

ID26 : X-RAY SPECTROSCOPY ON ULTRA-DILUTE SYSTEMS

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The ESRF beamline ID26 is dedicated to x-ray absorption spectroscopy on ultra-dilute systems (XAUS) in the spectral range 2.3 - 30 keV. The aim of the beamline is to extract structural and electronic information on dilute samples for which the concentration of the absorbing element ranges from a few ppm up to 10 000 ppm.

A wide range of applications is covered in biology, catalysis, chemistry, environmental sciences, solid state physics... The beamline accepted the first users in November 1997. We give herein a brief description of the beamline and we report on recent instrumentation developments.

The x-ray source consists of three phasable planar undulators. Each of them has a magnetic period of 42 mm and a length of 1.65 m. The energy of the fundamental harmonic is 2.35 keV at the minimum gap value (16 mm). The whole energy range is obtained by exploiting different harmonics of the undulators emission spectra. The design of the beamline optics is optimized in order to reduce background radiation and to provide an efficient harmonic rejection. The first component is a flat silicon mirror that deflects the beam laterally apart from the bremsstrahlung emission cone of the ring. This mirror damps the thermal power of the x-ray source and protects the other optical components. The x-ray beam is focused by two segmented piezoelectric bimorph silicon mirrors in a Kirkpatrick-Baez configuration, which are located in the monochromatic section of the

beamline. The typical focal spot size at the sample location is 200 μm (horizontal) x 15 μm (vertical). The photon flux on the sample is 10^{13} photons per second. Smaller spot size could be achieved (H : 80 μm x V : 7 μm) with a lower flux (10^{12} photons/s). Each mirror has three reflective layers: silicon, chromium and platinum.

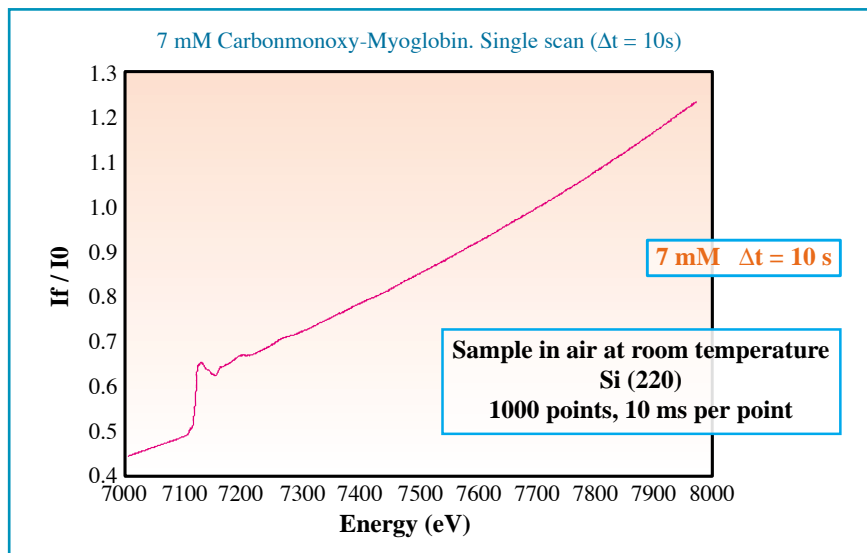
A two-crystal fixed-exit Kohzu monochromator is inserted after the first horizontally deflecting mirror. The monochromator is equipped with two pairs of crystals Si (111) and Si (220) cooled down to -140 °C. The crystal pairs can easily be exchanged using a lateral translation of the monochromator.

Two experimental stations are used: a small fluorescence chamber operated at room temperature and a fluorescence station equipped with a continuous flow liquid helium cryostat. The temperature

range covered goes from 4.8 K to 293 K. The cryostat is equipped with a very accurate (1 μm) vertical sample translator and a rotary stage with an angular accuracy of 0.13 mrad.

XAS spectra are recorded in the fluorescence excitation mode. To reach high dilution, three main difficulties had to be overcome : **i)** The fluorescence signal is usually buried into a large radiation background (mainly elastic or inelastic scattering) originating from sample matrix. One has to get rid of this background which degrades the fluorescence signal statistics. **ii)** Since the narrow emission peaks of the undulator spectra (typ 100-200 eV) are not suitable to record a whole EXAFS scan, we had to extend the gap scan techniques recently developed at the ESRF [1]. **iii)** Due to the very high flux delivered at the ID26 beamline, sample radiation damage is usually a major source of difficulties, especially in the case of biological samples. In order to overcome these difficulties, different data acquisition strategies have been developed.

Fig. 1a: EXAFS spectrum of a 7 mM/l Carbonmonoxy-Myoglobin sample recorded at the Fe K-edge measured in one scan of 10 seconds.



CONTINUOUS OR QUICK EXAFS FOR MODERATE DILUTIONS

For absorber concentrations above 1 mM/l (50 to 500 ppm depending on sample matrix), the fluorescence detection is performed using silicon PIN photodiodes operated in the photovoltaic mode. The diodes are associated with a low noise current to voltage amplifier and then to a high linearity voltage to frequency converter [2]. The output signal is fed into a gated integrator (ESRF VDL

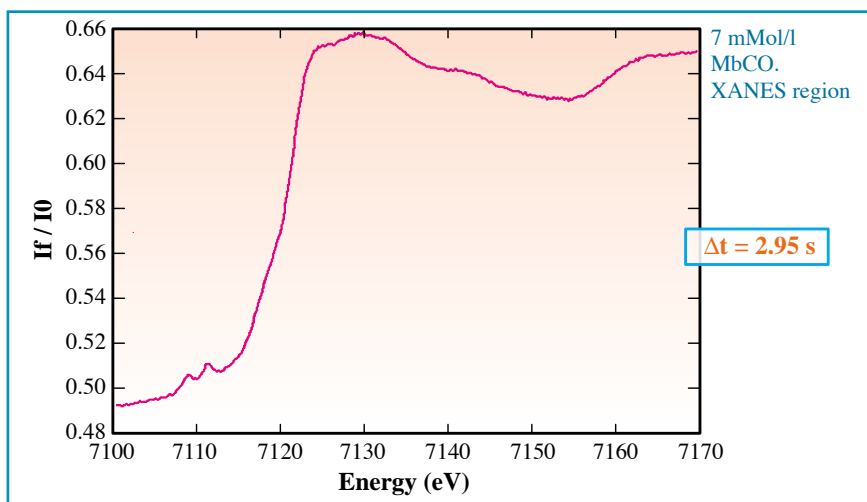


Fig. 1b: XANES region of a 40 second EXAFS scan of 7 mMol/l Carbonmonoxy-Myoglobin sample. The (220) crystal pair of the monochromator was used. The data acquisition for the XANES region is less than 3 seconds.

board). The diode can be operated with absorption filters in order to minimize the amount of background radiation reaching the detector. The IO intensity monitor is also a silicon diode associated with a scattering or fluorescence foil in an optimized geometry which minimizes the sensitivity to the x-ray beam instabilities. We take full advantage of the high saturation level, high linearity and low noise of silicon diodes which allows us to accept the very high flux delivered by the source. In the continuous gap scan technique, the monochromator Bragg angle and the undulator gap are scanned simultaneously during the measurement of the EXAFS spectra. Excellent performances were achieved: **Figure 1a** reproduces the EXAFS spectrum of a 7 mMol/l myoglobin sample measured in 10 seconds. **Figure 1b** shows the XANES part of the same EXAFS spectrum but recorded in 40 seconds. The data acquisition time of the XANES spectra was less than 3 seconds.

Averaging on several spectra indeed improves the signal-to-noise ratio. The main advantage is that radiation damage can be minimized by displacing the sample after each scan. Alternatively, the evolution of fragile samples can be monitored on a short time scale. Furthermore, there is some possibility to perform time-resolved experiments on dilute samples with a slow time evolution.

SILICON DRIFT DETECTORS

For higher dilution, it is necessary to discriminate in energy the fluorescence from the radiation background. Due to the severe counting rate limitations of energy resolving detectors, the development of

large arrays of detectors (up to 100 channels) is mandatory in order to restrict the data acquisition time within realistic limits. Over recent years, we have developed new energy resolving detectors: Silicon Drift Diodes (SDD) [3]. These detectors feature a very small readout capacitance which is independent on the active area. This results in the possibility of preserving good energy resolution together with high counting rates. These detectors are associated to multichannel digital shaping amplifiers designed at the ESRF. There are clear advantages in favor of this technology: **i)** The output rate can be improved in comparison with analog shaping amplifiers. **ii)** The cost per detection channel is much lower. **iii)** The set-up of the detector array is controlled by software and can be automated. A first prototype array (12 channels) has been evaluated at the beamline. **Figure 2** shows

an EXAFS spectrum recorded from a 200 μ mol/l aqueous solution of cobalt acetate (cobalt concentration 12 ppm) during a test experiment. The data acquisition time was 9 hours, the signal to noise ratio can be improved with longer data acquisition times. At present the highest dilution which can be achieved is 5-10 ppm depending on the absorber and the sample matrix composition. A 35 channel SDD array is under production in collaboration with Eurisys Mesures Inc. and should be operational by September 98. We expect to be able to lower the dilution limit down to 1-5 ppm. ■

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Fig. 2: XAS spectrum of an aqueous solution of cobalt acetate recorded at room temperature in air with a 12 channel SDD array. The sample dilution was 200 μ mol/l (12 ppm cobalt concentration). Data acquisition time was 9 hours.

