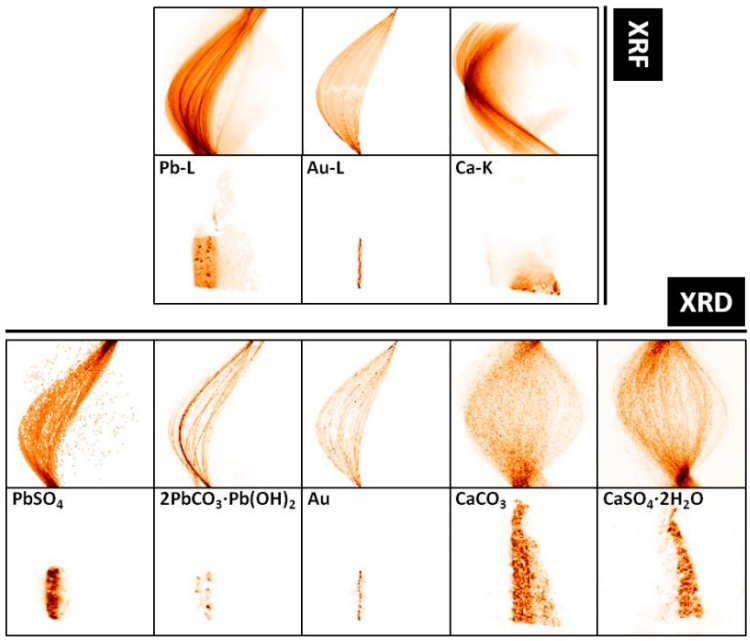
Combined µ-XRF/µ-XRD tomography on historical paint microsamples

F. Vanmeert[1], G. Van der Snickt[1], S. Legrand[1], and K. Janssens[1]

[1]Department of Chemistry University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

Two-dimensional (2D) X-ray powder microdiffraction mapping experiments have been shown to provide useful information on complex heterogeneous crystalline samples in the field of cultural heritage e.g., for the identification of the various pigments and materials used in works of art [1], as well as degradation products responsible for the discoloration of cadmium yellow [2][3] and the darkening of vermillion [4][5]. An intrinsic limitation of the 2D projective images is the loss of depth information, although limited depth-resolution can be obtained from the shift in the sample-detector distance for the different crystalline compounds present. To overcome this limitation X-ray microbeam computed tomography can be used to visualize the inner structure of a sample without destructive sample preparation [6][7], which is important for unique samples from works of art as the samples need to remain unchanged for preservation purposes or for further future analyses. The constructed virtual slices obtained by combined X-ray fluorescence and X-ray powder diffraction microbeam (µXRF/µXRPD) computed tomography contains both elemental and crystalline phase-specific information. Because of the time-demanding point-by-point sequential scanning procedure, the measured volume is usually limited to one or a small stack of two-dimensional slices.

Combined µXRF/µXRPD tomography experiments have been performed in the micro probe hutch of the P06 beam line using a photon energy of 21 keV. The energy was selected by means of a Si(111) double crystal monochromator. The beam was focused to 0.4 × 0.4 µm^2 (hor. × vert.) employing a Kirkpatrick-Baez mirror optic. A Keyence optical microscope equipped with a perforated mirror allowed for positioning of the sample. Diffraction signals were recorded in transmission geometry with a Pilatus 300K area detector. Simultaneously, X-ray fluorescence signals were recorded using a Si-drift detector with 50 mm^2 active area. Elemental and phase-specific distribution maps were collected from original paint microsamples with 2 – 4 µm lateral and 1.5 – 3.5° angular step size with an acquisition time of 1 sec/point. The high readout speed of the Pilatus detector (< 5 ms) allowed for fast mapping with minimal overhead time (< 1 sec). XRF spectral fitting was performed using the PyMCA software package [8] while the ensuing XRD data analysis and tomography reconstruction was performed with the XRDUA software [7]. Several original paint microsamples from works by Memling, Rubens and Van Gogh were analyzed.



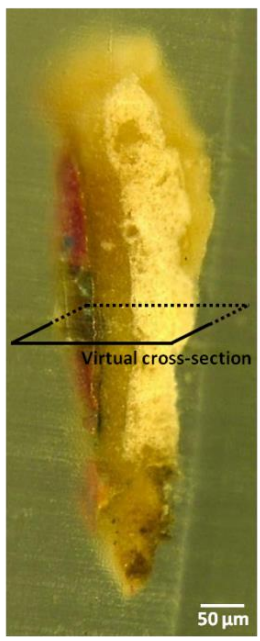


Figure 1: (left) Sinograms and tomographic reconstructions for selected elements (XRF) and crystalline phases (XRD) obtained on an original paint microsample. (right) Optical image of the paint microsample embedded in a resin.

Tomographic reconstructions were performed using the maximum-likelihood expectation maximization (MLEM) algorithm. No corrections for absorption effects were taken into account. The absorption effect becomes clear in the reconstructed Ca-K image because of the low fluorescence energy compared to Au-L and Pb-L lines. Although the diffracted signals also suffer from absorption through the sample, they do so in a lesser extent as the scattered X-rays maintain their primary energy. The results obtained from this experiment show that it is possible to perform XRF/XRPD tomography experiments on original paint microsamples employing a submicrometer beamsize.

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