A new Grazing-Exit-XRF setup at HASYLAB beamline L

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Total reflection x-ray fluorescence analysis (TXRF) operates with the incident beam impinging below the critical angle of total reflection on the surface of a flat polished surface of reflector. The interference between incident and reflected beam causes in case of microcrystalline samples an intensity increase of the fluorescence signal by a factor (1+R) where R is the reflectivity numerically close to 1. The additional effect due to the penetration depth in the nm region is a low background. Both effects are leading to excellent detection limits in TXRF and are widely used in ultra trace element analysis. Grazing incidence XRF uses (GI-XRF) the angle dependent wavefield intensity in order to characterize the structure of layered materials and the composition gradient of materials that are inhomogeneous along the direction perpendicular to the surface. The inverse GI-XRF with the incident beam perpendicular to the reflector surface carrying the sample and collection of the fluorescence under grazing angle can also be applied [1]. This mode of analysis was named grazing exit x-ray fluorescence (GE-XRF) and is theoretically based on the reciprocity theorem [2]. The interference in this case is not between primary and reflected beam but among the superposition interference of the fluorescent waves emitted from the sample and observed under the critical angle of total reflection crit.

A GE-XRF experiment was performed at HASYLAB beamline L using the newly designed equipment from the Atominstitut Vienna x-ray group. In figure 1 the fundamental arrangement is shown. The setup was designed with the axis of rotation of the detector exactly in the plane of the reflector. The sample holder was designed to mount this reflector in a precise geometry. Easy sample changing by a motorized translation stage is available. The sample is a dried spot prepared after pipetting a few microliters of a solution with known concentration in the center of the reflector. The experiments are performed with the aim to study XANES self-absorption effects, which were observed previously in GI-XRF geometry.

Angle dependent measurements of an As droplet sample were carried out by rotating the detector around the sample in the center of the reflector. In figure 2a the result of the angle dependent fluorescence signal is displayed showing the typical shape with double intensity at angles below the critical angle when compared to larger angles. An effect caused by the missing contribution due to surface reflections of the fluorescence signal in this region. Another test was performed with a bulk germanium reflector. The experimental data and the theoretical curve showed good agreement and are displayed in figure 2b. The distance between detector entrance slit and sample is 40mm and the slit width of the defining diaphragma in front of the detector is 40μm. This gives a theoretical angular resolution of 1mrad. However the divergence determined by the fitting was estimated to be 0.3mrad. This can be explained with a misalignment of the slit relative to the reflectors surface. The mentioned effect was expected and was not corrected in order to have a higher angular resolution.

The detector used is a Peltier-cooled Si drift detector with 50mm! active area. The effective area of collection is therefore roughly 40μm x 8mm. In order to achieve measurements with higher lateral resolution a polycapillary half lens was used to produce a focal spot of 40μm in diameter.

A series of dried residues with different total amounts of arsenic masses on quartz reflectors were scanned. As an example a surface scan of a droplet of 1μl 20ppm dried As is shown in figure 3. Scanning parameters were 31 x 18 steps with a step size of 40μm (total scanned area 1280μm x 760μm). Fluorescence intensities were calculated by region of interest integration because the spectra are practically background free.
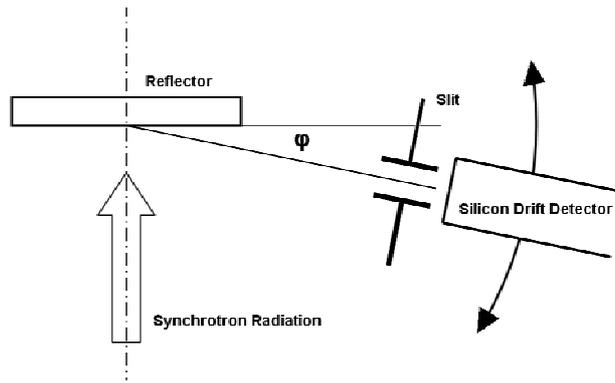
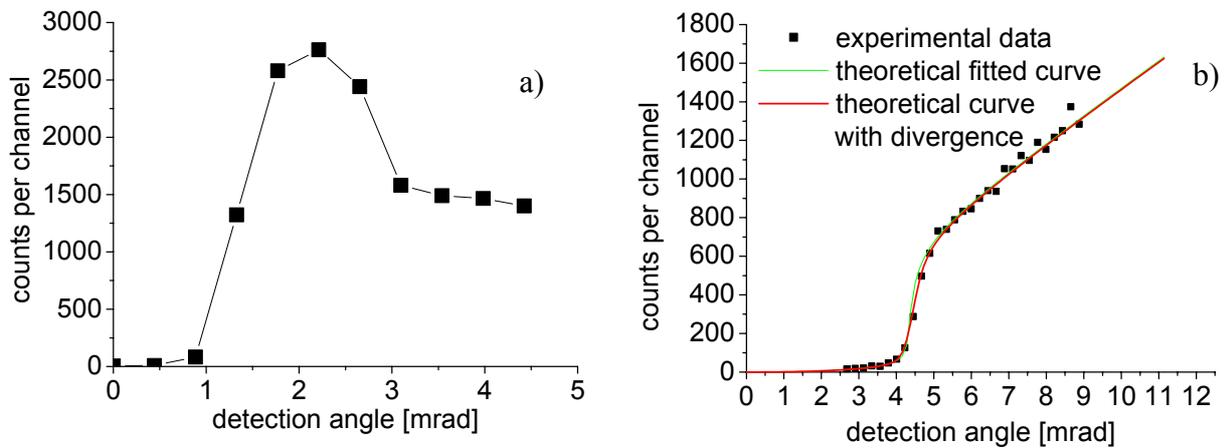Figure 1: Experimental setup of the GE-XRF spectrometer.

Figure 2: a) Measured angle dependence of the As-Ka fluorescence intensity of a droplet sample. b) Measured and calculated angle dependences of the Ge-Ka fluorescence intensity of the bulk sample.
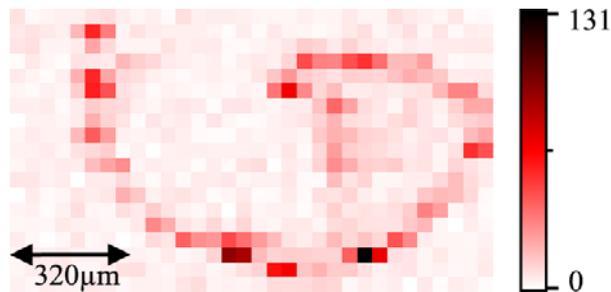

Figure 3: 2D-scan of the dried residue of the 1µl 20ppm arsenic sample.

References

[1] T. Noma, A. Iida, K. Sakurai, Fluorescent-x-ray-interference effect in layered materials, Physical Review B 48 (1993) 17524.

[2] R.S. Becker, J.A. Golovchenko, J.R. Patel, X-Ray Evanescent-Wave Absorption and Emission, Physical Review Letters 50 (1983) 153.