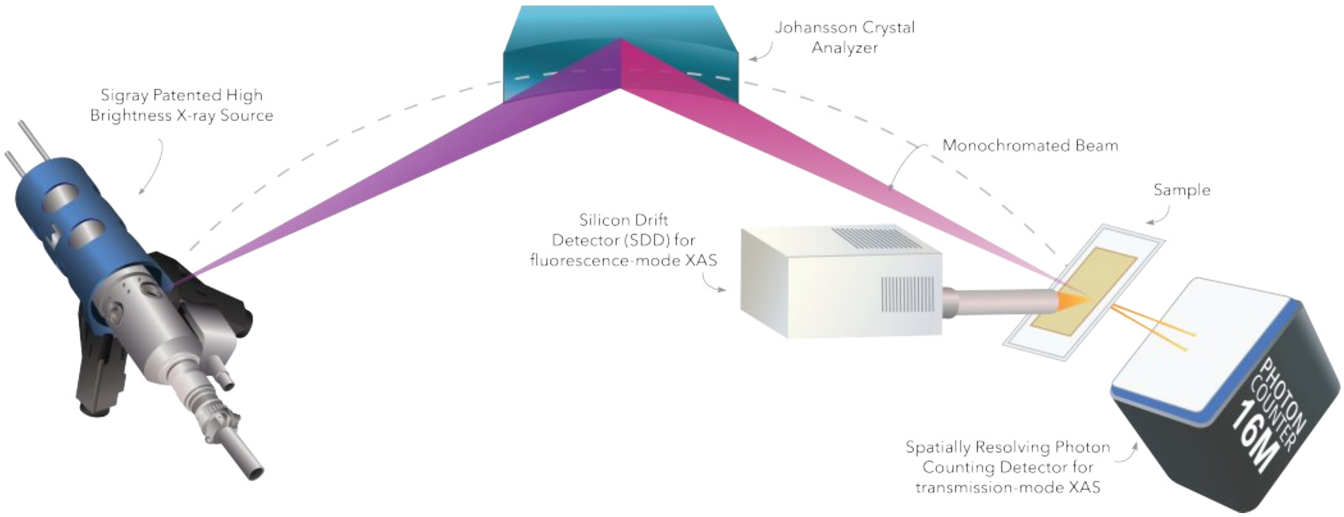

Figure 9: *QuantumLeap Rendering, showing its system design and its two detectors (SDD and photon counting detector), which are used for fluorescence and transmission mode XAS respectively.*

3) Secondary Detector for f-XAS Mode

Another innovation in the QuantumLeap-H2000™ is its patented approach for fluorescence mode XAS. Sigray uses the combination of a line source and an SDD detector configured to maximize the solid angle of collection from the sample. This approach enables not only high energy resolution for f-XAS but also sufficient flux for high signal-to-noise (SNR), enabling high quality EXAFS in fluorescence mode.

For more information about QuantumLeap's fluorescence mode and to see examples of spectra collected in f-XAS, read Sigray's technical white paper on [QuantumLeap H2000 fluorescence XAS mode]*.

Summary

Sigray QuantumLeap-H2000™ combines recent advances in key x-ray components (x-ray source and detector) with innovations in system design for low Bragg angle acquisition and an optimized acquisition approach to maximize performance and throughput. As a result, the system regularly achieves synchrotron-quality results within minutes for a broad range of elements.

*Additional white papers and applications notes are available upon request with your sales representative or by emailing sales@sigray.com.

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