Journal of large-scale research facilities

Journal of large-scale research facilities, 2, A101 (2016) http://dx.doi.org/10.17815/jlsrf-2-115

Published: 15.12.2016

mySpot: a versatile microfocussing station for scanning methods at BESSY II

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Abstract: mySpot is a versatile microfocussing station for scanning methods with resolution down to 1.5 μm, providing a combination of methods which can be performed simultaneously at the same sample position. It is especially designed (but not limited to) for the study of hierarchically structured biological samples. Structural information from different length scales (XRD - crystalline, SAXS - nanometer, Video-microscope - micrometer, sample translation - milimeter) can be combined with chemical information (XRF-mapping, EXAFS, XANES) and molecular information (Raman) providing unique insight into the mutual dependencies of different parameters.
The beamline provides focal spot of about 500 x 50 μm, which can be refocused at the sample using capillary optics. Capillary optics is used for two main reasons: 1) the focal spot does not depend on the energy which makes EXAFS and XANES measurements very simple, and 2) the optics is positioned very close to the sample which improves the stability of the focus at the sample. This allows the focal spot of 1.5 μm in 2D scans, as well as very parallel beam for scattering experiments down to 10 μm, or volume element of 20 μm diameter for 3D XRF mapping.

1 Introduction

Many natural and human made materials are hierarchically structured from macroscopic dimensions down to the molecular and atomic level. Important structural properties of such structured materials can be studied using X-ray spectrometry and scattering using an X-ray beam focused to a micrometer spot. Spectrometric methods deliver information about the chemical composition and oxidation states, whereas the scattering methods deliver information on the structure in nanometre range and atomic level. Combining these techniques with the scanning, complex hierarchical structures can be studied

[*]**Cite article as:** Helmholtz-Zentrum Berlin für Materialien und Energie. (2016). mySpot: a versatile microfocussing station for scanning methods at BESSY II. *Journal of large-scale research facilities, 2*, A101. http://dx.doi.org/10.17815/jlsrf-2-115

from millimetre range down to angstroms. The mySpot beamline and experimental station operates in the energy range between 5 and 30 keV and provides the simultaneous use of following nondestructive methods:

- Small (SAXS) and Wide- (WAXS) angle X-ray scattering in scanning mode, resolution 5 μm
- Scanning X-ray fluorescence analysis (2D/3D) (XRF) resolution 3 μm
- Spatially resolved extended X-ray absorption fine structure (EXAFS) and near-edge structure (NEXAFS, XANES) in volume and on surface (2D/3D), resolution 25 μm for volume and 3 μm for surface scans.

The beamline was designed to allow different x-ray analytical methods to be operated under optimal conditions; the only specialization of the beamline is the small spot size. Special attention was paid to destruction free measurements. For this reason the beamline is equipped with cryogenic stream for biological samples, and the whole experimental hutch is kept air conditioned to provide the museum environment for archaeological findings. The primary applications are in the fields of biological materials, archaeometry, photovoltaics and other fields where the hierarchical structure of material is important.
The station was built in 2004 in cooperation with Max-Planck-Institute of Colloids and Interfaces (MPIKG) Golm, Technical University Berlin (TUB), and Federal Institute for Materials Research and Testing (BAM). The scattering part of the experiment was constructed by MPIKG Golm. Fluorescence and spectroscopy experimental station was built by the workgroup "Analytical X-ray Spectroscopy" from Technical University Berlin, as a part of the BMBF-funded project. After the project was finalized in 2007, the TUB part of the beamtime is offered to external users.
The HZB portion of the beamtime is operated by the Institute for the Nanometre Optics and Technology, which is oriented in developing and building of the focussing X-ray optics. This influences the strategical developments of the beamline and experimental station and the part of the in-house research on this beamline.

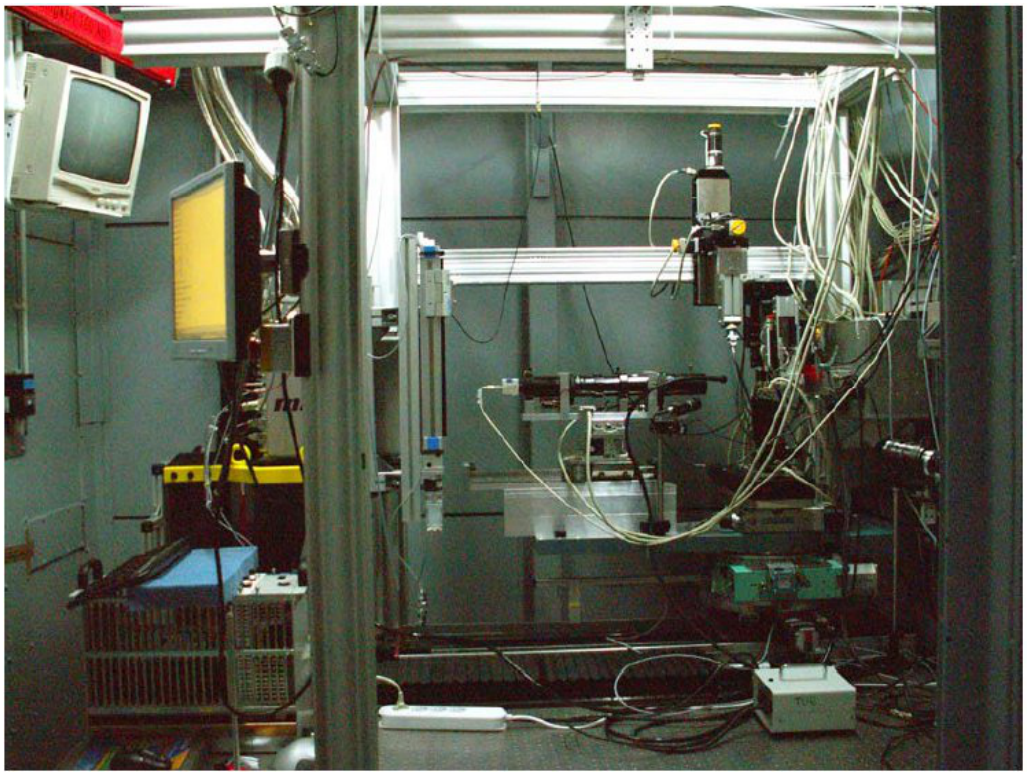

Figure 1: A view though the door of rather small experimental hutch.

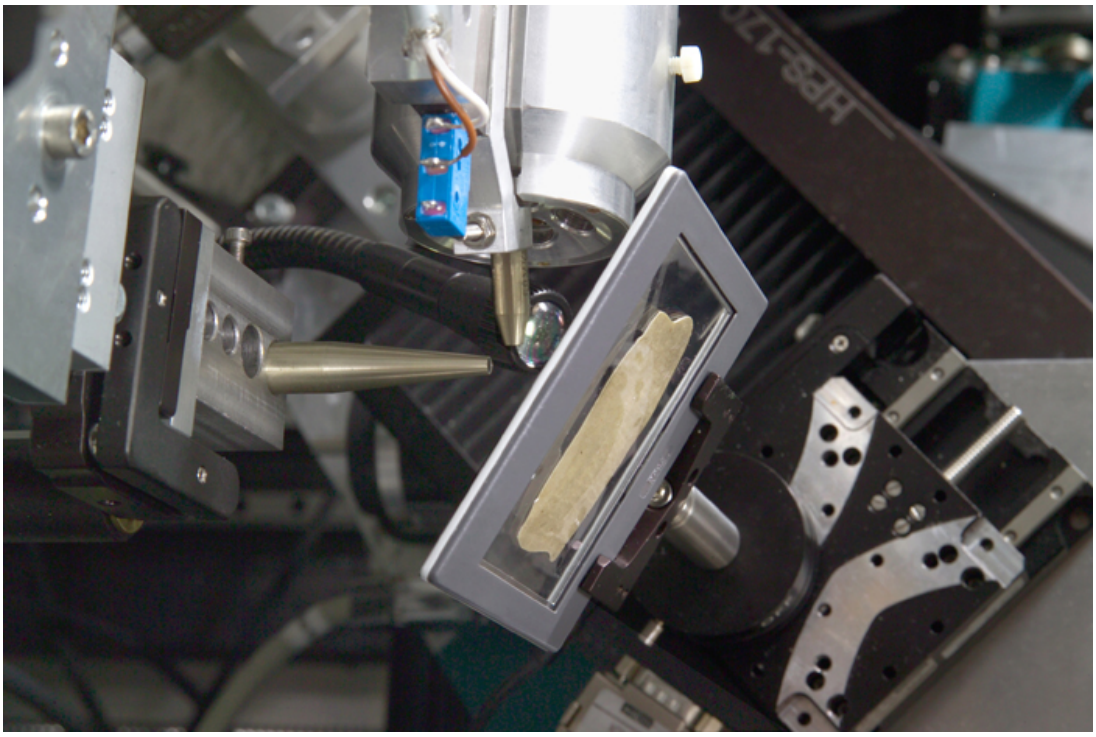

Figure 2: 3D fluorescence mapping on a piece of Qumran parchment.

2 Instrument Application

The mySpot experimental station is specialized for mapping experiments using different methods. Depending on the required method the focus varies between 1.5 and 100 μm. Most methods can be combined. However, the user should take into account that the beam requirements vary for different methods. Example: For XRF mapping with 1.5 μm focus the beam is strongly focused to the sample, providing enough intensity to perform even EXAFS at selected positions. If small angle scattering from the same position is required, this strong focusing is not possible, rendering simultaneous micro-EXAFS and SAXS with 1.5 μm focal spot impossible.

2.1 Optical microscope

An optical microscope is available for alignment purposes The microscope can be rotated around the sample to align the sample, X-ray beam (using fluorescent screen) and the focus of the Raman laser. Additionally, the microscopy images can be saved at every measurement coordinate, so that the correlation between the measured data and the microscopy is rather simple.

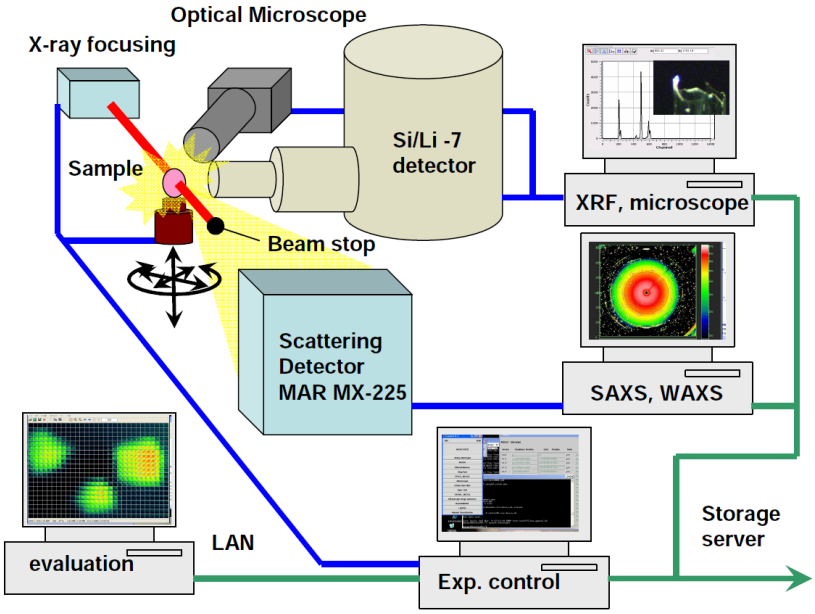

Figure 3: Experiment control at mySpot beamline. All the components are connected transparent for the user. During the measurement the evaluation can be performed as soon as the data is saved.

2.2 X-Ray Scattering

Detectors for scattering measurement:

- MarMosaic 225 (SAXS/WAXS detector, 16 bit CCD coupled with fibre-optic taper to a 225 mm Phosphor, 3072x3072 pixels, pixel size 73 μm, readout time 1 s, low noise) Distance between the detector and sample can be changed automatically.
- Silicon Drift Detector (Ketek) – In case that, due to the sample environment geometry, it is not possible to mount the 7-channel Si(Li), a small drift detector can be used to simultaneously measure the scattering, another, smaller energy dispersive detector is available at the beamline.
- Calibrated Photodiode mounted suitably for transmission measurements.

Additional equipment:

- He-Tube for SAXS measurements – in order to minimize the air scattering
- Microbeam for SAXS/WAXS

The special feature of the SAXS station is the usage of very small beamstopers (100-200 μm diameter). Due to very small beam size, it is possible to mount the beamstop very close to the sample and avoid the transmitted beam traveling through the air for a long distance. This minimizes the air scattering and the available q-region in small angle regime. The current setup is suitable for (scanning) microbeam SAXS/WAXS experiments with simultaneous XRF detection. The small-angle resolution (minimum $q=4\pi \sin\theta/\lambda$) due to beam divergence for all energies is about 0.1 nm^{-1} . Up to 3 orders of magnitude in q can be covered simultaneously (simultaneous SAXS/WAXS).

Capillary	Length (mm)	Focal Length (mm)	Larger window diameter (mm)	Smaller window diameter (mm)	Focal Size (μm)	Flux gain
58mkl01	12	4	2.1	1	17	300
58mkl10	12.2	5.2	2	1.4	17	660
51mls03	106	7.4	6.7	2.5	25	3000

Table 1: Parameters of the polycapillary lenses used at the mySpot beamline.

2.3 X-Ray Absorption Spectroscopy

At the mySpot beamline XANES and EXAFS measurement can be performed in transmission or in fluorescence geometry. Following equipment is available:

X-ray detectors used for Fluorescence measurements:
- Two ionization chambers calibrated for absolute flux measurement
- Two calibrated PIN-diodes for absolute flux determination
- A 7-element Si(Li) array detector with digital signal electronic for XRF and XAFS (high throughput mode for XAFS)

Further detectors are available on demand
- Small goniometer with xyz stage and 2 tilt axes for alignment of the focusing optics
- Glas polycapillary lenses with spatial resolution of ca. 15 and 25 μm.
- Single capillary lens
- pinhole collimators with different pinhole sizes

2.4 micro-XRF mapping

Detectors available: 7 channel Si(Li) detector with 210 mm^2 surface or 80 mm^2 Silicon drift detector. The smaller detector is used for combined scattering/XRF measurements. Resolution depends on the used optics and can be selected between 1.5 and 20 μm. Primary beam energy range is 6 keV-30 keV.

2.5 3D XRF-Mapping

The 7-channel detector is used, although only one channel is assigned to the volume mapping. This allows for the acquisition of the fluorescence signal from different directions and estimation of the inelastic scattering. For this method we use polycapillaries with focal distance of about 3 mm and focal spot of about 15 μm.
Using two polycapillary half-lenses it is possible to perform volume analysis with a resolution down to 15 μm. A half-lens is converting the parallel x-ray beam into focused (focusing orientation) or a beam radiated from the point source into the parallel beam (collecting orientation). The first lens is used for condensing the X-ray beam by focusing it onto the sample. The second lens is used to limit the field of view of the detector to several micrometers.

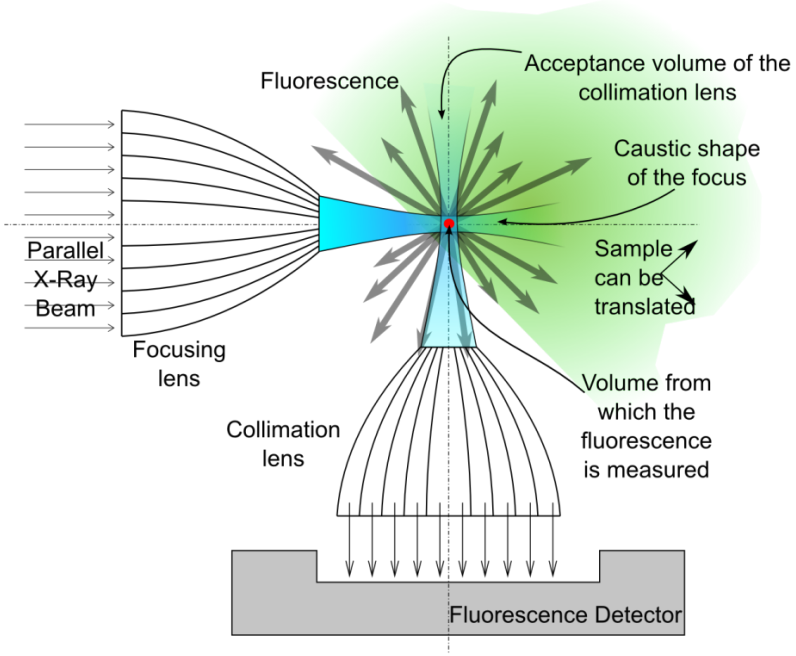

Figure 4: Working principle of the confocal lens setup. The focusing lens condenses the rays into a caustic shape with the focus in its waist. Similar shape determines the volume where the collimation lens lets the intensity through. If the sample is translated through the common focal spot, the 3D elemental distribution can be acquired.

Figure 4 shows the principle of the focusing with the confocal setting. The lenses are mounted normally to each other so that the focuses are at the same position. The fluorescence is induced only on the part of the sample which is inside the caustic volume of the primary beam. The collecting lens transmits only the intensity irradiated from its caustic surface. The photons which originate from outside of this volume are not detected. At the mySpot beamline we use the lenses with the focal length (distance between the aperture of the lens and focus) of 4-7 mm, and with the focal size of 15-30 μm. The large focal distance allows measurements several micrometers below the sample surface (as deep as the absorption allows).

Since the pre-focused beam in the beamline is stabilized during energy scans, it is possible to perform not only the volumetric XRF analysis, but also the spectroscopy (XANES, EXAFS) of the selected volume regions underneath the sample surface. When acquiring the fluorescence from the voluminous sample, both the incident beam, as well as the fluorescence are passing through the parts of the sample and must be corrected for the absorption. The knowledge of the consistence of all the sample regions through which the beam is passing through is necessary to perform this correction. Since we can acquire only a part of the spectrum, not all elements are detected. To be able to make some assumptions on those unknown elements, the Compton scattering is measured simultaneously. The model is developed by the Work group of B. Kanngießer at the TU Berlin, and works for finite and for layered samples (Kanngießer et al., 2012; Lühl et al., 2013; Mantouvalou et al., 2011).

All the capillaries were produced by Institut für Gerätebau Berlin. Flux gain is measured as the ration between flux through the 5 μm large pinhole without the lens and through the same pinhole positioned in the focus of the lens. To facilitate the sample alignment, an optical tele-microscope with a CCD camera and the field of view of about 1 mm is mounted normally to the sample. The sample image can be seen on the color monitor and in a special graphical program for the sample alignment.

Several different archaeological objects were studied at the mySpot beamline in last several years, including scrolls found in the region around the Dead Sea, corrosion of reverse-glass paintings, as well as several old paintings containing the blue pigment Vivianite compared to the artificially aged pigment.

Since the depth resolution is around 30 μm, individual layers in a painting can be studied without taking an in-depth section of the painting. At different depths in the painting, a XANES measurement can be performed to obtain the information on the oxidation state of the pigment constituting atoms. The flexible sample mounting stage at the beamline allows mounting of the paintings as large as 1 m^2.

2.6 micro-EXAFS and XANES

Capillary optics allows the acquisition of the energy-dependent absorption spectra on selected position at the sample. Energy range is, due to low intensity, limited to 20 keV.

2.7 Visible/NIR Raman scattering

It is possible to acquire Raman spectra in combination with X-ray measurements. For this two different Raman systems are available. In-line Renishaw Raman spectrometer (in cooperation with MPIKG Golm) allows for very precise Raman spectra to be acquired, using laser excitation parallel to the X-ray beam. For the combination with XRF measurements, a smaller and faster (down to 0.1 s per spectrum) system (Ocean Optics Ventana) can be mounted where the laser excitation is illuminating the sample at the 45° with respect to the X-ray beam. Both systems provide wavelengths 532 and 785 nm.

3 Technical Data

Monochromator	Selective Si(311), Si(111), W/B_4C Multilayer
Experiment in vacuum	No
Temperature range	180 - 320 K
Detector	Several ionisation chambers and calibrated PIN Diodes, 7-channel Si(Li) energy dispersive detector (210 mm^2 area), Si-Drift energy dispersive det. (100 mm^2 area), Mar X-ray CCD area detector for scattering, Renishaw Raman spektrometer, Ocean Optics Raman Spectrometer, CCD (visible light) built in the online microscope
Manipulators	Several goniometers and translation stages, to be used depending on the sample size
Energy range	6 - 30 keV as excitation for XRF, for spectroscopy 5-25 keV
Energy band width Si111	4000 E / dE
Energy band width ML	500 E / dE
Energy band width Si311	8000 E / dE
Raman options	Parallel with X-ray beam for scattering , normal to the sample surface for fluorescence
Raman wavelength	532 and 785 nm

Table 2: Technical parameters.

4 Sample environments

Different scanning environments for different sample sizes (from several micrometer to 150 mm) are available at the beamline. Rotational units are available for both scattering and fluorescence methods. There is no vacuum environment available at the beamline, but it is possible to mount sample environments or reactors at the available 1-circle goniometer in the experimental hutch. Different experiments were successfully mounted at the station, including in-situ stretching devices, plasma chambers, laser-levitation sample holders, ultrasound levitation chambers, flow chambers…
The experimental station is situated in a small radiation protection hutch. Same sample manipulation unit and same beam conditioning devices are used for all experimental methods. Non-destructive chemical analysis is very important for the study of archaeological findings. The mySpot beamline experimental hutch is equipped with the air conditioner which is able to control the environment temperature in the range from 18 to 24 °C with precision of 1 °C, and the relative humidity in the range between 40 and 55% with precision of 1% relative humidity. The temperature and humidity sensor is positioned near the sample to achieve fast and smooth regulation of the environment. This makes possible to study the irreplaceable artifacts under the same conditions, under which they are stored in the museum providing a real destruction-free measuring method.

- Two separate XYZ sample stages (20 mm or 150 mm travel, resolution down to 0.1 μm, load up to 10 kg), sample rotation about vertical axis.
- A long distance microscope with a resolution of 2-3 μm. CCD-camera mounted on the 2Θ goniometer arm and frame grabber for image acquisition
- Independent 5-axes / 2-axes positioning systems for pinholes or capillaries for beam definition, 3-axes beam stop positioning system.
- Air condition in the hutch to minimize thermal dilatation during micro-focus experiments.
- Sample cooling for very small samples (~1 mm) is available through cryogenic stream down to -150 °C (KGW Isotherm).
- For larger samples (~1 cm) a Linkam cryo-scanning chamber is available, providing temperatures between Liquid Nitrogen and 500 °C. Only clean, non-gassing samples are accepted for heating experiments. Sample can be translated inside of the chamber using motorized slits.
- For complex user experiments, where the user-provided device has to be correlated with the X-ray or Raman experiment a multitude of triggering possibilities are given in the experimental hutch, so that fully automatized experiments can be performed for longer time.

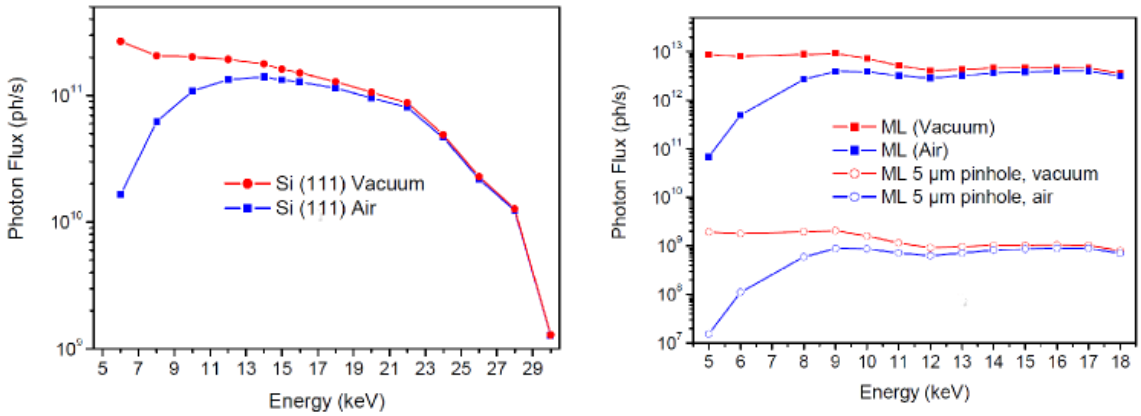

Figure 5: Photon flux Photon Flux depends on the monochromator and divergency. Image shows the flux for the Si111 and Multilayer monochromators.

Since all the devices are movable (most of them motorized) the experimental station can accommodate relatively large samples and complicated user-provided sample environments, like heating chambers,

process chambers, or mechanical testing devices for in-situ measurement.

The complete experiment is controlled from one personal computer, running Certified Scientific Software application spec. Spec is used at many scattering and fluorescence beamlines on different synchrotron sources, especially on ESRF and on Hasylab, and many experienced users are already familiar with it. The software can be used without graphical interface, by typing commands using keyboard. This provides the total control over all beamline components and detectors, and a possibility to automatize any kind of data acquisition. In this mode it is also easy to establish a communication to the user-supplied devices. Additionally, a graphical user interface is available at the beamline for standard experiments, on the basis of custom made Python programs. The graphical interface is written in cooperation between HZB, TUB, MPIKG, and ESRF. For standard experiments a partial evaluation during the experiment is possible.

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