# Structural and elemental X-ray microanalysis with synchrotron radiation in confocal geometry

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## ABSTRACT

A spectrometer for 3D structural and multielemental X-ray microanalysis with synchrotron radiation is presented in this work. It is based on the combination of the energy dispersive X-ray fluorescence and diffraction with polycapillary optics. The 3D spatial resolution was achieved by the superposition of the foci of two lenses arranged in confocal geometry. The parameters that affect the performance of the spectrometer were study in detail giving rise to a simplified calibration method for depth profile analysis. Two specific examples were included to illustrate the use of the spectrometer in order to identify their possible application fields.

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## 1. Introduction

A recent development in X-ray microanalysis is the expansion of spatial resolution into the depth with the help of a confocal set-up using X-ray optics. The foci of two lenses, one in the excitation channel and other in the detection channel, define a micro-volume for probing the sample. Fluorescence and scattered radiation, ideally, are detected only from this volume. During the last years, experiments with confocally aligned X-ray lenses have been performed at various laboratories around the world [1–5]. This setup proved to be capable to supply three-dimensional or depth-sensitive information on the elemental composition of a sample with a minimum spatial resolution of 10 μm. The usefulness of the new 3D micro-XRF method has already been shown at several applications [1–5].

The confocal setup implemented with polycapillary optics and polychromatic sources allows expanding its applications not only for elemental analysis but also for structural analysis. Effectively, the X-ray scattering produced by a continuous excitation spectrum in the probing volume can be used to obtain a diffraction pattern of the sample by means of Micro X-ray Diffraction Analysis (micro-XRD) in the Energy Dispersive (ED) configuration [6,7]. The continuous spectrum of the polychromatic source creates Laue diffraction peaks that originate from different crystallographic planes according to Bragg's condition. Then, the X-ray optics in the detection channel has to collect X-rays photons with a wide energy range. Polycapillary lenses are the ideal candidate to successfully satisfy this requirement, since they allow a broad energy bandpass.

In the energy dispersive X-ray diffraction the dispersion angle is fixed and the detected energy is scanning through the range source. It can be electronically done by an energy dispersive X-ray detector. Thus, it is possible to implement simultaneously the 3D micro-XRD and the 3D micro-XRF without the inclusion of any other additional component as an expensive goniometer or monochromator. It is a modern concept in X-ray spectrometry developed in the last few years which could be very useful for elemental and structural analysis with spatial resolution [8].

In this work confocal three-dimensional energy-dispersive micro XRD and micro-XRF was implemented using polycapillary optic. We used half lenses manufactured in our laboratory which were characterized using an experimental process described in a previous paper [9]. The lenses have low divergence in the order of milliradians allowing obtaining a good angular resolution and can efficiently focus the synchrotron beam. A characterization of the spectrometer which includes the determination of the sensitivity of the confocal setup and the lattice spatial resolution of the diffractometer is presented in this work.

## 2. Materials and methods

The experiment was carried out in the D09B-XRF beamline of the Brazilian Synchrotron Light Source (LNLS) using white beam. A silicon drift X-ray detector with 150 eV of resolution at 5.9 keV

was positioned at 44° to the photon beam on the horizontal plane. This system was mounted on a motorized XYZ stage with manual goniometers to tilt the detector. Suspended from the snout of the silicon drift detector, a fixed holder holds a half monolythic polycapillary with its optical axes centered and normal to the window of the detector. In the excitation channel a similar glass polycapillary was mounted in a special motorized gimbal. Both lenses had a focal distance of 20 mm with a focal dimension of 75 μm, a divergence of 2 mrad and a transmission efficiency of 20% for the mean energy of the excitation spectrum [9]. Samples were mounted vertically at 22° of the incident direction on a motorized XYZ sample stage with spatial resolution of 0.6 μm. Aligned ionising chambers at the entrance of the first polycapillary and behind the sample holder were used to align efficiently the excitation channel. In addition, a CCD camera was placed behind the sample holder to determine the position of the incident beam. A digital optical microscope focused on the sample was employed to distinguish details on the area excited by the incident beam. The experimental arrangement with the relevant geometrical parameters is shown in Fig. 1.

Once the polycapillary of the excitation channel was aligned, we oriented the axis of the polycapillary of the detection channel at 44° from the incident direction on the horizontal plane. Then, a silicon wafer (1 1 1) was placed in the sample holder. Using the motorized XYZ stage on the detector holder, we positioned the end of the polycapillary at 20 mm from the excitation point of the sample. Once a preliminary alignment of the setup was found, several linear scans of the probing volume through the normal direction of the foil were performed to improve the position of the polycapillary of the detection channel. For all scans, the counting live-time for each point was 10 s/step and the step size was 10 μm. The maximum of the diffraction peaks were recorded for each linear scan. They were considered as a test parameters of the quality alignment of the polycapillary. The greatest value registered for these intensities corresponds to the optimal alignment of the polycapillary. In this way the incident and emergent angles could be defined with high precision.

To determine the sensitivity of the spectrometer, we performed linear scans through the normal direction of pure foils. We used standard ultra thin foils (Micromatter) of Ti, V, Fe, Cu. ZnTe and Au with high purity (99.9%) and thickness in the order of the micrometer. For all scans, the counting live-time for each point was 40 s/step and the step size was 10 μm. As a final result, scanning curves of the XRF intensity versus depth were obtained for each element present in the set of thin films. To determine the detection limit for elemental analysis, we measured two biological tissues prepared as presses pellets. One of the samples was the reference material NIST 1577c of dried bovine liver and the second

was a dried rat liver analyzed in a previous work [10]. They were scanned in depth with a counting live-time for each point of 60 s/step and a step size of 10 μm.

## 3. Theory

### 3.1. Confocal micro-XRF

Assuming a homogeneous film of thickness $D$, the intensity of a specific X-ray fluorescence line of an element $i$ excited by a polychromatic source as a function of the normal coordinate $x$ can be written as [11]:

$$Ip_i(x) = \int_0^{E_m} \rho_i I_0(E)\, \tau_{F,i}(E) \left( \int_0^D \eta_i(E, x' - x)\, \exp(-\tilde{\mu}_i(E) x')\, dx' \right) dE \tag{1}$$

where $E_m$ is the maximum energy of the incoming photons, $I_0(E)$ is the incoming photon flux of energy $E$, $\rho_i$ is the density (in g/cm$^3$) of the $i$-element in the sample, $\tau_{F,i}$ is the production cross section (in cm$^2$/g) for the measured X-ray line of the $i$-element at energy $E$, $\eta_i(E,x)$ is the sensitivity profile of the spectrometer for the $i$-element at position $x$, and $\tilde{\mu}_i$ is the effective linear mass attenuation coefficient at energy $E$ for the $i$-element defined as follows:

$$\tilde{\mu}_i = \sum_{j=1}^{r} \rho_j \left( \frac{\mu_j(E)}{\sin(\theta_0)} + \frac{\mu_j(E_i)}{\sin(\theta_1)} \right) \tag{2}$$

where $\rho_j$ is the density of the $j$-element, $\mu_j(E)$ is the mass attenuation coefficient of the $j$-element at energy $E$, $E_i$ is the energy of the X-ray line of the $i$-element, $\theta_0$ and $\theta_1$ are the medium angle of the impinging beam and detected beam respectively.

The formula shown in Eq. (1) is the key for the quantitative multielemental analysis by fundamental parameters method. Besides of the input of emission and absorption probabilities, the calculations require the precise knowledge of the sensitivity profile of the spectrometer.

### 3.2. Confocal micro-XRD

The confocal micro-XRD combines the Energy Dispersive X-ray Diffractometry (EDXRD) with the 3D spatial resolution of the confocal setup. EDXRD is a well known method which can be implemented without complex mechanical motions of the detector or source since the diffraction angle is fixed. It takes advantage of the semiconductor X-ray detectors technology to electronically scan the scattered intensity for energy, looking for Laue diffraction peaks. These peaks originate from constructive interference in the different crystallographic planes according to Bragg's condition:

$$d = \frac{6.199}{E \sin \theta} \tag{3}$$

where $d$ is the interplanar spacing of the lattice planes in Ångstroms, $2\theta$ is the diffraction angle and $E$ is the scattered energy in keV. The full with at half maximum of a diffraction peak $\Delta E_{FWHM}$ can be taken as the minimum energy separation between two resolved diffraction peaks. Considering that the diffraction angle at the maximum of the diffraction peaks is $\theta$, then, the lattice spacing resolution of the spectrometer is related with $\Delta E_{FWHM}$ by means of the following Eq. (12):

$$\Delta d = -\frac{6.199}{E \sin \theta} \Delta E_{FWHM} \tag{4}$$

Evaluating the width of different diffraction peaks of a monocrystalline sample, it is possible to obtain directly the lattice spacing resolution of the spectrometer for different energies. Fur-
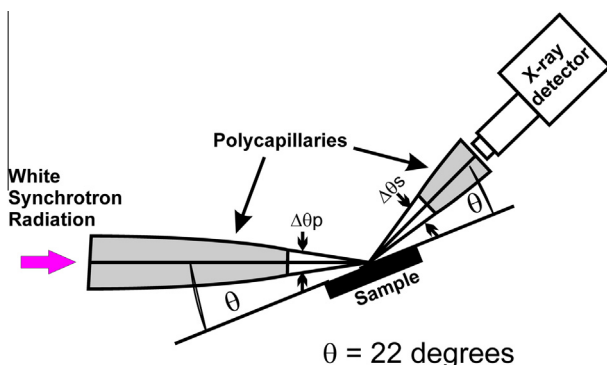


**Fig. 1.** Experimental setup of the spectrometer. The contribution to the angular resolution of the divergence of both lenses is shown.

θ = 22 degrees