Pink-beam and monochromatic micro-X-ray fluorescence analysis at the beamline L

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Introduction

Micro-X-ray fluorescence analysis has been introduced at HASYLAB beamline L almost ten years ago. Using white bending magnet radiation for excitation, all trace elements with 20<Z<84 can be analyzed simultaneously by means of their K-lines. Monocapillaries of various shapes are employed to form the white micro-beam with sizes down to 2 µm [1]. Especially applications in geosciences, where quantitative analysis of the element distribution of Rare Earth Elements and other heavy elements is required on a microscopic scale, benefit from the high-energy excitation conditions provided by a bending magnet at DORIS III [2].

During the last two years the beamline was equipped with a monochromator and a focussing system in order to extend the range of scientific applications beyond white beam experiments [3,4]. The first and most significant application of the new X-ray optics is microscopic X-ray absorption spectroscopy [5]. Recent improvements of polycapillary optics performance with respect to focus size and transmission makes also monochromatic (and pink-beam) micro-X-ray fluorescence analysis interesting for our bending magnet beamline. Monochromatic excitation generates in general higher ratios of fluorescence signal to background scattering, enables selective excitation of elements by tuning the energy and speeds up the calculation for quantitative analysis based on fundamental parameter or Monte Carlo approaches. However, the transmission characteristics of the polycapillary limits the maximum excitation energy to 20 keV and elements with Z> 42 need to be analysed using the L-lines when a polycapillary is applied.

Experimental Setup

The schematic layout of the beamline and experimental setup is shown in Fig. 1 and was explained in detail already in the last HASYLAB annual report [4].

![Figure 1: Experimental setup of the micro-X-ray fluorescence beamline L](image)

In short, the new optics comprises two separate fixed-exit double crystal monochromators, equipped with Si(111) and Si(113) crystals for high energy resolution and multilayer structures (NiC, W/C) for high flux applications, respectively. Both monochromators cover the energy range 2-100 keV. A pair of X-ray mirrors can be moved into the beam in order to (pre-) focus the beam and to cut off the high-energy part. For micro-focussing of the monochromatic and pink beam a
polycapillary half-lens (X-Ray Optical Systems, Albany, New York) is applied. The routinely achievable spot size is around 10-20 µm FWHM both vertically and horizontally in the energy range 5-20 keV. The gain factor of the polycapillary of about 2000 results in a photon flux in the focused beam of up to 10^9 photons/s using the Si(111) monochromator. The large focal distance of 5 mm of the polycapillary makes it easy to place collimators at the exit of the capillary and at the detector entrance in order to achieve spectra free of fluorescence lines originating from the capillary material. The sample is mounted on a sample stage containing three translational motor stages. The horizontal and vertical scanning range is 30 \cdot 30 mm^2. The intensities of fluorescence and scattering from the sample are detected by a Si(Li) detector (GRESHAM Sirius 80) of 80 mm^2 active area and 4 mm thickness with a 12 µm thick Be window throughout this study. HPGe detectors are available, too. The semiconductor detector is placed in 90° geometry to the incoming linear polarized X-ray beam and in the storage ring plane in order to minimize the intensity of the scattering. The angle between beam and sample and sample and detector is fixed to 45° each, in order to minimize the path length of X-rays in the sample. The detector is placed on a motorized translation stage, allowing optimisation of the detector position. Ionization chambers in front and behind the sample are used in order to monitor the intensity of the incoming and focused beam. A microscope coupled to a high-resolution CCD camera allows for a visual control of the micro-beam position on the sample. A Canberra 2060 Digital Signal Processor was used for collecting the spectra and the AXIL software package was used for evaluation of the spectrum.

**Relative And Absolute Lower Limits of Detection**

Besides the spatial resolution the most common parameter to describe the quality of a micro-fluorescence set-up is the lower limit of detection (LLD). The absolute and relative limits of detection can be determined by measuring standard reference materials (SRM) with well known elemental composition:

\[
C_{MDL,i} = \frac{3\sigma_{bgri}^i}{N_i^i} C_i = \frac{3\sqrt{I_i,B}}{I_i} C_i
\]

where \(C_{MDL,i}\) is the detection limit of element \(i\) with 99.86% confidence level, in ppm or mg cm\(^{-2}\), \(\sigma_{bgri}^i\) is the standard deviation of the background intensity measured under the characteristic X-ray peak of element \(i\), \(N_i^i\) is the net peak area of element \(i\) in counts, \(I_{i,B}\) and \(I_i\) are the measured background and characteristic X-ray intensity of element \(i\) in counts per second live time. \(t\) is the live time, which is the effective collection time of the multi channel analyser. The live time already compensates for events rejected due to pile-up and processing time (dead time). \(C_i\) is the concentration of element \(i\) in the standard sample in ppm or mg cm\(^{-2}\) [6].

The LLD is determined by the peak-to-background ratio, the intensity of the exciting beam and the measurement time. The background results mainly from the low energy peak tailing of the energy-dispersive semiconductor detector. In (ultra-) trace element analysis the scattering peak (Compton, Rayleigh) is often the most intense peak. The scattering intensity depends strongly on the degree of linear polarization of the impinging radiation. A value of 92% linear polarization was estimated for the conditions used for the measurements at beamline L described in the following. For comparison, a value > 99.5% was reported for the micro-X-ray fluorescence endstation ID18F at ESRF [6].

Standard reference materials from the National Institute of Standards & Technology (NIST) with two different matrix materials were used for the measurement of the analytical characteristics of the beamline: SRM 612 trace elements in silicate glass matrix (100 µm thin, polished on both sides), and SRM 1577b bovine liver (pressed pellet of 10 mm diameter and 100 µm thickness). The standards were measured at two different energies (10 keV and 17.5 keV) and under different excitation conditions: with and without prefocussing by X-ray mirrors (+ mirr, - mirr), with and
without micro-focusing by the polycapillary (+ cap, - cap), employing monochromatic beam (Si(111) monochromator) or pink beam (NiC monochromator) or filtered white beam. In all cases the same sample - detector geometry was employed. The solid angle of detection and the air path and volume of air seen by the detector were determined by a Ta collimator with an opening of 2.2 mm in diameter. The distance between sample and collimator was 12 mm and between collimator and detector crystal 15 mm, i.e. only a fraction of the active detector area was used.

In order to derive the illuminated sample volume and mass for the calculation of the absolute limit of detection, the size of the focused beam at the sample position was measured by scanning a tungsten wire of 10 µm diameter through the beam. After correction for the wire diameter, beam sizes of 18 µm (FWHM) at 10 keV and 13 µm (FWHM) at 17.5 keV was determined. Details of the beam profile characteristics are given in Ref [4,5]. The size of the beam at the entrance of the capillary was 1000 × 1000 µm².

The figures 2 (a) und (b) show spectra of SRM 1577 (bovine liver) and 10 keV and 17.5 keV at various excitation conditions. All spectra were normalized to 1000 s live time and a ring current of 100 mA for a comparison of intensities. The intensity of the Si(111) monochromatized unfocused beam was of the order of $10^9$ photon s⁻¹ at 10 keV. Using the polycapillary for focusing, the intensity is reduced only by a factor of 2 compared to the free beam. If the focusing X-ray mirrors are applied the intensity is increased by a factor of 8 without significant increase of the scatter peak or focus size. However, for the “pink” beam generated by the NiC multilayer an intensity gain of 80 was observed relative to monochromatic beam. Also for pink beam conditions no broadening of the focus size and only a small increase of the scatter peak was observed. Though, under the described conditions the pink beam generates count rates of 100000 cts/s for the 100 µm thick organic standard, which, at sufficient resolution, results in more than 80% deadtime. The high intensity of the pink beam is exploited only for thin samples.

The relative and absolute limits of detection, which are derived from these measurements and measurements on the 100 µm thick SRM 612 silicate glass standard are shown in Fig. 3 (a) and (b), respectively. Since the different beam conditions did not effect the ratio of peak to background, the detection limits decreases with increasing flux and decreasing excitation energy. On SRM1577 relative detection limits of < 0.1 ppm for elements of Z > 25 are achievable for a measuring live-time of 1000 s. For 33 < Z < 38 relative detection limits at the 10 bbp level are reached in pink beam mode. The absolute detection limits are below 10 fg for Z > 25 and even below 1 fg using pink beam.

The detection limits on SRM 612 glass standard are considerable higher because of the increased scattering from the dense matrix and peak overlaps with L-lines of high Z elements, which are included in this standard. Relative to the bovine liver standard, the glass standard generates three times higher count rates and the pink beam mode could not be employed without changing other conditions. For comparison, detection limits achieved with white beam modified by a 0.2 mm Cu absorber and collimated to 20×20 µm² beam size are shown. These conditions are typical for applications in mineralogy and are optimised for K-shell excitation of high-Z elements. The detection limits are about one order of magnitude higher than for monochromatic excitation for elements with Z < 35.

In conclusion, the detection limits at beamline L are close to the (preliminary) results presented for the micro-X-ray fluorescence end-station ID18F at ESRF in Ref. [6]. The low degree of linear polarisation is compensated by higher flux on the sample, which is due to the high transmission and wide collection area of the polycapillary in combination with broad bandwidth monochromatisation.
or prefocussing. However, the beam size is vertically one order of magnitude broader at beamline L than at ID18F.

Figure 3: Spectra of SRM 1577 bovine liver measured at different incident beam conditions at excitation energies of 10 keV (a) and 17.3keV (b). The spectra were normalized to a measurement live time of 1000s.
Figure 3: Relative and absolute limits of detection derived from measurements of SRM 1577 bovine liver (a) and SRM612 multi-element silicate glass standards (b).

Applications

Two recent applications are shown in Fig. 4 and 5 in order to illustrate the capability of the micro-X-ray fluorescence experiment at beamline L for fast two-dimensional element mapping.

The first example is a quartz mineral from the Ehrenfriedersdorf Complex hosting melt and fluid inclusions [7]. Melt and fluid inclusions in minerals are formed during crystal growth and may record the melt and fluid phase that was present during the formative process. Many generations of inclusions are often present within the same mineral host, which makes it important to analyse every individual inclusion separately.

An area of 200 × 400 µm² was scanned and about 600 X-ray spectra were measured for 15s (real) time. A combination of focusing mirrors, Si(111) monochromator and polycapillary was chosen in
order to achieve count rates 50000 cts/s maximum on the quartz sample of 100 µm thickness. A spectrum collected at the position of the biggest inclusion is shown in the centre of Fig. 4. The peak areas of the fluorescence and scatter peaks for all spectra were fitted and displayed on-line in two-dimensional elemental maps automatically during the measurement using the AXIL and MICROXRF2 software. The intensity distribution in the elemental maps (intensity increases from blue to red) resembles very well the arrangement of inclusion as seen in the optical microscope, when the distortion due to different viewpoints of X-ray beam and microscope on inclusions of different depth is taken into account. Fluid and melt inclusions can easily be distinguished by their Fe and Cs distributions, but also variations in composition between individual melt inclusions are observed. The vapour phase inclusion is not visible in the maps because of its low trace element content. For a conversion of the intensities displayed in the elemental maps into concentrations the size and depth of every inclusion has to be taken into account separately.

Figure 4: Fluid (F), melt (M) and vapour phase (V) inclusions in a quartz host of 100 µm thickness. An optical micrograph, a single point X-ray fluorescence spectrum and maps of selected fluorescence line intensities are shown. Excitation conditions: Si(111) monochromatization at 17.5keV, focussing mirrors and polycapillary, sample time / pixel: 15 s, pixel size: 15 x 10 µm².

The second example represents a rapidly growing field of applications of micro-XRF at beamline L: quantitative element analysis of thin slices of human or animal tissue. The investigations are performed in order to reveal the role of metals in the pathogenesis of, in this case, neurodegenerative disorders like the Alzheimer disease. In tissue most metals are bound to proteins and their biological effect is based on the impact of these proteins. In neurodegenerative disorders, like the Alzheimer disease, pathological protein aggregations are formed, which are deposited in the brain and affect the nervous system. There is evidence from several in vitro experiments that Cu, but also Fe, Mn, Se and Zn may be involved in the processes leading to Morbus Alzheimer.
Investigations on Morbus Alzheimer were performed by M. Kühbacher, G. Weseloh, and D. Behne from the Hahn-Meitner Institut, Berlin, T. Ohm, Charité, Berlin and G. Falkenberg. Affected part of a human brain was prepared as 16 μm thin slices (with 800 nm thin polyethylene backing) in order to obtain samples which are homogeneous across the complete sample thickness and to employ the full spatial resolution of the micro-beam.

An area of 1000 × 400 μm² was scanned and 1350 X-ray spectra were measured for 3s (real) time each. A combination of NiC multilayer monochromator and polycapillary was employed in order to achieve count rates of 20000 cts/s. Figure 5 shows a spectrum (which is collected at the position of highest Fe peak intensity) and intensity maps of selected elements. The light elements P, S and K show qualitatively the same pattern, which reflects inhomogeneities of the organic matrix smaller than +/- 20 %. The element maps of Fe and Zn resemble this pattern, but an additional pattern is superimposed consisting of a single spot of double intensity for Zn and broader patches of up to double intensity for Fe. Since the distribution of mayor elements is homogeneous in this sample and the trace element distribution can be regarded as homogeneous across the sample thickness the quantification modul of the MICROXRF2 program can be employed, which performs a fully automated conversion of peak intensity maps into concentration maps by Monte Carlo simulation. The non-destructive nature of the XRF technique allows to measure the same sample area with complementary techniques subsequently. Finally, an assignment of the measured element distribution patterns to pathological and non-pathological protein aggregations by staining the sample is forseen.

Figure 5: Morbus Alzheimer affected part of a human brain. A single point X-ray fluorescence spectrum and maps of selected fluorescence line intensities are shown. Excitation conditions: pink beam (NiC multilayer) at 11.5keV excitation energy and polycapillary for focussing, sample time / pixel: 3s, pixel size: 15x15 μm².

Conclusion

The performance of the micro-X-ray fluorescence beamline L has been evaluated for various excitation conditions. Basic focussing element is a polycapillary half-lens generating a spot size of 10 – 20 μm in the energy range 5 – 20 keV. Relative detection limits of < 0.1 ppm for elements
with $Z > 25$ are achievable for a measuring time of 1000 s on organic reference materials. For $33 < Z < 38$ relative detection limits at the 10 ppb level are reached in pink beam mode. The absolute detection limits are below 10 fg for $Z > 25$ and even below 1 fg using pink beam. The low detection limits make fast two-dimensional element mapping feasible, which may be employed for quantitative trace-element imaging of heterogeneous samples. (Ultra-) fast scans are also used to find locations of interest for micro-X-ray absorption fine structure measurements. The experimental setup is identical for both techniques. Only the excitation conditions need to be adapted for moving from micro-XRF mode to micro-XAFS mode, which is feasible within minutes.

References

   accepted for publication in X-Ray Spectrometry (2003).