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Microspectroscopic Investigation of Metal Soaps in Oil Paintings--a Case Study on late 19th Century Cobalt Green ($(Co_xZn_{1-x}O)$ Paint

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The reaction between metal ions (from metal-containing pigments or modifiers) and hydrolyzed long-chain fatty acids from an oil binding medium leads to the formation of metal soaps. Since the late 1990s, metal soaps have been systematically detected in oil paintings and could be linked to their deterioration, by causing brittleness, increasing transparency, or other phenomena [1, 2].

In order to study the metal soaps formed within the overpainted region of the oil painting by Jean-Baptise-Camille Corot, *Gypsy Girl with Mandolin* (National Gallery of Art Collection No: 1951.21.1), one cross-section sample and dispersed pigment samples from the uppermost layers of the overpaint were collected and analyzed using multi-analytical micro-spectroscopic and imaging techniques.

Photomicrographs (Figure 1(a-b)) and SEM-EDX element maps of the cross-section sample showed the structure consisted of fifteen layers. The pigment cobalt green ($Co_xZn_{1-x}O$) was found dispersed within lead white in the top layers of the overpaint. It was characterized using polarized light microscopy and SEM/EDX. In addition to Co and Zn, the pigment contains Mg, as do historical samples examined. ATR-FTIR mapping (Figure 1(e-f)) of a region where absorbance of COO^- occurs indicated that metal soaps had formed in the vicinity of cobalt green particles in the paint.

Photoluminescence was observed within the cross-section, especially within the top layers (Figure 1(c-d), Figure 2(a-b)), associated with cobalt green pigment, metal soaps, zinc oxide, and the binding medium. Backscattered electron images showed a low atomic weight phase surrounded the unreacted cobalt green particles (Figure 2(c-d)). Elemental analysis showed the presence of Mg and Zn in this phase. The combination of results suggests that this is a Zn-Mg metal soap [3].

References:

[1] C Higgitt, M Spring and D Saunders. National Gallery Technical Bulletin **24** (2003), p. 75.
[2] G Osmond *et al* , Applied Spectroscopy **66** (2012), p. 1136.
[3] The authors thank Kathryn Harada for sampling and preparing the cross-section and dispersed samples. Dr. Melanie Gifford and Michael Palmer are thanked for useful discussions and contributions to this work.

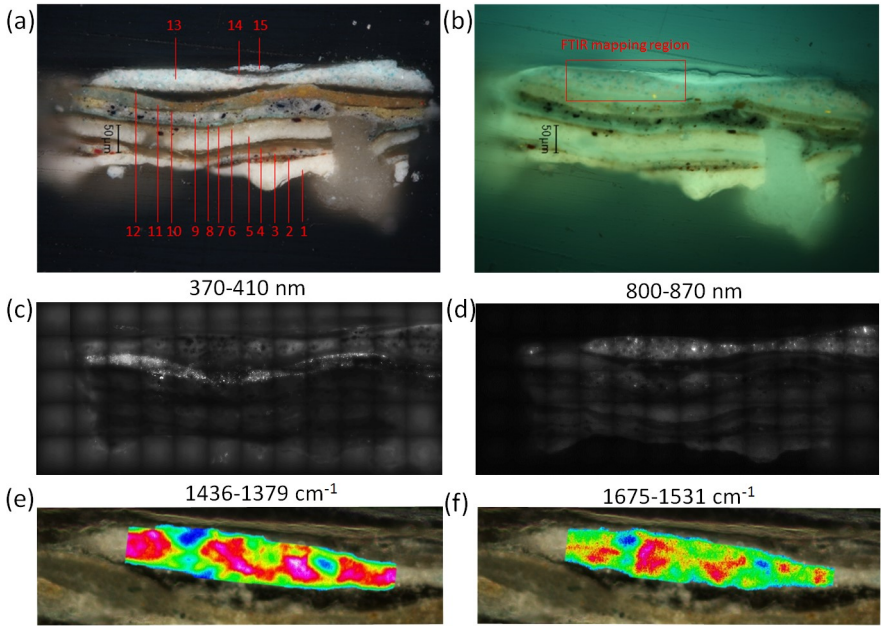

Figure 1. (a-b) Visible light and luminescence images of the cross-section sample: (a) under visible light illumination; (b) using filter cube D (UV/violet illumination, 355 nm $\leq \lambda_{exc} \leq$ 425 nm; dichroic mirror cut off, 470 nm $\leq \lambda_{exc}$). (c-d) Photoluminescence image of the cross-section under 280 nm excitation and 370-410 nm and 800-870 nm bandpass emission respectively. (e-f) ATR-FTIR mapping results on the first layer of the cross-section (mapped region as shown in (b)): (e) map of the integrated absorption between 1436 and 1379 cm^{-1} ($\nu_{as}(CO_3^{2-})$ of lead white); (f) map of the integrated absorption between 1675 and 1531 cm^{-1} ($\nu_{as}(COO^-)$ of the metal soap formed).

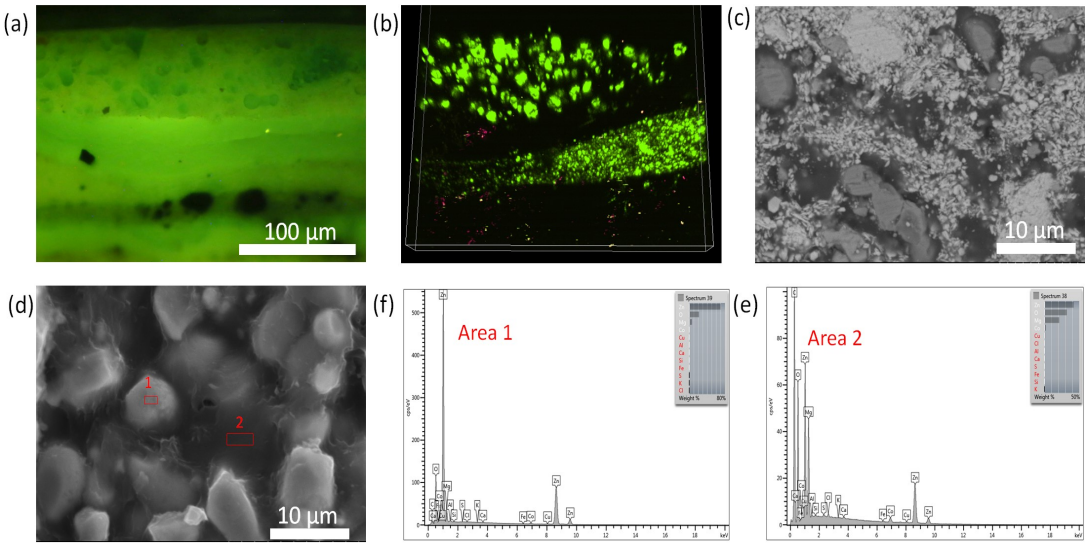

Figure 2. (a) Luminescence images of the first few layers of the cross-section using filter cube D; (b) 2-photon excitation spectroscopy of the region in (a), showing zinc white and intact cobalt green; (c) BSE image of the cobalt green pigment dispersed throughout lead white; a low atomic weight phase is surrounding the larger cobalt green particles; (d) SE image shows cobalt green particles and their surrounding medium; (e-f) EDX analysis of areas 1 and 2 indicated in (d) showing the composition for the cobalt green pigment and the metal soaps respectively.

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