Full field spectroscopic imaging at the ANKA-XAS- and -SUL-X-Beamlines

Stefan Mangold1*, Ralph Steininger1, Tomy dos Santos Rolo1 and Jörg Göttlicher1

1 Karlsruhe Institute of Technology, Institute for Synchrotron Radiation (KIT-ANKA), P.O. Box 3640, D-76021 Karlsruhe, Germany

stefan.mangold@kit.edu

Abstract. Full field transmission spectroscopic imaging is a powerful method for screening complex and large systems to map the distribution of valence state and electronic configuration of elements. Here, we describe an optimized hardware set-up and data evaluation tool chain for spectroscopic X-ray imaging. We tested this system successful on a ferruginous quartz (SiO2) sample.

1. Introduction

Full field transmission spectroscopy can be applied in radiography and tomography mode and is started to be used to gain insight into complex and large sample systems in catalysis, environmental science and biology [1]. Its usefulness can be attributed to the fact that spectral information is collected in parallel, thus avoiding the time consuming scanning of the sample through a micro-focussed X-ray beam. To demonstrate the full potential of this technique, we optimized measurement and data evaluation procedures and tested it at the ANKA-XAS beamline on a ferruginous quartz sample containing iron (oxyhydr)oxides of up to three different structural environments. Measurements were performed in radiography mode, collecting 440.000 spectra simultaneously. Similar data evaluation procedures have been reported from other groups [2].

2. Experimental

2.1. Hardware

As shown in figure 1, the sample was placed between an ionization chamber as primary flux monitor and the detector system. Due to the absence of any focusing mirrors the ANKA-XAS beamline delivers a beam of very uniform intensity across 9 x 1 mm² and is therefore well suited for radiography of laterally extended samples. The SUL-X beamline with a 27 pole wiggler has higher flux that is needed for tomography, but at a small beam size of about 0.5 x 0.3 mm². The smaller homogeneous beam size is not a limitation, since the transmitted signal through the cylindrical sample needs to be on the order of 20% for a good signal to noise ratio in the case of tomography.

We used a high-resolution X-ray imaging detector system, where the visible light image created by the single crystal scintillating screen is relayed by a diffraction limited microscope objective onto the camera sensor. The detector system consisted of a YAG fluorescence screen, a vertically reflecting mirror for the visible light, a Mitutoy long working distance microscope objective and a PCO camera (type ‘edge’ and ‘4000’) [3]. With a 2 by 2 binning, a physical pixel size of 9 µm and an optical
magnification of 3.6 X, the effective pixel size on the sample was 5 by 5 µm². This detector configuration gave rise to 440,000 X-ray Absorption Near Edge Structure (XANES) data sets in each radiogram. Normalization images were acquired for each energy step by moving the sample out of the beam. Using these additional images, the influence of the beam profile, the detector system and its energy dependence were eliminated.

Figure 1. Sketch and photograph of the imaging set-up

2.2. Software

To retrieve the maximum information from the raw data, a prototype of an advanced data evaluation tool chain has been developed in the language IgorPro [4]. The steps performed to calculate the spectra in each pixel are described in table 1.

Table 1: Data evaluation steps

| Data evaluation step   | Description                                                                 | Time needed per core (standard intel CPU – not optimized) |
|------------------------|------------------------------------------------------------------------------|----------------------------------------------------------|
| Calculation of spectra | Calculation of spectra by ln(measurement without sample/ measurement with sample) for each detector pixel (ln = natural logarithm) | < 5 min per 2Gb                                          |
| Calculation of the vertical energy shift | Used for correction of the vertical energy drift over the image | 9h (440000 spectra); only once per edge                   |
| Correction of the vertical energy shift | Used to correct the beamline dependent vertical energy shift                  | < 1 min (440000 spectra)                                |
| Edge filtering         | Filter out all pixels, which contains no reasonable spectrum                 | < 2min                                                   |
| PCA analysis           | Detection of components (PCA = principal component analysis)                 | ~15 min                                                  |

Due to the illumination of the flat monochromator crystal with a divergent beam, a small energy drift in the vertical direction on the detector is expected and can be seen in figure 2 and 3. The drift is corrected by a reference measurement with the metal foil of the element of interest. The shift per spectrum was determined by aligning all spectra to a spectrum from the center of the image. The
remaining shift was reduced from 2 eV to below 0.2 eV between all XANES data sets of the radiogram (figure 4). While the determination of the energy drift over the metal foils up to now takes a few hours per core, the correction of the energy drift needs less than a minute for a complete radiogram. To exploit the full potential of the principal component analysis (PCA) and to speed up the data correction steps, XANES spectra containing no important physical information were removed from the radiographs. A simple but very stable edge-screening algorithm accomplished this by selecting only spectra with an edge jump of sufficient height. Additionally, an early prototype of a highly reproducible automatic background correction is in use.

Figure 2. Relative energy distribution across the beam profile at ANKA-XAS

Figure 3. Edge region of the raw Cu spectra across the vertical beam profile.

Figure 4. Cu spectra (edge region) of vertical beam profile, energy calibrated to the central spectrum.

3. Results and discussion

Prior to the full filed data evaluation, goethite (FeOOH) and hematite (Fe₂O₃) have been determined in this study by μ-XANES spectroscopy in the ferruginous quartz test sample at the SUL-X beamline to derive reference spectra (figure 5). A third spectrum belongs to a not yet identified black phase of most probably mixed Fe(II,III) valence. In the full field measurements, irrelevant spectra were removed by using the robust edge filter prior to the processing with the PCA. For the studied sample this reduced the number of spectra to process by a factor of ten (figure 6).

Figure 5. Fe K-edge μ-XANES spectra of orange and red particles with goethite and hematite reference spectra (measured at the SUL-X beamline; Si(111) monochromator crystal pair, beam size at sample position ~ 50 x 50 μm²)
Figure 6. Top: transmission image of the sample; bottom: white areas are used for further processing.

We were able to extract three important components from the PCA (figure 7). They are sufficient to reconstruct all spectral types extracted from the full field measurements.

Figure 7. Graphs show the first 3 components of the PCA analysis.

Figure 8 shows the distribution of the two unambiguously identified spectral components across the sample area (goethite (FeOOH) green, hematite (Fe₂O₃) blue). The particle shown in the optical microscope image mainly consists of goethite FeOOH (orange) and hematite Fe₂O₃ (red). The lower part of the particle shows only a very low amount of iron and is therefore not suited for transmission measurements.

Figure 8. Comparison of light microscope image and the results of spectral analysis (goethite FeOOH, green; hematite Fe₂O₃, blue):

4. Conclusion and outlook

The test measurements illustrate that full field spectroscopic radiography is a powerful tool for screening large samples. Nevertheless, the raw data has to be carefully corrected to eliminate undesired effects introduced by the beam line and detector system. To further improve the method, a background correction on the complete data set is required. We are developing such a background correction method based on a robust algorithm with a combined pre- and post-edge fit. Each step of the procedure is described in table 2 and is based on simple, but very fast fits (time of all steps 0.1 s per core).
Table 2: Steps of the background fit

| Fitting step                                      | Description                                                                 |
|--------------------------------------------------|-----------------------------------------------------------------------------|
| Pre-edge background correction                   | Options: line fit and polynomial (second degree), edge position is automatically detected |
| Sigmoidal fit                                    | Needed to correct the pre- and post-edge in one step afterwards             |
| Combined pre- and post-edge background           | Fits the rest of the spectra with a polynomial fit (edge region is omitted)  |
| Adding sigmoidal fit and interpolate data        | Adding the data of the sigmoidal fit produces to the spectrum again; the data will be interpolated subsequently |

Optimized detector systems are currently in the design phase, which will decrease the required integration time by one order of magnitude, enabling us to perform in-situ studies of catalysts and other fast processes, as well as to increase the sample throughput significantly.

References

[1] Meirer, F.; Cabana, J.; Liu, Y.; Mehta, A.; Andrews, J.C.; Pianetta, P., 2011, J. Synchrotron Rad. 18, 773–781
[2] Liu, Y.; F. Meirer, F.; Williams P.A.; Wang J.; Andrews, J.C.; Pianetta, P., 2012, J. Synchrotron Rad. (2012). 19, 281-287
[3] Cecilia, A.; Rack, A.; Douissard, P.-A.; Martin, T.; dos Santos Rolo, T.; Vagovič, P.; Hamann, E.; van de Kamp, T.; Riedel, A.; Fiederle, M. & Baumbach, T., LPE grown LSO:Tb scintillator films for high-resolution X-ray imaging applications at synchrotron light sources, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 2011, 648, Supplement 1, S321 - S323
[4] IgorPro - http://www.wavemetrics.com/