

Combined MA-XRF, MA-XRD and MA-FTIR scanning on a 17th C Still life painting by J.D. De Heem: slowly towards comprehensive imaging of chemical species

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In his paper ‘Slowly towards improved infrared reflectography equipment’ Van Asperen De Boer reviewed the impact of introducing Infrared Reflectography (IRR) in the late sixties.¹ IRR was then considered to be a major breakthrough in the young field of heritage science as it allowed non-invasive sub-surface probing of features and materials (i.e., carbon-based underdrawings) to which more established methods such as X-ray radiography and UV induced visible fluorescence photography was insensitive.

However, none of above imaging methods allow direct chemical identification of painting materials; to some extent this is possible with more recently developed imaging spectroscopic imaging techniques such as hyperspectral and MA-XRF. Combining a number of these techniques brings us slowly towards the ultimate goal: imaging *all* chemical species in a painting *in situ*, in a non-invasive manner, and with a relevant depth selectivity.

While the value of MA-XRF scanning was extensively illustrated in the last decade,² being an element-specific imaging method, its applicability is somewhat curbed by a lack of specificity. In spite of these limitations, De Keyser et al.³ recently demonstrated how the insights obtained by MA-XRF scanning on a complex multi-pigment and multi-layered still life by De Heem can be considerably expanded by SEM-EDX analysis of a single cross-section. Here we will present how one or more compound-specific scanning techniques can be used to obtain missing information *in a similar but non-invasive manner*. MA-XRPD and reflection mid-MA-FTIR permit to visualize the distribution of low *Z* materials such as ultramarine that are not detectable by MA-XRF. The additional ability to differentiate between pigments with a similar elemental composition proved particularly valuable for instance for understanding the copper-based foliage between the flowers. Here, combined MA-XRPD/MA-FTIR was able to clarify the particularly well-preserved deep green tones by revealing the combination of blue verditer with yellow lakes, instead of the expected verdigris. The surplus of recording species-selective maps *in situ* became even more clear when degradation products are considered. For the De Heem painting, MA-XRPD succeeded e.g. in recording maps of potassium salts related to lake substrates and arsenic compounds that are in line with the recently established degradation pathway of orpiment.^{4,5}

¹ Van Asperen De Boer, J.R.J. ‘Slowly towards improved infrared reflectography equipment’. Recent Developments in the Technical Examination of Early Netherlandish Painting: Methodology, Limitations and Perspectives. Brepols Publishers. 2003.

² Van der Snickt, G. et al. Large-Area Elemental Imaging Reveals VanEyck’s Original Paint Layers on the Ghent Altarpiece (1432), Rescoping Its Conservation Treatment. *Angew. Chemie*, 56 (2017) 4797-4802.

³ De Keyser, N. et al. Jan Davidsz. de Heem: a technical examination of fruit and flower still lifes combining MA-XRF scanning, cross-section analysis and technical historical sources. *Heritage Science*, accepted 2017.

⁴ Keune, K. et al., Tracking the transformation and transport of arsenic sulfide pigments in paints: synchrotron-based X-ray micro-analyses, *J. Anal. At. Spectrom.*, 30 (2015) 813-827.

⁵ Vermeulen, M. et al., Visualization of As(III) and As(V) distributions in degraded paint micro-samples from Baroque- and Rococo-era paintings, *J. Anal. At. Spectrom.*, 31 (2016) 1913-1921.