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Comparison of ATR-FTIR and O-PTIR techniques for characterization of a degraded oil paint cross-section

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ATR-FTIR (Attenuated Total Reflection Fourier-Transform InfraRed) spectroscopy is widely used to characterize the complex composition of layers in cross-sections extracted from painted works of art. However, some limitations, such as poor contact of ATR crystal with sample or sample area of interest below the IR diffraction limit, prevail.
Recently, a novel O-PTIR (Optical- Photothermal InfraRed) spectromicroscopy claims to open a new avenue for non-destructive, efficient and reliable analysis at sub-micron resolution without the need to touch the sample. O-PTIR produces transmission-like FTIR spectra for interpretation.
This work reports a comparison of O-PTIR and ATR-FTIR techniques applied to a thin cross-section (about 15 μm thickness) delaminated from a late 19th - early 20th century "Portrait of Mr Tan Beng Wan", a zinc white oil-based painting belonging to the National Heritage Board, which depicts a crucial Peranakan figure in the shipping industry of early Singapore.
Zinc soap (palmitate / stearate) is a common degradation product in zinc white oil paints, of which the crystalline form is known to cause paint delamination and flaking problem. In the ageing of oil paints, fatty acids derived from the hydrolysis of oil components are mobile and tend to move through layers and form aggregates. It was postulated that the haze developed on the painting's surface was brought about by the migration of zinc soaps from the ground to the paint layers, which subsequently interact with atmospheric pollutants to form the haze (gordaite in this sample). Zinc lactate, another degradation product that is less reported in oil paints, is soluble in water and its detection suggests for a water-sensitive paint that can lead to implications in conservation treatments.
During O-PTIR analysis, various degradation products that have formed in the cross-section, including zinc palmitate / stearate (both crystalline and amorphous), zinc lactate and gordaite (NaZn4Cl(OH)6SO4.6H2O), were identified with better signal to noise ratio and resolved at the sub-micron resolution. These compounds, though detected with ATR-FTIR imaging, could not be well resolved. Knowing the spatial locations of the degradation compounds characterized at the haze-paint interface is beneficial in understanding the paint's condition and behaviour during conservation.

Primary author: BANAS, Agnieszka (Singapore Synchrotron Light Source, Singapore)

Co-authors: BANAS, Krzysztof (Singapore Synchrotron Light Source); Dr CHUA, Lynn (Heritage Conservation Centre, National Heritage Board of Singapore)

Presenter: BANAS, Agnieszka (Singapore Synchrotron Light Source, Singapore)

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