EDXD3H: The New EDXD Diffractometer at Rome Sapienza University - High Speed, High q and High Savings

EDXD3H

In frame of this project I propose to build a new Energy Dispersive X-Ray Wide Angle Diffraction Instrument. This instrument would be a successor to the existing EDXD machine and would be placed at the Chemistry Department of "La Sapienza" University of Rome. The innovative design proposed, in its horizontal geometry, would take full advantage of EDXD method potentialities, reducing drastically data acquisition time and delivering enhanced performance that turns out to be comparable with Synchrotron Wide Angle X-Ray beamlines, without requiring the access to Large-Scale Facilities. At the same time the new instrument would possess an extended sample environment portfolio to address potential scientific goals. The new design would also have the added value of low cost and time savings, together with the resulting higher environmental sustainability. Once the new instrument will be completed and fully operative, I plan to broaden the objectives of the scientific projects in the field of ionic liquids and on cultural heritage already started in my group, and meanwhile I plan to offer a scientific service to the national and international academic and industrial communities, to make them profit of the outstanding features of the new EDXD instrumentation. Besides data collection, the scientific collaboration will envisage data elaboration and interpreting model formulation, for which the new computing clusters recently developed in my group will be made available.The suggestion of a potential second panel for the review of the proposal is motivated by the strong versatility of the instrument we are planning to build. Besides the most finely detailed structural characterizations, the new EDXD machine proposed is also capable of investigating chemical (e. g. analytics) or even biophysical problems.

Extended Synopsis of the scientific proposal

X-Ray diffraction is probably the best experimental tool for structural studies of matter, since X-ray's wavelength is comparable to interatomic distances. The output of X-ray interaction with matter is a scattered intensity modulated by the interference with the sample, which is related to the Fourier Transform of the atomic structural correlations. A common X-ray scattering based approach to investigate morphology is the Angle Dispersive X-Ray diffraction (ADXD), where a scattered monochromatic beam is monitored as a function of a scattering angle. In contrast, Energy Dispersive X-ray Diffraction uses a continuous **polychromatic** X-ray beam, while a solid state detector (germanium) is placed at a fixed angle. The modulus of a scattering vector **q** is related to the incident beam energy **E**and to the diffraction angle **θ** by the equation

[1] $\mathbf{q = (4\pi/hc)E\ sin\theta}$

where **E** is the energy of the incoming beam, and **θ** is the scattering angle. Therefore, the **q** range available in a measured spectrum depends on the choice of the angle **θ** and on the energetic spectral range of the source. ADXD is limited in its accessible **q** region by the relationship $\mathbf{sin\theta=1}$ (since E is fixed). On the other hand, in the EDXD method, at a given scattering angle, the maximum **qmax** value accessible is determined by the highest energy component of the white beam. Accordingly, using a power supply voltage of 50kV, the maximum energy is 50 keV. At an angle $\theta=40°$, the theoretical **qmax**is about 30 Å-1, although the actual **q** range may be reduced by the strong X-ray absorption and consequently low diffracted intensity near the upper limit of the spectrum. **However, we stress that measurements collected at just a limited number of scattering angles are sufficient to account for the description of the whole structural pattern over a wide momentum transfer range (and hence wide spatial range).**

The typical beam used in the ADXD technique is based on the fluorescence lines K∝ of heavy elements, such as Cu or Mo. In contrast, the beam used in EDXD is the Bremsstrahlung radiation that is produced by the deceleration of fast electrons impinging on a W target. The intensity concentrated in fluorescence lines is at least one order of magnitude lower than the intensity distributed in the continuous spectrum used by EDXD. Moreover, in the EDXD technique data are collected simultaneously for different **q** values. These two features lead to considerably shorter collection times as compared to ADXD techniques, thus making the EDXD method mode efficient for

structural investigations of liquid and amorphous systems, soft matter and other samples, where a high q resolution is not required.The EDXD instrument currently available at the Rome University (Italian Patent n° 01261484) makes use of a standard Seyfert Tungsten tube operating at 50 kV and 40 mA as X-ray source. Its Bremsstrahlung radiation is used as a white beam, whereas the detecting system is composed of an EGG liquid nitrogen-cooled ultrapure Ge solid state detector. The diffractometer operates in vertical θ-θ geometry. It is equipped with step motors and a collimation system so that both the X-ray tube and the detector can rotate around their common center in which the sample is placed. All details can be found in [R. Caminiti, V. Rossi Albertini, Int. Rev. Phys. Chem. 18, 2, 1999 and M. Carbone, R. Caminiti, C. Sadun, J. Mater. Chem. 6 (10), 1709-1716, 1996]
Presently the main drawback of the technique is the relatively long data acquisition time necessary to obtain high statistics in the q range 0.1-19 Å-1 (about 36/48 hours).

In this view, my collaborator and I elaborated a novel design for a EDXD machine that will lead to a marked increase of the intensity, to shorter acquisition times and to the access to a large momentum transfer range, thus making the instrument more flexible in achieving best (and new) results.

Basic Design

The proposed instrument would operate in 0-2θ**horizontal planar geometry (see Fig. 1). In this way a X-ray generator tube will be fixed at 0 angle, while detectors would move along a horizontal platform to different 2θ values. Four detectors will be used simultaneously for data collection, all capable of being moved along the horizontal platform. The first detector (DET1) would be positioned at high angle (2θ above 60°), covering the high q range (approximately 6-25 Å-1 using 50 kV). A second detector (DET2) would operate on low-to-middle scattering angles (2θ 1-30°), covering a low and intermediate range of q. DET3 would be placed in the central region (0-6 2θ in the “negative” half-plane), while DET4 would be placed at high angle, symmetrical to DET1. In this way, it will be possible to perform twin measurements at the same angle (absolute value), obtaining twice as much counts for the spectral region where the intensity is lower (high angle).**

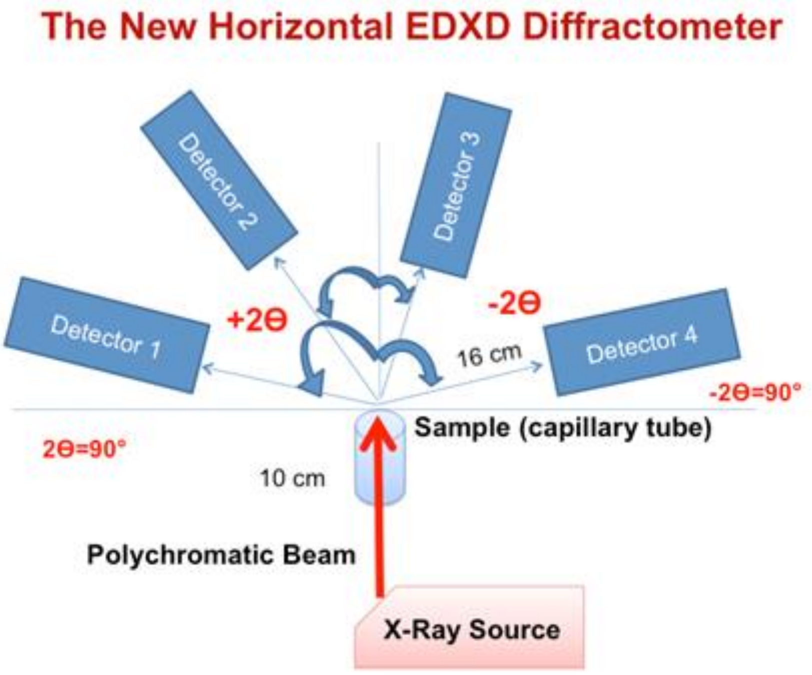

Fig 1: The new horizontal EDXD instrument proposed in this project

Detector arms would be moved manually, if necessary, and will be mechanically fixed at predefined 2θ values. This concept leads to a major cost reduction (since no motors are required). More

importantly, the definition of the diffraction angle 2θ becomes precise, while in the present vertical instrument we have to deal with an uncertainty Δθ in the angle and consequently with a Δ**q** in the scattering variable. A quartz capillary tube would be used as standard sample holder.
The full simultaneous movability of the detectors could actually be hindered in some cases, owing to the contact between the detector heads; in any case, the possibility of measuring additional angles is granted. This could be important in some cases, for instance, when the sample contains elements which have fluorescence lines falling amid the bremsstrahlung, so that the usable portion of the radiation is beyond the line [see, e. g. M. Carbone, L. Gontrani, AIP Conf. Proc. 1603, 47 (2014); http://dx.doi.org/10.1063/1.4883041].

As mentioned, this novel design will lead to:

- **Increase of intensity**

The proposed 0:2θ horizontal planar geometry allows to locate the Tungsten X-ray source very close to the sample stage, increasing the incoming beam intensity, since the latter is inversely proportional to the square of the distance, according to the relation

[2] I0=Ibeam/R2

where I0 is the intensity irradiating the sample, while Ibeam is the beam intensity generated by the X-ray tube, and R is the distance between source and sample. Changing it from the current 20 cm to 10 cm leads to a four-fold intensity increase. Such generator positioning in the present instrument would be impossible, since the θ:θ geometry requires the symmetry of “generator-sample” and “sample-detector” distances.

- **Shorter acquisition times**

Since the new instrument operates with 4 detectors, the diffracted intensity will be collected at different 2θ simultaneously. As the scattering signal at high **q** is low, the acquisition time will be defined by the statistics on the DET1 and DET4 only. The present EDXD instrument operates with a single detector, and the average acquisition time necessary to span all the scattering variable range, that in the current geometry with 50kV voltage goes from 0.06 Å^{1} up to 25 Å^{1}, is 36/48 hours (3-4 days). The largest part (24 hours) of this period is dedicated to collect the pattern at high angle. Due to intensity increase of the incoming beam, and to the use of two symmetrical detectors (DET1 and DET4, see above), that will double the number of counts for the same high angle, which is characterized by an intrinsic low intensity scattering (see Eq. 1), the average experimental time to collect the whole spectrum could be shortened up to 3 hours only. Such a short overall acquisition time, in combination with the relatively low energy of the beam, would result in a global low X-Ray dose (operation power = 50 kV * 40 mA = 2000 Watt) and allow us to investigate biological samples very sensitive to radiation damage [e. g. G. Caracciolo, D. Pozzi, R. Caminiti, C. Marianecci, S. Moglioni, M. Carafa, Chem. Phys. Lett., 463, 307, 2008].

- **Larger momentum transfer range**

The experimentally accessible **q** range is defined by Emax of the incoming beam and the maximum 2θmax value (see Eq 1). A 50 kV power supply voltage produces a beam with Emax equal to 50 keV. Accordingly, at 2θ=90° we would collect the structural pattern up to 36 Å-1. The currently used geometry (vertical θ:θ) implies a mechanical limitation on the detector position, making very high angles (above 60°) inaccessible. Further extension of momentum transfer range could be achieved applying higher voltage on the X-ray generator, provided the radiation sensitivity of the sample allows it. A large momentum transfer could prove very important to perform PDF studies (e. g. for amorphous systems).

- **Further possibilities**

The intensity gain and widening of accessible momentum transfer range will provide new enhanced experimental potentialities. Under the new proposed conditions, very short scans would be accessible, thus paving the way for in situ and kinetic studies. Parallel data acquisition at different angles would make the instrument very flexible to the scientific goals. While low q (<1 Å^{1}) will be collected at low angle (detector 3) in short times, the q-range above 1 Å^{1} (to more than 20 Å^{1}) will be covered by the other detectors simultaneously, providing information about high resolution Pair Distribution Function (PDF, P(r)). Moreover, very small samples amounts could be used, if required (this is often the case for very specific “unique” samples).

Summarizing, the short acquisition times coupled with the large momentum transfer accessible and to its complete flexibility render our project a smaller, cheaper and competitive alternative to Large-Scale Facilities (Syncrotron) for the solution of a large variety of physical and chemical problems. This appealing new possibility of performing high-level X-Ray diffraction experiments with laboratory devices has received a widespread interest in the scientific and industrial community, as indicated by the numerous expression of interest received by different physics or chemistry departments in Italy (12) and Europe (6) that would find the proposed instrument very suitable to satisfy their research needs.

As an example, we report an excerpt from the support letter of Prof. Edward Castner, (Rutgers University, USA, Associate Editor of J. Chem. Phys):

“While it will continue to be desirable to make some measurements at synchrotrons, the availability of new EDXD instrument will make even more detailed investigations of liquids possible without the wait and expense of travel to synchrotrons. The broad range of scattering vectors made available by the multiplex acquisition of the X-ray scattering of a broadband X-ray beam will permit rapid data acquisition, and facilitate use of samples where the temperature and pressure can be systematically varied. I wish you rapid success in obtaining the funding to complete an EDXD instrument, and I look forward to fruitful collaborations with your group in the future.”

In the wake of this interest, after the necessary period to fully set up all the new instrumentation (estimated time: 6 months – one year), throughout this project we plan to offer to the international academic and industrial community (from Europe and abroad) a scientific service for all the issues that can be studied with EDXD, ranging from material science to the structure of molecular or ionic liquids, as well as amorphous solids and nanomaterials, etc. The collaboration would include the preliminary assessment of the problem and the full management of the diffraction experiment, as well as the data processing necessary to obtain the final diffraction patterns (as Diffracted Intensity, Structure Function, Total Radial Distribution Function, PDF, etc).