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Combination of X-ray synchrotron radiation techniques to gather information for clinicians

Solenn Reguer [a,*], Cristian Mocuta [a], Dominique Thiaudière [a], Michel Daudon [b], Dominique Bazin [c]

[a] Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France
[b] Service d'Explorations Fonctionnelles, AP-HP, Hôpital Tenon, 4, rue de la Chine, 75020 Paris, France
[c] CNRS–LCMCP–UPMC, Collège de France, 11, place Marcellin-Berthelot, 75005 Paris, France

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ABSTRACT

Among the different techniques specific to synchrotron radiation, the combination of X-ray absorption spectroscopy with X-ray scattering experiments is a powerful tool to characterize samples with a capability to gather structural and electronic information at the cellular level. In the present contribution, selected examples making use of such techniques point out as well the information that one can have access to. Via the presentation of the physicochemical data, this paper focuses on displaying the information that has a significant clinical character.

1. Introduction

The possibility to obtain complementary information such as crystalline structure, elemental composition and chemical speciation using non-destructive techniques is a necessary requirement in the research proposals applied to medical investigations as metal alloys and prostheses, elasticity and probes, and trace elements and nephrotoxicity. Indeed, the samples studied, coming from human bodies' specimens, are precious, volume limited and complex. They often present a heterogeneous distribution of chemical elements. In addition the morphology and structure of crystallites (or amorphous compounds) constituting the samples are supposed to be pathology dependent. The most important objective is to determine the local environment of specific chemical elements, and particularly metal ions in such biological compounds. This is however generally a difficult task. The measurements have to be done at the micrometer scale to determine both local order and elemental distribution in the samples studied.

The purpose of the present short review is to describe the opportunities given to the medical community by the use of X-ray synchrotron radiation techniques. The intent is not to provide a comprehensive summary of all the work described in the literature but to give to clinicians useful information by concentrating on particular studies using synchrotron radiation.

The examples presented in this paper were mostly performed at the DiffAbs beamline, implemented at SOLEIL synchrotron (France). This beamline led to numerous major scientific breakthroughs in materials sciences, thanks to the available almost simultaneous combination of the following techniques: X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and X-ray Absorption Spectroscopies (XAS). As an aid toward a better description of the sample, the combination between XRD, XRF and XAS is of primary

* Corresponding author.
E-mail address: solenn.reguer@synchrotron-soleil.fr (S. Reguer).

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importance in the case of pathological calcifications in which it is thus possible to assess the environment of trace elements and get a precise structural description of the calcification. In addition, the possible access to a local probe (about a few μm) allows us to determine the distribution of the characterized compounds on the studied materials.

After a brief description of the DiffAbs beamline, recent results obtained on different kinds of biological entities including pathological calcifications will be presented [1,2]. Of note, the very first set of data collected on the SOLEIL Synchrotron was on the DiffAbs beamline and from kidney stone samples [3,4].

2. DiffAbs beamline

At SOLEIL Synchrotron, the DiffAbs beamline is located on a bending magnet. A permanent magnetic field of 1.71 T yields a critical energy of 8.6 keV and the horizontal angular aperture is 6 mrad. The beamline provides a monochromatic X-ray beam, tunable in the 3–23 keV energy range and can presently operate in two modes detailed hereafter: the standard beam mode obtained with the main optics and the microbeam mode by adding a secondary focusing optics.

The main optical system includes a monochromator located between two long mirrors (50 nm Rh-coated Si). The use of these two mirrors that collimate and focus the beam in the vertical plane results in a high rate of harmonic rejection and an increase of the energy resolution. The fixed-exit double crystal monochromator is composed of two independent Si(111) crystals. The first crystal, that is flat, allows the monochromatisation of the incident beam by setting the incident angle and thus selecting only the X-ray energy for which the Bragg law is fulfilled. The second crystal, that is mechanically bendable, restores the parallelism between the incoming and outgoing beam and provides a sagittal focusing (in the horizontal plane) of the monochromatic beam. This main optical set-up allows us to obtain a monochromatic beam size less than $300 \times 300\ \mu m^2$ (H × V, Full Width Half Maximum) at the sample position, with a photon flux of about 10^{12}–10^{13} ph s^{-1}.

The secondary optical system consists of two trapezoidal shaped orthogonally placed curved mirrors (Rh coated) under grazing incidence (in the Kirkpatrick Baez geometry): each of them is focusing the X-ray beam in one direction. The beam size obtained at the sample position is about $5 \times 5\ \mu m^2$ (H × V, FWHM) with a flux close to 10^{10} ph s^{-1}. Apart from the obtained small and intense X-ray spot, one of the great advantages of using KB focusing optics is their achromaticity, making them the optics of choice for laterally resolved spectroscopic experiments, in particular EXAFS (Extended X-Ray Absorption Fine Structure) measurements. The applications presented in the present paper and performed at DiffAbs were mainly realized using the microbeam set-up.

The main experimental instrument on the DiffAbs is a 6 + 2 circle diffractometer (Fig. 1). This high mechanical precision instrument offers an exceptional potential for all experiments on the beamline. The diffractometer consists of a goniometric system with 4 circles in the Kappa geometry for the sample orientation and a goniometric system with 2 circles, concentric with the first one, for detector positioning in the vertical and horizontal planes. This geometry corrects and improves the mechanical performance and leaves a large free volume for heavy and bulky sample environments. In addition, a motorized table for the sample position in the X-ray beam and a microscope allow us to adjust the sample on the diffractometer and perform X-ray imaging.

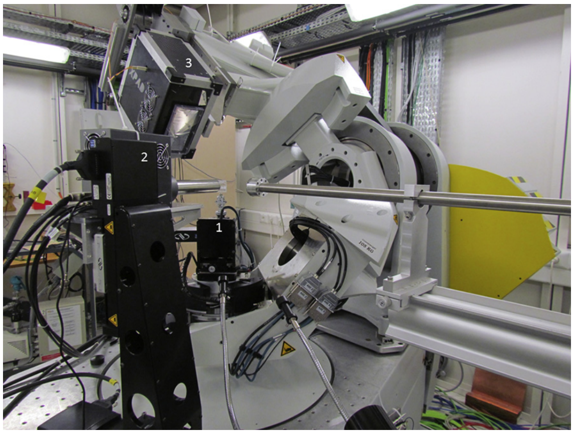

Fig. 1. The 6 + 2 circles diffractometer in Kappa Geometry on the DiffAbs beamline with (1) sample positioning using micrometric motorized tables, (2) SDD-4E detector for XRF measurements, (3) hybrid pixel area detector XPAD for XRD measurements.

Making use of the elastic scattering and the absorption processes, several synchrotron analysis techniques based on XRD or XAS and XRF spectroscopies are available on the beamline (Wide Angle X-ray Scattering, Reflectivity, Anomalous Scattering, Diffraction Anomalous Fine Structure…). All the measurements are performed on the diffractometer using different and well-adapted detectors. Moreover, all these techniques can be used in the whole 3–23 keV energy range for both standard and micro-beam modes and with various sample environments. This originality makes it the beamline of choice to study a large variety of materials as illustrated by many different topics [5–7]. In addition the coupling of XRD, XAS and XRF spectroscopies is available to correlate the information under the same experimental conditions. It means the same X-ray spot position on the sample and thus the possibility to analyze the same area of the sample under the same physico-chemical conditions.

From XAS measurements, it is possible to determine the local order, that is the environment of the probed atoms (geometry, distance of neighbors, and speciation). By XRD, long range order is accessible, allowing, for example, the determination of the crystallized phases, the orientation, and other characteristics of crystals. The combination with the microbeam scale and XRF measurements allows a good description of the structure and distribution of the different compounds constituting the samples studied.

Thanks to these characteristics, the DiffAbs beamline is thus well adapted for a great part of biological samples, though no direct access to sub-cell lateral resolution, but it gives a lateral resolution good enough for a lot of studies.