Modern developments of the powder diffraction technique have allowed the investigation of systems with large unit cells such as proteins [1]. Protein powder specimens consist of a large number of randomly oriented diffracting micro-crystals. These micro-crystals are usually formed rapidly by batch crystallization. Frequently, the resolution and quality of the data are limited mainly by rapid deterioration of the protein crystal structure during exposure to the intense synchrotron X-ray beam. In a typical single crystal diffraction experiment radiation damage can be minimized by collecting diffraction data under cryocooled conditions (typically 100K) which requires the addition of a cryoprotecting agent to the protein sample to prevent freezing of the mother liquor. In this study, we succeeded in obtaining various cryocooled samples of human insulin at 100K avoiding ice formation. Powder diffraction data were collected at both room temperature and under cryocooled conditions (ID31, ESRF, Grenoble, France). As expected both the cryoprotectant and the sample container have a remarkable impact on the data quality. Significant variation of the lattice parameters and peak widths with the type and concentration of cryoprotecting agent has already been observed and will be presented for the case of insulin. Preliminary data interpretation correlating these changes with the structural and microstructural characteristics of the systems under study will be shown.

[1] Margiolaki, I. & Wight, J. P. *Acta Cryst.*, **2008**. A64, 169-180

Keywords: proteins; powder diffraction; cryocooling

FA5-MS01-P12

Two Quinoline Zirconium Phosphate Structures Solved Using Powder Charge Flipping. Dubravka Sisak[a], Christian Baerlocher[a], Lynne McCusker[a], Lei Liu[b],Jinxiang Dong[b]. *[a]ETH Zurich, Laboratory of crystallography, Zurich, Switzerland.[b]Taiyuan University of Technology, Taiyuan, Shanxi, China.*
E-mail: dsisak@mat.ethz.ch

Two novel zirconium phosphate compounds with the chemical formulae $|(C_9H_8N)_4(H_2O)_4|[Zr_8P_{12}O_{40}(OH)_8F_8]$ (ZrPOF-Q1) and $|(C_9H_8N)_2|[Zr_2P_2O_4(OH)_2F_4]$ (ZrPOF-Q2) were synthesized hydrothermally in the HF-ZrO_2-P_2O_5-quinoline-H_2O system. Because they could only be obtained in polycrystalline form, their structures had to be analyzed using powder diffraction techniques. Both diffraction patterns (ZrPOF-Q1 : synchrotron, SNBL at ESRF; ZrPOF-Q2 : laboratory, Stoe) could be indexed with triclinic unit cells, but the dimensions and volumes are significantly different (ZrPOF-Q1: ; a = 10.7567Å, b = 13.8503Å, c = 14.8994Å, α = 109.6°, β = 101.1°, γ = 100.5°; V = 1979 Å^3, and ZrPOF-Q2: ; a = 7.7058Å, b = 12.3546Å, c = 6.5851Å, α = 97.0°, β = 89.7°, γ = 101.9°; V = 610 Å^3). In both cases, reflection intensities were extracted from the powder diffraction pattern using the Le Bail method and then used as input to the powder charge-flipping (pCF) algorithm [1] in the program Superflip [2]. In this implementation, the original single-crystal charge-flipping algorithm of Oszlányi and Sütő [3,4] has been modified to include a second type of perturbation of the electron density map. This is based on a histogram matching algorithm and is performed prior to a repartitioning of the intensities of reflections that overlap in the powder pattern. The histogram used simply reflects the chemical composition per unit cell. The electron density maps obtained from Superflip showed localized electron densities in the form of tetrahedra and octahedra, which were interpreted as PO_4 and $Zr(O,F)_6$ groups. Some residual, less well-localized electron density, assumed to be due to the quinoline species, was also observed, but was not used in constructing the initial model for Rietveld refinement. Instead, the positions of the quinoline C and N atoms were derived from a series of difference Fourier maps. The structure of ZrPOF-Q1 (60 non-H atoms, 3909 of 4522 reflections overlapping, R_F = 0.053, R_{wp} = 0.144) consists of zirconium phosphate layers with quinolinium ions and water molecules in between. The layers are unusual in that they have isolated ZrO_2F_4 octahedra anchored on their surfaces that protrude into the interlayer space. The ZrPOF-Q2 structure (19 non-H atoms, 928 of 1265 reflections overlapping, R_F = 0.059, R_{wp} = 0.162) consists of zirconium phosphate chains with an unusual Zr:P ratio of 1.0, interspersed with quinolinium ions. The charge-flipping algorithm allowed a straightforward structure solution in both cases, although the degree of reflection overlap is considerable. The effect of the various charge-flipping parameters on the structure solution will be presented.

[1] Baerlocher, Ch.; McCusker, L.B.; Palatinus, *L. Z. Kristallogr.* 222, 47-53, **2007**. [2] Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* 40, 786-790, **2007**. [3] Oszlányi, G.; Sütő, A. *Acta Crystallogr.* A60, 134-141, **2004**. [4] Oszlányi, G.; Sütő, A. *Acta Crystallogr.* A61, 147-152, **2005**.

Keywords: charge flipping; structure determination; X-ray powder diffraction

FA5-MS01-P13

High Throughput Phase Diagram Mapping of Urate Oxidase via Powder Diffraction. Ines Collings[a], Sotonye Dagogo[a], Yves Watier[a], Irene Margiolaki[a], Andrew N. Fitch[a], Jonathan P. Wright[a], Marion Giffard[b], Francoise Bonnete[b], Richard Kahn[c]. *[a]European Synchrotron Radiation Facility, Grenoble, France. [b]Centre Interdisciplinaire de Nanoscience de Marseille, France. [c]Institut de Biologie Structurale, Grenoble, France.*
E-mail: ines.collings@esrf.fr

Modern developments of the powder diffraction technique have allowed the investigation of systems with large unit cells such as proteins [1]. Polycrystalline protein precipitates are frequently obtained under a variety of crystallization conditions and thus powder methods can be employed for structural characterization of small proteins when single crystals are unavailable. The recombinant urate oxidase from Aspergillus flavus (Uox) is a protein used to reduce toxic uric acid accumulation and also for the treatment of hyperuricaemia which occurs during chemotherapy. In this study, we investigate the effects of pH, salt and polyethylene

glycol (PEG) concentration on the structural characteristics of Uox uncomplexed and complexed with 8-azaxanthine (AZA) using powder diffraction data collected on ID31 [2] at the ESRF.
Previously unknown phases of Uox were observed depending on the presence and type of salt whereas PEG and pH variation had a minor affect on the cell dimensions. All phases have been successfully indexed, and the known I222 orthorhombic phase of Uox complexed with AZA was solved by molecular replacement using software designed for single crystal diffraction data [3]. The phase diagram of Uox and its relevant crystallizing conditions will be presented.

[1] Margiolaki, I., Wright, J. P. *Acta Cryst.* **2008** A64, 169-180. [2] Fitch, A. N. **2004**. J. Res. Natl Inst. Stand. Technol. 109, 133-142. [3] Collaborative Computational Project, Number 4 **1994**. Acta Cryst. D50, 760-763.

Keywords: protein crystallography; powder diffraction analysis; phase diagrams

FA5-MS01-P14

Use of Rietveld Method in Quantitative Analysis of Weldments in Duplex Stainless Steels. Jorge L. Garin[a], Rodolfo L. Mannheim[a], Manuel A. Camus[a]. [a]*Department of Metallurgical Engineering, Universidad de Santiago de Chile, Santiago, Chile.*
E-mail: jorge.garin@usach.cl

Duplex stainless steels (DSS) are an important class of engineering materials, currently been considered for welding applications among many other industrial requirements. They have approximately equal proportions of the body-centered cubic ferrite and face-centered cubic austenite phases in their microstructure. The main advantage of DSS over conventional stainless steels are strength, chloride stress-corrosion cracking resistance and pitting corrosion resistance. Although the weldability of DSS is generally good, the high alloy content and the existence of a ferritic matrix render SDD susceptible to embritlement and loss of mechanical properties due to precipitation of sigma-phase in the microstructure. This phase is a complex intermetallic compound of Fe and Cr, based upon an ideal stoichiometric composition AX_2, Pearson's code tP30 and space group P_2/mnm. Owing to the usually complex diffraction pattern of these alloys, which disclose many overlapping reflections and strong preferred orientations caused by the welding process, the Rietveld method was used to resolve those difficulties in welded joints of commercial duplex stainless steels (21-23 Cr - 4.5-6.5 Ni). The Rietveld refinements were performed based upon typical measurement and global parameters. The powder diffraction patterns of the weldments resulted in strong preferred orientation effects due to the uniaxial solidification of the weld metal-pool, which was corrected in the Rietveld refinement by using the March-Dollase function. The pseudo-Voigt function was used for the simulation of the peak shapes, while the background was modeled by a 3rd order polynomial in 2θ with refinable coefficients. A total of three phases, namely ferrite (Cr,Ni), austenite (Ni,Cr) and sigma phase (Fe_7Cr_6) were identified and considered in the quantitative analysis. The results obtained have assessed the application of the Rietveld method to quantify the microstructural components of weldments in duplex stainless steels. The main advantage of this methodology was the use of the March-Dollase model for correcting the strong texture effects on the diffraction pattern, which yielded the lower R-values and much better represented the relative amount of phases in the samples.

Keywords: duplex stainless steel; rietveld; sigma phase

FA5-MS01-P15

Laboratory X-ray Microdiffraction - Limits and Applications in Forensic Science. Ivana Jebavá[a], Viktor Goliáš[a], Marek Kotrlý[b]. [a]*Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague.* [b]*Institute of Criminalistics Prague.*
E-mail: Iva.Jebava@seznam.cz

The aim of this work was to evaluate and prove abilities and limits of laboratory x-ray powder microdiffraction and to create the methodical procedure for applying of this technique in forensic science.
X-ray powder microdiffraction is a progressive non-destructive analytical method that allows analysing very small area on a sample. X-ray beam was in our case focused by monocapillary with an exit diameter 100 or 800 μm. Monocapillary is a hollow glass tube in which there is a total reflection of X-ray beam.
Several problems were investigated. Microdiffraction technique was compared with standard powder diffraction method in Bragg-Brentano instrumentation on identical small-volume samples and capabilities of identification of more phases in mixture were verified. Results showed that microdiffraction reflections are 2-3 times broader than the Bragg-Brentano ones (FWHM 0.13 vs. 0.27° 2Θ for (012) line of corrundum). Peak shape can be fitted by conventional profile functions approach only with difficulties. However, in case of analysing of small-volume samples, microdiffraction technique usually identify more phases.
The next task was to determine limit of microdiffraction with respect to grain size in a sample. This was carried out on commercially produced alumina of several different granularities and results were compared with scans from imaging plate. Studied material contains pure alumina (α-Al_2O_3) and minor concentration of β-Al_2O_3 that was used for evaluation of quality of quantitative analyse from microdiffraction patterns. Upper grain size limit for 100 μm capillary was determined 10-15 μm (static sample) and 25 μm (rotated sample). For 800 μm capillary the upper granularity limit is 50 μm (static sample) and 100 μm (rotated sample).
The determination of detection limit of minority phase in mixture was our next step. We studied the mixture of quartz and fluorite in several concentrations. The detection limit was defined as 0,5 wt. % of fluorite.
The optimized step was defined 0,05º 2Θ for both 100