

# Improvements for Absorption Spectroscopy at Beamlines A1, C, E4 and X

*E. Welter for the XAFS-Team*

Apart of the commissioning and start of operation of beamline C as a new XAFS beamline for in-situ investigations in the energy range 6 – 44 keV [1], several new devices will further improve the conditions for XAFS spectroscopy at beamlines A1, C, E4 and X. Among these improvements are additional detectors for fluorescence yield XAFS, a new liquid Helium cryostat, a mass spectrometer for in-situ measurements and a new sample cell for liquid samples.

## 7 pixel HPGe detector

The majority of recent proposals demonstrate that measurement of XAFS spectra in fluorescence mode is necessary due to samples which are too dilute or too thick for normal transmission measurements. To cover the growing demand for an energy dispersive x-ray detector which could no longer be fulfilled by the one 7 pixel Si(Li) detector, a 7 pixel HPGe detector was obtained and commissioned in 2006. The new detector has 7 independent pixels arranged on a hexagon around one central pixel; each pixel has an active area of 100 mm<sup>2</sup>. It was build by Canberra-Eurysis (Olen, Belgium).

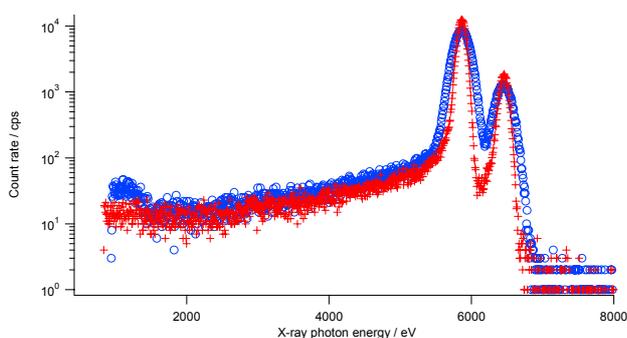


Figure 1: Mn K emission spectra from an <sup>55</sup>Fe source, pixel 6, 3 μs shaping time (crosses) and 0.2 μs shaping time circles

Pixel	FWHM @ 3 μs	FWHM @ 0.2 μs
1	128	244
2	130	239
3	133	242
4	137	239
5	168	242
6	128	242
7	132	235

Table 1: Measured resolution (FWHM of Mn Kα<sub>1,2</sub>) of all seven pixel of the new HPGe detector

Figure 1 displays spectra from a <sup>55</sup>Fe source. In table 1, values for the spectral resolution of all 7 pixels using peak shaping times of 3 μs and 0.2 μs are listed. The spectra were measured using a fast Canberra spectroscopy amplifier (2026x) and a Canberra ADC (8715) for signal processing. The incoming count rate was 10 Kcps for 3 μs shaping time and 40 Kcps for 0.2 μs shaping time. A shaping time of 0.2 μs is typically used for fl-XAFS measurement where count rates of up to 100 Kcps are wanted. Using this setting the energy resolution (FWHM @ Mn Kα<sub>1,2</sub>) is ~240 eV. This resolution is more than sufficient for almost all possible applications.

## PIPS-Detector

Many applications in x-ray absorption spectroscopy require detection in fluorescence mode since the concentration of the absorbing atom is too low for transmission mode. Usually, multi-element Si or Ge-detectors are used, which have excellent energy resolution, and allow discrimination of fluorescence lines of different elements. This is not always necessary, for example if the absorption edges of different species in the sample are well separated, so that there is no overlap of the edges in the respective EXAFS-regions. In these cases, it is possible to use a PIPS-detector (Passivated Implanted Planar Silicon) [2] for fluorescence detection. A PIPS-detector is in principle a photodiode with a large area: An incident photon gets absorbed, and excites electrons across the band-gap. These electrons give rise to a small photo-current, which can be measured by an amp-meter, like a Keithley current-amplifier. A typical photo-current for an 8 μm Cu foil in a monochromatic beam with an intensity of 10<sup>9</sup> Hz at 9 KeV is 50 nA, with the detector at a distance of 5 cm. Since the detector is operated in current mode, the noise-level is determined by the noise of the amplifier

and of additional electronics, and the number of detected photons, which is not the limiting factor in most cases. The PIPS-detector can be used for similar applications as a Lytle-detector, with the difference that the PIPS-detector is significantly easier to use. The drawback is that the PIPS-detector detects photons of any energy, including visible light, which requires that it is well shielded with a thin Al-foil or aluminised Mylar-foil from visible light. Another drawback is that the detector cannot be used at high temperatures: When the detector becomes warm, the bandgap decreases, thus increasing noise. If the temperature is too high ( $>130^{\circ}\text{C}$  sample temperature), the bandgap vanishes, and thermal excitations are sufficient to cause a significant current. This problem can be overcome by cooling the detector and Al-window with water.

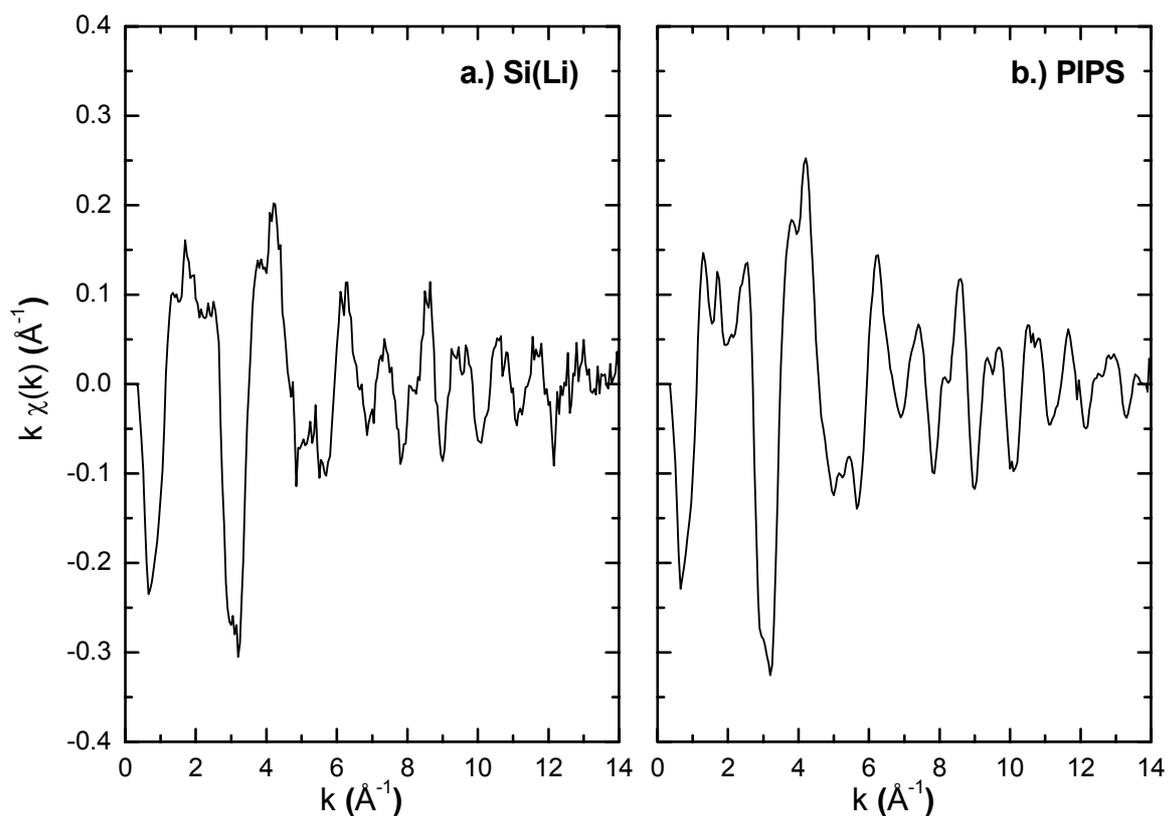


Figure 2: Fluorescence yield spectra of a thin film Ga oxide sample measured with a.) the Si(Li) and b.) the PIPS detector, spectra courtesy of D. Samuelis and M. Martin, RWTH Aachen University.

In figure 2, we show a comparison of data collected with the PIPS-detector and with the seven element Si(Li)-detector. The Si(Li) –detector is limited in its maximum counting range, which determines the statistical accuracy. The data collected with the PIPS-detector extend to much higher momentum transfer, and the counting time was reduced by a factor of 2. The conclusion is that the multi-element detector can be replaced in some cases with a PIPS-detector, and results in better or at least similar quality data.

## Mass spectrometer

At least seven XAFS user groups regularly use a mass spectrometer for the analysis of reaction products during in-situ investigations at HASYLAB. Up until now they had to bring their own mass spectrometers to the beamline. Because almost identical devices are used by all these groups it was possible to improve the experimental conditions for in-situ measurements by obtaining a similar mass spectrometer. After discussions with the involved user groups it was decided to buy a Pfeiffer

Omnistar GSD 301C with corrosive gas equipment. Inlet and outlet tubes are made of stainless steel. It can be used in the mass range 1 – 200 amu. The pressure at the inlet can be up to 1 bar.

It is available for general user use and will mainly be used at beamline X1. The inlet capillary uses a 1/16 inch swagelock connector. Adapters, if necessary to connect special in-situ cells, should be provided by the users.

## **Liquid Helium cryostat**

The liquid He flow cryostat, which was used over several years for deep temperature XAFS experiments, developed a vacuum leak, which only opened at cold temperatures, in spring 2006. Due to this leak the pressure in the isolating vacuum is larger than  $10^{-2}$  mbar. This makes it impossible to reach temperatures below 60 K. As a repair turned out to be too costly, a complete new cryostat was ordered from Oxford Instruments (Wiesbaden, Germany). It is a slightly modified standard model (Optistat CF). The modifications include a sample changer for four samples, which can be mounted simultaneously and which can be changed via remote control, and the window material. The windows are now made from 50 $\mu$ m Kapton foil, even though Kapton is not He tight. But experience with the old cryostat which also used Kapton windows showed that this is not problematic as long as the isolating vacuum is continually pumped with a turbo pump. The temperature working range of the cryostat is 3.5 – 300K. In this range, any temperature can be set and will be stable within less than 0.1K.

## **Sample holder for liquids**

X-ray absorption spectroscopy (XAS) is well known as a powerful method for the investigation of the solid state. XAS beamlines at Hasylab, i.e. A1, CEMO, E4 and X cover the entire energy region from 2400 eV to 80000 eV and are suitable for in-situ and ex-situ measurements of solids. However, the need for the investigation of liquid samples resulted in the design of the sample holder for liquids, suitable to XAS beamlines. The new liquid sample holder (LSH) is presented in figure 3

The design of the LSH allows measurement of liquids in transmission as well as in fluorescence mode, separately or simultaneously. The quasi-continuous change of the optical path, from 2 mm to 40 mm allows measurement of samples with between 0.5 ml and 22 ml. The outer frame is build from stainless steel and is isolated from liquid samples by an inner Teflon frame. The windows at the front and back of the LSH are made from 25 - 75  $\mu$ m Kapton foil depending on the energy. Thus the samples are not in contact with any metals.

The sample can be introduced into the cell in two ways:

- by two small holes in the front of the cell (see figure 3), which fit to the size of the tip of a small syringe,
- by using syringe needles, e.g. non-metallic needles, directly into the sample area.

By using a stop flow system, it is also possible to measure the kinetics of the reaction or intermediate products, for example by using Quick XAS at beamline X. The syringes, needles and stop flow system must be supplied by the users.

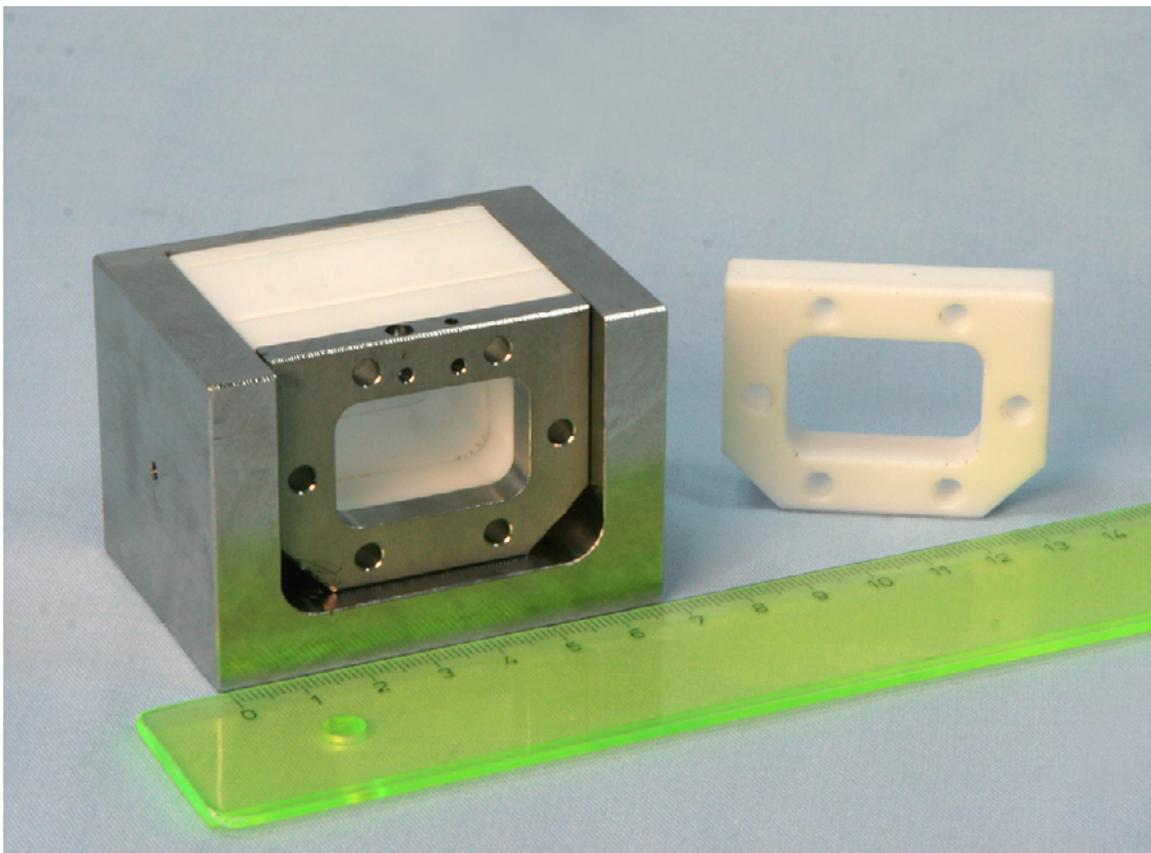


Figure 3: The liquid sample holder designed for XAS beamlines at Hasylab.

## References

- [1] K. Rickers et al., this Annual Report
- [2] Canberra Eurysis: <http://www.canberra.com/products/505.asp>