X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), a surface sensitive technique, uses the photoelectric effect to produce quantitative elemental information regarding a sample. XPS is useful for valence shell, core level, and Auger emitted photoelectrons. Since bonding effects the relative binding energies of an element, these chemical shifts are observed in XPS spectra and details regarding functionalities within a sample can be gathered. Because the emitted photoelectrons are characteristic for the binding energies of an element, complex mixtures can be analyzed. Due to advancements in instrument design, imaging is also possible with spatial resolution down to 1 µm.

While XPS is related to X-Ray Fluorescence (XRF), it is a more sensitive technique for evaluating the elemental and molecular composition at the surface of a sample as it measures electrons instead of X-rays. Future applications for art conservation may include pigment characterization, artificial aging studies, surface/pigment degradation phenomena, and the identification of organic materials.

Analytical Challenges

One of the greatest analytical challenges facing the conservation community involves the specific identification of paint binders, notably complex mixtures of layered systems. Advancements in data interpretation and instrumentation have encouraged conservation professionals to look beyond conventional methods of analysis such as cross-sectional staining (Fig 2), Fourier-transform infrared spectroscopy (Fig 3) and chromatography methods coupled with mass spectrometry (e.g. GC-MS). While the latter continues to provide scientists with useful results, chromatographic techniques are often not able to answer questions relating to the distributions of organic materials in complex layered systems. Fatty acids ratios are often used to distinguish between different drying oils and egg-containing materials, however unforeseen pigment interactions as well as poor detection limits can dramatically alter these numbers (Fig 4). Similar issues are encountered when performing protein analysis, making egg-oil systems extremely challenging to interpret.

Egg-Oil Paint Systems in Art

The early adoption of oil-painting techniques in 15-th century Italy has been revealed by both research and the scientific analysis of relevant works of art. Combinations of egg and oil have been discovered in easel paintings by several Italian paintings of the early Renaissance, including Giovanni Bellini, Carlo Crivelli, and Antonello da Messina. The gradual transition towards oil painting was likely inspired by the artistic traditions associated with painters active North of the Alps like Van Eyck and Rogier van der Weyden. Unless an artwork can afford several paint samples, it is extremely difficult to distinguish tempera grassa (true egg-oil mixtures or emulsions) from egg-oil layered systems (oil glazes atop an oil mixture) from egg tempera samples. It is extremely difficult to prove the presence of oil as paint layers, further research is still needed to confirm this theory. The advent of oil-painting in the works of art. Combinations of egg paints to create his Annunciation (1445/50). The study was carried by one of the authors, Kristin deGhetaldi in collaboration with National Gallery Senior Scientists Suzanne Q. Lomax.

Figure 1. A 2009-10 study conducted at the National Gallery of Art in Washington revealed that Frans Hals used both egg tempera, oil paints to create his Annunciation (1445/50). The study was carried by one of the authors, Kristin deGhetaldi in collaboration with National Gallery Senior Scientists Suzanne Q. Lomax.

Figure 2. Cross-sectional analysis demonstrated the necessity of the fluorescent state Alpha FLUOR® 488 and an amino acid diazo stain, Amido Black (magenta above). Although pigment interference may explain why the two stains were not able to identify egg yolk in the paint layers, further research is still needed to confirm this theory. An aged reference sample containing lead white/tempera paint over a gypsum-plaster ground (1680s) is shown in normal visible light (A) and stained with Amido Black (B). The same procedure was performed on a reference sample containing yellow ochre/tempera paint on in 1680s (C) and (D). All images were taken using a camera fitted with a Hoya R72 warm red filter (Fig 4).  Similar issues are encountered when performing protein analysis, making egg-oil systems extremely challenging to interpret.

Figure 3. The series of FT-IR spectra shown above correspond to a range of egg-oil mixtures containing yellow ochre to demonstrate the detection issue often encountered when proteinaceous materials are present in complex mixtures. For a range of egg-oil paints containing lead white, azurite, and vermilion the peaks associated with protein (area circled in red) become increasingly difficult to detect when the egg yolk consisted of half or less than half of the overall binding medium. Note that pigments typically interfere with the fingerprint region in the 1700-400 cm⁻¹ range. Further research is still needed to confirm this theory. An aged reference sample containing lead white/tempera paint over a gypsum-plaster ground (1680s) is shown in normal visible light (A) and stained with Amido Black (B). The same procedure was performed on a reference sample containing yellow ochre/tempera paint on in 1680s (C) and (D). All images were taken using a camera fitted with a Hoya R72 warm red filter (Fig 4).  Similar issues are encountered when performing protein analysis, making egg-oil systems extremely challenging to interpret.

Some preparations of pigments can lead to misinterpretation of the results (e.g. an egg-oil system can be mistaken for simply comprising of walnut oil). These issues are related to interactions between common and usual reifications in the conservation literature.

Currently work is being performed to obtain similar elemental information from oil-containing paints and mixtures.

Figure 4. Chart illustrating fatty acid ratios used for identifying egg and oil containing materials. Note that mixtures of oils and egg or oil can lead to misinterpretation of the results (e.g. an egg-oil system can be mistaken for simply comprising of walnut oil). These issues are related to interactions between common and usual reifications in the conservation literature.

Figure 5. The VG Scientific 200i XL X-ray photoelectron spectroscopy (XPS) at the University of Delaware. Surface Analysis Laboratory includes a monochromatic high flux microfocused Al Kα X-ray source for high resolution, high sensitivity work, a magnetic immersion lens for high collection efficiency and stable charge compensation, and a unique detector system for spectral and imaging data acquisition.

Figure 6. This series of spectra were collected using XPS and represent the surfaces of unpigmented glue (A), unpigmented egg yolk (B), and a series of egg tempera paints (C-F). Note the consistent ratio of O, N, and C present throughout all egg-containing samples. The ratios yielded by the glue sample were noticeably different, with much higher amounts of O and N.

Figure 7. The ION-TOF TOF-SIMS IV system at the University of Delaware can obtain images with a resolution better than 100 nm and can be achieved with very high mass resolution (m/Dm > 10,000). Several operational modes are now available in the facility including static mode and imaging.

Figure 8. This series of spectra were collected using TOF-SIMS and represent the surfaces of gypsum (calcium sulphate) in collagen (A), unpigmented collagen (B), lead white (basic lead carbonate) in leaded oil (B), and lead white in egg yolk (D). Note that the glue, egg yolk, and oil binders all generated spectra with characteristic features. This confirms that TOF-SIMS is not only able to distinguish between egg and oil binders, but also between proteinaceous materials (glue and egg yolk).

Time-of-Flight Secondary Ion Mass Spectrometry

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a surface technique that provides molecular information regarding a sample. TOF-SIMS uses a primary ion beam to bombard a surface to produce secondary fragment ions, which are analyzed via a TOF mass spectrometer. As with any other mass spectrometry technique, molecular information is provided by looking at mass fragments derived from a sample. TOF-SIMS is well suited for imaging, as the instrument can raster the primary ion beam across the sample surface, and unique mass fragments can be selected during analysis. Lastly, WS-SIMS is a technique applicable for multivariate analysis, as an image is comprised of pixels (e.g., 128x128) where each pixel is a single spectrum allowing for high data rate acquisition. To date only a handful of studies have applied WS-SIMS to issues relating to art conservation.