Conservation Studies of Heritage Materials Focus Topic
Room: 313 - Session CS-ThA

Conservation Studies of Heritage Materials 2

Moderator: H. Frederick Dylla, American Institute of Physics, Robert Opila, University of Delaware

2:20pm **CS-ThA1 A Conservator's Perspective of Technical Studies and Scientific Analysis**, ***Patricia Favero***, The Phillips Collection **INVITED**

The nature of technical studies is necessarily interdisciplinary as they address various questions about works of art and artifacts: What materials did the artist use ; how did he use his materials; and most importantly, what is the significance of this information for a greater understanding of the artist and his work? What is learned in technical studies often both augments art historical research and informs conservation treatment decisions.Collaboration between conservators, scientists, and art scholars is becoming ever more common in the study of works of art. Results of in-depth studies are now featured in exhibitions and scholarly publications, and their importance is increasingly recognized within larger art historical studies of an artist's oeuvre.

In this light, this presentation will consider two recent technical studies carried out at The Phillips Collection in Washington, D.C. The first, a study of a group of Georges Braque's mid-career paintings, was conducted in collaboration with conservation scientists from Harvard Art Museums and curators at the Phillips and the Kemper Art Museum in St. Louis. The results of the study were featured in the exhibition *Georges Braque and the Cubist Still Life, 1928-1945* and in the related publication. The second study focuses on one painting, *The Blue Room* (1901), an early Blue Period picture by Pablo Picasso in the collection at the Phillips. Ongoing research of this picture is being conducted in collaboration with independent Picasso scholars and scientists from the Winterthur Museum in Delaware, Cornell University, and the National Gallery of Art.

Both studies began in the conservation studio with the conservator carefully examining each painting in good light and under magnification, considering each artist's technique and how it may have influenced their material choices. Other examination techniques, such as UV-induced fluorescence, infrared imaging, and x-radiography were also employed.

In both studies, paint samples were taken and analyzed to positively identify the artists' materials and understand them in context. In the Braque study, the increasingly wide-spread use by conservators of portable x-ray fluorescence (pXRF) spectroscopy allowed for comparative pigment analysis of eight paintings from five different collections. For the Picasso, three non-invasive techniques—reflectance imaging spectroscopy, fiber optic reflectance spectroscopy (FORS), and XRF intensity mapping—were used.

The presentation will consider the collaborative nature of both studies and evaluate what made them successful in addition to discussing the process and outcome of each project from the conservator's perspective.

3:00pm **CS-ThA3 State of the Art: Probing Complexity in Paint**, ***Francesca Casadio***, *F. Pozzi, L. Chang,* The Art Institute of Chicago, *D. Kurouski, S. Zaleski, N.C. Shah, R.P. Van Duyne,* Northwestern University, *V. Rose*, Argonne National Laboratory **INVITED**

In recent years, the scientific analysis of painted surfaces has made a giant leap forward. At the same time as innovative standoff macro-scale imaging modalities have been developed to deliver elemental mapping (using macro X-ray fluorescence spectroscopy) and molecular imaging (with Ultra-Violet/ Visible, Near Infrared, Mid-Infrared reflectance, fluorescence, and Raman imaging), our ability to probe local paint chemistries and mechanical properties at the nanoscale has grown exponentially. These recent developments have fundamentally changed the way conservators, curators and conservation scientists approach the study of works of art, leading to cutting-edge research on pigment degradation phenomena and enabling us to retrieve otherwise lost information on altered colors or hidden compositions that make up the original aspect of masterpieces.

This talk will present recent research employing high resolution nanoprobe synchrotron X-ray fluorescence (XRF) mapping of metallic impurities with 30 nm resolution in single grains of zinc oxide pigments used in early 20th century paints formulated for artists and other commercial uses and widely employed by Pablo Picasso (1881-1973). Such highly detailed chemical characterization of paints at the nanoscale opens the path to a better understanding of their historical fabrication and chemical reactivity.

For the characterization of organic molecules used in paintings Surface-Enhanced Raman Spectroscopy (SERS) has recently been developed into a robust, reliable and highly sensitive technique to detect and unambiguously identify minute quantities of organic colorants. SERS has seen the field of cultural heritage become one of its foremost research and application areas, resulting in improved analytical protocols applicable to several other fields such as pharmaceuticals and forensic analysis. In particular, our efforts to develop methods to identify more than one colorant on a single sample using combined Thin Layer Chromatography / SERS and microfluidics SERS approaches will be discussed. Pushing the envelope of in-situ SERS analysis, first results on the use of Tip-Enhanced Raman spectroscopy (TERS) for the high spatially resolved, highly sensitive and non-invasive investigation of dyes used on paper supports will be discussed and preliminary results presented. This first demonstration of TERS spectral acquisition directly on a paper substrate confirms the analytical potential of TERS to identify organic colorants in artworks with high sensitivity, high spatial resolution, and minimal invasiveness opening the way to future developments for the nano-scale mapping of organic constituents of works of art.

4:00pm **CS-ThA6 The Degradation Mechanisms of Cadmium Pigments in Works by Henri Matisse, Edward Munch, and Their Contemporaries**, ***Jennifer Mass***, Winterthur Museum, *E. Pouyet,* ESRF, France, *F. Meirer,* Utrecht University, Netherlands, *M. Cotte,* ESRF, France, *A. Mehta*, Stanford Synchrotron Radiation Lightsource **INVITED**

Cadmium carbonate ($CdCO_3$) has for several years been identified in the altered cadmium yellow (CdS) paints found Impressionist, early modernist, and post-Impressionist works. When it is concentrated at the surface of the painting, $CdCO_3$ appears to be a result of the photo-alteration of CdS, likely through a $CdSO_4$-containing phase. However, in other cases $CdCO_3$ is distributed throughout the paint layer. This is significant because $CdCO_3$ is highly insoluble (K_{sp} of 1.0×10^{-12}), and if it were formed solely as a result of photo-alteration it would not be expected to migrate away from the painting's surface. In cadmium yellow paints in works such as Edvard Munch's c. 1910 *The Scream* (The Munch Museum, Oslo), Plahter et al. have recently proposed that $CdCO_3$ is present because this compound was used in the indirect wet process synthesis of CdS (through, for example, the reaction of $CdCO_3$ and Na_2S). This would mean that the $CdCO_3$ is a residual starting reagent rather than a photo-alteration product. Such an interpretation is supported by the identification of $CdCO_3$ in the unaltered cadmium yellow paints of early modernist works such as Pablo Picasso's *The Blue Room* (The Phillips Collection, 1901) and Henri Matisse's *Flower Piece* (The Barnes Foundation, 1906).

To address this question of $CdCO_3$'s role, a flake of apparently nondegraded cadmium yellow paint was removed from Henri Matisse's *Flower Piece* so that the distribution of $CdCO_3$ could be studied, both as a function of depth in the paint layer and in individual pigment particles.

X-Ray microspectroscopy and microdiffraction were respectively carried out at ESRF ID21 and Petra III, supplemented by light microscopy, backscattered electron microscopy with X-ray microanalysis, and Fourier transform infrared spectroscopy. This presentation will focus on results from X-ray microspectroscopy: μ-X-ray fluorescence (XRF scanning) allowed precise mapping of local elemental distribution, and Full Field X-ray Near-Edge Absorption Structure (FF-XANES) for mapping the chemical speciation using the Cd-L_3 and S-K edges.

FF-XANES imaging of a 15 micrometer thin section at CdL3-edge revealed the presence of three Cd-based phases: CdS, $CdSO_4$, and $CdCO_3$. The $CdSO_4$ was concentrated on only one surface of the sample, suggesting its role as a photo-alteration product. Cadmium carbonate was found to comprise the bulk of the individual pigment particles, suggesting that it is a synthesis starting reagent. CdS was found to be concentrated on the surface of these $CdCO_3$ particles. $CdSO_4$ could also be observed to surround some of the $CdCO_3$ particles, suggesting the beginnings of photo-oxidation of the thin CdS coating.

4:40pm **CS-ThA8 Characterisation of Modern Watercolour Paints using XPS, HIM, ToF-SIMS and Principal Component Analysis Techniques**, ***Naoko Sano***, *P.J. Cumpson,* NEXUS, Newcastle University, UK, *E. Cwiertnia, B.W. Singer*, Northumbria University, UK

To conserve old masterpieces is, of course, critical but modern fine/contemporary arts also need preservation as future cultural heritage. Therefore, nowadays many modern artistic works have been studied using scientific techniques to preserve their condition. As with easel oil paintings, modern watercolour paintings represent some of our great cultural heritage from artists such as J.M.W. Turner, Paul Klee or Georgia O'Keeffe. For conservation scientists, the characterization of the binder and pigments in

modern paintings is especially important yet problematic in terms of conservation treatments and environmental conditions for display or storage.

In investigation of modern paintings it is often critical to identify the origin of organic molecules in the paintings, since modern paintings have commonly used artists' paints containing synthetic organic pigments due to their greater selection of colours. In addition, in terms of watercolour paints, commonly used binders such as gum arabic, gum tragacanth or honey are not straight forward to identify due to their organic content.

To contribute to a better understanding of modern artists' paints for conservation, this study presents a scientific investigation into commercially prepared watercolour cakes and binders from the 20th century. Analysis focuses on the characterisation of commercial watercolour paints (red colour) that may contain quinacridone and/or saccharide materials, and shows different surface chemistries of the paint between powder and cake types. Moreover, we attempt the identification of the synthetic organic pigments and the plant gum binder from the watercolour paint using surface analysis techniques and principal component analysis (PCA). Especially, we feel surface analysis techniques such as x-ray photoelectron spectroscopy (XPS), helium ion microscopy (HIM) and time of flight secondary ion mass spectrometer (ToF-SIMS) are powerful techniques for cultural heritage preservation.

5:00pm **CS-ThA9 The Analysis of Egg-Oil Binding Media by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Zachary Voras***, *K. DeGhetaldi, D. Clark,* University of Delaware*, J.L. Mass,* Winterthur Museum*, T.P. Beebe, Jr.*, University of Delaware

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is quickly becoming a critical tool in the field of art conservation. This technique provides high-resolution spatial maps of both inorganic and organic components located across and below the surface of a paint cross-section or other art object. With recent advancements in surface analysis, ToF-SIMS can now be used to identify specific amino acids present in protein-containing materials as well as fatty acids present in drying oils. For example, the detection of the ion fragment associated with the amino acid hydroxyproline can be used to confirm the use of animal glue in a paint sample. As an analytical technique, ToF-SIMS avoids the need for derivatization/silylation reagents, with no interference by the presence of reactive or unreactive pigments. Furthermore, the layered systems that are often encountered in historical paint samples remain intact throughout the analytical procedure. This allows for the co-localization of organic and inorganic species in specific layers (e.g., eggyolk paint atop a glue ground). Because of this ability to localize the analytical signal to approximately 1μm or less, the mass spectral information can be used to produce mass-resolved and spatially resolved images which can be correlated to previous studies of the same preserved samples. In this study, ToF-SIMS was used to analyze paint cross-sections obtained from various time periods. A focus will be on works by Italian artists such as Raphael (from the Walters Art Museum) with additional mentions of a painting by Matisse (from the Barnes Foundation) and Henry Ossawa Tanner (from the Smithsonian American Art Museum).

5:20pm **CS-ThA10 The Right Snuff? A Technical Study of Two Snuff Boxes from the Winterthur Museum Collection**, ***Marlene Yandrisevits***, Winterthur/ University of Delaware Program in Art Conservation*, J.L. Mass, C. O'Grady, C. Matsen,* Winterthur Museum Scientific Research and Analysis Laboratory*, E. Torok*, Winterthur/ University of Delaware Program in Art Conservation

The nasal inhalation of snuff tobacco stored in vanity boxes was a fashionable custom among the colonial European elite. From the late 18th to the early 19th century, small decorative enameled boxes were manufactured in England to supply a bourgeois demand for stylish, but less expensive, imitative snuff boxes. The utilization of traditional materials and techniques for later 19th/ early 20th century repair and revival fabrication of enameled boxes introduces a serious challenge in distinguishing the original from the copy or the heavily restored. This study examines two enameled boxes at the Winterthur Museum with the goal to contribute technical data to provenance and dating discussions. Ultraviolet-induced visible fluorescence surface examination, x-radiography, energy dispersive x-ray fluorescence spectroscopy, microRaman spectroscopy, cross-sectional microscopy with visible and UV illumination, scanning electron microscopy – energy dispersive x-ray spectroscopy/ back-scattered electron imaging, Fourier transform infrared spectroscopy, and gas chromatography – mass spectrometry were used to characterize the composition and stratigraphy of the materials comprising the boxes, followed by comparison to period materials and techniques reported in historical sources and to the findings of previous research. As characterized in this study, aluminosilicates were inferred as the enamel network forming agent combined with lead arsenate and tin oxide opacifiers and potash flux on both boxes, with soda flux additionally on one box. Enamel colorants were metal-based (including iron oxides in red, pink and purple overglazes; colloidal gold in pink and purple overglazes; cobalt oxides/ glass in blue and green overglazes; and Pb-Sb-Sn oxides in yellow and green overglazes). Findings suggest that, while significant titanium-containing restoration overpaint and synthetic coatings are present on both boxes, the enamel and mount materials of one box are consistent with the early production. The majority of materials on the other are also consistent with the early stage of enameled snuff box production in England, with the possible exceptions of chromium-based green enamels, iron oxide pink and purple enamels, and brass-based imitation gilding in localized areas which may represent an early restoration campaign. The materials identified on both boxes are consistent with the findings of previous analyses, excluding a yellow colorant identified in previous research as Naples yellow ($Pb(SbO_3)_2$/ $Pb_3(Sb_3O_4)_2$) now detected in this study and recharacterized as a related Pb-Sn-Sb triple oxide ($Pb_2(SnSb)O_6$), which may suggest further research towards a reliable dating scheme.

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