Combined micro-XRF/XRPD tomography on historical and modern paint multilayer samples at Beamline L

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Combined micro-XRF (X-ray fluorescence) and micro-XRPD (X-ray Powder Diffraction) experiments have been performed successfully at Beamline L on various materials [1,2]. However, in several situations, the scattering material is not a fine-grained powder but a polycrystalline material of which only a few crystals find themselves in the path of the micro-focused primary X-ray beam. These give rise to only a few single reflections instead of complete Debye rings in a two-dimensional diffraction pattern. By performing conventional 2D scanning μ-XRF/μ-XRPD experiments (xy), projected elemental or phase distributions of three-dimensional samples can be obtained. Similar distributions in virtual planes inside heterogeneous materials may also be obtained by performing μ-XRF/μ-XRPD scanning in tomographic (xθ) mode, involving translation along the x-coordinate and rotation along a perpendicular axis (θ). Since this form of tomography requires the object to be rotated while collecting x-ray fluorescence and diffraction signals, reflections associated with individual single crystals will appear and disappear from the recorded diffractograms during the rotation, as the crystals will only fulfill Bragg’s law at specific orientations.

Pigment grains in historical and modern paint layers often show diffraction patterns between that of an ideal powder and of a single crystal. In order to evaluate the feasibility of performing XRPD tomography measurements, two multilayered paint fragments were investigated at Beamline L: (a) a paint fragment from a 17th C. painting “The Prodigal Son” of P.P. Rubens and (b) a modern car paint multilayer sample. The entire analysis procedure was completely non-destructive. These materials were irradiated by means of an X-ray beam, focused by means of an elliptical single-bounce capillary to a diameter of 15 µm. A double multilayer monochromator (Mo/Si in case of the car paint and Ni/C for the Rubens paint fragment) produced a ~30keV beam. A Silicon Drift Detector acquired the XRF spectra and a MarCCD area detector (2K×2K, 80µm pixel size), positioned at ~20 cm behind the sample, collected the 2D diffraction patterns.

In Figure 1, the sinograms and tomograms derived from the recorded XRF spectra and XRD patterns for the Rubens paint fragment is shown. Only for the three most important elements, the XRF distributions are shown in the first row. On the right-hand side, an overlay image provides an elemental composition.

Figure 1. Sinograms and tomograms (first row: XRF, second and third row: XRD) from a paint fragment of Rubens’ “The Prodigal Son”. Colored elemental overlay image: Ca (green), Pb (purple), Cu (blue) and support tape (red). Phase overlay image: calcite (green), hydrocerussite (purple), azurite (blue) and supporting polymer foil (red).
overview, showing a calcium-rich base layer (green) and a layer containing Pb (purple) and Cu (blue). The Ti-Kα intensity (red) was used to visualize the adhesive polymer foil that supported the paint fragment during the analysis. These data are consistent with the fact that the paint sample originate from an area of the painting depicting the sky in the "The Prodigal Son", where the Cu-containing blue pigment Azurite was used in combination with lead-white in order to obtain a light-blue tint.

In the corresponding XRD distributions, three phases could be identified: Calcite [CaCO₃, 72-1652], Hydrocerussite [Pb₅(CO₃)(OH)₂, 13-0131] and Azurite [2CuCO₃·Cu(OH)₂, 01-0564]. In order to obtain the sinograms of the second row of Figure 1, the intensity of a single non-overlapping reflection in the azimuthally integrated diffractogram was calculated for each phase. This procedure leads to adequate results in case the pigments involved are sufficiently finely grained so that for each orientation, on average the same number of crystals are in Bragg orientation. The sinogram for Azurite shows the result when a coarse grained powder is present in the paint layer: under some orientations, more crystals diffract then under other orientations, leading to a non-uniform sinogram; the corresponding tomogram shows many artefacts and is of little use for visualising the distribution of Azurite in the virtual section.

To overcome this problem, it is possible to employ Pawley fitting of the diffractograms collected at each (x,θ). Instead of extracting the intensity of a single reflection in order to obtain a sinogram, all reflections of a phase are fitted simultaneously to a line pattern, consisting of a series of d-spacings and their associated relative intensities. These relative intensities are kept constant so that only one free parameter, the phase scaling factor, is determined during the least squares procedure. This factor is obtained at all (x,θ), resulting in a sinogram showing a much smoother intensity variation vs. θ than in the case only the intensity of a single reflection is considered. The relative intensities for each phase are extracted from the ICDD PDF-2 database. The third row of Figure 1 presents the result of the Pawley fitting method; it shows that a meaningful virtual cross-section of the Azurite-containing layers can be obtained in this manner.

A more complicated layered structure was encountered in the second paint layer fragment. The tomographic XRD results are shown in Figure 2. The identified phases were Rutile [TiO₂, 76-0318], Crocoite [PbCrO₄, 08-0209], Aluminum [Al, 04-0787], Hematite [Fe₂O₃, 33-0664], Talc [Mg₃Si₄O₁₀(OH)₂, 13-0558], Zinc yellow [K₂Zn₄O(CrO₄)₄·3H₂O, 08-0202]. In this sample, the presence of in total nine layers could be resolved with a maximum of three crystalline compounds in one layer. The thickness of these layers varies from approx. 40 to 200 µm. As before, phase scaling factors were used to obtain the sinograms.

![Figure 2. Reconstruction of a car paint multilayer structure using XRD phase scaling factors. Scan dimensions are (81×15µm) × (61×3°).](image)

It can be concluded that Pawley fitting provides a solution for tomographic reconstruction from diffraction data obtained from non ideal powders. Relatively complex layered structures could be resolved with the µ-XRF/XRPD tomography setup at Beamline L.

References
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