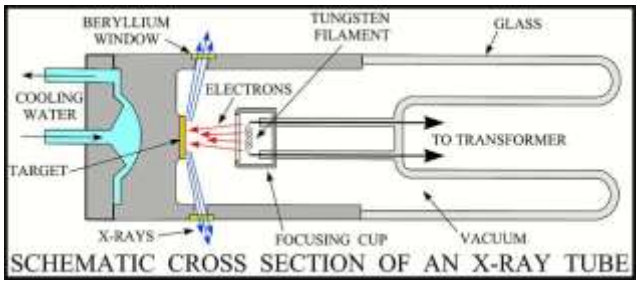
Seminar by Prof. Ruggero Caminiti

EDXD_3H

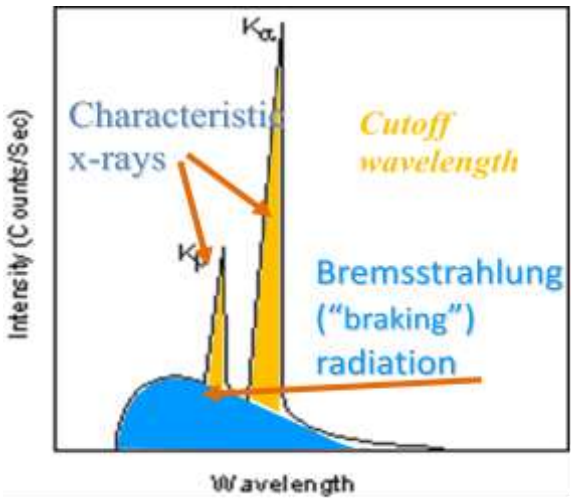
A DAY OF INNOVATION

Monday, February 29th, 2016,11 am
Chemistry Department – Cannizzaro Building
Room "La Ginestra",.

SAPIENZA
UNIVERSITÀ DI ROMA



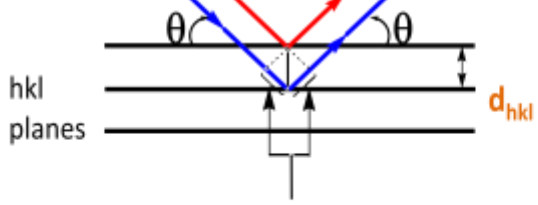
SCHEMATIC CROSS SECTION OF AN X-RAY TUBE



Bragg's Law

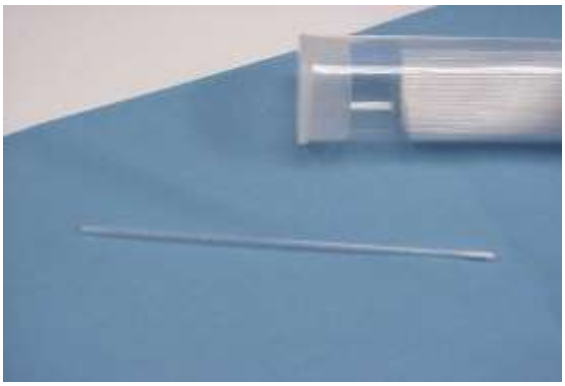
Wavelength= λ

$\lambda = 2d_{hkl} \sin \theta_{hkl}$

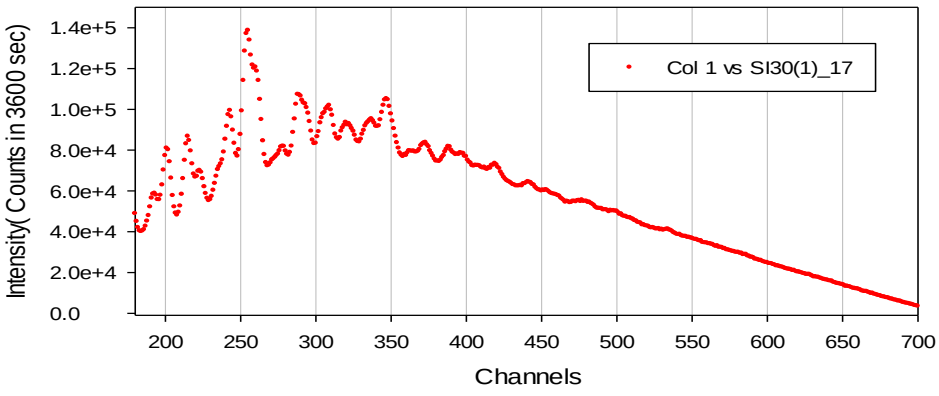


$2d_{hkl} \sin \theta_{hkl} = n\lambda$

$$q = \frac{4\pi \sin\theta}{\lambda} = k\,E \sin\theta$$



DETECTOR 1
TETA 30
Si powder (Standard)



A NEW ENERGY-DISPERSIVE X-RAY DIFFRACTOMETER FOR THE STUDY OF LIQUID AND NANOSTRUCTURED SYSTEM STRUCTURAL CHARACTERIZATION OF NEW MATERIALS FOR APPLIED SCIENCES

The first prototype of laboratory Energy-Dispersive Diffractometer was built and patented by my research group about twenty years ago [1,2]. In the following years, our EDXD allowed to study a large number of liquid and low-crystallinity solid samples, with very short measuring time (about one tenth of the time required to gain a full structural pattern with the traditional angular-scanning instruments)[3]. It was thus possible to study systems variable with time, whose transformation kinetics had a short time duration, up to about ten minutes [4]. In particular cases, like the study of hydration/dehydration of lipid multi-layers supported on silicon, that are characterized by very intense diffraction peaks, scattering patterns could be collected every second. This allowed to follow processes lasting 100 seconds in real time [5].

Two years ago, owing to the new and every day urgent machine-time requirements, we conceived a second generation instrument that can yield the same results in one tenth of the original time.

This has been made possible by "**re-thinking**" the diffractometer and its geometry, and by a massive use of the devices available:

1) X-Ray source

2) Germanium solid-state detectors (ORTEC-AMETEK)

The 36-hour time necessary to perform a high-statistics structural measurement with the first EDXD machine nowadays, will drop to about three hours with the new prototype.

The energy and money savings are REMARKABLE and EVIDENT

The technical details of the project are:

1) **Very compact instrument configuration**
2) **Use of 0-2teta geometry**
3) **Cylindric sample-holder**
4) **Trasmission measurements**
5) **Use of three Germanium solid-state detectors placed at different angles, that collect the radiation diffracted by the sample in parallel**

The white radiation employed in EDXD is generated by a single Tungsten X-Ray lamp. The data elaboration software, coded 25 years ago by myself, was updated to account for the contemporary use of three detectors. One of the new themes that will be investigated in the immediate future is the large-angle diffraction of highly concentrated protein solutions (60 mg/mL); in the next three-year period the current project about **the structure of ionic liquids [6-10] will be extended to include new-generation liquids for electrochemistry and for cellulose extraction from algae**

References

[1] R. Caminiti, C. Sadun, V. Rossi Albertini, R. Felici, F. Cilloco**, Brevetto Diffrattometro RM 01261484, 1993**

[2] R. Caminiti, V. Rossi Albertini, **International Reviews in Physical Chemistry** (**1999**) 18(2) 263-299

[3] **http://webcaminiti.chem.uniroma1.it**

[4] R. Caminiti et al., ***J. of Macromol Sciences***: Part B, Physics (**2006**) 45(6), 1005

[5] R. Caminiti et al., ***Chem. Phys. Letters*** **(2005)** 414 (4), 456

[6] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, D. Xiao, L. G Hines Jr, R. A. Bartsch, E. L. Quitevis, N. Plechkova, K. R. Seddon, **Journal of Physics: Condensed Matter** (**2009**) 21(42) 424121

[7] E. Bodo, L. Gontrani, R. Caminiti, N. V Plechkova, K. R. Seddon, A. Triolo,**The Journal of Physical Chemistry B** (**2010**) 114(49) 16398-16407

[8] A. Triolo, O. Russina, R. Caminiti, H. Shirota, H.Y. Lee, C.S. Santos, N.S. Murthy, E.W. Castner**Chemical Communications (2012)** 48(41) 4959-4961

[9] M. Macchiagodena, L. Gontrani, F. Ramondo, A. Triolo, R. Caminiti,**The Journal of Chemical Physics (2011)** 134(11) 114521

[10] S. De Santis, G. Masci, F. Casciotta, R. Caminiti, E. Scarpellini, M. Campetella, L. Gontrani, **Physical Chemistry Chemical Physics (2015)** 17(32) 20687-20698

Prof Ruggero Caminiti

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Marco Petruccetti(technician),form I.N.F.N., that constructed and assembled all the mechanical parts needed by**E.D.X.D. 3H** diffractometer

Co. Met. Art (Menta e figli) that built the box that houses the diffractometer

Dr. **Vittorio Moroni** , Eng. **Antonio Colucci** and **Davide Sacchi** from Ortec –Ametek that gave valuable support to buy the three detectors, supplied by X-cooler and electronic equipment

To Colleagues, chemists, physicists and geologists who, sharing with me their research projects, have made possible the reaching of high level positions in the field of **Ionic Liquids** by my research group:

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And to all my Colleagues chemists, physicists, biologists Italian and foreigner that have used out instrument for their research projects in these years

A SPECIAL AND GRATEFUL THANK TO PROF. ALDO LA GINESTRA AND PROF. FRANCESCO PAOLO RICCI WHO IN 1988 BELIEVED IN MY IDEA AND SUPPORTED THE CONSTRUCTION OF THE FIRST EDXD DIFFRACTOMETER

EDXD_3H
The New EDXD Diffractometer at Rome Sapienza University
High Speed, High q and High Savings

A new Energy Dispersive X-Ray Wide Angle Diffraction Instrument is the object of this project. 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 fully operative, the scientific objectives will be broadened to include, for instance, ionic liquids, electrochemistry and cultural heritage studies, already started in the research group, and meanwhile a scientific service to the national and international academic and industrial communities will be offered, 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 the group will be made available. The new EDXD machine proposed is not limited to the most finely detailed structural characterizations, but it is also capable of investigating chemical (e. g. analytics) or even biophysical problems, proving its very high versatility.

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 Eand to the diffraction angle θ by the equation

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

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** to 4π/hcE, since the maximum angle is 90° and E is fixed. On the other hand, in the EDXD method, at a given scattering angle, the maximum **q**(max) 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

θ=40°, the theoretical **q**(max) 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 Seifert 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 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 0-2θhorizontal 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. Three 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 (2θ6-20°), covering a low and intermediate range of **q**. DET3 would be placed in the central region (0-8 2θ) in the “negative” half-plane

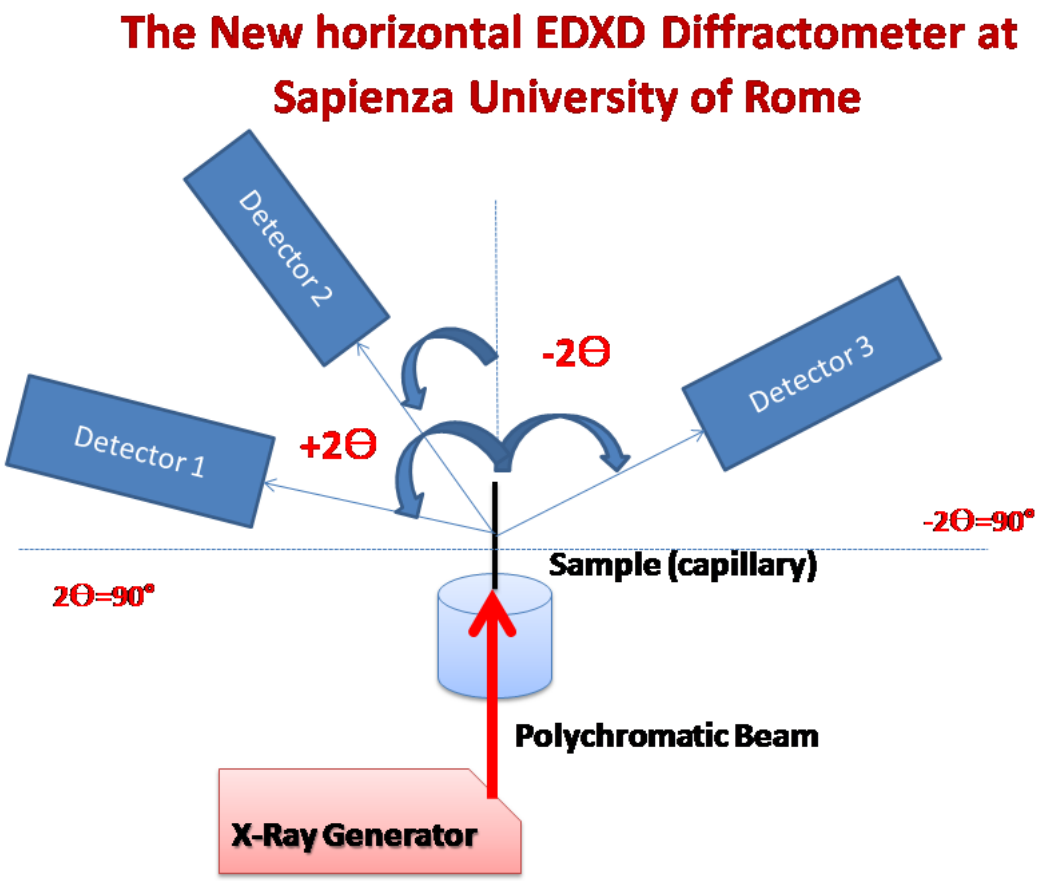


Fig 1: The new horizontal EDXD instrument proposed in this project

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

$$I(sample)=I(0)/R^2 \qquad [2]$$

where I(sample) is the intensity irradiating the sample, while I(0) 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 3 detectors, the diffracted intensity will be collected at different 2θ simultaneously. 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 50 kV voltage goes from 0.06 $Å^{-1}$ up to 20 $Å^{-1}$, is 36/48 hours (1-2 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, 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 E(max) of the incoming beam and the maximum 2θ (max) value (see Eq 1). A 50 kV power supply voltage produces a beam with E(max) equal to 50 keV. Accordingly, at 2θ=90° we would collect the structural pattern up to 36 $Å^{-1}$. The previously 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.

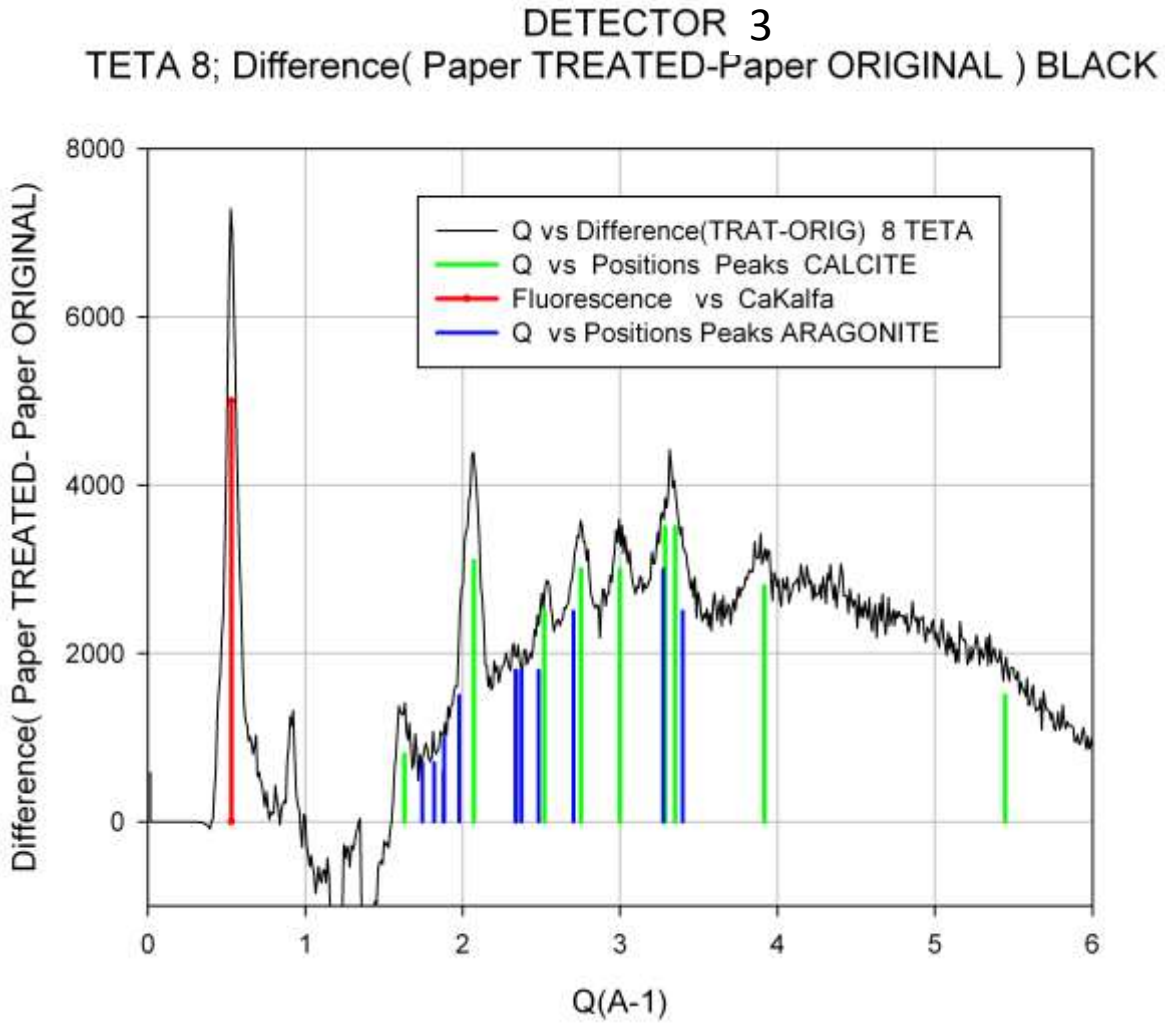
As an example, we report an excerpt from the support letter of Prof. Edward Castner, (Rutgers University, USA, Associate Editor of J. Chem. Phys):

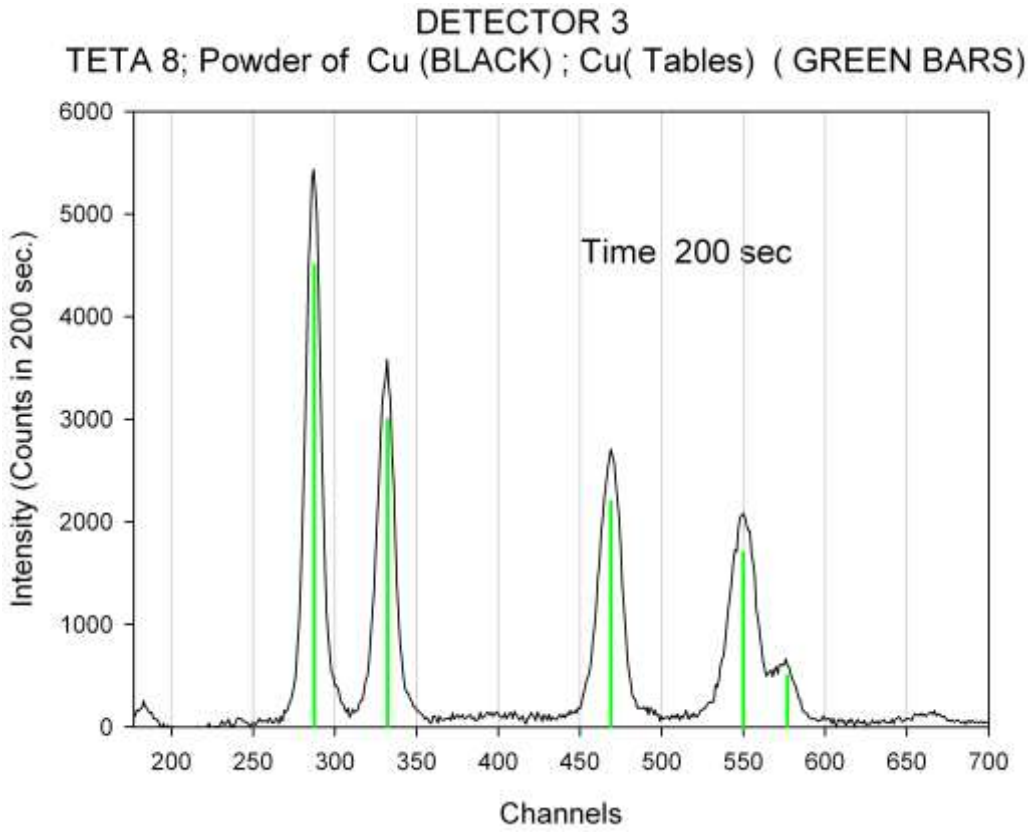
"*While it will continue to be desirable to make some measurements at synchrotrons, the availability of new EDXD instrument will make even more detailed investigations of liquids possible without the wait and expense of travel to synchrotrons. The broad range of scattering vectors made available by the 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*."

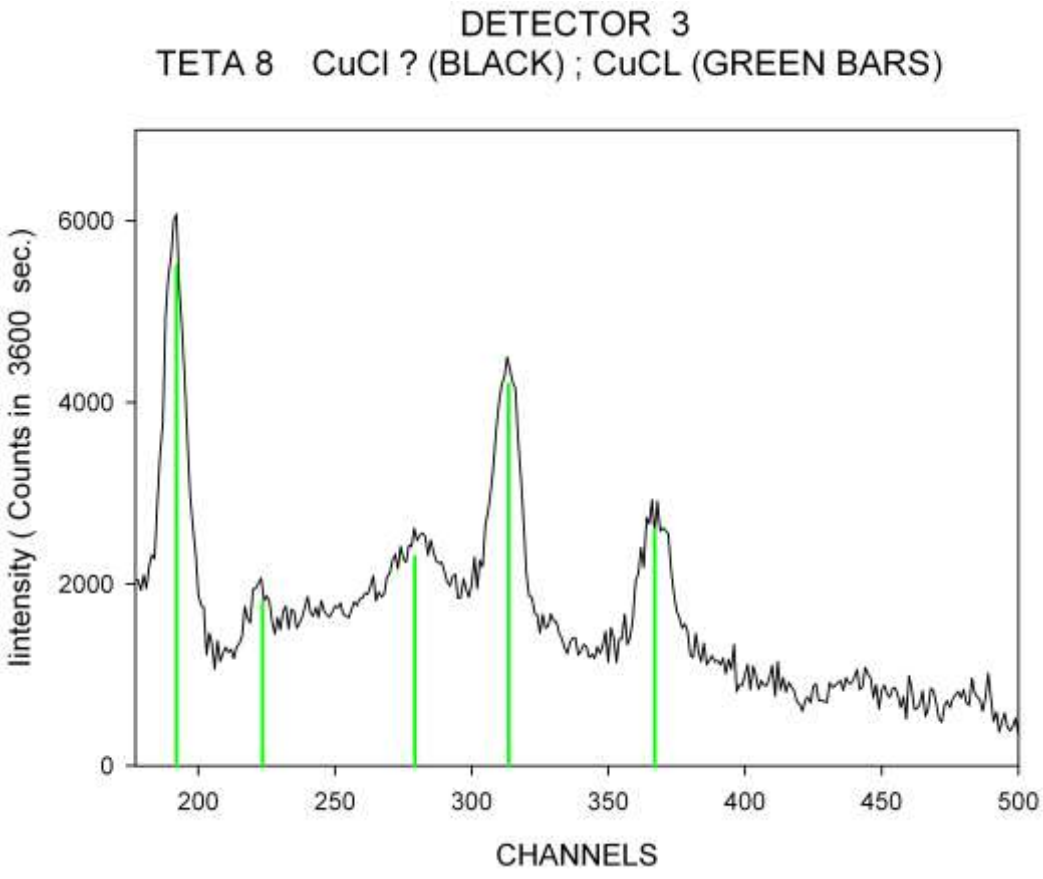
In the wake of this interest, after the necessary period to fully set up all the new instrumentation (estimated time: 6 months – one year), throughout this project we plan to offer to the international academic and industrial community (from Europe and abroad) a scientific service for all the issues 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).

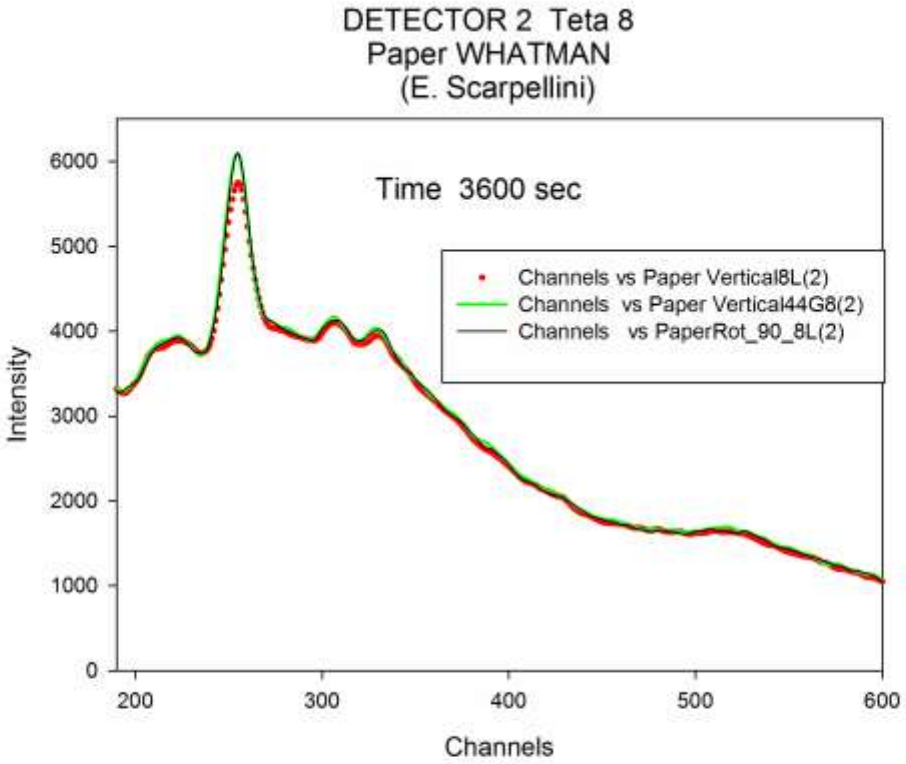
Applications

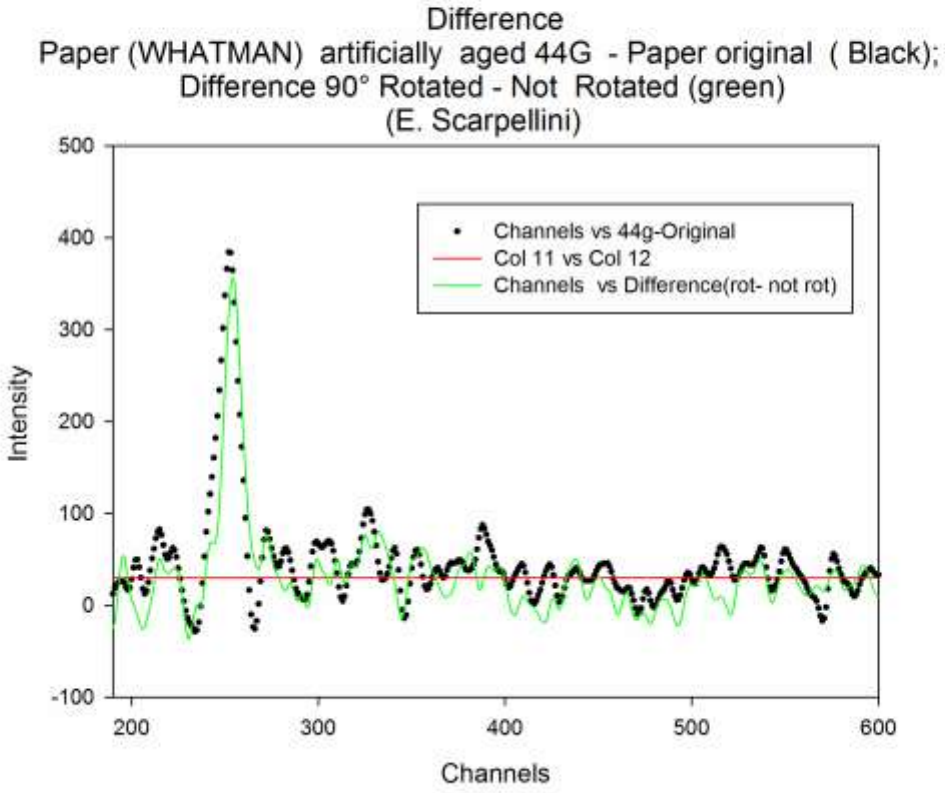
(Prof. Luigi Campanella)

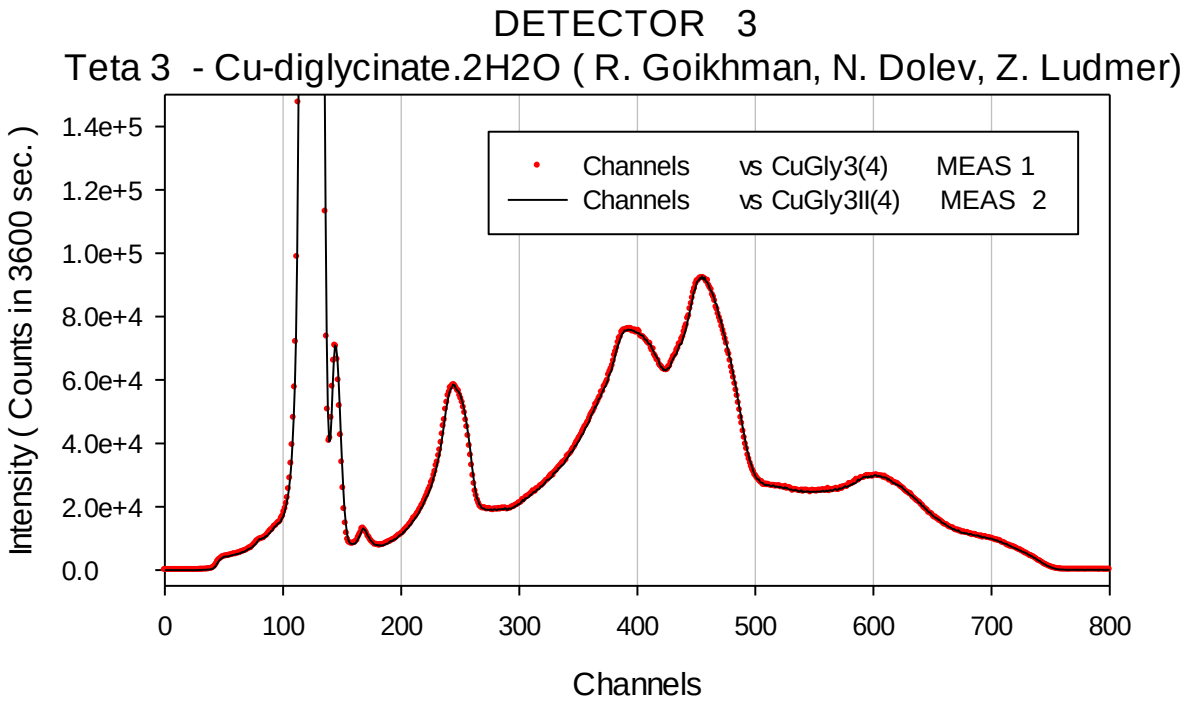


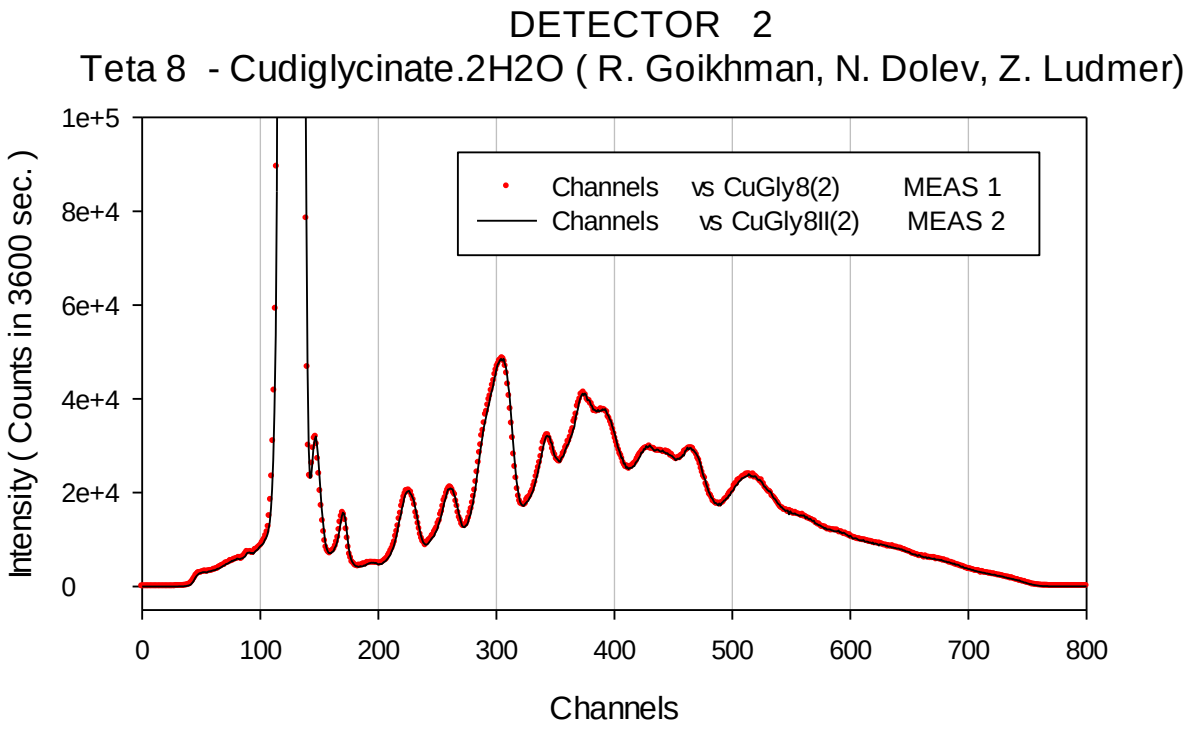

DETECTOR 3
TETA 8; Powder of Cu (BLACK) ; Cu(Tables) (GREEN BARS)
Time 200 sec
Intensity (Counts in 200 sec.)
Channels
0
1000
2000
3000
4000
5000
6000
200
250
300
350
400
450
500
550
600
650
700


DETECTOR 3
TETA 8 CuCl ? (BLACK) ; CuCL (GREEN BARS)
Iintensity (Counts in 3600 sec.)
CHANNELS
0
2000
4000
6000
200
250
300
350
400
450
500


DETECTOR 2 Teta 8
Paper WHATMAN
(E. Scarpellini)
Time 3600 sec
Channels vs Paper Vertical8L(2)
Channels vs Paper Vertical44G8(2)
Channels vs PaperRot_90_8L(2)
Intensity
Channels
0
1000
2000
3000
4000
5000
6000
200
300
400
500
600

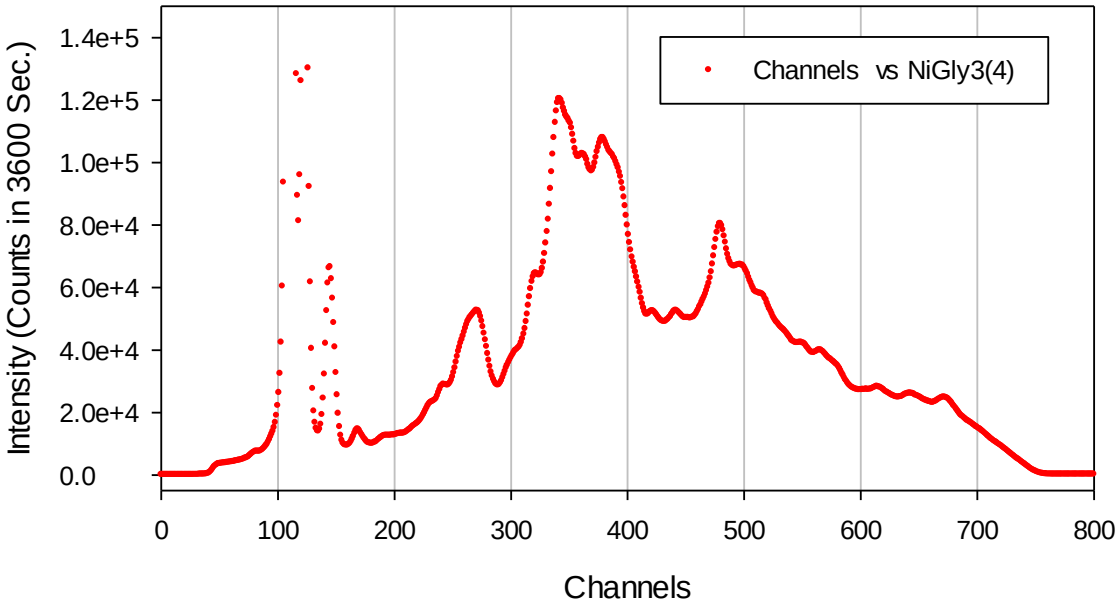

Difference
Paper (WHATMAN) artificially aged 44G - Paper original (Black);
Difference 90° Rotated - Not Rotated (green)
(E. Scarpellini)
Channels vs 44g-Original
Col 11 vs Col 12
Channels vs Difference(rot- not rot)
Intensity
Channels
-100
0
100
200
300
400
500
200
300
400
500
600


DETECTOR 3
Teta 3 - Cu-diglycinate.2H2O (R. Goikhman, N. Dolev, Z. Ludmer)
Intensity (Counts in 3600 sec.)
1.4e+5
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
Channels vs CuGly3(4) MEAS 1
Channels vs CuGly3II(4) MEAS 2
0
100
200
300
400
500
600
700
800
Channels


DETECTOR 2
Teta 8 - Cudiglycinate.2H2O (R. Goikhman, N. Dolev, Z. Ludmer)
Intensity (Counts in 3600 sec.)
1e+5
8e+4
6e+4
4e+4
2e+4
0
Channels vs CuGly8(2) MEAS 1
Channels vs CuGly8II(2) MEAS 2
0
100
200
300
400
500
600
700
800
Channels

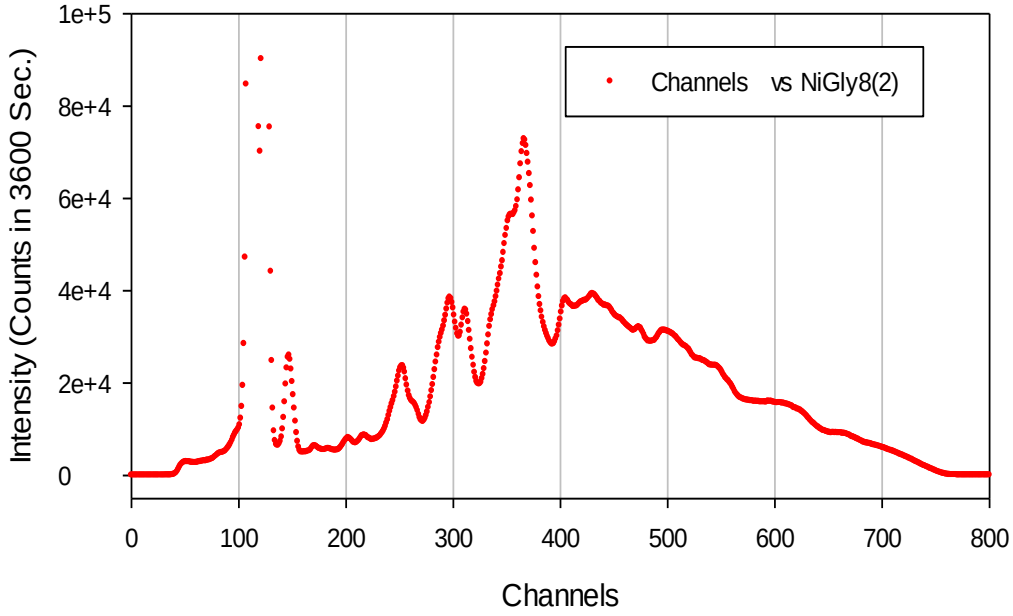
DETECTOR 3

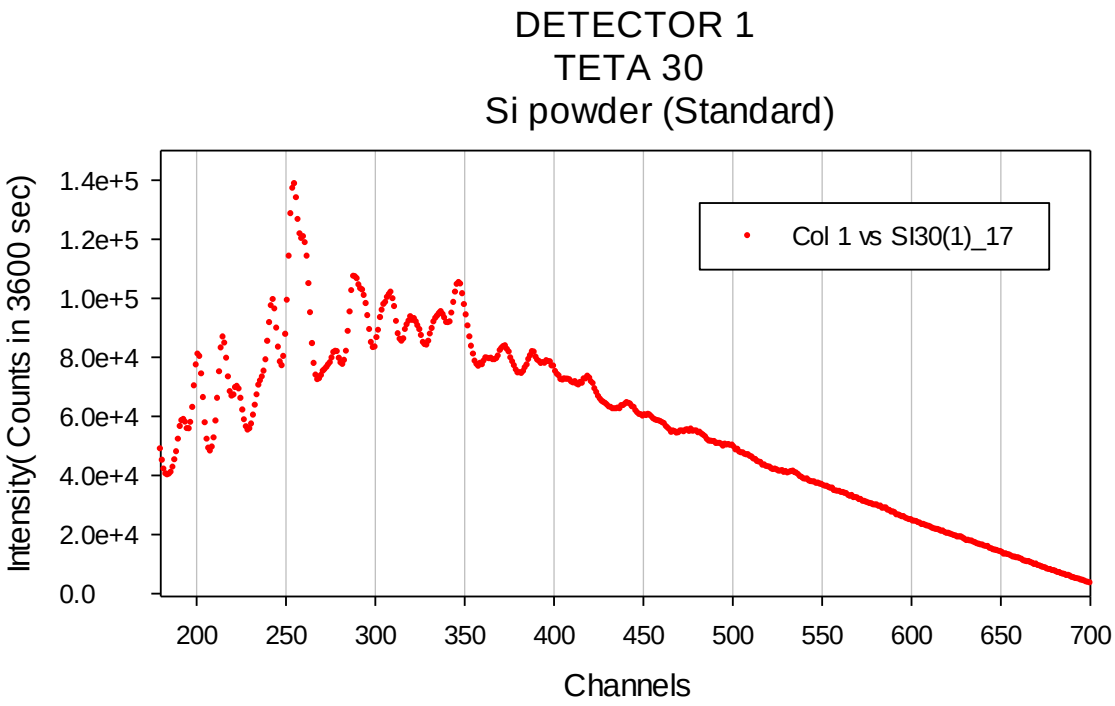
Teta 3 - Ni-diglycinate.4H2O (R. Goikhman, N. Dolev, Z. Ludmer)

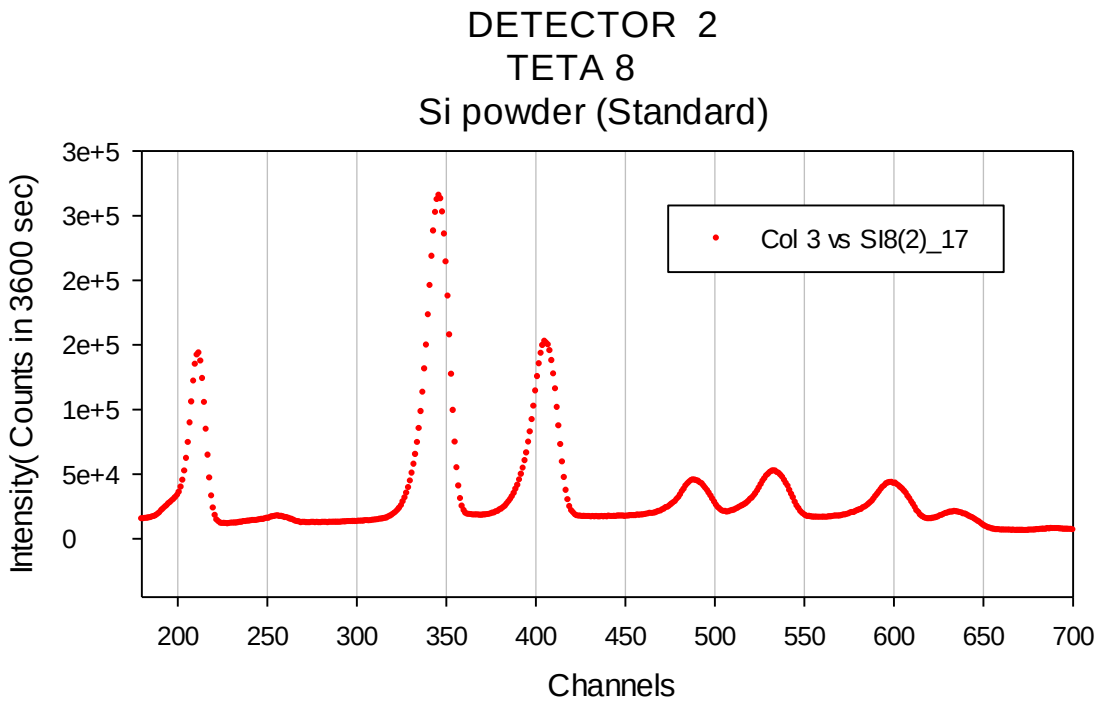


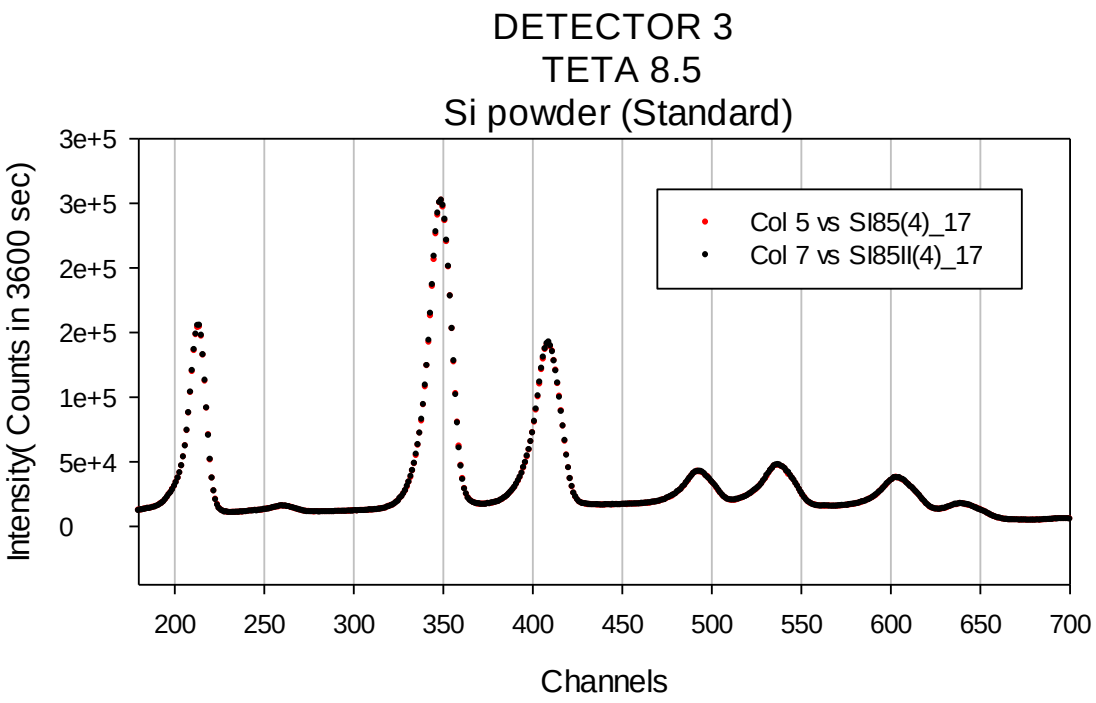
DETECTOR 2

Teta 8 - Ni-diglycinate.4H2O (R. Goikhman, N. Dolev, Z. Ludmer)

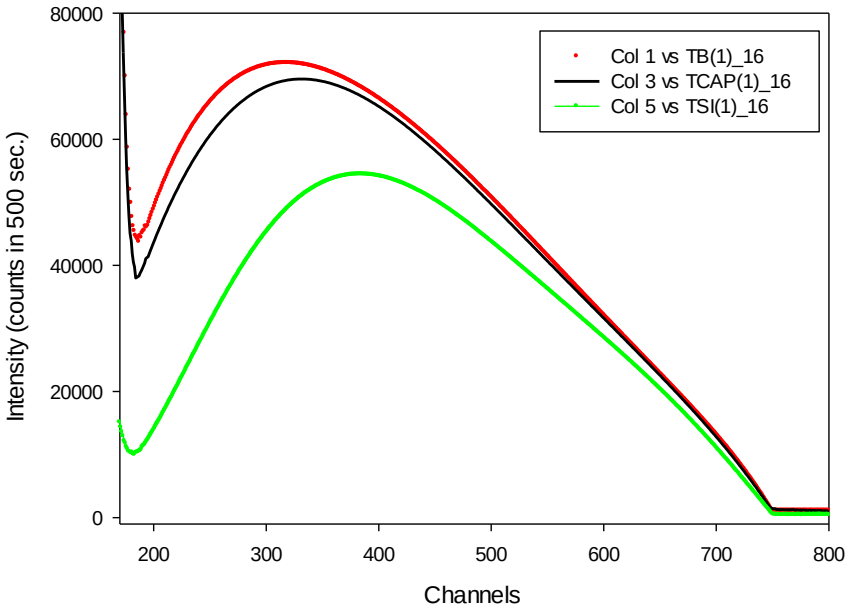


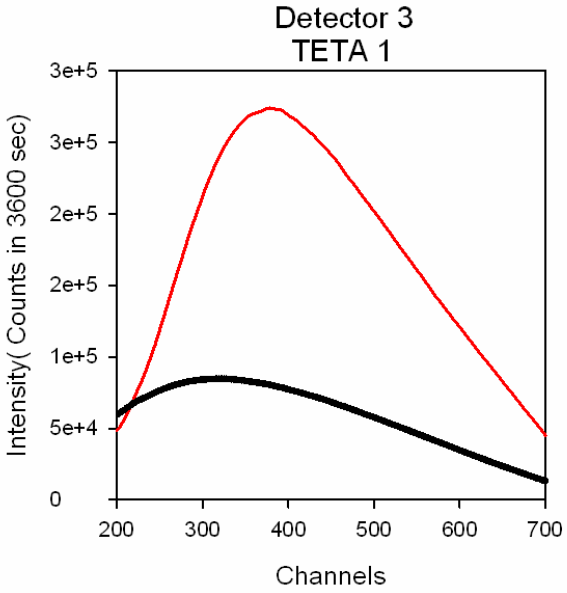

DETECTOR 1
TETA 30
Si powder (Standard)
Intensity(Counts in 3600 sec)
1.4e+5
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
Col 1 vs SI30(1)_17
200
250
300
350
400
450
500
550
600
650
700
Channels


DETECTOR 2
TETA 8
Si powder (Standard)
Intensity(Counts in 3600 sec)
3e+5
3e+5
2e+5
2e+5
1e+5
5e+4
0
Col 3 vs SI8(2)_17
200
250
300
350
400
450
500
550
600
650
700
Channels



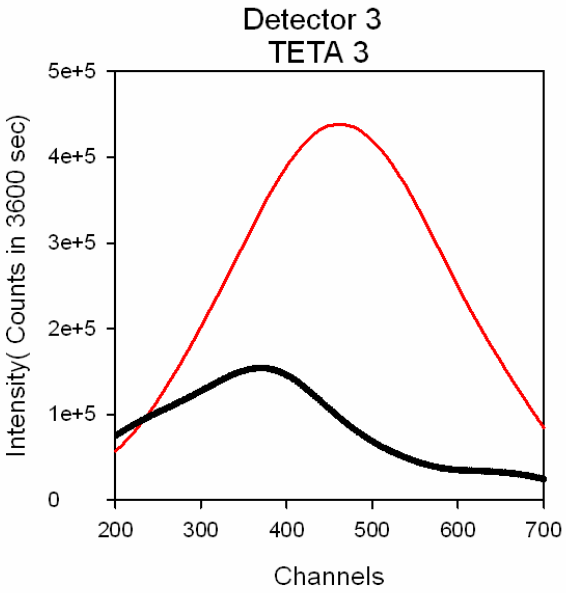
Source (RED), TRASMISSION CAPILLARY(BLACK)
TRANSMISSION Si powder (GREEN)
SLITS 0.1 mm * 0.2 mm after Source
0.1 mm * 0.2 mm In front of Detector
POWER 50kV*10mA

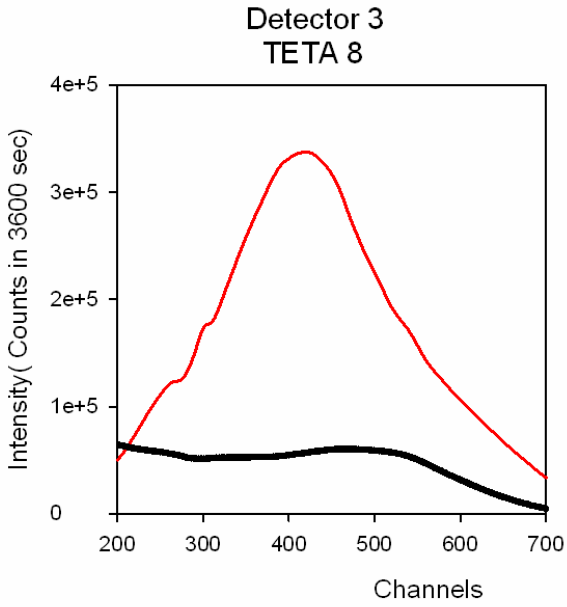




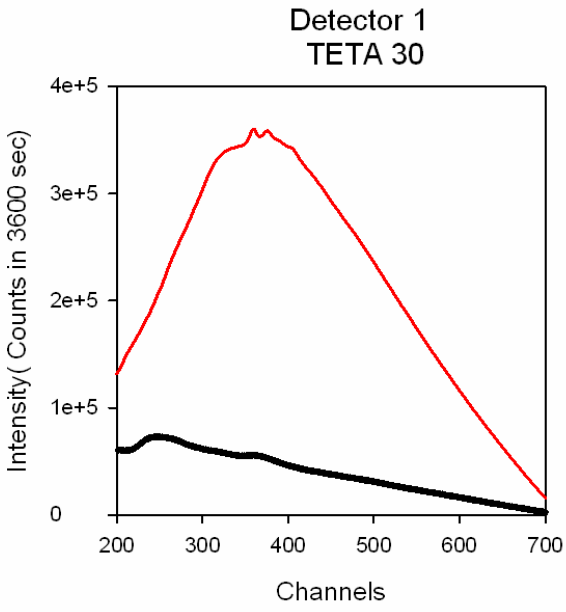
(M. Pasquali ; F. Scaramuzzu)
(S.B.A.I.)

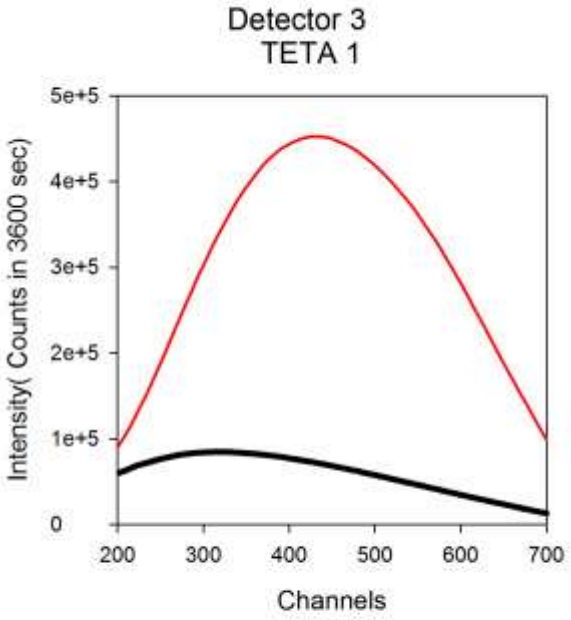
TiO2Amorphous(Red);
Capillary Tube(Black)





TiO2Amorphous(Red);
Capillary Tube(Black)





(S. Brutti , Univ. Potenza)

PYR14TFSI(Red); Capillary Tube(Black)