MS48-O4 Provenancing of clay-based pigments in paints using quantitative X-ray micro-diffraction analysis

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One of the main reasons why individual clay minerals are not being properly detected in colour and preparatory layers of paintings regardless of their often significant contents is a missing methodology of its analysis. None of the micro-spectroscopic or spectrochemical analytical methods frequently used in the field leads to reliable differentiation of clay minerals due to their variable chemical composition, structural similarities and low Raman scattering. For their identification, it is necessary to employ powder X-ray micro-diffraction that is the only microanalytical method that allows a reliable differentiation of individual clay minerals' structures in colour and ground layers of paintings. It has not yet been satisfactorily tested for correct and unambiguous discrimination of clay structures in paint layers and, eventually, for reliable quantitative analysis of their relative contents. To overcome this lack of knowledge, several sets of laboratory experiments with model mixtures and reference samples imitating real paint layers have been performed and general rules for proper discrimination of clay structures have been described. Besides the common limitations of micro-pXRD (e.g. worse resolution, small size of irradiated area etc.), the accuracy of quantitative microanalysis of clay minerals in mixtures with other minerals in earth pigments is characterised by total bias values in the range of 3 – 10 wt. %. While in the case of conventional Bragg-Brentano geometry, the total bias does not exceed 6 wt. %. However, a more critical issue seems to be the effect of heterogeneity of natural materials, which tends to be more pronounced in small irradiated volumes. In our study, the newly determined accuracy of quantitative microanalysis was found to be sufficient for differentiation of red earths from two historical sources in Bavaria and Bohemia, respectively, both in reference samples and in micro-samples of Baroque grounds of paintings by, e.g., the famous Czech painter Karel Škréta. Further, as a specific sign of material's origin, randomly ordered illite-smectite interstratified structures were differentiated from pure smectites in painting grounds used by Baroque Venetian painters. These and other examples demonstrate the practical usability of this methodological approach for the comparative studies on paintings focusing on differentiating their regional provenance.

Keywords: x-ray powder micro-diffraction, clays, artworks, quantitative phase analysis

MS49 How to...: crystallization for small and large molecules

Chairs: Aurelien Crochet, Andrew Maloney

MS49-O1 Some Tricks for the Single Crystal Growth of Small Molecules

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While there exist helpful articles that describe the crystallization of small molecules for X-ray analysis[1], it is our experience that some systems still present a challenge to be crystallized. We have summarized our assembled knowledge of the crystallization of small molecules over the last 15 years in a tutorial that is intended to be inspiring for the beginner as well as the more advanced chemist.[2] The techniques described in this tutorial are all being applied at room temperature. In more recent times, we have studied the influence of the temperature upon the formation of molecular single crystals as well as the possibility of growing high quality crystals from few milligrams of material within few hours by thermal recrystallization.

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(2) Spingler, B.; Schnidrig, S.; Todorova, T.; Wild, F. *CrystEngComm* **2012**, *14*, 751.

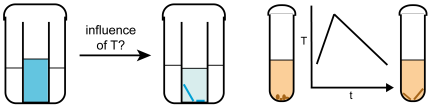

Figure 1. Different ways of obtaining single crystals. Left: Vapour diffusion at a constant temperature; right: thermal recrystallization.

Keywords: Single crystal growth, molecular compounds, crystallization, solvent/antisolvent