Performance of B18, the Core EXAFS Bending Magnet beamline at Diamond

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Abstract. B18 has been operational since April 2010 and has hosted a total of 63 EXAFS user experiments up to Jan 2012. B18 is contributing to research programs across a wide range of scientific disciplines, e.g. solid state physics and materials, catalysis, chemistry, soft matter, surfaces and biomaterials. We present a review of its present performance and capabilities.

1. Introduction
B18, Core EXAFS is the Bending Magnet beamline within the Diamond Spectroscopy Village. B18 complements I18, the micro-focus beamline, and I20, I20-1 the twin-branch, multi-pole wiggler-based beamlines, proving a scanning and a dispersive section, and in the future I08-STXM and I14, the Diamond Phase III nano-focus spectroscopy and SAXS beamline under construction.

Considering this ample portfolio, the B18 design has focused on reaching a high flexibility on a stable beamline, to provide the UK user community an effective and reliable tool, able to deliver high quality data and allowing fast experimental turnover.

2. Beamline design and optical layout
B18 covers a wide energy range, from 2 to 35 keV, covering K-edges from phosphorus to iodine, and LIII-edges from yttrium to uranium. This requires using mirrors with at least two different metal coatings. The choice for B18 has been to use Pt, allowing to reach high energies with a mirror of reasonable length (1.2m, at 2.3mrad grazing angle), and Cr. The latter is used for the low energies, to avoid the Pt M absorption edges and provide a cutoff energy at 22 keV useful for harmonic rejection in the commonly used, intermediate energy range. However, the availability of two coating branches usually requires horizontal translation of mirrors to swap between configurations. Instead, the B18 design profits from the wide fan available from a Diamond bending magnet front-end (3 mrad) and adopts a configuration with two beamline branches, fixed in position, 1mrad wide. This layout almost eliminates the need to realign the beamline after every mirror configuration change. The first mirror (Si, coated with two stripes, Pt and Cr as mentioned) is always fully exposed to the 3 mrad-wide white...
beam, reducing instabilities due to thermal drifts likely after each branch change with a conventional configuration. The operational beamline branch is selected just downstream of the primary mirror, using a pair of secondary white beam slits, which translate horizontally to allow an 1 mrad-wide section of the beam to reach the monochromator.

The first mirror is flat, cylindrically bent to provide optimal collimation in the vertical direction. This setup provides consistently the best energy resolution and high flux, removing the need to adjust the gap of vertical selection slits to match the beam divergence with the desired monochromatic beam resolution.

The beamline routinely provides focused beam, to allow the study of small samples with high flux density. The beam is focused using a double toroidal mirror placed after the monochromator. The mirror is a single bent, 1.2m long, silicon unit, with two cylindrical grooves, slightly divergent (1.4 mrad) so that the cylinder axes are aligned with the two beam branches. The mirror is placed at 25m from the bending magnet source, and focuses the beam on the sample placed a further 12.5m downstream. This focusing geometry (2:1) in combination with the primary collimating mirror minimizes optical aberrations and provides a regular, elliptical focal shape. The beam can be quickly focused down to 150 x 200 µm² (HxV), or defocused to about 700 x 700 µm by changing the mirror pitch to move the position of the horizontal focus and then adjusting the mirror bending radius to further expand the vertical footprint on the sample.

Running at low energies requires removal of the higher energy harmonics. To this purpose, we use short mirrors placed in the beam path at high grazing angles. When working at energies lower than 7 and 11 keV on the two branches, we insert a pair of pre-aligned and parallel Si mirrors, Pt- and Ni-coated, with a 7 to 17 mrad incidence angle. The mirrors are separated vertically by 2 mm, so the beam height change of approximately 4 mm is compensated by lifting the experimental table, which also translates horizontally (by circa 60 mm) according to the focal position of the selected branch.

![Figure 1. B18 optical layout.](image-url)

### 2.1. Monochromator

The double crystal monochromator (from IDT) hosts two pairs of Si(111) and Si(311) crystals. The whole mechanics is in vacuum. This allows rapid crystal change without breaking the vacuum, reduces leak risks due to the absence of rotating mechanical feedthroughs and minimizes interferences to the
motion from the torque exerted on the primary axis. The monochromator mechanics translates horizontally to four predetermined positions, allowing use of both crystals on each beamline branch. The first crystals are directly cooled with water. To guarantee a good thermal control and the absence of vibrations, we developed a Peltier-based water chiller system, including a pressurized water vibration damping system. An intermediate vacuum path surrounds the water circuit, protecting the beamline vacuum by avoiding direct water-to vacuum joints.

The monochromator is designed to carry out both conventional and continuous-scan (QEXAFS) measurements. The Bragg axis is fitted with an in-vacuum, DC brushless motor that guarantees a continuous motion with a wide angular speed range, from 0.4 degrees/s to 0.1 mdeg/s. This means we have the possibility to acquire full QEXAFS spectra in the full energy range of the monochromator (including the low energy range, from 2.05 kev at 70 degrees), with fixed exit, with acquisition times variable from a few seconds to several minutes. In addition from the possibility to study time-dependent phenomena, continuous scan operations have demonstrated a decisive advantage over the step-scan acquisition strategy traditionally used on EXAFS beamlines even for long acquisition times. Indeed, by minimizing the acquisition dead times, slow fluorescence experiments on diluted samples profit sensibly from the adoption of the QEXAFS setup. This is therefore the default mode of operation for the beamline.

3. The continuous scan (QEXAFS) acquisition system

The acquisition system in Quickexafs mode is based on a dedicated hardware, developed at Diamond. The system acquires directly the quadrature signals from the monochromator encoders, providing a 250 ns triggering signal used to synchronize all the acquisition electronics, through the beamline time frame generator. The system is partially independent of the monochromator motion control system, which takes care only of the angular motion with the desired speed, and provides the overall gating signal to the triggering system, used to calculate the absolute angular position. This design implies that the gating signals are hardware-based, and do not rely on slow software readouts of the encoder positions. This guarantees a very high angular positioning accuracy (limited by the encoder interpolated step size only) and fast response, with a maximum pulse output frequency of 1.4 MHz. It has to be noted that the amount of data generated is the same as per a single traditional step scan, and does not require dedicated preprocessing, such as binning and averaging, as required for fast-scanning Qexafs mechanisms.

![Figure 2. B18 Quick Exafs acquisition system schematics.](image-url)
To evaluate the quality of the QEXAFS data obtainable on B18, we ran a series of comparative measurements with the classic step-scan modality, on the same samples representing very different data acquisition conditions. The measurements consisted in the acquisition of step-scan and qexafs acquisitions on a Cu foil, in transmission mode, and on a copper nitrate solution, 10 mMolar, in fluorescence mode, using B18 9-element Ge detector with XSPRESS-II acquisition electronics [2].

**Figure 1.** Comparison of step-scan and QEXAFS acquisition on a Cu foil and a 10 mM copper nitrate solution in fluorescence using B18 9-element Ge detector with XSPRESS-II [2] electronics. Top: Cu foil, RT. 1 x step-scan (30 min), 1 x 10-min QEXAFS, 10 x 1-min QEXAFS, 10 x 1-min QEXAFS, rebinned as per step-scan. Bottom: CuNO3, 10mM, 5 x 30 min step scan (blue), 60 x 1-min and 6 x 10-min QEXAFS.
We extracted then the experimental noise by subtraction of a smoothed signal calculated using a simple running-average on 5 points after normalization. The spectra were normalized adopting a linear fit for the pre-edge region and a second order polynomial fit for the post-edge region. The noise on the normalized spectra is evaluated then by calculating the standard deviation of the residual in a range far away from the absorption edge, in a region from 500 eV after the edge to the end of the spectrum.

**Figure 4.** Noise (N/S, normalized) behaviour for QEXAFS acquisitions on Cu foil (top) and 10 mM fluorescence (bottom panel). Average over up to 60 scans– 1 minute each. In red, $N^{-1/2}$ theoretical curve.

In Figure 3 and following we report the result of this analysis. We can anticipate that the results show a decisive advantage in terms of total acquisition time for the continuous scan mode. The N/S estimates (standard deviation of the residual) are plotted as a function of the number of averaged spectra for QEXAFS repeated scans. Experimental data (dots) trend is plotted along with the result of a power function curve fit and the ideal $1/N^2$ trend. The noise, both in transmission and fluorescence modes, follows closely the $1/\sqrt{N}$ curve, down to a N/S level (signal is the absorbance normalized to the absorption jump in both cases) in the range of $2 \times 10^{-5}$ for transmission for a total 1h acquisition time, and is remarkably consistent with photon-limited statistics as $B18$ estimated flux is in the range $10^{10-5} \times 10^{11}$ ph/s (with $5 \times 10^{11}$ ph/s one can expect, on a foil, N/S to be $\sim 1.10^{-5}$, for 1s acquisition /point). It has to be noted in addition that the noise values shown are calculated for constant step, constant monochromator speed acquisition. This means that binning the data on a constant photoelectron $k$-step mesh as usually done during EXAFS analysis will result in increasing acquisition times, proportional to $k^2$, and correspondingly increased acquisition statistics. For fluorescence data, the data quality is naturally dominated by the fluorescence photon counting statistics. In the case of
transmission measurements on copper, the experimental curves tend to deviate slightly from the theoretical behaviour (the fitted power exponent is 0.49), showing a weak tendency to reach a plateau.

A close inspection of the averaged data shows some indication of little dispersive-like localized structures coming from a residual signal from non-fully compensated monochromator glitches (whose amplitude can reach 10% of the monochromatic beam intensity in the region explored), not visible above the noise in the non-averaged, single spectra. Those structures are usually removed by the user during the pre-processing steps of the EXAFS analysis, indicating that, also for realistic experiment conditions, a beamline ‘detection limit’ had still to be reached in the present measurements. In addition, because the signal has been acquired using the conventional voltage-to-frequency converter system (with 100 kHz/V conversion ratio) feeding pulses to the beamline scalers, we are actually reaching the resolution limit of the acquisition system, as the measurement on both I0 and It channels resulted in 7000/4500 pulses respectively per step in a 1 minute scan. A simple error propagation calculation on the absorbance expression shows that this resolution is matching the N/S value we get from the experimental data on a single scan. This indicates that for faster acquisition times, a higher resolution system as the 24 bit simultaneous ADC system under commissioning at the moment on B18 will be needed to reach photon-counting statistics in this case.

4. Sample environments and detectors

As mentioned before, B18 default setup consists in a set of 30cm-long ionization chambers for intensity monitoring and transmission measurements, and a 9-element Ge detector with XSPRESS-II [2] electronics. In addition a 4 element SDD and a gas microstrip are available on the beamline for fluorescence experiments at low energies, and a high resolution Si-microstrip detector (Dectris, Mythen [3]) covering 60 degrees.

The B18 sample space has been designed to be very flexible to accommodate complex user experimental setups. Experiments requiring stop-flow systems, electrochemical cells, low temperature XEOL detection have been successfully installed and are commonly used on the beamline. The beamline provides to users several default sample environments. All operate in transmission and fluorescence geometry for XAS, and additionally, simultaneous XRD measurements are possible in the majority of cases. Environment hardware and software controls have been integrated into the B18 data acquisition software.

For low temperature studies, three cryostats are available operating down to 77 K. Two systems are used for loading single samples with a rapid cool down, and a large cryostat for loading and automated translation for up to 50 samples is available for high-throughput experiments. In the Soft X-ray experimental section (in vacuum, 10-5 mbar), up to 10 samples can be loaded on a cold finger sample holder. This automated motion stage operates down to 77 K. Where samples are not suitable for use with a conventional cryostat, a variable temperature cryojet operating down to 77 K, is available. In this case, a RT N2 gas flow shield limits condensation and sample icing. Finally, a low-vibration pulse tube refrigerator operates down to 1.5 K and holds 3 samples. After the first cryostat cooling, the cool down time to base temperature for a new sample is ~60 minutes.

High temperature experiments, typically for catalysis studies are quite common on B18. We can provide as default a purpose-built, furnace operating up to 1000°C. The atmosphere can be continuously purged with bespoke gas mixtures. Samples (one only is allowed in the heated chamber) are mounted on a rail system allowing rapid sample exchange. For liquids, a heating liquid sample system (250°C) incorporates a variable path length liquid sample holder, sample being held between 2 windows (typically mica, Mylar or Kapton, others feasible). If the experiment requires precise control of the sample atmosphere, a heated catalysis reaction system (developed by Diamond, Industrial Group) allows a controlled flow of User defined gas mixture over a sample held in a capillary (typically quartz). A rapid gas switching manifold allows the gas mixture being flowed over the sample to be quickly changed (switching <1s) to change the reaction conditions. An integrated controllable hot gas blower can rapidly heat the sample up to 700°C. Finally, a High throughput
system (Southampton University) [4] is available to the Users: This system was designed for catalyst research but is ideal for any experiment that requires spectroscopic analysis of samples, use of a controlled gas atmosphere, or use of the other analysis techniques available. The system is fitted with an automated motion sample manipulator to move between several samples. The sample can be heated up to 900°C. A confocal Raman system with adjustable optics and CCD camera can position the Raman sampling point coincident with X-ray beam position on the sample. A turbo pump allows the sample chamber to be evacuated and operated under vacuum; and a mass flow controller allows the chamber to be purged and filled with bespoke gas mixtures. An internal capillary adjacent to the sample is connected to a mass spectrometer to monitor gas/sample evolution in real time. The data is collected simultaneously with the XAS/XRD data acquisition.

5. Conclusions
B18, after the initial periods of commissioning with users started on April 2010, is now fully operational. The beamline can provide reliably high quality data in a wide energy range, and the continuous scan acquisition mode is becoming increasingly adopted due to its clear advantage in terms of data collection times respect to the usually adopted step scan mode. The beamline design allows quick turnaround times, allowing experiments requiring different optical configurations to be scheduled without interruptions, improving the overall efficiency. With the availability of a wide portfolio of detection systems and sample environments, B18 is providing the user community an all-round, reliable and effective instrument for XAS spectroscopy.

References
[1] Dent A J, Cibin G, Ramos S, Smith A D, Scott S M, Varandas L , Pearson M, Krumpa N, Jones C 2009 Journal of Physics: Conference Series 190 012039
[2] Farrow, R., Derbyshire G E , Dobson B R , Dent A J , Bogg D, Headspith J, Lawton R , Martini M, Buxton M 1995 Nucl. Instr. Meth. Phys. Res. B 97 567
[3] Schmitt B, Brönnimann C, Eikenberry E F ,Gozzo F, Hörmann C,Horisberger R, Patterson B 2003 Nucl. Instr. Meth. Phys. Res. A 501, 267-272
[4] M. Tromp, Russu S, Dent A J, Mosselmans J F W , Harvey I, Hayama S, Russell A E, Guerin S, Hayden B E ,Suchsland J-P, Meacham K, Surridge M, Frey J G, Tsapatsaris N, Beesley A M,Schroeder S L M,Newton M A, Fiddy S, Safonova O V , Glatzel P, Binsted N, Evans J 2007 AIP, CP882 858