XAFS data acquisition with 2D-detectors: Transmission mode XAFS and grazing incidence EXAFS spectroscopy

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Abstract. XAFS-experiments in transmission and reflection modes have been performed using a Pilatus 100K pixel detector. Transmission mode XAFS spectra from a Co metal foil and Co3O4 were recorded to evaluate the data quality offered by this 2D-detector. Furthermore, the pixel detector was also used to measure reflection mode grazing incidence EXAFS data. Using different regions of interest in the collected scattering patterns, we will show that the diffuse scattering can be separated for the different contributing surfaces and interfaces, allowing simultaneous investigations of surfaces and buried interfaces within multi-layered samples.

1. Introduction
The quality of transmission mode EXAFS measurements rely on the homogeneity of the investigated samples in the region transmitted by the X-ray beam. Lateral thickness variations, holes or inhomogeneous sample composition may lead to severe distortions of the EXAFS spectra. So the amplitude of the EXAFS oscillations is reduced compared to a perfect sample, and the determined coordination numbers and Debye-Waller factors are erroneous [1]. A careful sample preparation may prevent such artifacts in the case of ex-situ experiments. In in-situ studies, however, there are many situations where the sample considerably changes, e.g., in the case of catalysts in a reacting environment [2] or a battery material during charge [3]. While ionization chambers measure the average absorption through the sample, a 2D-area pixel detector may provide local absorption spectra for each position within the sample. Recent experiments have demonstrated the capabilities of such a setup for in-situ experiments of battery materials, where the charging / discharging occurs [3]. In this contribution, we will present transmission mode EXAFS data of model samples measured with a large, unfocussed beam of a wiggler source in order to evaluate the data quality offered by pixel detectors also for real samples.

In a second series of experiments, we addressed grazing incidence X-ray absorption spectroscopy measurements with a 2D-detector, where the X-rays impinge on the surface of the sample under a small incident angle $\phi_i$. Besides the specular reflected beam (incident angle $\phi_i = \phi_e$), a second distinct scattering peak (Yoneda-peak) occurs if $\phi_e = \phi_c$, the critical angle of the scattering material [4], with $\phi_c(Au)\approx 0.35^\circ$ and $\phi_c(Bi)\approx 0.25^\circ$. From related XAFS experiments, a depth profiling of the sample is feasible and structural information of the surface and buried layers may be obtained [5, 6]. If ionization chambers are used as detectors, the EXAFS has to be measured sequentially for the different scattering (exit) angles, which makes Yoneda-XAFS experiments extremely time-consuming. Using a 2D-area detector, the entire scattering pattern is acquired simultaneously for each energy in the EXAFS scan, and a wealth of information is available in a moderate time. Here we will discuss the feasibility of Yoneda-XAFS measurements for the investigation of multilayered samples.

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2. Experimental details
A Pilatus 100K detector was used for all experiments [7]. Transmission mode studies were conducted at beamline 10 at the DELTA storage ring [8], where incident and transmitted intensities from the sample were monitored by N₂-filled ionization chambers, and the 2D-detector was placed behind the second ionization chamber in order to measure the lateral distribution of the transmitted X-rays. The unfocussed incident beam from the Si(111) channel-cut monochromator was defined by two slit systems in front of the sample. Kapton foils downstream the second ionization chamber were used to adjust the photon flux on the Pilatus detector in order to avoid counter overflows and not to exceed the maximum countrate accepted by the detector (10⁶ counts s⁻¹ pixel⁻¹). Co metal foil and Co₃O₄ powder samples were investigated, with about 0.5 s – 1 s integration time per data point (ca. 25 min/spectrum).

For the conducted grazing incidence X-ray scattering experiments, the 2D-detector was directly placed in the scattered radiation fan without a second ionization chamber. The measurements were done at the MRH endstation of the ROBL beam line BM20 at the ESRF using a Si(111) monochromator and a mirrored, focussed beam. Test sample was a Bi (20 nm)/Au (200 nm)-bilayer on a float glass substrate prepared by vacuum deposition. The entire scattering pattern was evaluated for each energy while scanning across the Au L₃ (11919 eV) and the Bi L₃ (13419 eV) absorption edges.

3. XAFS experiments
3.1. Transmission mode EXAFS
In order to study the feasibility of laterally resolved XAFS experiments and to evaluate the data quality that can be achieved, first tests were performed using a Co metal foil. In figure 1(a), a map of the beam behind the sample is shown in the right inset for an acquisition time of 1 s. The illuminated region of the sample consists of ca. 6 pixels vertically and 40 pixels horizontally. With a pixel size of 172 μm ([7], see inset), this corresponds to a beam size of 1 x 7 mm². The raw absorption data measured using the ionization chambers are compared to different areas of the pixel detector. Obviously, the data quality of a spectrum calculated from a single pixel is excellent with respect to the reproduction of sharp absorption features close to the edge as well as to the low noise of the k³-weighted χ(k) data depicted in the inset. A vertical cross section of the beam, i.e. a line of 6 pixels, is used for the calculation of an absorption spectrum, the data quality slightly improves, and if the entire region of the sample that is illuminated from the beam is taken into consideration (40 lines of 6 pixels = 240 pixels), the obtained spectrum is almost indistinguishable to that from the ionization chamber.

Figure 1. (a) Comparison of the K-edge X-ray absorption spectrum of a Co metal foil measured in transmission at room temperature using ionization chambers as detectors (—) and using the intensities on the 2D-detector (1 s / point). Different regions of this detector were used for spectrum calculation: a single pixel (—), a vertical cross section of 6 pixels (—) and the entire illuminated area (40×6 pixel,—). The insets show the k³-weighted EXAFS oscillations χ(k)k³ for the different spectra depicted, and the intensity distribution on the Pilatus detector measured at E = 7600 eV. (b) Raw absorption data (0.5 s / point) for an inhomogeneous Co₃O₄ powder sample with an intensity map. (c) χ(k)k³ data extracted from a single pixel (—) and 5 neighboring pixels (—) compared to the ionization chamber data (—).
While no substantial differences can be seen in the extracted $\chi(k)$ data up to ca. 12 Å$^{-1}$ for all the different measurements, uncompensated glitches are visible at about 14.4 Å$^{-1}$ and 16 Å$^{-1}$ in the data of the pixel detector, limiting the usable k-range here. The EXAFS of a Co$_3$O$_4$ powder sample is shown in figure 1(b). The inhomogeneous intensity distribution on the 2D-detector is directly reflected in the variation of the edge jump on two selected positions (arrows in figure 1(b)). Moreover, the EXAFS oscillations measured using the ionization chamber have substantially smaller amplitudes compared to the data of single pixels, especially at larger k-values, see figure 1(c). Thus, it should be promising to measure laterally resolved EXAFS spectra of inhomogeneous samples containing variations of thickness, composition, etc., with a lateral resolution of the pixel size, i.e. ca. 200 μm in the present case.

3.2. Grazing incidence XAFS

Some selected scattering patterns obtained from the Bi/Au-bilayer sample are shown in figure 2 for three different energies in the vicinity of the Au L$_3$ edge and $\phi_i=0.5^\circ$, placing the 2D-detector 0.6 m behind the sample. As can clearly be seen, the intensity of the diffuse scattering strongly depends on the X-ray energy and the scattering angle, i.e. the diffuse scattering from the smaller exit angle, i.e. the outer Bi-air surface with smaller density (ROI 2), is not dramatically affected when the energy is scanned through the Au L$_3$-edge. In contrast, the pattern related to the larger exit angle (ROI 2), the inner Bi-Au interface with the larger Au density, dramatically drops down in this energy range (figure 2(c)).

![Figure 2](image-url)

**Figure 2.** Scattering pattern from a Bi / Au / glass sample for different photon energies in the vicinity of the Au L$_3$-edge and an incidence angle $\phi_i=0.5^\circ$: (a) 11800 eV, (b) 11919 eV, (c) 12000 eV. The intense feature at the y-coordinate of about 173 ± 3 pixel ($\phi_e \approx 0.25^\circ$, ROI 2) corresponds to the Yoneda peak of the outer Bi-air surface, and the less intense, smaller spot at y = 167 ± 2 pixel ($\phi_e \approx 0.35^\circ$, ROI 1) belongs to the inner Bi-Au interface, respectively. Regions of interest (ROIs 1 and 2) were defined around these two spots for the collection of representative diffuse EXAFS data.

This behaviour is also observed in the EXAFS spectra calculated from these diffuse X-ray scattering profiles. As can be seen in figure 3, the intensity measured for the Yoneda-peak with the larger $\phi_e$ (smaller y-coordinate in figure 2) is always smaller compared to that related to the smaller $\phi_e$ (larger y-coordinate). While a distinct Au L$_3$-edge can be seen in the first Yoneda peak, no edge can be seen in the scattering related to the second feature. Furthermore, the Bi L$_3$-edge spectrum related to the first Yoneda peak shows a fine structure similar to that of metallic Bi, while that of the second peak resembles that of Bi-oxide Bi$_2$O$_3$. The qualitative interpretation of these observations is clear: The diffuse scattering related to the larger $\phi_e$ is related to the inner Au-Bi interface, where both elements are present in a metallic form. On the other hand, no gold is present at the outer surface of the bilayer,
and thus no Au L₃-edge is observed for the smaller \( \phi_e \). Due to the chemical reactivity of Bi metal, the latter metal is oxidized at its air-side surface, forming a thin oxide layer of about 1-2 nm thickness [9]. Although the incidence angle is larger than \( \phi_c \), the technique appears to be extremely surface sensitive [5]. Thus, the X-ray absorption fine structure in the diffuse scattering reveals features similar to that of Bi₂O₃ (see e.g. [10]) due to strong contributions of the outermost surface to the scattered signals [5].

Figure 3. Non-specular reflection mode EXAFS experiments at the (a) Au L₃- and (b) Bi L₃-edges for an incidence angle \( \phi_i = 0.5° \) and exit angles according to the Yoneda peaks shown in figure 2, i.e. \( \phi_e \approx 0.25° \) (---) and \( \phi_e \approx 0.35° \) (——). The inset depicts a model of the layer structure of the sample.

A detailed modelling of the measured data (for calculation details see [5]) is currently in progress in order to determine the thickness of the Bi oxide layer at the surface. Furthermore, the formation of a gold-bismuth alloy at the inner interface can be initiated by an annealing process of the bilayer. Such an alloy formation may result in substantial modifications of the EXAFS detected at the Yoneda peak at larger exit angles, and, thus, a careful analysis may identify these interfacial phases, their thickness and their changes with temperature and time, which will be subject of a forthcoming publication.

4. Conclusions
We have investigated the feasibility of transmission and reflection mode EXAFS experiments using a 2D-pixel detector. The results show that acceptable data quality can be achieved even if a short acquisition time and a single detector pixel is used for the evaluation, and the data quality improves if the signals from several pixels are averaged. For surface sensitive grazing incidence X-ray absorption spectroscopy, the pixel detector allows the simultaneous measurement of the entire scattering pattern, thus the structure of different surfaces and interfaces can be investigated in parallel.

References
[1] Bridges G, Li GG and Wang X 1992 Nucl. Instrum. Meth. A 320 548
[2] Schroer CG and Grunwaldt J-D 2013 In: In-situ characterization of heterogeneous catalysts. Eds.: J.A. Rodríguez, J.C. Hanson, and P.J. Chupas. John Wiley & Sons pp. 49 - 73.
[3] Tanida H, Yamashige H, Orikasa Y, Oishi M, Takanashi Y, Fujimoto T, Sato K, Takamatsu D, Murayama Y, Arai H, et. al. 2011 J. Synchrotron Rad. 18 919
[4] Yoneda Y 1963 Phys. Rev. 131 2010
[5] Keil P, Kühn R and Lützenkirchen-Hecht D 2010 Corrosion Sci. 52 1305
[6] Lützenkirchen-Hecht D, Keil P and Frahm R 2007 Surf. Sci. 601 4232
[7] Kraft P, Bergman U, Broennimann A, Dinapolli R, Ekenberry EF, Henrich B, Johnson I, Mozzanica A, Schlepütz CM, Willmott PR and Schmitt B 2009 J. Synchrotron Rad. 16 368
[8] Lützenkirchen-Hecht D, Wagner R, Szillat S, Hüsecken AK, Iстomin K, Pietsch U and Frahm R 2014 J. Synchrotron Rad. 21 819
[9] Atkinson R and Curran E 1985 Thin Solid Films 128 333
[10] Jiang N and Spence JCH 2006 J. Phys.: Condens. Matter 18 8029