

# Improvements for Absorption Spectroscopy at Beamlines A1, E4, X1

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For an improvement of the conditions of XAFS spectroscopy at the HASYLAB beamlines A1, E4, and X1 several technical modifications and amendments were made or started in 2002. For low concentration samples a new fluorescence detector is available. It can be operated in vacuum. Air and humidity sensitive samples can be manipulated in a glove box under inert argon atmosphere. New Si(311) channel cut monochromator crystals for the monochromator at beamline A1 make it now possible to perform measurements between 15 - 35 keV at this station.

## Fluorescence Yield XAFS

A new 7 pixel Si(Li) detector (Gresham Scientific Instruments) was commissioned in 2002. It is already used in normal user operation for the detection of fluorescence yield XAFS spectra. It was especially designed for use at lower energies (2-10 keV) but can as well be applied for energies up to 20 keV. Technical key parameters were already given in last years technical report [1]. The new detector will mainly be used at the beamlines E4 and A1. The older 5 pixel HP-Ge detector, which shows a higher photon counting efficiency at energies > 20 keV, will be used at the X1. The new

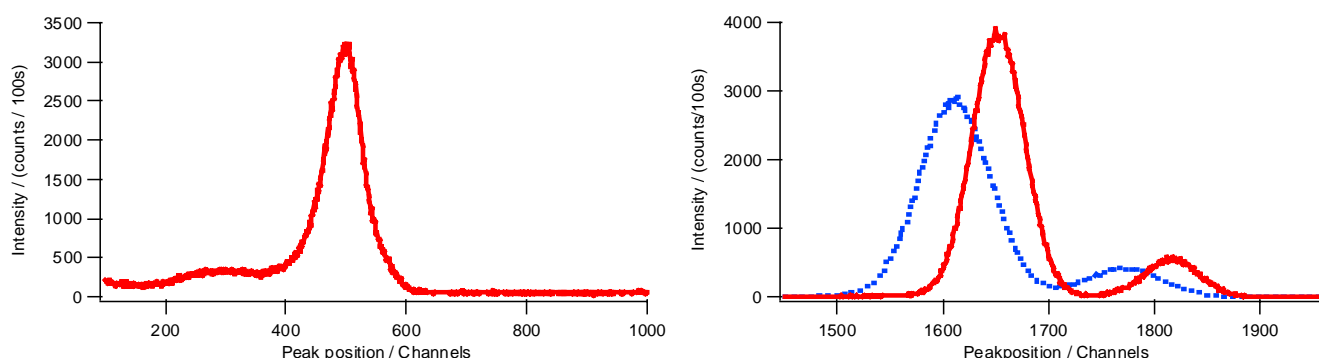


Figure 1:  $K\alpha$  and  $K\beta$  emission lines of Mn measured with the 5 pixel HPGe detector (left) and with the new SiLi detector (right), blue measured with the conventional analog electronics, red with the digital signal processing electronics

detector offers several advantages compared to the previously used HP-Ge detector. First of all it shows a higher energy resolution. Figure 1 shows the emission spectra of a  $^{55}\text{Fe}$  source. It is clearly visible that the Ge detector produces one peak with poor energy resolution (no separation of  $K\alpha$  and  $K\beta$ ) while the Si(Li) detector completely separates the Mn  $K\alpha$  and Mn  $K\beta$  peaks.

The main reason for the different energy resolution is, that the Ge detector uses a resistor feedback preamplifier while the Si(Li) uses a transistor reset preamplifier. The latter produces much less noise. Resistor feedback preamplifiers are the optimal choice for extremely high count rates at high photon energies, that means applications where a large amount of charge is produced in the detector crystal. This is because they are discharged continuously while the reset of the transistor feedback models produces additional dead time during which the detector can not measure pulses. For X-ray spectroscopy (photon energy < 20 keV) at count rates of about 100 kcps the transistor reset models are preferable, because the additional dead time is negligible.

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The new Si(Li) detector is equipped with Canberra digital signal processor electronics (DSP, Model 2060). A comparative test of the DSP and analog peak shaping electronics (Canberra 2026x main amplifier and 8715 ADC) showed that the DSP yields better energy resolution at high count rates and is more convenient to use. With this electronics the registration of the complete fluorescence spectrum at every single point of a XAFS scan will be the standard mode of operation.

This mode of operation allows the user to use the whole amount of information contained in the fluorescence spectra and thus to extract absorption spectra individually after the measurement. This is useful for samples which contain elements with closely neighbouring absorption edges. The amount of data and the produced number of files (300-500 files/XAFS spectrum, i.e. 50 MB) made it necessary to develop procedures for an automated extraction of the XAFS spectra. Software that uses IDL 5.1 under Linux was developed. It handles the following tasks:

- reading in all the fluorescence spectra corresponding to one single XAFS-scan
- calculating the integral intensity of a fluorescence line of interest for each of the according fluorescence spectra (done by summing all events in the respective interval) and for each of the N detector pixels
- writing a standard FIO-file that contains N+1 columns: energy, integral pixel 1,... , integral pixel N

The produced FIO-output can be read and processed by another program also written in IDL, which calculates a weighted sum of the individual FIXAFS-spectra (including a correction for the dead-time of the experimental signal chain).

At present the program is not able to calculate the intensity of the fluorescence line of interest using a fit-procedure (e.g. Gauss-fit). It is foreseen to implement a routine to do this soon. This important step will allow to reduce noise effects, subtract background signals and to disentangle overlapping fluorescence lines. The quality of the resulting FIXAFS-spectra will hence be significantly increased.

Since IDL is not available for all user groups it should be mentioned that two alternative programs are available for the pre-processing of the large data sets. One is written in Igor Pro [2] the other is an EXCEL worksheet [3]. Both read all the fio-files that contain the fluorescence spectra , perform a peak fitting (already with gaussians) and store the results in a new fio file in standard format. One should contact the authors directly if interested in using these programs.

### **Air-sensitive samples**

A glove box (M.Braun GmbH, Garching, Germany) enables users to handle samples under an oxygen and water free atmosphere. This device is operated with Ar as inert gas. In a standard mode of operation both oxygen and water concentrations are < 1 ppm. The glove box is equipped with an analytical balance and with a hydraulic press for the preparation of sample pellets (figure 2). The glove box was already used to fill *in situ*-cells with air sensitive catalysts and to work with metals like Li under inert gas atmosphere.



Figure 2: Glove box for air and moisture sensitive samples, equipped with an analytical balance and a hydraulic press

### Si(311) monochromator crystals at A1 beamline

New Si(311) channel cut crystals can be used in the A1 monochromator in regular user operation. As an example, figure 3 depicts a Cd K-edge XAS spectrum that was measured during the commissioning phase. It was acquired in transmission mode using a 25  $\mu\text{m}$  Cd foil. During first user beamtimes the Si(311) crystals were used for measurements at the PbL3, HgL3, AsK and UL3 edges (corresponding energy range: 13-17 keV). The experimental conditions (beam parameters, sample holders etc.) are comparable to those found at beamline X1. By now only the two-crystal mode is tested, but experiments using the 4-crystal mode are expected to be possible.

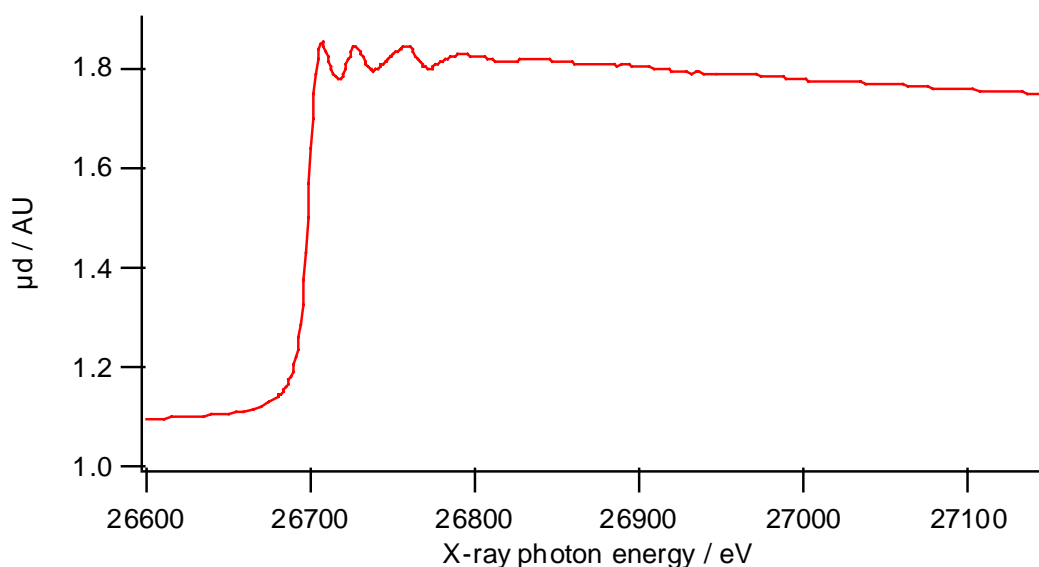


Figure 3: Cd K-edge XAS spectrum measured at beamline A1 using the new Si(311) channel cut crystals.

The exchange of the monochromator takes about 12 hours. This is because the large monochromator tank must be opened to exchange the crystals and must then be pumped down to  $6.5 \cdot 10^{-6}$  mbar before the beamshutter can be opened. The adjustment of the crystals after an exchange is relatively simple, because the position (height and angle theta) of the crystals (311 and 111) is reproducible and quite similar.

### **New gas connector system at X1**

A new gas connector system provides an easier and safer gas handling at X1. Figure 4 shows a photograph of the new components: The gas connector at the pressure reducer was changed from Swagelok 6 mm to Swagelok 'QC'-series (note pressure of 2 bars displayed on the pressure-meter, indicating that this connector is gas tight when unplugged). The gas lines equipped with according connectors (and) can easily be "click-plugged" to the pressure reducer and the gas distribution system for gases at the beamline and in the chemistry lab. For high safety and overall convenience coloured labels and respective different types of connectors will be deployed to correlate gas lines and pressure reducers. By this e.g.  $H_2$  cannot be plugged to  $O_2$ -containing lines. How colors/plugs and gas types are will be assigned is shown in table 1.

<b>Colour</b>	<b>Gases</b>
blue	CO, $O_2$
black	NO
orange	$H_2$
yellow	$SO_2$ , $H_2S$ , mixture gases containing $H_2S$
red	$N_2$ , mixture gases, noble gases, technical air

Table 1: Assignment of colours to gases

The new gas system is being installed for the user (experimental and lab) gases first, and a change of the connectors for the ionisation chamber gases is foreseen for February 2003.

### **Planned improvement of the E4 monochromator**

While the other two XAFS beamlines use angle encoders (Heidenhain) to control the angle theta of the monochromator crystals, the E4 monochromator still uses only the stepping motor values to determine the X-ray photon energy. Recent measurements at the Ca *K* edge [4] showed that this is not sufficiently precise, since the goniometer (Huber) shows an unavoidable periodic worm gear error. Consequently, additional oscillations are introduced to XAFS spectra. At low energies (corresponding to large theta) the frequency of this spurious signal is comparable to the frequency of the EXAFS oscillations.

This problem will be addressed by installation of a Heidenhain ROD-800 angle encoder. This encoder offers an angle resolution of  $5 \cdot 10^{-5}$  degree (0.035 arcsec). Together with the possibilities offered by the digital monochromator stabilisation this will add significantly to the ability to perform high precision XAFS measurements between 2.8 and 7 keV at the beamline E4.

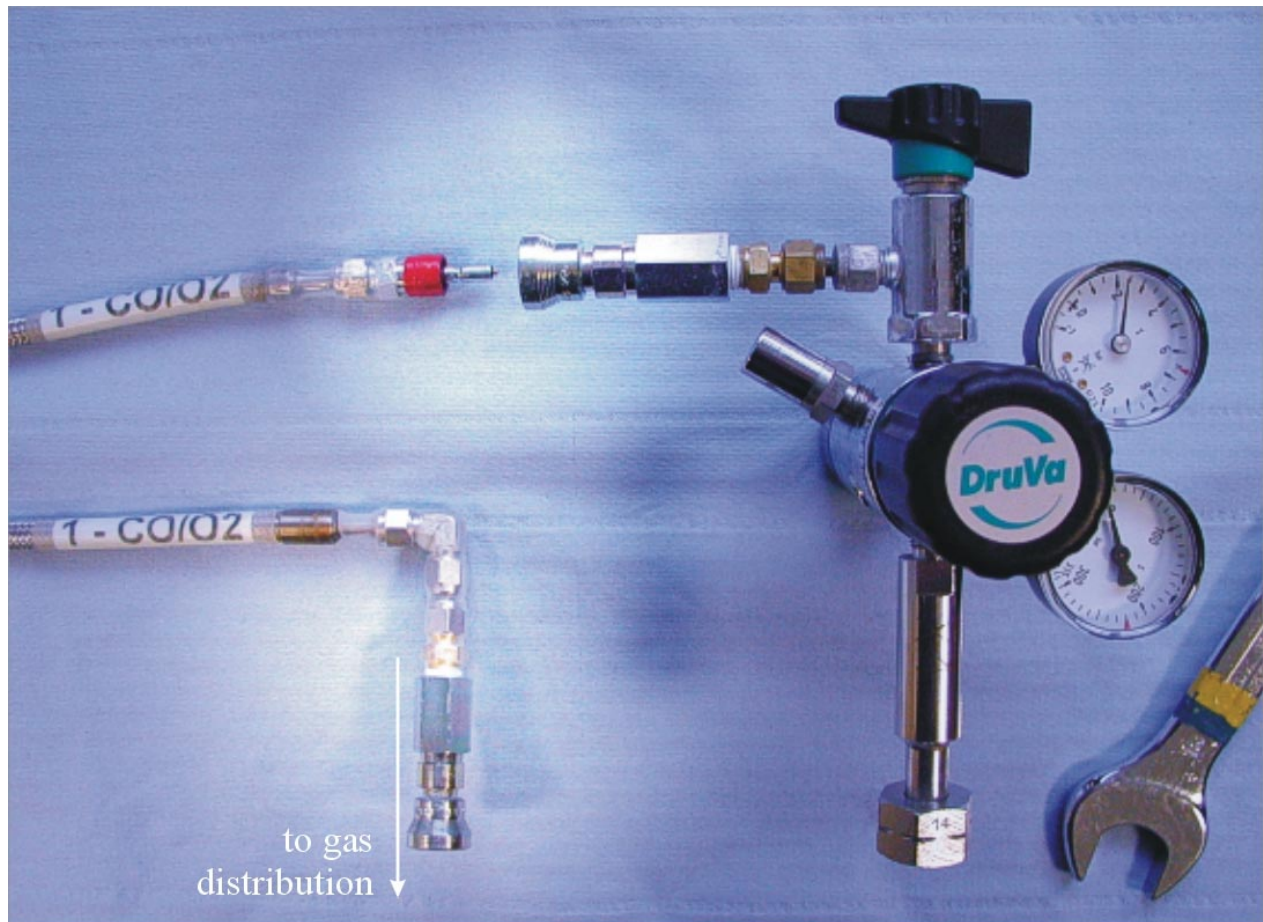


Figure 4: Photograph of the new gas connectors for X1.

## References

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