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An Examination of Light-Induced Color Change in Anoxia and Hypoxia using the Microfading Tester

Vincent Beltran, Jim Druzik, Andrew Lerwill & Christel Pesme

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An Examination of Light-Induced Color Change in Anoxia and Hypoxia using the Microfading Tester

Vincent Beltran, Jim Druzik, Andrew Lerwill & Christel Pesme

2014 AIC Annual Meeting, San Francisco
Presentation Outline

• Introduction
• Experimental method
• Microfading Tester (MFT) results
• Comparison of MFT results to those from 2012 Halogen Lightbox study
• Future Work
Introduction
Light is a primary agent of deterioration for collections. Shown here is a century-old blue dress faded after 10 years of modern museum display. (Photo Credit: Stefan Michalski, CCI)

Listed are typical means by which light damage to collections may be reduced. The focus of this research examines the use of anoxic & hypoxic environments as another way of mitigating light-induced damage.
Photooxidation is a major mechanism of light damage.

The rationale behind the use of anoxic or hypoxic conditions is to limit the availability of oxygen that can be used in reactions creating reactive species that may cause irreversible damage.

It should be noted that in the absence of oxygen, other photochemical reactions may occur.
The conservation literature on the use of anoxia has highlighted the potential benefit of anoxia in limiting color change. In addition to the issues listed above, it has also identified other colorants for which color change may be enhanced in anoxia (e.g., Prussian blue).

Note that the color change of Prussian blue in anoxic environments has also been shown to regain color upon re-exposure to air.
Here we summarize the results of a previous anoxia study published in 2012 in *Studies in Conservation*. This study used a halogen lightbox (LB) to expose the samples to light, while the environment was established (and samples housed) within a hermetically-sealed case. Note that temperature was actively regulated by use of water-chilled cooling panels within the case, and the gas was humidified before purging of the case to set the humidity level.

As a follow-up study, it was decided to rerun the study using select fresh samples exposed to the Whitmore-designed Microfading Tester (MFT), thus allowing a comparison of color change results between the two techniques (Lightbox and MFT).
Experimental Method
This image shows the MFT being used to assess samples through glass. The following slide will show a schematic of the experiment.
The analysis was carried out through a ¼” pane of glass on the case’s top surface. To allow for alignment of the xenon and spectrometer spots, the samples were positioned ~5 mm below the glass.

While reducing the illuminance on the samples, the glass has minimal effect upon the spectral power distribution (SPD) of the light source.
Four gases (compressed air, nitrogen, and 1% and 5% oxygen balance nitrogen) were used to establish the various oxygen environments within the case. The oxygen concentrations of the air and hypoxic environments were verified using a head-space oxygen analyzer, while the concentration for the anoxic environment was assessed using a trace oxygen analyzer. Though containing an oxygen concentration of 200 ppm or less, this environment will be considered “anoxic” for this experiment.

While case temperature was determined by the air conditioning in the room (which remained fairly constant), case humidity was established by the addition of moisture to the gases (which initially are dry streams) prior to purging the case.
This image shows reflectance curves produced by the MFT during varying intervals of exposure to the high-intensity xenon light source.
From the reflectance spectra (which were collected every minute), curves for the colorimetric variables of \( L^* \) (upper left), \( a^* \) (upper right), and \( b^* \) (lower left) were generated as a function of exposure time. The colorimetric data was then used to calculate curves of color change or \( \Delta E \) (lower right), again as a function of exposure time, with the reference colorimetric values being those collected at \( t = 0 \).

Note that the \( \Delta E \) reported here is based on the 1994 calculation.
To facilitate comparison to the 2012 halogen lightbox study, we will focus on MFT data collected following 203 minutes of exposure, which corresponds to an approximate light dose of 17.5 Mlux-hours.
The 18 samples examined have known compositions and were previously examined in the 2012 halogen lightbox study. Samples were chosen to encompass a range of colorant types and color change values/behaviors as observed in the 2012 study.

Note that the study includes two samples of Prussian blue: Kremer and Winsor & Newton (WN) watercolor.

Regarding the Canadian Museum of Nature (CMN) leaf and grass samples: though these dried specimens remained in dark storage for a number of years before analysis, they continued to maintain a green color, likely due to skilled preservation techniques by the collector. Thus, any degradation processes concomitant with only being dried and stored in air had run their course or arrived at a state of reasonable stability prior to testing.
Microfading Tester Results

The Getty Conservation Institute
This plot shows the MFT color change in air of the 18 samples examined. Note the wide range in color change values in air.

Recall that the data shown on this plot and on the plots to follow display values following a light dose of approximately 17.5 Mlux-hours.
The color change of each sample can then be ranked by its Blue Wool Equivalent (BWE). In addition to connecting a sample’s color change to a Blue Wool internal standard, this categorization becomes particularly useful when comparing results between the MFT and the halogen lightbox study.
This plot compares the MFT color change in air and anoxia for each sample. Though generally less than that in air, note that the color change in anoxia is not insignificant. Thus, anoxic color change may be utilizing the residual oxygen (< 200 ppm) remaining in the “anoxic” environment, or other photochemical pathways that do not need oxygen are being utilized and causing color change.

To ease comprehension, one can calculate the ratio between MFT color change in air (numerator) and anoxia (denominator). This ratio will be shown in the next slide.
The Y-axis now shows the ratio of MFT color change in air (numerator) and anoxia (denominator).

2 thresholds are shown at ratios of 0.8 and 1.2. A ratio above 1.2 indicates higher color change in air, a ratio below 0.8 indicates higher color change in anoxia, and a ratio between the two indicates roughly equal color change in the two environments.

In addition, the further a sample’s ratio is above 1.2 or below 0.8 indicates a larger difference between that sample’s color change in air and anoxia. For example, a ratio of 2 indicates that a sample’s color change in air is two times greater than that in anoxia, while a ratio of 10 indicates that a sample’s color change in air is ten times greater than that in anoxia. Conversely, a ratio of 0.5 indicates that a sample’s color change in anoxia is two times greater than that in air.

12 samples showed a color change ratio above 1.2, 1 sample showed a color change ratio less than 0.8 (WN Prussian blue), and 5 samples showed a ratio between 0.8 and 1.2.
Color Change in Hypoxia
This plot shows MFT color change curves for Blue Wool 1 when exposed to four different oxygen environments. Note that the curves at 1% and 5% oxygen remain close to the anoxia curve, indicating that hypoxic concentrations continue to impart much of the benefit provided by anoxia.
This plot shows MFT color change curves for WN Rose Malmaison when exposed to four different oxygen environments. Note that the curves at 1% and 5% oxygen are much closer to the air curve. Thus, the benefit of anoxia in reducing the color change of WN Rose Malmaison seems to be quickly lost when exposed to hypoxia.
The Y-axis shows % of MFT color change in air for samples exposed in anoxia and 1% oxygen. (Anoxia bar = color change in anoxia divided by the color change in air, while the 1% bar = color change in 1% oxygen divided by the color change in air. 100% represents the color change of the sample in air.)

Note the similarity between anoxia and 1% bars for most samples, indicating that exposure to 1% oxygen did not dramatically increase the color change of these samples. (Though the 1% bars are slightly lower than those of anoxia for several samples, we are assuming here that they are essentially equivalent.)

Three samples – WN Rose Tyrien, WN Rose Malmaison, WN Fluorescent Yellow – showed much higher color change in 1% oxygen than in anoxia.
This plot builds upon the previous slide by including the bars for exposure in 5% oxygen. (5% bar = color change in 5% oxygen divided by the color change in air.)

For those samples that showed little difference in color change between anoxia and 1% oxygen, exposure in 5% oxygen typically resulted in only a slightly higher color change result which remained much lower than that in air.

For the 3 samples – WN Rose Tyrien, WN Rose Malmaison, WN Fluorescent Yellow – showing much higher color change in 1% oxygen compared to anoxia, exposure in 5% oxygen produced even higher color change values.
This plot shows the Y-axis as the % MFT color change of WN Prussian blue in anoxia for samples exposed in 1% oxygen, 5% oxygen, and air. The Y-axis was changed since WN Prussian Blue WC shows the most color change in anoxia. (Air bar = color change in air divided by the color change in anoxia, 5% bar = color change in 5% oxygen divided by color change in anoxia, 1% bar = color change 1% oxygen divided by the color change in anoxia. 100% represents the color change of the sample in anoxia.)

Note that the color change of WN Prussian Blue WC at 5% oxygen was only slightly higher than that in air. The implication of these results is that intermediate oxygen concentrations (e.g., 5%) might be useful when an object contains both Prussian blue, resulting in a slight increase in color change compared to its exposure in air, with other colorants such as Crystal Violet for which hypoxia would greatly reduce its color change compared to in air.

Summary of MFT Results

- 12 of 18 samples exhibited more color change in air
- 1 sample showed more color change in anoxia (WN Prussian Blue WC)
- Hypoxic exposures (1% and 5% O₂) typically show much less color change relative to air
  - Prussian Blue: hypoxia shows much less color change relative to anoxia

This slide lists a summary of the results from the data generated by the MFT. The remainder of the presentation will compare the MFT results to those obtained in the 2012 halogen lightbox (LB) study.
Comparison of Microfading Tester and Halogen Lightbox
This slide compares the experimental details of the MFT and halogen lightbox (LB) studies.

The two light sources have different spectral power distributions (SPD), with the xenon SPD roughly constant across the visible range, while the halogen SPD increases continuously with higher wavelengths, crossing the xenon SPD at ~ 570 nm.

Note the disparity in light intensity and its consequent effect on the duration to reach 17.5 Mlux-hours. The shorter exposure time of the MFT compared to the LB study allow us to generate more rapid results for individual samples. Note that the lower light intensity of the LB study (0.01 Mlux) remains much higher than what would occur in a typical low-level gallery lighting situation (0.00005 Mlux or 50 lux).

The near-simultaneous results provided by the MFT also allow for an examination of the kinetics of color change and provide a gauge by which the analysis can be terminated when a threshold color change value has been reached. Finally, the small spot size of the MFT analysis limits the aesthetic impact of any resulting color change.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Microfading Tester (MFT)</th>
<th>Lightbox (LB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Source</td>
<td>Xenon</td>
<td>Halogen</td>
</tr>
<tr>
<td>Light Intensity</td>
<td>5 Mlux or 5 million lux</td>
<td>0.01 Mlux or 10,000 lux</td>
</tr>
<tr>
<td>Duration (17.5 Mlux-hrs)</td>
<td>3.5 hours</td>
<td>1750 hours or 2.5 months</td>
</tr>
<tr>
<td>Analysis</td>
<td>Continuous</td>
<td>Start/End</td>
</tr>
<tr>
<td>Exposure</td>
<td>4 mm spot</td>
<td>Broad</td>
</tr>
</tbody>
</table>
This slide reviews the concept of reciprocity. If reciprocity does not hold between the MFT and LB, this would limit extrapolation of these results using different light intensities or exposure times.
This plot shows the color change in air for the 18 samples examined by the MFT.
This plot now compares the color change in air for the samples examined by the MFT and LB studies. Note that in general the color change in air is greater in the LB study compared to in the MFT study. We’ll return to this comparison following an examination of Blue Wool Equivalence between the two techniques.
This slide repeats the Blue Wool Equivalent (BWE) categorization of the samples examined by the MFT in air.
This slide now categorizes the Blue Wool Equivalent (BWE) of the samples examined by the LB in air.
The BWE in air for the MFT and LB studies was within 0.5 BWE for half of the samples and 1 BWE for nearly all samples. Four samples indicated BWE within 1.5 BWE – we will discuss CMN Aster and Scirpus in a later slide.

Though not shown here, the BWE for samples exposed in anoxia showed a similar correlation, with most samples showing MFT and lightbox BW rankings within 0.5 BWE.
Here we return to a plot of color change in air for the samples examined by both the MFT and LB studies.

It is again helpful to look at ratios of color change. While previous slides looked at the ratio of color change in air and anoxia, the next slide will now plot the ratios of color change in air for the MFT (numerator) and LB (denominator). This ratio will be shown on the next slide.
This plot now shows the ratio between color change in air for the MFT (numerator) and the LB (denominator).

Two thresholds are again shown at 0.8 and 1.2. In this case, a ratio above 1.2 indicates higher color change in the MFT, a ratio below 0.8 indicates higher color change in the LB, and a ratio between the two indicates roughly equal color change determined by the two analytical techniques.

Since most samples did not exhibit ratios between 0.8 and 1.2, reciprocity does not generally hold between samples analyzed with the MFT and lightbox. Only three samples – WN Rose Malmaison, WN Periwinkle Blue, and WN Flesh Tint – potentially showed reciprocity holding between the two techniques and all had borderline ratios of ~0.8.

Further, 12 of the 18 samples showed higher color change in air for the LB than for the MFT (ratios below 0.8), indicating that the MFT typically underestimated the color change compared to the LB study. Only 3 samples – WN Prussian Blue, K Prussian Blue, and WN Fluorescent Yellow – showed higher color change in air for the MFT than for the LB (ratios above 1.2). Here the MFT study overestimated the color change in air compared to the LB study.

Of particular interest are the results for CMN Aster, CMN Scirpus, and CMN Dryopteris, which showed the lowest ratios of any sample, indicating that the MFT severely underreported the color change in air compared to the LB study. These samples will be discussed further in the next slide.
This table highlights the large difference in color change in air for the natural history samples as determined by the MFT and 2 lightbox studies.

The second lightbox experiment (Halogen, Mark 3 filter) corroborated the results from the first lightbox study. (Note that this study was carried out in a different lightbox that did not control temperature and humidity.) Though the light dose of the second lightbox experiment (1.8 Mlux-hours) was roughly only 10% of those for the MFT and first lightbox study (17.5 Mlux-hours), the resulting color change values from the filtered halogen experiment far exceeded those obtained from the MFT study and were roughly 50% of the values from the first LB study.

The second halogen study also represented an attempt to modify the halogen SPD by removing light above 640 nm. (As stated previously, the SPQ of xenon is relatively constant, while the SPD of halogen increases continuously, exceeding that of Xenon above ~570 nm.) The region above 640 nm also coincides with peaks in the action spectrum of Chlorophyll a and b. Thus, it was hypothesized that removal of light above 640 nm for the halogen light source would limit chlorophyll activity and provide a rough comparison to the lower xenon SPD in this wavelength region. However, exposure of the samples to this modified halogen SPD seemed to have little effect as they continued to exhibit larger color change values relative to those from the MFT.

This discrepancy between the color change of these natural history samples obtained with the MFT and lightbox studies remains an open question that will be examined further by exposure under varying MFT conditions (e.g., lower light levels) and analysis of a variety of natural history samples.
Relative Color Change Behavior in Air and Anoxia for MFT and LB
This table is an attempt to compare the relative color change behavior in air and anoxia as determined by the two analytical techniques.

Categorized for both the MFT and LB studies, the symbols are as follows: + indicates that the sample showed more color change in air than in anoxia; - indicates that the sample showed more color change in anoxia than in air; and 0 indicates that the samples showed roughly equal color change in both environments.
13 of 18 samples showed similar relative color change behavior as determined by the MFT and LB studies (i.e., both techniques resulted in the same category of relative color change behavior). This result suggests that the MFT can be reliably used to assess relative color change behavior.
This is a plot of the MFT color change ratio between air (numerator) and anoxia (denominator) for samples exhibiting higher color change in air than in anoxia.
This plot now builds upon that shown in the previous slide by adding the LB color change ratio between air (numerator) and anoxia (denominator) for samples exhibiting higher color change in air than in anoxia.

Of the 11 samples exhibiting higher color change in air compared to anoxia for both the MFT and LB experiments, 8 samples showed a higher color change ratio (air/anoxia) when assessed by the lightbox. This indicates that, for these samples, the difference between the color change in air and anoxia is much greater in the lightbox study than it is in the MFT study. This suggests that, while it may be reliably used to qualitatively assess relative color change behavior, the MFT may not be suitable as a quantitative comparison between color change in air and anoxia.

Among these samples, only two showed a higher color change ratio for the MFT (LC Brazilwood/P and WN Rose Malmaison) and one sample showed a roughly equivalent color change ratio (LC Brazilwood/L).
This plot shows the color change ratio between air (numerator) and anoxia (denominator) for WN Prussian Blue WC as determined by the MFT and LB studies. This was the only sample in this study to exhibit more fading in anoxia than in air. Similar to the previous plot, the difference between color change in air and anoxia is greater in the lightbox study than for the MFT study. (Note that a ratio further below the 0.8 threshold indicates a greater difference between the higher color change in anoxia and the lower color change in air.)
Five samples – WN Periwinkle Blue, WN Fluorescent Yellow, CMN Aster, CMN Scirpus, and K Prussian Blue – showed different relative color change behaviors between the MFT and lightbox studies (i.e., both techniques resulted in different categories of relative color change behavior). The next slide will compare the color change ratios for each.
This table focuses on the color change ratios between air (numerator) and anoxia (denominator) for the samples highlighted on the previous slide that showed different relative color change behavior.

As previously discussed, CMN Aster and CMN Scirpus were affected by the inability of the MFT technique to induce a color change near that seen in the LB study, contributing to the different categorizations of relative color change behavior (MFT: equal color change in air and anoxia, LB: more color change in air than in anoxia).

Though technically showing different relative color change behaviors by the two techniques, the MFT color change ratio of Kremer Prussian blue (0.8) was on the border between equal color change and more color change in anoxia. Thus, replicates of this sample should be tested to see if subsequent results show similar relative color change behavior as the LB study (i.e., more color change in anoxia than in air).

The disparate relative color change behaviors of WN Periwinkle Blue and WN Fluorescent Yellow require further assessment by replicates and similar samples and variation in the experimental details of the MFT. For example, previous work by Hoyo-Melendez and Mecklenberg suggested that reciprocity held for the MFT at light intensities below 1 Mlux.
Summary of MFT/LB Comparison

- Blue Wool Equivalence in Air for MFT and LB is typically within 1 BW step
- Reciprocity failure between color change in air for LB and MFT (5 Mlux)
  - MFT ΔE94 in air generally less than LB ΔE94 in air
- Inability of MFT to induce color change for leaves and grass

This slide and the one that follows summarize the results from the comparison of the MFT and LB studies.
Summary of MFT/LB Comparison

- Relative color change behavior in air and anoxia typically consistent between MFT and LB
  - Compared to the LB, MFT shows a smaller differential between the color change in air and anoxia
Future Work

- Replicate analyses for current sample set
- Additional samples from 2012 anoxia study
- Effect on reciprocity for MFT exposures at reduced light intensities (< 1 Mlux)
- Examine relationship between color change and humidity

Note that the results shown in this presentation were based on a single analysis of each sample in each environment. This was due to the prolonged MFT exposures (5 hours) and a desire to present results for a varied sample set in time for this presentation. Thus, replicate analyses will be necessary to verify the results of the MFT study.

As previously stated, Hoyo-Melendez and Mecklenberg showed that reciprocity held for the MFT when lower light intensities were employed.
Following the presentation, it was asked if the halogen lightbox (LB) results would be more representative of what might occur in a typical low-lighting gallery setting, particularly since this presentation showed that reciprocity generally did not hold between the MFT and lightbox studies.

The author’s response stated that the conventional thinking was that the lower light intensities posed by the lightbox study (0.01 Mlux) compared to the MFT (5 Mlux) were thought to result in color change values closer to what one might see in a gallery setting. However, the question remains if reciprocity holds between the lightbox study and typically gallery lighting. Thus, extension of accelerated aging results as a quantitative predictor of the effect of low-level gallery lighting conditions remains an approximation.
Concealable strain monitoring and modeling of relative dimensional changes in art objects

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Presented at the RATS session
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San Francisco, CA, May 27-June 1, 2014
This presentation describes a novel way to monitor small displacements without intermediation of stress. It is concealable and suitable for monitoring strain in cultural heritage objects both in laboratory and display environments.
The following outline describes the scope of this presentation.

Outline

1. Objectives
2. Sensor description
3. Sensing relative motion
   1. Applications
4. Lab experiments
   1. In wood
   2. In textiles
5. Data gathering for analytical models
6. Deployment at Hampton Court Palace
Due to the fact that art objects are exposed either to strictly controlled or otherwise to uncontrolled environments (particularly with respect to temperature and humidity conditions), our objective is to investigate the use of strain sensors to correlate mechanical changes with environmental fluctuations for better understanding conservation approaches.

This slide describes the desirable properties of the sensors that enable it to best achieve the goals above.
This slide describes the giant magneto resistance (GMR) sensor-magnet configuration. The chip has a GMR element in a Wheatstone bridge. The voltage between the two legs of the bridge changes in response to GMR resistor variation due to change in the magnetic flux (in our case provided by the excitation magnet), resulting from variation in the chip-magnet distance. The sensor chosen for the experiment (NVE AAL002-02) has a linear output between 1.5 and 11.5 Oersted, and an operating temperature range of -50 to 125 degrees C. A more comprehensive list of properties is reported by the manufacturer on their website. The GMR element is shielded using a high permeability metal shield so that it responds only to variations of the magnetic field component along the axis of sensitivity. In the preferred mode of operation, the field is provided by a small rare earth magnet positioned with its axis aligned with the axis of sensitivity of the GMR element.

The properties described above underscore the advantage of this type of sensor in that, after suitable calibration of sensor output voltage versus relative displacement, the relative motion between chip and magnet, which are mechanically decoupled, can be measured.
For calibration experiments, the chip was mounted in a fixed location while the magnet was aligned with the chip axis of sensitivity on a platform with micrometer displacements along three axes.

The chip was powered with 3.2 DC voltage, and the voltage output versus magnet position was recorded with 0.1 mV resolution. The magnetic field was generated by a rare earth magnet 3.2 mm in length and 1.6 mm in diameter that was mounted on a 3D stage controlled by micrometers that had a displacement accuracy of 2.5 µm.

The sensitivity of the sensor with respect to the distance X to the magnet is only constant (linear response) within a region centered around a fixed X/D ratio value, where D is the diameter of the magnet. For the magnet used to produce the data shown in this slide, this linear response region encompasses +/- 0.75 cm with respect to its midpoint, which is sufficient to probe the expected strain range. For the same magnet, it is shown that the curves are fairly insensitive to small lateral displacements and exhibit cylindrical symmetry, in agreement with the use of cylindrical magnets. Furthermore, the range of the lateral insensitivity increases with the diameter D of the magnet.
The sensitivity $S_{ij}$ is the slope of the sensor output voltage versus the chip-magnet distance along the axis of sensitivity, and it is used to obtain the curve of voltage versus distance using the formula:

$$X_{ij} = X_{ij-1} + S_{ij} \times (V_j - V_{j-1})$$

where $i = x, y, z$ axis, and $j$ values are consecutive measurement data points.

The top figure in this slide shows the chip response for two different magnet diameters, and shows that there is a compromise in choosing the magnet. Smaller diameter increases the sensitivity, but decreases the midpoint of the linear response region, and decreases the region of insensitivity to lateral movement. The bottom figure plots the variation in voltage due to a lateral displacement of the sensor (perpendicular to the axis of sensitivity, the $x$ axis) at a fixed $x$-value (mid-value) within the linear region on the axis of sensitivity. Notice that within a lateral displacement of $+/- 0.6$ cm this variation is less than $4\%$. 
Strictly speaking, due to the nature of the chip, it could be argued that a variation in voltage could be generated not only by a change in the position along the axis of sensitivity, but also by a lateral movement produced by a shear strain.

In order to take the latter effect into account, we developed a three-element node, which has been applied to an experiment that monitored strain in wood objects, as shown in the next slide.
Having determined the calibration parameters for the particular chip and magnet arrangement described before, two wood objects of different shape and kind were selected to test the performance of the sensors. Object 1 was a piece of cedar 8 mm thick cut along the fibers, and which had an incipient crack. Object 2 was a piece of pine 20 mm thick which was cut across the fiber, exposing the growth rings.

In order to assess the effect of lateral displacements, the node is defined as described in the top figure, which shows a schematic representation of the way three identical sensors are deployed in Object 1. In Object 2, the x direction is the radial direction, and thus the y direction is tangential to the ring at the insertion of the sensor in direction x. In addition, we deployed a control sensor in which both the chip and magnet were attached to a glass slide. The actual orientation of the sensor and magnet mounting is shown in the bottom figure.
This slide describes the equations used to limit the non-linear effects on the strain determinations for a given direction due to strain in the orthogonal directions. It is an iterative calculation that converges very fast to a stable value.
The wood objects with mounted strain sensors and corresponding magnets were mounted in a regulated temperature-humidity chamber. The chamber was run so that the temperature was kept constant at 25 degrees C, and the relative humidity (RH) was abruptly ramped from 50% at time zero to 85%, a process that took about 20 min. This type of change mimics a situation in a museum room in which the air conditioning stops while a door is opened on a humid day. The GMR sensors outputs were sampled every 30 seconds. After 48 hours, the RH was reversed down to 50%. The displacement results for Objects 1 and 2, including the iterative corrections in different colors, are shown on the left side of this slide.

To assess the reversibility of the process, the calculated displacements at the beginning and end of a set of two consecutive runs are shown in the table on the right hand side of this slide.

The results indicate that for Object 1 the deformation is mostly reversible with the exception of the crack opening, which exhibits an irreversible increase of about 15% of its maximum incursion after the RH goes back to its initial value at the end of the second run. However, the experiment may have not been long enough for the “irreversible” deformations to achieve their initial values.

For Object 2 the dimensional change in the z direction is small, but there is irreversible change in the x, y plane, with a contraction along the x direction and an expansion along the y of about 3% and 5% of their maximum incursions, respectively. For this object, the largest variation occurs along the y direction, which is tangential to a growth ring and perpendicular to the radial direction of the sensor along the x axis. It is interesting then to estimate the variation of a chord linking two points on a ring (the position of the two sensors). The corresponding equations are shown in red in this slide, and suggest that the deformation is not just pure radial expansion.

The objective of this work is not to make a detailed study of the deformation of wood upon changes in RH; a larger sensor array would be necessary for that. However, the results shown above demonstrate the usefulness of the sensor assembly and correction methods to study in detail the deformation of wood objects, and it should be underscored that the conditions of the experimental T/RH chamber mimic a possible interruption of well-controlled conditions in a museum environment on a humid day. The above results in our experimental pieces also imply that the objects’ response to a sudden change in RH may be relatively fast (less than one hour) in a museum environment if the T and RH conditions are suddenly disturbed.
We propose that this type of sensor is suitable to monitor strain in textiles, and this slide shows a possible way of non-destructive attachment of both sensor and magnet.
This slide shows the results of measuring the evolution of a piece of cotton fabric as it dries. The short wavelength oscillations respond to air pressure fluctuations due to opening or closing of the lab’s doors. The long term variation reflects the shrinkage measured in two different parts of the cloth.
The above results, and the sensor characteristics (concealment because of its small size, stress-independence, low energy consumption) are a dramatic demonstration of the advantages that the described assembly offers in terms of monitoring this type of object, in-situ in a museum, compared to previously used sensors in these venues. A further advantage is that our sensors are well suited to be powered by small batteries (nominal voltage of 3.3 V) and embedded as part of remotely controlled radio elements (motes) capable also of carrying environmental sensing combined with power-efficient communication based on a time synchronized communication protocol.

One such implementation is the Low Power Wireless Mote Technology (LPMT) developed at IBM that is utilizing off-the-shelf radios (Linear Technology) and microcontrollers (Texas Instruments). The time synchronized communication allows radios to “sleep” for most of the time and then wake up to transmit the sensor data to the gateways through a dedicated communication path, avoiding collision and multiple communication path searches. The optimized communication allows for over 5 years of operation utilizing a single AAA battery. Multiple sensors can be attached to the relevant motes to assase microenvironment fluctuations: temperature, humidity, air contamination, door position, presence sensors etc. The motes are self-organizing in a mesh network and create a rich ecosystem of sensing points that is valuable to assess museum collections, IT equipment, hospitals rooms, etc. The sensor data can be acquired individually or one parameter acquisition can trigger the measurement of a second parameter (to assess, for example, how the presence of one person would change the local relative humidity value around an object of art). The sensor network is characterized by reliable, low power, and small form factor sensors that can be attached to objects of art in a concealable fashion.
To further test these sensors, IBM and Historic Royal Palaces established a Joint Scientific Agreement to monitor valuable tapestries in the Great Hall at Hampton Court Castle, aiming at creating dynamic models of deformation correlated with micro-environmental fluctuations.
This slide describes the Great Hall and the mode of attachment of the sensors and magnets to the tapestries.
This slide shows the details of the installation process.
This slide shows a schematic description of the attachment and location of the magnets, motes and sensors.
This slide shows a real-time data collection viewing which is attained by logging on to the server. These data can be grabbed for analyses by anyone with access to the server website.
This slide shows an example of data acquisition for a period of three days.

Notice that the variations are fairly well correlated with temperature. A disturbance occurs at the time of the Great Hall’s opening to the public. Keep in mind that the room is not T/RH controlled. As expected, the bottom level of the tapestry exhibits the largest movement.
This slide shows the variation of the displacement data correlated with dew point temperature to take into effect the air moisture. Notice that the variations are better correlated with dew point temperature.
Summary

- Demonstrated the suitability of GMR strain sensors for long term monitoring the response of wood and textile objects to local environmental fluctuations.
  - Produced algorithm to correct the effects of sensors misalignment
  - Demonstrated the advantages of integrating the sensors with Low-Power Mote Technology (LMT) for general wireless data gathering and control.
  - Showed sample of results arising from the installation of the described technology at Hampton Court Palace, London, UK.

- Planned activities
  - Continue collaboration with Historic Royal Palaces
    - Monitor environmental risks of the tapestries in the Great Hall at Hampton Court Palace
    - Sense tapestry movements in response to fluctuations in temperature and relative humidity in real time
      - Long term sampling will allow modeling the best structural support for the tapestries using data from the actual historical pieces
      - Create a model for assessing the response of the tapestries to environmental dynamics
  - Collaborative PhD project with University College London (UCL)

- Develop Analytics and Models in novel environments
  - Extend relationships with cultural institutions to promote the use of a universal platform for analytics in the area of environmental effects on cultural heritage preservation
  - Microclimatic dynamics effects on objects
  - Risk management across different geographies
  - Helping to revise existing standards.

This slide summarizes our results and highlights future work.
Accurate Measurement and the Quantification of Surface and Material Property Change Using New RTI and AR Techniques

Carla Schroer¹, Mark Drew², Mark Mudge³, Mingjing Zhang⁴

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Presented at the RATS session
42nd Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
San Francisco, CA, May 27-June 1, 2014
This paper presents new work in the area of Reflectance Transformation Imaging (RTI) and the use of color and surface normals data. It includes work by Cultural Heritage Imaging, prepared by Mark Mudge and Carla Schroer, and research from Simon Fraser University by co-authors, Mark Drew and Mingjing Zhang. In addition, some collaborative work from Sema Berkiten and Szymon Rusinkiewicz of Princeton University is included, as well as recently published work from the Georgia O’Keeffe Museum and several collaborators.
This paper will discuss some exciting new work with Reflectance Transformation Imaging (RTI) and related techniques that use the same types of captured image data sets as RTI.

It will start with some background on the technique and describe what surface normals are. Then it will present an RTI example.

The bulk of the paper will focus on additional uses of RTI data sets starting with examples of Algorithmic Rendering from Princeton University.

Then it will look at ways in which RTI data can be used to track changes in surfaces over time, and also recent research to improve the accuracy of the calculated surface normals. Finally it will take a brief look at the importance of evaluating the resulting images for quality, reliability and reuse.
All of this work takes place in the context of computational photography. What I mean by this is that instead of taking a single image, you take a sequence of images. Then using computer algorithms you extract information from that set of images to create a new type of image (or result) not possible from a single image.

There are many examples of computational photography, and this is a field that has much active research.
Reflectance Transformation Imaging (RTI)
Let’s begin by looking at an example of an RTI.

This example is a Japanese Woodblock Print from the mid 19th century in the collection of the Fine Arts Museums of San Francisco.

Note: The RTI example shown in the presentation at AIC has been replaced in this postprint due to publication restrictions. In addition, a live demonstration of an RTI example was included. Here we substitute some still images taken from an RTI.
With an RTI we can dynamically relight the subject from any direction. We have collected both color and shape information, so we can look at just the surface shape, and we can also apply mathematical enhancements to the view. In this image the lower left shows the “default” or “normal” view from the RTIViewer while the upper right shows the surface shape with no color, and with the surface rendered as specular (or shiny) so that we can see the fine surface details.

Note: A live demonstration was given in the conference presentation. Here we substitute an image created from 2 views within the RTI viewer. A video demonstrating details from this example and showing the interactive relighting and mathematical enhancements in action, can be seen here: http://vimeo.com/16942430
So, here are the basics for creating an RTI:

We have a camera and a subject in fixed positions. Then we take a sequence of images with light in different positions around the subject. We have to know where the light is in each image in order to calculate the RTI. The result is a 2D image that carries 3D information.

This is based on work by Tom Malzbender and Dan Gelb from HP Labs, first published at SIGGRAPH in 2001. [http://www.hpl.hp.com/research/ptm/papers/ptm.pdf](http://www.hpl.hp.com/research/ptm/papers/ptm.pdf)
There are 2 primary ways to collect RTI data. First I’m going to talk about Highlight RTI.

In 2006, Cultural Heritage Imaging and Tom Malzbender co-invented Highlight RTI.

Highlight RTI can determine the light positions after the capture session.

We place shiny black spheres in the photo scene.

The light makes a sharp highlight on the sphere’s surface.

The location of the highlight on the sphere’s surface indicates the position of the light source, which can be calculated in software after the images are taken.

The invention of Highlight RTI enabled broad adoption of the technique because the cost to capture RTI data was small, and the setup is flexible for a wide range of sizes and capture environments.
This is a simple Highlight RTI configuration.

The camera is pointing down toward the subject. There are two small ball bearings in the field of view, used to collect the light position information. A string is used to keep the distance of the light to the subject constant. We trigger the flash unit using radio triggers on the camera and flash. In this case we are also connected to a computer so we can fire the camera, download the images, track file naming, and be able to check test images in detail. A tethered computer isn’t required, but we recommend it whenever possible.
The light position is moved and another shot is taken.
Here is a third light position for this image set.
We can do this for vertical subjects by mounting the spheres and placing them in the image.
Here is another vertical setup, this time in a gallery. We are shooting a detail of this large panel, and we have placed the flash unit on a longer pole so we can get it all the way around the area we are imaging.
Copy stands, found in many museum and library studios, provide a great environment for capturing RTIs.
RTIs can also be captured using a light array or dome. Prior to the 2006 invention of highlight RTI, domes were the primary method of capturing RTI data. They are still very efficient for working with larger collections of smaller objects.

This is the most recent example of a light array built by Cultural Heritage Imaging. It has 45 lights and can image subjects up to 12 inches in diameter. The lights have a radius of 24 inches from the center of the subject. The light array has many features for flexibly placing the camera and subject in the environment. It takes 2.5 minutes to capture the 45-image sequence.
How RTIs work:

1. Mathematically, the direction that is perpendicular to the surface at any given location is represented by a vector (direction) called a normal. Technically it is a vector that is perpendicular to the tangent plane at any point on the surface, as real surfaces are in 3 dimensions and this graphic is only 2-dimensional.
2. Light bounces off of surfaces such that the incident angle of the light and the reflected angle of the light are equal angles to the surface normal. Since the camera is in a fixed position, and we know where the light is coming from in each image, and because we sample from a variety of light positions, we can calculate the surface normal per pixel in the image.
3. The mathematical description of the normal is saved per pixel, along with the RGB (red-green-blue) color information of a regular photograph. This ability to record efficiently the color and true 3 dimensional shape information is the source of RTI's documentary power.
Software to create and work with RTIs is free and open source. Also available are a free capture guide and instructional videos. All these are accessible on the Cultural Heritage Imaging’s website.

http://culturalheritageimaging.org/downloads
It is also possible to combine the RTI technique with UV and IR light spectrums, as well as to do RTI under the microscope.
RTI Adoption Breakthrough

- Significant RTI adoption is happening in museums
- Adoption by many museums including:
  - Yale University Digital Collections Center
  - The Metropolitan Museum of Art
  - The Smithsonian Institution, Museum Conservation Institute
  - The Museum of Modern Art
  - Staatliche Museen, Berlin
  - Worcester Art Museum
  - Georgia O’Keeffe Museum

We have seen significant adoption of RTI in museums in recent years, largely driven by museum conservation. Here are just a few of the museums that are actively using RTI today.
A recently completed grant from the Institute of Museum and Library Services was an important aid to RTI adoption. The grant included funding for 10 4-day training sessions. CHI was able to train 150 participants representing 45 different institutions. This included all of the ANAGPIC graduate programs in art conservation in North America as well as 4 regionally hosted training sessions where museum professionals could participate without a training fee. Participants were chosen through an application process.
Algorithmic Rendering

Cultural Heritage Imaging
Let’s take a quick look at a technique called Algorithmic Rendering (AR).

This uses the same sets of images that are collected to create RTIs.

It is based on work from Szymon Rusinkiewicz (and team) from Princeton University.

The approach allows you to apply various signal processing algorithms to the color and shape information collected in an RTI image set and use them to create technical drawings that allow you to emphasize certain features while suppressing other features.

This paper describes much of the early work of Szymon and team on Algorithmic Rendering: Corey Toler-Franklin, Adam Finkelstein, and Szymon Rusinkiewicz. Illustration of Complex Real-World Objects using Images with Normals. International Symposium on Non-Photorealistic Animation and Rendering (NPAR), August 2007.

There is a range of styles that can be applied to the same data.
Here is a petroglyph example from Legend Rock in Wyoming. In the lower right are a series of zoomorphs that are very difficult to see in a conventional photograph (or with the naked eye). However, with the collection of color and surface normal data contained in an RTI image set...
...this representation can be produced using the AR technique, which clearly shows the zoomorphs. Note that this could not be accomplished with a single photograph because you only have color data, and there is no color change that can make these zoomorphs visible. Because we also have shape information (in the form of surface normals), this allows the creation of this representation.

This data set was collected by Cultural Heritage Imaging in summer 2006, and the AR result was produced by Szymon Rusinkiewicz.
This example illustrates the idea of fusing information from multiple images to create a result that supplies the most information-rich rendering, not found in any one image by itself.
One technique that can be applied with AR is exaggerated shading. This is used to bring out small changes in the surface shape and make them more visible.
Here is an example from a petroglyph in the Owens Valley near Bishop California.

The same data set was processed as an RTI, and several AR examples were also made.

This first image is from the RTI in the RTIViewer default viewing mode.

The data was collected in May 2013 by Cultural Heritage Imaging and we appreciate the help of Greg Haverstock of the US Bureau of Land Management and rock art specialist David Lee.
The next image is also from the RTI, this time with the mathematical enhancement, specular mode and no color.
The last example from the RTI shows an image rendered using the diffuse gain mode.
Now we will look at some examples where we apply Algorithmic Rendering to the same data set.

First, just color with no shape. The color is “illumination independent.”
This next slide shows exaggerated shading with very little color. The exaggerated shading is applied to the surface normal data calculated from the image set.
This AR example shows exaggerated shading applied to the larger (low frequency) details.
This final example shows exaggerated shading which emphasizes very small surface changes.
CHI is working with the team at Princeton to create the CARE tool, which will be open source. We have a National Science Foundation Grant that supports this project.
Now I’d like to talk about recent work to use surface normals to track changes in a surface.
This work was presented in a paper at the Digital Heritage Conference in Marseilles in the fall of 2013.

You can find the full paper here:
http://www.gokmconservation.org/scientific-methods/rti/
The first step was to look at the repeatability of RTI data. This was done by imaging the same subject several times, moving the camera slightly between each image capture, then aligning the image sets and comparing the produced results. What the team found was that the Polynomial Texture Map (PTM) algorithm is not very repeatable, whereas the Hemispherical Harmonics (HSH) algorithm is very repeatable. Note that the use of both algorithms is supported in the free RTIBuilder software.

A discussion of the differences between using the PTM and HSH algorithms can be found on the CHIForums here:  
http://forums.culturalheritageimaging.org/index.php?/topic/190-hsh-or-ptm-how-to-choose-the-best-fitter/
Once the team understood the variability in the results, they created a test subject, a drawing they imaged with RTI, then damaged, then imaged again. The goal was to determine whether, by just doing a mathematical comparison of the surface normal data produced by the RTI, the changes to the drawing could be detected.
They only considered pixels that were offset by more than 1.9% to be changed.
Next they were able to create a map of the changed pixels, which clearly shows the modifications to the drawing.

This work is just the beginning, and more needs to be done using different types of surfaces. However, this is very promising work and shows how this kind of data can be used quantitatively to detect change.
Because we are looking at additional uses of this color and surface normal data, we want to understand how we might improve the accuracy of surface normals.
In order to understand the next set of images it is important to understand how to view a normal map.

A normal map is a false color visualization of the direction of the surface normals for a surface.

This graphic shows the surface normal map of a sphere.

Pixels shown as pink and magenta are pointing to the right and down, green pixels are pointing up. Variations in the shading depict changes in the direction of the surface normals.
This is a detail of a boomerang from Australia.
Here is the normal map for this same detail when an RTI is created using the Hemispherical Harmonics or HSH algorithm.
Here is the normal map for this same detail when calculated using the Polynomial Texture Mapping (PTM) algorithm.

You can see that there is a significant difference in the result, especially where the edges of the subject are in the image. This is due to limitations in the PTM approach in areas that have significant shadows from some illumination angles.
This graphic shows the difference between the HSH and PTM normal maps.

It is clear from the normal map comparison that the HSH algorithm is calculating more accurate surface normals for the edges of the subject when compared to PTM.
In the latest version of the RTiViewer (1.1) the ability to look at normal maps, and also save them as image files, is now available.

There are other new features in this update as well. You can download it, along with documentation and examples, here:

http://culturalheritageimaging.org/What_We_Offer/Downloads/View/index.html
Here is a screen shot of the latest version of RTIViewer, which includes several new features.
As part of the National Science Foundation grant project with the Princeton team, PhD student Sema Berkiten and Professor Szymon Rusinkiewicz have done research on aligning image sets of the type captured for RTI and Algorithmic Rendering. They worked with image sets of 30-100 images where the camera and the subject are in a fixed position, and the light is moved from image to image. Even though the camera and subject are fixed, there can be small movements due to unstable floors, wind in outdoor environments, slight rolling or movements of the subject, and so on.

They began testing different algorithms and approaches for how to best get sub-pixel alignment across the image set. In addition, they tested the impact to the resulting calculated normal maps before and after alignment.

An open source alignment tool for RTI and AR data sets, based on this work, will be released in the future.

A paper with details on this work is available:
The next few images show the results of image alignment on the surface normals.

Here is a surface normal map for the petroglyph from the Owens Valley in California, which was discussed earlier. This shows the surface normals created from images that were not aligned.
Here is the normal map after the images are aligned.

From this zoomed out view, we cannot see the difference.
When we zoom in and compare again, the difference will become clear.

This is from the unaligned images.
This is the same area after alignment.

You can see that the alignment has noticeably improved the surface normal map.
Improved Surface Normal, Color, and Specularity Accuracy

- Current research at Simon Fraser University, Vancouver, BC, Canada
  – Mark S. Drew, Mingjing Zhang
- Problem: The PTM algorithm has difficulty with shadowed and specular surface areas
  – Does not calculate accurate normals for these areas
  – Appearance in the RTI viewing environment is incorrect, when compared to ground truth
- HSH algorithm is better than PTM for shadows and highlights. It still has inaccuracies.

Additional research is underway to improve the accuracy of surface normals, as well as the color and specular accuracy calculated from RTI image sets.

This work is by our co-authors, Professor Mark S. Drew and recent Masters graduate Mingjing Zhang of Simon Fraser University.

As was partially demonstrated earlier, the problem is that the Polynomial Texture Map (PTM) algorithm does not properly handle highly shadowed areas on a surface nor really shiny or specular areas. This problem manifests itself in two ways. First, the surface normals are not accurate in these areas; and second, the appearance in an RTI viewing environment is incorrect when compared to “ground truth.” The ground truth used in this case is an input photograph from the image set compared to the view of the subject within the viewing environment with the light in the same position as the photograph.

While the Hemispherical Harmonics (HSH) algorithm does a better job than the PTM algorithm, it still has inaccuracies.
This work has been an active area of research at Simon Fraser University since 2009.

The team has worked with multiple approaches and algorithms, and has been refining their approach based on their results.

To improve surface normal accuracy, they are separating the shadows and specularity so that the normals are calculated only on the matte (or Lambertian) surface.

Then they apply robust regression techniques so that the impact of outlier data is reduced. The outlier data in this case is caused by highlights and shadows. The robust regression approach limits the impact of the highlights and shadows on the overall calculation.
To improve the highlight and shadow appearance within the viewing environment, a different technique is applied.

The team uses Radial Basis Functions to ‘weight’ the impact of lighting on the rendered image. Thus, the final rendered result is more heavily influenced by the sampled light that is closest in position to the light direction being modeled in the viewing environment.
There are several published papers on this work. The next few slides will include the references for some of them.


Robust Estimation of Surface Properties and Interpolation of Shadow/Specularity Components

Image and Vision Computing, vol.30 (no. 4-5), May 2012
– Mark S. Drew - Simon Fraser University
– Yacov Hel-Or – The Interdisciplinary Center, Herzliya, Israel
– Tom Malzbender – HP Labs
– Nasim Hajari - Simon Fraser University

More Papers

- “Robust Surface Normal Estimation via Greedy Sparse Regression” Mingjing Zhang, Msc Thesis, School of Computing Science, Simon Fraser University, 2014


“Robust Surface Normal Estimation via Greedy Sparse Regression” Mingjing Zhang, Msc Thesis, School of Computing Science, Simon Fraser University, 2014

Here are some visual examples to demonstrate the results.

This image is a photograph that was part of the set of images collected to make an RTI. In this case it is image number 34.

This data set of a Celtic Gold Stater was collected by Cultural Heritage Imaging. All processing shown in these slides was done by Mingjing Zhang and Mark Drew.
This is the interpolated image using the above mentioned techniques. The light direction in the viewing environment is the same as the light direction applied to the photograph.
This image shows the rendered image from the PTM using the same light position.
This shows just the calculated Matte surface of the coin. The surface normals are calculated from this data.
This slide shows just the calculated highlights and shadows.
Here is the surface normal map produced by this approach.
Here is the normal map produced by the PTM.

You can see that the edges of most of the details are incorrect in that they appear to show a steep directional change in the surface. These areas all have shadows in some of the sampled images.
This is the normal map produced from the RTI created using the HSH algorithm.
In the AIC presentation, a live demo of the software showing this work was presented using an additional example.

Cultural Heritage Imaging is currently working with Mark and Mingjing to incorporate the calculation of more accurate surface normals into the open source tools released to the RTI community.

Simon Fraser University and CHI

- CHI is working with Mark and Mingjing to incorporate calculation of more accurate normals into the open source RTIBuilder tool
- Expected release – late 2014
Evaluating Digital Imaging Quality and Reliability
I’d like to close the talk with a brief discussion of the importance of the scientific method to aid in the evaluation of images produced using these methods.

An essential element of traditional scientific inquiry is the systematic gathering and sharing of observations about the world. These observations of the senses are labeled ‘empirical’.

Within scientific discourse, the methodology employed in the process of generating scientific information has been traditionally called the inquiry’s ‘provenance’.

This provenance explains where the information came from and how it was used in order to allow evaluation of the results, and also to allow others to replicate the work.
Collecting and managing this type of data enables distributed scholarship and also greatly improves the likelihood that data collected today can be reused in the future, including reprocessing existing image sets using better software and new approaches.
The Digital Lab Notebook

- **Collect and Manage** data about the digital surrogate throughout its lifecycle
  - Setup – equipment, filters, lighting, etc.
  - Location, people involved, institutions, etc.
  - Image capture (and image sequence capture)
  - Processing (and reprocessing for different uses)
  - Analysis and generation of derivatives

The Digital Lab Notebook is intended to both collect and manage all the necessary data about a digital representation. It includes information about how the data was collected, why it was collected, who was present, and all subsequent processing steps.
The current methodology and tools for RTI and AR collect this information, but it is not organized in a way that is truly useful.

CHI is currently working to manage this data, including relationships of the data, using the CIDOC Conceptual Reference Model (CRM) and producing Linked Open Data.
CHI recently received an NEH Digital Humanities Start-up grant to allow us to further this work. A primary focus of this project is 2 case studies to be done with the Georgia O’Keeffe Museum and the Classics Department at University of Texas, Austin.

A project page with more information about this project can be found here: http://culturalheritageimaging.org/What_We_Do/Projects/neh-startup/
Conclusions

- RGB + Normals data – “not just for interactive relighting anymore”
- Quantitative comparisons are possible
- Normal accuracy is improving
  - Work on alignment at Princeton University improves normal accuracy
  - Recent research from Simon Fraser University is dramatically improving normal accuracy and appearance of surfaces
- Computational Photography lends itself to good practice for process history tracking (DLN)

So, please remember that collecting RTI data is not just for interactive relighting!

This type of data can be used for quantitative comparisons.

Work is also underway to improve surface normal accuracy.

Computational Photography also lends itself to good practice for tracking all the needed information to allow data reuse and evaluation by others.
Kristin deGhetaldi 1, Zachary Voras1, Eric Gordon2, Glenn Gates3, Karen French4, Pamela Betts3

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Presented at the RATS session
42nd Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
San Francisco, CA, May 27-June 1, 2014
This paper will present research I have conducted in collaboration with the Walters Art Museum, a project that we have been working on for almost two years.
But before I discuss the project, I want to give some context to our research. My PhD dissertation topic focuses on the transitional period in 15th century Italy when artists began to shift away from tempera paint and embrace drying oil as their favored medium.
Until fairly recently scholars have often dealt with this complex period using an over-simplified approach, which I think is clear from the quote on the slide above. Today, most of us now realize that this issue is much more complicated, especially in light of new technological advancements in the analytical field.

“...if the painting is done in egg tempera then the panel dates before 1450, if it is executed in oil it is likely to be later.” – Curator/scholar (anon.), 1993, excerpt from the NGA Conservation Files
Clearly, the oil method was a skill sought after by both clients and artists alike. Oil paintings from the north were highly valued by the Italian elite. An inventory of the Medici collection dated to 1490 differentiates tempera paintings from those done using drying oils by explicitly designating the latter as “pittura ad olio”.

Portraits of the Italian Banker Tammaso Portinari and his wife
by Hans Memling
(oil on panel, c. 1470, Metropolitan Museum of Art)
While the identification of oil medium in a painting may imply an economic significance, it has also been used to help with attribution. Thanks to the Masaccio and Masolino project, we are aware that the oil technique was being used by Italian artists as early as 1428. Archival documents helped scholars to identify which sections of the Santa Maria Maggiore altarpiece were painted by Masaccio before his death in 1427, something that was further corroborated by analysis of the paint. Sections finished by his collaborator Masolino, however, were found to contain oil, a technique that he likely learned during his travels in Hungary between 1426-7.
“How you are to make an oil, good for a tempera, and also for mordants, by boiling it with fire – You ought to know how to make this oil, since it is one of the useful things which you need to understand; for it is used for mordants, and for many purposes.”

- Cennino Cennini (trans. D. V. Thompson, 1954)

But what of primary sources? In 2001 over 450 treatises on artists materials were identified, however only a handful of them have been translated into English. Even our much quoted Cennino Cennini suffers from translation problems. The word temper, for example, meaning to mix, can obviously be confused with the word tempera, a term that is now associated with aqueous media. Furthermore texts have been altered, corrupted, and edited over hundreds of years, something that scholars are now attempting to address. Cennini’s text is currently being re-interpreted by scholar Lara Broecke and I know that many of us are eagerly awaiting her updated translation.
So what were traditional Italian painters up against when faced with this sudden influx of Northern oil paintings? The two types of media could not be more different as demonstrated by these didactic painting reconstructions.
Tempera strokes shown on the left dry almost instantly when applied onto the absorbent gesso ground, making blending impossible and forcing the painter to often work in fine, individual hatched strokes. Drying oils, however, completely coat the pigments, creating paint that can be very transparent, dark, and saturated while its long dry time allows for effortless blending. But what if an artist used both egg and oil or if the painting is hidden beneath layers of restoration? Such subtleties cannot be differentiated by eye and we must turn to an analytical approach.
I feel that David Bomford’s 2010 sentiment at the bottom of the slide above sums up the root of this problem very well.

If I have learned anything throughout this study it’s that pigment analysis can be very difficult, but organic analysis can be next to impossible. While there are countless texts on the chemical components and properties of pigments, concrete specifics about binding media have proven far more challenging for scientists to qualify. I am only including a few texts to demonstrate this point.
Just as we have learned to become more cautious when interpreting Vasari’s historical accounts, conservation scientists continue to refine certain techniques while largely abandoning others, something that is not always apparent to conservators and art historians reading older literature. Thin layer chromatography (TLC), for example, was often used during the 1980s and 90s, yet there were clearly problems with the technique when dealing with binding media, as Raymond White recounted in his 2009 Oral History interview.

“TLC really wasn’t of any great use and sometimes gave sort of falsely possible things”.

And returning now to our study... Before requesting samples from various institutions we reviewed an extensive number of scientific studies and found that three techniques are frequently used to characterize egg oil paint systems: cross-sectional analysis, Fourier-transform infrared spectroscopy (FTIR), and chromatography/mass spectrometry.
Making paint references that replicate 500 year old films is nearly impossible, but as with most cultural heritage studies, references still play an important role. Egg and oil can occur as mixtures, often referred to as tempera grassa or as multi-layered systems, both of which are being considered in our study. I have now made a number of these reference paints, including pigments such as yellow ochre, lead white, vermilion, azurite, verdigris, charcoal black, and red lake.
I was perhaps overly hopeful when I first attempted to stain some of my paint outs, bearing in mind that they were only artificially aged for a period of about 3 weeks. I selected two types of stains that are used to identify proteins, Amido Black and Alexa Fluor 488, with the assistance of conservation scientist Michael Palmer and research conservator Melanie Gifford.
The result from both stains was rather depressing. While the glue ground gave a wonderful positive reaction, nothing was observed in the egg-containing paint layers. Ultimately we decided to look into other techniques to characterize samples that may contain egg tempera.
This then brings me to FTIR, a technique that is wonderful for certain materials, but as expected, we found it less than definitive when analyzing mixtures or layered paint systems, even in reflectance mode.
One is really limited to the region shown above, paying particular note to the presence of the carbonyl stretching band as well as the three amide stretching peaks indicated here. Obviously, things become less clear when both egg and oil are present.
Finally, certain pigments can also mask areas of interest, as we found when analyzing a sample collected from an actual Italian painting which contained red lake. But, perhaps more importantly, FTIR cannot distinguish between different protein sources like egg and glue.
And so, turning finally to chromatography... For our project we are relying heavily on information generated by chromatography-mass spec methods, as they can readily distinguish between materials like egg and glue. As early as 1977, however, John Mills and Raymond White realized that if one is fortunate enough to extract protein from a 500 year old degraded paint film, protein analysis is only half the story. Using early Italian Renaissance paintings as a prime example, they described the challenges associated with fatty acid analysis in the very first volume of the Technical Bulletin Series. Ratios may not be especially helpful when determining whether or not oil is present in a tempera film.
More recently, scientists have teamed up with conservators to better understand these chemical markers, and have found that many of these ratios can be affected by several factors, all of which can in turn complicate the characterization of egg-oil paints. I have found that many of my colleagues are unaware that these issues are actively being revisited by the scientific community.
We have come quite far since the 1970s, but as with any technology, new advancements bring new headaches. After learning about the complexities involved with sample preparation, I promised myself that I would refrain from bombarding scientists with requests to identify traces of partially heat-bodied walnut oil that may be in my tempera painting. As our instruments have become more refined, more sensitive and more complicated, scientists have made extraordinary efforts to tackle these issues, developing elaborate methods to extract multiple components from a single tiny sample.

But this slide brings up another issue. For the purposes of our research, it became apparent that it was impossible to compare the analytical results coming out of one lab with that of another, unless both are using the same exact method for preparing samples. While we certainly continue to rely heavily on chromatography in our research, we decided that comparing the various protocols was well outside the scope of our project.
Despite its strengths, gas chromatography–mass spectrometry (GC/MS) cannot provide spatial information, which finally brings me to time-of-flight secondary ion mass spectrometry (ToF-SIMS). We are not the first to apply ToF-SIMS to the analysis of easel paintings and much of our work to date is built on the foundation of previous studies carried out by the MoLART group in the Netherlands.
What has continued to improve, however, is the ion beam technology associated with SIMS. We are currently working with a bismuth beam which allows for a higher level of resolution and sensitivity than previous systems.
This image gives you an idea as to how the fragmentation process occurs, with smaller ions traveling up to the detector at a much quicker rate than larger ion fragments, hence the name “time of flight”. There is a minimal amount of damage that occurs on the surface of the sample, but this area is less than 3 nm in diameter.
There are three main benefits to using SIMS, starting with resolution. For each primary ion pulse, a full mass spectrum is obtained by measuring the arrival times of the secondary ions at the detector and then performing a simple time-to-mass conversion. Compared with other mass spectrometry techniques, ToF-SIMS is more successful at identifying individual fragments with the same nominal mass.

For example, because of the higher resolution, SIMS can detect up to four separate fragments at around 86 m/z (as opposed to one), which can be very helpful when trying to identify both of the ion fragments associated with the amino acids hydroxyproline and isoleucine/leucine.
This large amount of data then allows for the simultaneous collection of both inorganic and organic information.

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry)

Three main benefits to using Imaging ToF-SIMS:

a) ToF-SIMS is capable of performing high-resolution chemical imaging as the primary ion beam can be focused to 1-2 μm.

b) SIMS is able to simultaneously characterize inorganic and organic species in a sample.
Certainly a downside to SIMS is that sampling is required. However, cross-sections exist by the hundreds and our findings suggest that this technique can be used to revisit those samples to obtain new information.
Extremely careful sample preparation is required due to the technique’s sensitivity. Our greatest enemy is the excess resin that surrounds the paint sample because this can lead to an unwanted buildup of charge, which can complicate data acquisition.
Here you see my colleague Zach preparing samples using a microtome equipped with a diamond knife. The extremely sharp edge of the diamond allows us to not only trim away the excess resin but also to remove extremely thin sections (about 1-2 microns) from the surface to get rid of any unwanted grime or residue. After analysis we then re-cast the sample in a larger block of embedding resin before returning it to its parent museum. We are continuing to look into ways to improve our sample preparation methods.
And here is an image showing the chamber inside the SIMS system, as well as the parameters that we have been using during analysis.
This past year the Conservation Department at the Walters Art Museum generously leant us cross-sections from a number of Italian paintings.

I will begin with this painting attributed to Raphael. This sample was collected from the arm of the Christ Child and contains a thick ground covered by a medium-rich interlayer with a fractured paint film along the surface.
This medium-rich layer exhibited strong auto-fluorescence in UV light, and questions remained about whether it contained oil, resin, or another material. It was also difficult to tell whether the dark line between the paint and the medium-rich layer was a void in the cross-section or in fact another layer altogether.
To double check this it can be helpful to consult the total ion count (TIC) image, which represents the sum of all peaks in a spectrum, both elemental and molecular.
The dark areas in the TIC image indicate air pockets on the surface like the one created by the bubble in the bottom left, and so we were able to confirm that this line is in fact a gap between the ground and paint in the cross-section. For comparison, you can see a very strong signal for the medium-rich layer atop the ground.
Like SEM, ToF-SIMS imaging can also generate elemental maps.

You can see that we are not getting any elemental signals from either the void or that medium-rich layer. In this map, the green represents the calcium in the ground while the red indicates the presence of lead in the paint layers.
But one of the main advantages of SIMS is that it can spatially map for compounds as well as elements. For example, in negative mode we were able to confirm the presence of gesso in the ground with the calcium sulfate map shown in the bottom right.
Recent improvements in beam technology now enable us to identify protein-containing materials. Here you can see a map for organic species in negative mode. The red signal represents protein, while the teal color on top is a combination of the green and blue signals corresponding to the presence of palmitic and stearic acids in what appears to be an oil-rich paint layer.
This system is also able to map individual amino acids in positive mode. We detected a strong signal for hydroxyproline along that medium-rich layer. As hydroxyproline is unique to animal glue, this layer is undoubtedly a glue-size layer. Note that we also got a faint signal in the gesso-glue ground as we would expect. I have only included alanine on the slide, but we did obtain similar maps for an additional six fragments associated with the amino acids listed above.
So what does this tell us about the painting? The artist in this case deliberately chose to add an additional layer of animal glue to size his gesso ground before applying oil paint, a technique that painters began to embrace by the mid-16th century. In comparing these results to other works belonging to Raphael’s post-Rome period....
....analysis of Alba Madonna at the National Gallery in Washington DC revealed a similar “glue-sealing” layer in a number of cross-sections. More research is certainly needed, but we hope that these results will ultimately help in understanding the methods used by Raphael or artists related to his circle.

So now to compare this 500 year old oil painting with works done in egg tempera. Again on the left you see the Raphael sample with the red signifying protein and the blue and green indicating fatty acids.
We were somewhat puzzled after analyzing this sample collected from the Sienese tempera painting shown above in the upper right. It appears that there is a slight depletion of fatty acids towards the surface of the painting, as demonstrated by the lack of green and blue signals in this region. So what exactly is going on here?
Although it is difficult to tell, the Raphael sample also shows a lack of fatty acids along the paint surface as we should see a consistent line corresponding to the top of the paint film, which is better seen in the visible light image.
We have now analyzed samples from three other Renaissance paintings and all have revealed exactly the same pattern. An interesting theory was proposed after consulting the Walter’s resident scientist Dr. Glenn Gates and another scientist who has had extensive experience with this technique, Dr. Jaap Boon.

Certainly fatty acids remain mobile until they form complexes with reactive pigments and it is possible that we are seeing fragments from metal soaps that are present within the lower lead-containing layers in all of these samples.

Some of us, particularly conservators, have seen the hazy film that can form on modern tempera paintings. Analysis of these ghostly films have found them to be very rich in fatty acids. Finally, these paintings have undoubtedly experienced multiple restoration campaigns, some of which would have involved the use of harsh chemicals that could have further contributed to the leaching of these fatty acids near the paint surface.
We wanted to check whether we could see this pattern on younger paint films. Both of the primary fatty acid ion fragments are shown, which confirm that hardly any depletion has occurred. We hope to be able to further explore these observations using artificially aged samples in the near future.
Although I have been focusing on binding media I do want to discuss some of our findings relating to inorganic materials. Turning momentarily to this beautiful tempera by Giovanni di Paolo, we were also asked to examine the green pigment which prior to treatment had shown dramatic signs of chalking and flaking.
Again this cross-section had a void, but this time the separation occurred at the border between the ground and paint layers, mimicking the flaking pattern observed on the actual painting.
Here is the elemental map of the same sample showing the presence of copper throughout the paint layers with underlying areas rich in lead on top of a gesso ground.
So what about malachite? Fortunately we knew that detecting malachite was possible using SIMS because we had already confirmed the presence of green copper carbonate particles in *The Ideal City* by Fra Carnevale.
But we did not observe this in the Giovanni di Paolo. SIMS did, however, identify a number of copper oxides and hydroxides throughout the paint layers, which led us to believe that we were instead dealing with verdigris.
Due to the degraded nature of the paint and the reactive nature of the pigment, we had difficulty finding ion fragments associated with the intact copper acetate compound. One surprise, however, was the abundance of chlorides present throughout the paint, particularly copper chlorides.
Recipes recorded by Theophilus in the 12th century reference the occasional addition of salt and honey in the preparation of green copper acetate. In fact, this type of verdigris is also referred to as viride salsum or salt green.
A 1989 reconstruction of this recipe was found to produce excessive amounts of copper chlorides as well as a small amount of atacamite, a trihydroxychloride. Our analysis showed a similar trend, not only revealing large amounts of chlorides, but also a trace amount of atacamite, which you can faintly see in blue in the copper-rich paint layers.

The presence of these species may very well explain the instability of the green paint noted by the conservators prior to treatment. Chlorides would inevitably react with atmospheric water and oxygen, causing these unstable compounds to expand in volume upon conversion to other products, atacamite being one of them.
But as with everything, this technique only shows its strengths when used in tandem with other types of analysis. It was not until we performed SEM that we noted an extremely small area of gold leaf atop the surface of the cross-section. In addition, the co-localization of lead, tin and silica suggested the possible presence of lead tin yellow. Further analysis with Raman spectroscopy confirmed that lead tin yellow type 2 was present.
The fact that we missed this in our initial interpretation is really the fault of the analyst and not the instrument. With such high resolution it is relatively easy to miss a single ion fragment.
Fortunately with SIMS it is easy to revisit to the data set and in doing so we did confirm the presence of several fragments associated with lead tin yellow.
We missed the gold leaf for a different reason. Metals like calcium and lead are generally easier to detect in reduced form, so we tend to look for these signals in positive mode, but as you can see our signal for gold was poor at best.
To our surprise, however, negative mode appears to be much better suited for imaging heavier elements when they exist in metallic form, something that we are now taking into account as we continue to analyze samples from gold ground paintings.
It is always important to point out problematic aspects of any technique, and with SIMS sample preparation is certainly difficult, especially when dealing with samples that are less than 10 microns. But our team is starting to explore other sample preparation methods such as ion milling.
In closing, as we continue to pick apart the egg/oil question, I propose that ToF-SIMS is a powerful tool, able to provide both unique and complimentary data in combination with other techniques. Our team has also been incorporating chemometrics, specifically principal component analysis to assist us in the identification and differentiation of egg yolk, glues, and drying oils. With SIMS, extant cross-sections can now be re-visited to give both organic and inorganic information. While these instruments are not always the easiest to access, the center at the University of Delaware is open to partnering with museums and institutions and continues to welcome opportunities that foster interdisciplinary research and collaboration.
Acknowledgments…my collaborator Zachary Voras (voras@udel.edu)

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- Dr. Jaap Boon
Free Fatty Acid Profiles in Water Sensitive Oil Paints: A Comparison of Modern and 15th-Century Oil Paints

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AIC San Francisco, 2014

The Getty Conservation Institute

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The identification of organic materials in ancient and modern works of art, restoration materials, outdoor murals, and archeological objects is one of the most challenging research areas in conservation science. Specifically, the paint media may be contaminated by materials from parchment or the wood support, microbial by-products of deterioration, and exposure to soil and the environment.

This paper describes a novel stepwise method that provides quantitative data for fatty acids and amino acids, and qualitative analysis of natural resins and waxes. It utilizes Gas Chromatography/Mass Spectrometry (GC/MS) by analyzing extracts from several solvents and reagents in one vial. Soluble fractions identified in chloroform include waxes, resins and extractables such as treatment materials and plasticizers. The same sample is subsequently analyzed for free fatty acids and fatty acid soaps, total fatty acids from triglycerides and oils, and lastly for proteins. We are still refining this method so this paper represents a work in progress.
Here are some (but not all) of the factors that make it difficult to quantitatively identify all the fatty acids in oil paints: pigments, hydrolysis of the oil due to environmental factors, soap formation, water sensitivity, and addition of proteins or other components. In addition, it is possible that a previous restoration or cleaning removed fatty acids from the oil. And lastly, artists intentionally modify their oils to dry faster, or to make their paint more matte. All of these factors, and more, influence the drying rate of a paint and thus the fatty acids found in the paint over time. Nevertheless, we decided we wanted to develop a method that was easy to use in order to understand and get as much information out of a sample as possible.

"The chemistry of the drying of the linseed oil is so complex as to be unintelligible to anyone who is not a student of chemistry"

A.P. Laurie, The Painter’s methods and materials
The three components of oil that I will be talking about today are: triglycerides (fatty acids that are attached to glycerol), soaps (fatty acids combined with pigments), and free fatty acids. Ideally we would want to identify all three parts of the oil paint separately. However, with the method we developed we can only identify free fatty acids and soaps. For this talk we will call free fatty acids and soaps “Non-Glycerides” (NG). The second part of our analysis identifies the total fatty acids present as triglycerides, free fatty acids, and soaps, collectively called “Total”. The step in the method that analyzes the total fatty acids in oil paint is what is most commonly reported. The new data we acquire with our method is the free fatty acid and soap data.
Soaps can form naturally over time by the reaction of certain pigments with free fatty acids. Manufacturers may add pigment soaps to tube colors in order to change their working properties.
Meth-Prep II is a 0.2N methanolic solution of \( m \)-trifluoromethylphenyl trimethylammonium hydroxide (TMTFTH) in methanol (from Alltech). It is used to quantify the total fatty acids in oil paints. Methylation of fatty acids occurs in two reactions; first in the GC inlet, and the second is transesterification of triglycerides with methanol.
We developed a novel Meth-Prep II procedure using t-butanol. It is used to analyze for free fatty acids and soaps. Transesterification does not occur with Meth-Prep II if the methanol is evaporated and replaced with t-butanol because of steric hindrance.

To prepare t-butanol reagent: Evaporate 500 µl Meth-Prep II at 50 °C with nitrogen to remove all the methanol, then add 50 µl toluene and evaporate. Add 100 µl t-butanol and mix until salt is in solution. Add 500 µl toluene and mix.

Steps in the method:

Step 1. Weigh the sample (50-100 µg for easel paintings and 1-10 mg for mural paintings that are media poor) into a 100 µl Reacti-Vial.

Step 2. To analyze for extractives, add chloroform; it is a good solvent for beeswax, hydrocarbons, and plasticizers. Inject into the GC/MS. 25 M x 0.2 mm x 0.2µm DB-5HT. Helium 1ml/min. Splitless injection 280°C. Transfer line 300°C. Oven 80°C (2 min), 10°C/min to 340°C (12 min); 20°C/min to 360°C (5 min).

Step 3. To analyze for free fatty acids, soaps, waxes, resins, and hydrocarbons, evaporate the chloroform with nitrogen, add 1:1 acetone:water to the sample and heat at 60 °C for 1 hour. Crush the paint sample with a pipette to ensure soap dissolution. Add the t-butanol reagent (see lower left box) and heat at 60 °C for 1 hour. Inject into GC/MS, using the same conditions as above.

Step 4. To analyze for total fatty acids, evaporate the t-butanol reagent at 30 °C. Add 1:2 Meth-Prep II:toluene to vial. Inject into the GC/MS, using same conditions as above.
Step 5. To analyze for proteins, evaporate the Meth-Prep II and add 100 µl of 6N HCL and heat for 24 hours at 105°C. Evaporate and reconstitute in 60 µl water. Add 32 µl of ethanol, 8 µl pyridine, and 5 µl ethyl chloroformate (ECF). Shake for 5 seconds and add 100 µl 1% ECF in chloroform. Transfer the chloroform layer to a GC vial and extract the solution a second time, neutralize, concentrate and inject into the GC/MS. INNOWAX (30 M x 0.25 mm x 0.1 µm). Helium 1 ml/min; Splitless injection 240°C; Transfer line at 240°C. Oven 70°C (1 min), 20°C/min to 250°C (3.5 min). The identification of proteins by GC/MS is compared to the amino acids of standard reference materials using the method of correlation coefficients.
This slide compares the two chromatograms obtained from the new procedure. This is a free fatty acid standard. The standard was first treated with Meth-Prep II in t-butanol to obtain free fatty acid methyl esters, it was allowed to evaporate at room temperature, and Meth-Prep II was added as normal (with methanol), and injected again. Both chromatograms are comparable except that the smallest carboxylic acid (lauric acid) has decreased. There are some problems with the internal standard during evaporating, and that is the subject of future method development.
Reference paints were analyzed: paints made 20+ years ago that were artificially aged and naturally aged; and we analyzed different commercially available tube paints, some of which were water-sensitive.
This slide shows handmade paints from the Smithsonian, 1990 to 1992, made with cold pressed linseed oil. The great thing about these samples is that we are certain that soaps were not added. This is the type of data we should expect for relatively new oil paint that is handmade.

The top graph shows the free fatty acid and/or soap fraction of the paint (NG). The bottom graph is the total fatty acids present in the paint, data that is obtained with Meth-Prep II. The green bar is percent palmitic, red is percent stearic (this ratio should be roughly 1.2 to 2.2 for linseed oil), and the blue bar is percent azelaic acid. The paint sample name is given in the top center, and in parenthesis the percent hydrolysis is given. Percent hydrolysis is a quantitative value calculated by the amount of free fatty acids and soaps compared to the total. The lead white and malachite both have between 12 and 15% hydrolysis while red iron oxide and yellow ochre have between 50 and 57%. Perhaps we are not removing all of the fatty acid soaps from the lead paint because the results are different from the ochre. Soap formation should occur in the lead paint and yield a higher percent hydrolysis. Perhaps it may take longer for lead soaps to form. This work is ongoing.
This chart shows percent free fatty acids and soaps by weight. The paints that contain lead and zinc have much lower values than the others. Visually, it was nearly impossible to break up the lead paints in acetone and water, and they remained cohesive. It is possible that the reagent did not penetrate the paint, or that the soaps or free fatty acids have not formed yet, and more research is needed.
These are tube colors from Winsor and Newton that are water-sensitive. We wanted to investigate the differences (if any) that water-sensitive paints would show with the method. However, the top graph (% NG) is not that different from the bottom graph (% Total). Percent hydrolysis is within the normal range as compared to the less water-sensitive handmade Smithsonian paints shown in the previous slide. There is a difference in the NG palmitic acid fraction of the cadmium orange paint, which could be due to palmate soaps. For the most part, the difference is not easily seen in any of the other paints.
So what makes a paint water-sensitive? Unfortunately, we can’t get at the answer with this method. It is probably a combination of things, but cadmium paints in particular seem more sensitive to water. We analyzed a water-sensitive painting by Jack Youngerman, and the orange pigment was cadmium sulphide. This graph shows the fatty acid profiles in an orange paint that was easily disturbed by a wet swab roll. The NG fraction shown on the left contains quite a bit of free palmitic acid as compared to the total. This is similar to the Winsor and Newton cadmium water-sensitive paint shown on the previous slide.
In order to investigate the relationship to cadmium paints and water-sensitivity further, we prepared 2 paints with linseed oil - the first with cadmium and the other with chrome - and artificially aged them for 3 weeks in a Weatherometer. Both paints were applied to unprimed canvas and glass slides. The cadmium paint on both the glass and canvas was water-sensitive to a wet swab, while the chrome (lead chromate) was not. Both paints have the same percent hydrolysis; 7 to 14%. There are no major differences between the total fatty acids and the free fatty acids that may explain the water-sensitivity. Since we made the paint and did not add any soaps, this indicates that the water-sensitivity is a pigment effect in this specific case.
A summary of the oil paintings that I will be discussing in the next slides is shown here. Dates and percent hydrolysis data are shown. Percent hydrolysis is a quantitative value calculated by the amount of free fatty acids and soaps. Some paintings give a range of values due to multiple samples tested. Overall, higher values are seen in the oldest mural paintings compared to the youngest easel paintings.

<table>
<thead>
<tr>
<th>Oil Painting</th>
<th>Date</th>
<th>% Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Red-Vermillion&quot; Jack Youngerman, Norton Simon Museum</td>
<td>1961</td>
<td>20%</td>
</tr>
<tr>
<td>&quot;Water Lilies&quot; Claude Monet, Metropolitan Museum of Art</td>
<td>1914</td>
<td>7% to 32%</td>
</tr>
<tr>
<td>Ubaldo Gandolfi, &quot;Virgin and Saints&quot;, Panel Painting, Italy</td>
<td>1758</td>
<td>40 to 66%</td>
</tr>
<tr>
<td>Bartolomeo Cesi &quot;Prayer in the garden&quot;, Easel Painting, Italy</td>
<td>1595-97</td>
<td>22%</td>
</tr>
<tr>
<td>Bartolomeo Cesi &quot;Annunciation&quot;, Easel Painting, Italy</td>
<td>1595-97</td>
<td>27 to 65%</td>
</tr>
<tr>
<td>Cyprus, Asinou Church, Mural Painting</td>
<td>(11th-15th C)</td>
<td>70% to 90%</td>
</tr>
<tr>
<td>Cyprus, St. Neophytos Church, Mural Painting</td>
<td>(12th to 15th C)</td>
<td>44% to 83%</td>
</tr>
</tbody>
</table>
This is Monet’s “Water Lilies,” a very large triptych mural. According to MOMA’s website, the paint is very matte, contains lead pigments, and is sensitive to water and other solvents.

There are differences in the pink/orange paint where the free stearic and palmitic fatty acids are completely absent. The top graph also shows that soaps may have formed in three other paints: the green, lavender and black/red/white contain higher levels of free palmitic acid in the NG fraction, and that is different from the total fatty acids. It is expected that this painting would have more free fatty acids and soaps in its 100 year old oil paint. The fact that the lavender only has 7% hydrolysis is unusual and unexpected, and further study is needed.
The graph shows the total weight percent fatty acids in several paintings. The relatively low percent total fatty acid values in the samples by Monet indicates that his paints are medium-poor. The MOMA website states, “the paint from Water Lilies is matte and powdery”, and that Monet was said to remove oil from his tube paints with paper blotting, or it reflects pigment-to-binder conditions.
These samples are from Italian paintings from 1758 and 1595. It appears that some of the paints are starting to have more percent hydrolysis: the Virgin’s red dress has 66%. However, 200 years earlier, in *Prayer in the Garden* the red dress of St. John is 22%. This could be due to many factors as mentioned throughout this paper. You can see evidence of soap or free fatty acid formation in the *Virgin and Saints* brown robe, and the yellow area of *Annunciation*, 1595. The uncertain history of the cleaning and varnishing of such old paintings make the interpretation of the data difficult.
These samples were taken from the murals of a church from Asinou, Cyprus. The samples have a wide date range, but are the oldest oil paints tested. These results show that the percent hydrolysis are higher than we have seen before, 40 to 90%. This is expected due to the ages of the paintings. It also agrees with the current understanding that oil paint will hydrolyze over time and form close to 100 percent free fatty acids. Most of the paints shown here have evidence for soap or free fatty acid formation due to the high free palmitic and/or stearic acids in the NG fractions, especially the green paint in St. Neophyto.
The encaustic portrait shown here was analyzed using the novel Meth-Prep II in t-butanol procedure. The wax palmitate esters in the beeswax are not transesterfied.
The top chromatogram is 19th C beeswax and the bottom chromatogram is purple paint from the stripe in the portrait on the previous slide. The differences between the two samples are striking. The hydrocarbons (C_{25}-C_{31}) in the purple paint have evaporated as compared to the 19th C wax. Evidence for soaps in the purple paint are the relatively large peaks of lignoceric, palmitic and stearic acids. Soaps are associated with lead pigments found all over the portrait. Over time, the hydrocarbons have evaporated and the less volatile soaps remain.
The top chromatogram shows the total fatty acids found in a sample of light blue paint in *Mural*, 1943, Jackson Pollock. The fatty acid results match linseed oil, and is typical for most of the samples from this painting. The exception is a white paint that was applied throughout the painting. The bottom chromatogram shows that fatty acids were not detected in the white paint sample.
This chromatogram shows the subsequent protein analysis of the same white matches casein. Pollock’s use of mixed media in this painting is one of the earliest examples of his experimentation with retail trade paints. The GC/MS method that is presented here can quantitatively analyze free fatty acids and soaps, as well as total fatty acids and proteins. This study showed the earliest example of casein paint in Jackson Pollock’s “Mural” and identified fatty acid soaps in beeswax paint from a Fayum portrait. Lastly, as in the case of “Water Lilies” by Monet, art historical information is enhanced by analytical results.

In summary, paint media identification is inherently complex. Contamination, especially on objects that are exposed to the environment, should be addressed by running multiple samples to yield background levels. Pigment types (especially lead), fatty acid soap solubility, cleaning, and varnishing impacts will be the subject of future studies.
In summary, Oil paint media identification is inherently complex. The novel modified Methprep II procedure was used to quantify pigment soaps and free fatty acids (NG) in several different works of art and tube paints. Results showed that lead based pigments initially contain very low NG’s. This could be due to the soap solubility or the young age of the paint sample. Over time, the NG fraction of lead based oil paint (and all paints) approaches 100% as expected. Water sensitivity was not directly linked to the NG fraction, especially in the case of cadmium paints or Windsor Newton tube paints. The water sensitivity of oil paints is a subject of future studies.

Conclusions

• Pigment Soaps and Free Fatty Acids (NG) approach 100% as a painting ages.
• NG’s may be removed by cleaning
• Lead based pigments- initially low NG’s
• Oil Paint Water Sensitivity is wide subject for future investigations
Jennifer McGlinchey Sexton, Paul Messier, and Jiuian Jiuai Chen

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San Francisco, CA, May 27-June 1, 2014
UV Innovations Inc. was established by Paul Messier and Jiuan Jiuan Chen. It is a project of the Paul Messier Conservation Studio.

This paper will present the final stages of development and beta testing of the Target over the last two years. This work built on the considerable efforts of co-authors JJ Chen and Paul Messier since this project began in 2008.
The Target-UV and UV-Grey are color references for achieving repeatable and consistent photographic documentation of UV-visible fluorescence. White balance is set by the UV-Grey, while the Target-UV provides consistent RGB levels for setting exposure.

The first major point of this paper is a short discussion of why standardization is needed, particularly relating to this type of photo-documentation. From there it will get to its main focus, which is the general development of the Target, and the beta testing that we completed in 2013. To finish, it will briefly discuss the current design and what to expect.
This Target is designed for use with ultraviolet induced visible fluorescence – more specifically, UVA or longwave UV radiation. We hope to develop a future Target that focuses on UVC.

Image Credit: "EM Spectrum3-new" by NASA –
http://mynasadata.larc.nasa.gov/images/EM_Spectrum3-new.jpg
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UV-visible fluorescence has been in use by art conservators since the 1930s. This imaging technique is valuable to all specialties and disciplines of art conservation.

Here are some examples of the use of UV-visible fluorescence to characterize pigments and resins, uranium glass, mold, tidelines, bone, optical brightening agents, and minerals.
We need standards for all types of conservation documentation, including UV-visible fluorescence. The *AIC Guide to Digital Photography and Conservation Documentation* reads: "Targets act as the technical metadata by providing known RGB values within the image. Targets also provide a visual reference for the viewer."

Here are some examples of visible light targets, which are commonly used in our field to establish exposure and color balance. The UV-visible target we developed is similar in its goal and purpose.
UV-visible documentation is highly subjective. For example, can you tell which image here accurately reflects the fluorescence of this hand-painted photograph? The answer depends on the keenness of your eyesight, but also the nature of the UV source you are using, and many other factors. This paper will discuss the variables in more detail later, but note that these images vary considerably in both color and intensity.
Here you can see a list of the major goals of the project. Our first challenge was to find stable UV-visible pigments, which would act as the foundation of the Target. On the top right you can see some of JJ’s first experiments with commercially available paints. Unfortunately, these are mostly dye-based, so stability was a limiting factor.

Eventually, we settled on our current formulation, pictured on the bottom right. These paints are made from more stable inorganic phosphors that have been custom-made into paint for us by Golden Artist Colors. Once we had our paint, we could move onto other challenges, like: managing intensity, identifying and controlling variables, defining a neutral grey, testing the Target, and finally, producing the Targets.
Intensity presents a challenge that is somewhat unique to UV-visible documentation, since we are documenting an emissive source. For this reason, exposure will be dependent on the fluorescent intensity of the object you are documenting. Photographing objects of different intensities in the same image will cause over- or underexposure.
Here are some examples of this issue. On the left you can see that the largest object has been underexposed, while the fluorescent stamps next to it look great. On the right, the optically brightened label has been overexposed because the exposure has been set for the low fluorescence of the paper it is adhered to.
Early on, we decided that the best solution for this issue was to divide the Target into three different intensity levels.

- “Ultra” would be for items that were manufactured to fluoresce, such as paper with optical brightening agents and fluorescent dyes.
- “High” would match the intensity of bright, naturally fluorescent materials, like minerals and uranium glass.
- “Low” would be for many applications in conservation documentation, such as thin applications of resins, varnishes and pigments.
The next step was to formulate a neutral grey. The intent was to mix red, green and blue pigments to create a neutral grey to serve as the backbone of the project as discussed in the next slide. Let’s just say that this was not a straightforward process, and required significant experimentation to arrive at our current grey.

Greg Smith, conservation scientist at the Indianapolis Museum of Art, provided us with this spectrum which shows the emission of the grey as measured through common camera filtration. Peaks from blue, green, and red combine to produce the appearance of a neutral grey.
Defining the neutral grey may have been the most time-consuming and challenging aspect of this project. The main goals were for this grey to:

- Be interpreted by the camera as neutral. We’ll discuss this further shortly, but this proved to be an important point.
- Appear neutral to the viewer, but this also proved to be a more complex issue than originally hoped – more on that later too.
- Perform similarly under a variety of conditions, which, after all, is the point of any standard.

I’d like to point out some similarities with a traditional 18% grey card, which is designed to provide consistent parameters for normal light photography even under changing lighting conditions.
We had some variables to consider:

- The camera provides some pretty significant variables. Digital cameras vary considerably in their sensitivity based on manufacturer and sensor type.
- Filtration is also an issue. In this graph I have overlaid some common filters used for UV-visible documentation. In the blue is a “BG-38”, which is a typical in-camera filter designed to limit infrared, since digital camera sensors have more sensitivity in this range than we do. The grey coloration shows the transmission of the Wratten 2e filter. Overlapping with this is the green graph, showing the transmission of the PECA 918 UV-IR cut filter. As you can see in the center of this graph where all the filters overlap, the nature of the information coming into the camera sensor is significantly altered by this filtration. As a comparison, a final overlay is a typical photopic curve for human vision. Note how the filters bring us a little bit closer to that human vision curve.
Camera filtration and sensitivity present a significant set of variables that needs to be understood, especially when setting a standard neutral gray:

- First, digital cameras are designed to mimic human vision. This is done with internal filtration and proprietary software that interprets what the camera sees.
- Cameras also vary considerably in their sensitivities. The image (removed due to copyright restrictions, but found at www.fen-net.de/walter.preiss/e/slomoinf.html) on the right shows some of the differences between the two most common sensor types, CMOS and CCD. Due to these differences, manufacturers use filtration and software that best works with their components.
- External filtration is also an important factor.
- And finally, we see visible light differently than the camera does. This point seems obvious, but is often overlooked in normal light photography.
The next variable is the radiation source. To show some issues with this variable, we will review some common UVA sources.
The most common UV source is probably low pressure mercury in the form of a fluorescent tube. These are also called black lights. Their emission is typically very reliable, with major peaks around 368nm. This graph shows the emission of a SuperBright II made by UV Systems (orange line). This lamp has filtration over the bulb (shown by the blue line) that limits the visible light output.

Source of data for spectra: UV Systems.

Image credit: "Two black light lamps" by Chetvorno – Own work. Licensed under Creative Commons Zero, Public Domain Dedication via Wikimedia Commons – http://commons.wikimedia.org/wiki/File:Two_black_light_lamps.jpg#mediaviewer/File:Two_black_light_lamps.jpg
Another common type of radiation source is the high pressure mercury lamp, which uses mercury vapor. These require long warm-up times but create a lot of UV radiation. As you can see in this graph, the emission of this lamp (shown with the orange line) varies a bit from the low pressure mercury lamp. Significant filtration (blue line) is needed to limit the emission in the visible. Its main UVA peak is at 365nm, but it also has a secondary peak at 334nm.

Source of data for spectra of Mercury lamp and 18A filter: Zeiss and Kodak
Another UV source that is gaining popularity is LED. This is a UV flashlight that you may be familiar with made by Inova. Its LEDs emit at 398nm, which barely qualifies as UV. This graph from Greg Smith at the Indianapolis Museum of Art shows the emission spike at 398nm. This intense, narrow spike is characteristic of LEDs, but can be targeted to any range. Unfortunately, UV LEDs closer to 367nm are still a little hard to find and more expensive.
This slide shows the differences in fluorescence caused by the differing emission peaks in various UV sources. Here is a prototype of the Target photographed with settings calibrated for a low pressure mercury source. The set pictured on the bottom appears neutral because it was used to set the white balance.

However, the other sets (seen in the middle and top images) photographed with the same settings as the bottom image, appear very un-neutral. The LED source causes significant shift to the blue, while the high pressure mercury source shows a red shift. As suggested by the images, this color change is visually apparent when switching between these sources. While the visual difference is most striking, it is also important to note that these sources vary considerably in the intensity of radiation as well, which will effect exposure times.
This is where the Target comes in. White balancing with the UV-Grey should adjust for small differences in radiation sources. Such adjustments are analogous to setting the white balance in normal light photography when switching from a daylight source to a fluorescent or tungsten source.

Of course, our product cannot accommodate large shifts in UV radiation, so some limitations should be noted. For the purpose of standardization, UV sources should be limited to the most common types, which have main emission peaks between 360 and 370nm.

Image credit: "Metrostation-Sofia-University-white-balance-collage" by Vassia Atanassova – Spiritia – Own work.Licensed under Creative Commons Attribution-Share Alike 3.0-2.5-2.0-1.0 via Wikimedia Commons –
http://commons.wikimedia.org/wiki/File:Metrostation-Sofia-University-white-balance-collage.jpg#mediaviewer/File:Metrostation-Sofia-University-white-balance-collage.jpg
The final two variables are:
- Post processing, typically done with Photoshop or another raw editing program.
- User perception.

These are huge factors with this type of documentation. We will address them briefly in terms of the testing, but these variables deserve more discussion than we can give them here.
The next phase of the project was testing. We wanted to see how well the Target could accommodate all of these variables.

Two main variables are being controlled by the Target-UV and UV-Grey. These are the sensitivity of the camera and the specific radiation source being used. This means that the Target-UV should produce consistent results regardless of camera manufacturer or type, and using any radiation source that has a main peak between 360 and 370 nm. This includes most sources, but does cut out our handy LED flashlight.

Many of the other variables are controlled by external factors. This means standardizing filtration, limiting those UV sources, and instituting a workflow that regulates post processing. These are all significant variables that can be eliminated only by consistency in use. This final variable, user perception, is a tricky one. But, by setting our exposure values and color rendering to known values on the Target-UV, we are effectively eliminating this as a variable. This is easier said than accepted, but as you will see in the coming slides, things aren’t always as they appear.
The testing took place from February to May 2013. We assembled a group of easily transportable fluorescent objects that might commonly be documented in conservation. We attached these items to black Fome-Cor so they were easy to document. On the bottom of this slide you can see some normal light images of these objects. They were grouped by intensity level. These items went into a FedEx box with the UV-Grey card, Target-UV, and a set of filters. The box went around the world from site to site.
We chose the sites based on their availability, interest and equipment. Specifically, we wanted to choose sites that: had a UV workflow already in place; and represented some of the variables we were trying to test.

We are grateful to all these institutions for their time and participation in the testing. The final list is seen in the slide above.
Each site was asked to capture two sets of images. Set “A” would represent the testing sites’ existing internal workflow, which usually included a subjective adjustment of exposure and color balance. Filtration was also variable. Some used the guidelines set out in the AIC Guide to Digital Photography and Conservation Documentation, but most used color and exposure values based on visual perception during the documentation session.

The “A” set was meant to be a contrast to the next set of images – the “B” set. This was done using our workflow which standardized filtration, set the white balance from the UV-grey, and set exposure to values on the Target-UV. Our expectation was that we would see inconsistency among the testing sites in the A set, and hopefully consistency in the “B” set.
Ultimately, we had an excellent representation of variables. Common camera types and manufacturers were represented, as well as several sensor types. Cameras that had been modified to be sensitive to UV and infrared were also included. Radiation sources varied, with high pressure mercury, low pressure mercury, and arc lamps used. In addition, set “A” showed variability in filtration as well as user interpretation.
Here are the results for objects with “low” fluorescence. This slide represents all the “A” images. Each number represents a testing site. As you can see, there is quite a bit of variability here. On the whole the images are pretty dark, which would be expected for this intensity level. There are definitely some outliers.

Each user’s perception of the fluorescence is slightly, or significantly different. RGB values were collected from the images using Photoshop, and used to calculate the delta E (ΔE) values and standard deviation you see in the bottom right corner. For this group, those numbers are pretty high. Delta E is over 18 and standard deviation is 32.8 - a significant lack of consistency.

Delta E (or ΔE) is the distance metric used by the International Commission on Illumination (CIE) to indicate color difference. The 1976 formula was used: $\Delta E_{ab} = \sqrt{(L^*2 - L^*1)^2 + (a^*2 - a^*1)^2 + (b^*2 - b^*1)^2}$. A ΔE of 1 is commonly referred to as a “just noticeable difference” under ideal viewing conditions.
These are the low-fluorescent results using the UV Innovations settings, or the “B” set. As mentioned before, filtration and workflow were standardized and the exposure was set to values on the Target. The visual difference is clear. Delta E was reduced to 4.9, about one quarter of the previous value, and the standard deviation to 6.2.
To visualize this a bit better, these graphs plot the delta E values against the absolute deviation from the average RGB values for each image. This gives you an idea of the level of variability in the “A” images. The further out from zero, the more variable the image is from the average. There is a cluster in the bottom left here, of variability that hovers around 15 to 20 delta E with a similar absolute deviation. Again, notice some outliers in the top right as delta E values and absolute deviation increase.
This next graph shows a significant decrease in variability in the “B” images captured with the UV Innovations settings. There is only one group of similar images in the bottom left with no outliers.
Here is the set of “high” fluorescent items. This group of “A” images shows a similar level of variability with the user workflow that we saw in the “low” images. Delta E values and standard deviation are pretty similar to the “low” fluorescent images. It is a little easier to see the differences in color rendering and exposure here. Notice the differences that occur when user interpretation is a factor.
The “B” set again shows a significant reduction in the visual differences. These images are pretty similar. This is reflected in a reduction of the delta E values and standard deviation.
Here is a graph of the “A” images. There is a pretty wide spread of delta E values and absolute deviation like that we saw with low fluorescence.
There is a similar reduction in delta E values and absolute deviation in the “B” group that followed the UV Innovations settings.
Here is the last set – the “ultra” images. These “A” images show some differences in perception by the viewers. Some of these images reached maximum RGB values of 255, meaning they were overexposed beyond the capacity of the sensor. Again, delta E values and standard deviation are similar to the low and high-fluorescent sets. I hope you are beginning to see the amount of variability in user perceptions and workflows.
The “B” group, using the Target and UV Innovations settings shows more consistency, which is again reflected in the reduction of the delta E and standard deviation values. Can you see the power of standardization and consistent workflows?
A graph of the “A” set shows the variability in interpretation present in the user workflows.
As with the “low” and “high” fluorescence groups, the “B” set of “ultra” images shows that standardization reduces delta E and absolute deviation.
Some conclusions:

• There is a high degree of variability in current UV-visible documentation protocols and workflows at the institutions included in this test.
• Calibration with the UV-Grey card and Target-UV standards and workflow allows disparate sites and users to create images with similar results.
  • Visual comparisons and data show a significant reduction in variability among the testing sites.
• Image processing software proved to be another significant variable.

• There is a high degree of variability in their “A” images.
• Calibration with the UV-Grey card and Target-UV allows disparate sites to create similar images. The visual comparisons are clear. This means that the Target-UV successfully controlled the variables we laid out earlier.
• Image processing software proved to be another significant variable that we are still working out. This was most noticeable with the cameras that required post processing using proprietary software, like the Hasselblad and Phase One systems. All the DSLRs could be processed with Adobe Photoshop Raw.
We got a lot of valuable feedback on this testing. Most users noted a slight blue/green cast in the images, so the neutral point of the grey was adjusted to reduce this.

The most common comment we got related to intensity. Many users felt that the “low” images in particular were too dark, and hard to see. Though they may reflect an accurate rendering of intensity, most said that the images just weren’t useable. To deal with this issue, we increased the intensity rendering, as you can see here. The color change is also visible. This adjustment allows us to capture a lot more detail and reduces the tendency of the blue values of the image to max out. We also added a fourth intensity level (not pictured) to allow a bit more flexibility.
These products should be ready soon. We have partnered with Image Science Associates who will manufacture and sell the Target-UV and UV-Grey. They made the wonderful prototype pictured on the bottom here. We have a few more things to do, but we hope to have these available later this year. Up next are some much needed ageing tests to put a reliable replacement date on the pigments, but we expect them to perform well. We are also still working out some of the workflow issues.

Some future goals include a larger format Target and a UVC Target. For more information, you can visit our website at www.uvinnovations.com.
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Recommendations for the Standardization of Digital Radiography of Cultural Heritage Materials

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Image: X-ray of a landscape painting by FW Rogers used as a study piece for various techniques at the Museum Conservation Institute (MCI) from the personal collection of Mel Wachowiak.
I want to start this paper by telling you a little bit about myself. I do not want anyone to get the wrong impression that I am claiming to be an expert digital radiography user.

My background is as a Digital Imaging Specialist at the Smithsonian’s Museum Conservation Institute (MCI) using a variety of scientific and computational imaging techniques for the conservation and research of cultural heritage materials. Digital radiography is one of my newer techniques.

When I was hired in 2012 as an employee with the title of Digital Imaging Specialist, I was assigned to work towards the revitalization of the digital radiography program at MCI. In the fall of 2012, I completed training at General Electric (GE) for Nondestructive Evaluation (NDE) for digital radiography. After the training, I visited various conservation and research labs to learn more about digital x-ray in the context of cultural heritage.

With the lofty title of “Recommendations for the Standardization of Digital Radiography of Cultural Heritage Materials” my goal is to initiate the conversation about standardization of digital radiography of cultural heritage materials. I initially had the time and resources to support the community in this way.
Digital Radiography of Cultural Heritage Materials

- A non-destructive tool:
  - Condition Assessment & Documentation
  - Informing Care & Treatment
  - Increasing Understanding
- Radiography is not a new technique
- Useful for a range of objects, materials and sizes

Similar to digital photography, digital radiography of cultural heritage materials is used as a non-destructive tool for condition assessment and documentation, informing the care and treatment and increasing the understanding of an object.

Radiography is not a new technique for documenting and analyzing cultural heritage objects. According to Janet Lang and Andrew Middleton in “Radiography of Cultural Material”, radiographs were taken of archaeological artifacts including mummies shortly after the discovery of x-rays by Rontgen in 1895. The technique has seen growth in the past few decades for the examination of cultural heritage materials.

Depending on the source and energy, it can be used on a wide range of objects and materials.

Similar to other analytical techniques used in research and conservation of cultural heritage objects, digital radiography has been heavily developed by medicine and industry.
In medical radiography there is a standard known as Digital Imaging & Communications in Medicine or DICOM.
With the introduction of computed tomography (CT) followed by other digital diagnostic imaging modalities in the 1970's, and the increasing use of computers in clinical applications, the American College of Radiology (ACR) and the National Electrical Manufacturers Association (NEMA) recognized the emerging need for a standard method for transferring images and associated information between devices manufactured by various vendors. These devices produce a variety of digital image formats.

The American College of Radiology (ACR) and the National Electrical Manufacturers Association (NEMA) formed a joint committee in 1983 to develop a standard to:

- Promote communication of digital image information, regardless of device manufacturer
- Facilitate the development and expansion of picture archiving and communication systems (PACS) that can also interface with other systems of hospital information
- Allow the creation of diagnostic information databases that can be interrogated by a wide variety of devices distributed geographically.

*Text and information from The DICOM Standard, DICOM Part 1: Introduction & Overview
http://medical.nema.org/standard.html
*X-ray of Bull Mummy A413941-0 from the National Museum of Natural History, Smithsonian Institution
Industrial Radiography & DICONDE
Digital Imaging & Communication in Nondestructive Evaluation

- Industrial Radiography includes aviation, transportation, energy and defense
- ASTM E2339 – 11 DICONDE Standards
  - 1.1 This practice facilitates the interoperability of NDE imaging and data acquisition equipment by specifying the image data in commonly accepted terms. This practice represents a harmonization of NDE imaging systems, or modalities, with the NEMA Standards Publication titled DICOM...
  - 1.2 This practice has been developed to overcome the issues that arise when archiving or analyzing the data from a variety of NDE techniques, each using proprietary data acquisition systems. As data acquisition modalities evolve, data acquired in the past must remain decipherable. This practice proposes an image data file format in such a way that all the technique parameters, along with the image file, are preserved, regardless of changes in NDE technology. This practice will also permit the viewing of a variety of image types (CT, CR, Ultrasonic, Infrared and Eddy Current) on a single workstation, maintaining all of the pertinent technique parameters along with the image file.

*Text from ASTM E2339 – 11: http://www.astm.org/Standards/E2339.htm
*X-ray detail of Tibetan Shrine Bodhisattva LRR 7563 from the Freer|Sackler Galleries, Smithsonian Institution
These are similar issues to what we deal with in digital radiography for cultural heritage: archiving and analyzing, the evolving of data acquisition modalities, and preserving metadata.
The Need for Standardization

- Ensure stability of overall acquisition system and that it is functioning properly
- Provide a framework to assess image quality
- Improving reproducibility & comparison
  - Calibration
  - Post-processing
- Proprietary file formats & archiving
- Evolving technologies
  - Image acquisition modalities & file formats
- Maintaining viewable data
- Make it easier to share among institutions

*X-ray of a metal plate from the Museum Conservation Institute (MCI) study collection.

We need to standardize digital radiography for cultural heritage imaging.

How do you know your system is working? How do you know that the quality of your x-ray is such that you are seeing everything that is there, and that what you don’t see really is absent?
We have established that there is a need for standardization for digital radiography of cultural heritage materials, so now we need to start the conversation. The presentation of this subject at the 2014 AIC annual conference was a start to this conversation, as is a web resource that I created.
I have created a web resource for cultural heritage professionals working with digital radiography to pull together resources and encourage the conversation about standardization: http://my.si.edu/DigitalX-ray.
The website has a blog that will include guest bloggers discussing recent projects, challenges, trouble shooting, and anything and everything relating to digital radiography of cultural heritage materials.
The site also includes a page with profiles for institutions that have digital radiography capabilities.
The intent of these profiles is to allow users to reach out to others who may be using similar equipment or working with similar materials so that they may discuss, collaborate and troubleshoot together.
The final page is a list of resources for digital radiography. The page currently includes articles and books, but I would be happy to add links, technical notes/white papers, and other resources that will help us do our work better.
Participation is the key to the success of this web resource. It can only be as good as the contributions and participation of the community.

This web resource will only be as good as your contribution and participation!

With all of our experience and knowledge together, we can x-ray the world!

*X-ray of Bull Mummy A413941-0 from the National Museum of Natural History, Smithsonian Institution*
An example of taking steps towards standardization is Blythe McCarthy’s work with 3D printing for step wedges.
Examples of Image Quality Indicators (IQIs) for NDE radiography:

Hole-type IQI
- T equals the thickness of the material of the IQI. The three holes on the indicator have the diameter of T (thickness of the indicator), 2T (twice the thickness) and 4T (four times the thickness). The holes that can be resolved in the x-ray image indicate the image quality of the exposure.
  - Illustration from http://www.ndt.net/article/v08n08/shahout/shahout.htm

Contrast Sensitivity Gauge
- These gauges have varying thicknesses of partial holes that represent 1%, 2%, 3%, and 4% transmission so you can check the sensitivity of the contrast in your image. This gauge measures contrast sensitivity independently from the imaging system’s spatial resolution.

Duplex-wire IQI
- This IQI evaluates image unsharpness. The distance of the wire pairs is the thickness of the wires. As the unsharpness increases the line pairs begin to merge.

CR Phantom
- A kit that incorporates several test objects that are included in ASTM E2445 so that they can be shot with one exposure.

These are not inexpensive standards and some must be composed of the same material that is being evaluated. Within cultural heritage digital radiography it can be hard to obtain a standard for each of the materials that might be imaged.
Step wedges can be used to test the consistency of a radiography set-up. They can be used to determine the linearity or non-linearity of exposure response to changes in time and current as well as the exposure response to changes in thickness of the object being radiographed.

If using multiple imaging plates (IP plates), step wedges can provide an easy check for differences between the plates, and a method to track changes in the plates over time.

Calibration samples can make comparison between laboratories more straightforward. They can be used for comparison studies that incorporate objects from multiple museums/collections or adoption of techniques from other museums or other x-ray setups.

They can also be used to compare results from different detectors. If the power of two x-ray sources differs, you may need to adjust to get comparable exposures. The step wedge gives you a measurement to do so.

They are commonly used in film-based systems to guide selection of exposure conditions. This is generally not such a concern with digital systems due to their greater dynamic range.
Blythe McCarthy is working with a designer to develop calibration samples that could be printed on demand using 3D printing processes.
She carried out x-radiography of commercially available sample materials at a series of exposure conditions to see if colorants in the plastics would result in variable radiodensity. Colorants in the plastic (negative XRF results for inorganic pigments other than titanium suggest the use of organic dyes) did not result in variable radiodensity.

From these experiments, we have reduced our selection for further testing to two commercial plastics (“alumide” and “detail acrylic”) and two metals (stainless steel and silver). Note that with the exception of silver, most of the metals tested so far, regardless of their name, are plated stainless steel, hence the similarity in results.

The graph at lower right shows the variation in image intensity versus kV. Intensity was divided by test sample thickness to correct for differences in thickness.

We are currently working out options for step wedge thickness that would cover a broad range of exposure conditions, object thickness, and that would use design and materials to minimize cost.
While these will not have the accuracy of test pieces designed for the NDT community, they should be much more affordable. The hope is to end up with test objects (step wedges) that can be used by many labs and that will make sharing between labs easier.
Continued Work with Step Wedges

- Blog results of testing
- Test wedges available on web for purchase
- Continued Investigation
  - Possibility of incorporating holes in step to check contrast sensitivity
  - Possibility of using wires to measure unsharpness

*X-ray of Egyptian Glass Vessel F1909.430 from the Freer Gallery of Art, Smithsonian Institution*
Where do we go from here?

• PARTICIPATION—Contribute to the Web Resource
  – Have a profile for your museum/institution
  – Be a guest blogger
  – Recommend resources or allow us to link or list what you create

• COMMUNICATION—
  – Reach out to other institutions working on similar materials or using the same equipment

• Future digital/remote gatherings

* X-ray image of a Junkers Ju 88 A6 aircraft model A1943-101 from the National Air & Space Museum, Smithsonian Institution

Where do we go from here?

- Participation: please get involved with the website by contributing to the profile, blogging, resources areas.
- Communication: reach out to people working with similar materials or using the same equipment.
- Possible future digital/remote gatherings: in the couple of months preceding the 2014 conference, we had a panel discussion on Reflectance Transformation Imaging (RTI) using Google Hangout and YouTube.
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- Winterthur Museum
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*X-ray of a ceramic mug belonging to E. Keats Webb*
Mel Wachowiak, senior furniture conservator at MCI passed away on May 28 after a long struggle with cancer. Mel was the soul of MCI and a great asset for the Smithsonian. In his nearly 25 years there he brought in many imaging and microscopic techniques to the Smithsonian Institution, including 3D scanning, and he trained furniture conservators who are now in many of our nation’s museums. He was very generous in sharing his knowledge with everyone and will be deeply missed.
Thank You!

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http://my.si.edu/DigitalX-ray

X-RAY COMPUTED TOMOGRAPHY OF WESTERN RED CEDAR BARK

Pete Mc Elhinney, Nicole Little, Benjamin Ache, Brandon Walters.

42nd Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
San Francisco, CA, May 27-June 1, 2014

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Presented at the RATS session
42nd Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
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The research I am presenting today was completed as part of the Andrew W. Mellon Foundation Post Graduate Fellowship in Object Conservation at the National Museum of the American Indian (NMAI) in Washington DC.
My research at NMAI focused on understanding the deterioration mechanisms of Western Red Cedar in the collection there. Cedar bark is well represented in the collection...
... and objects are often accompanied with small tags marked ‘Inherently Fragile. Will Have Continued Loss.’ Being an inquisitive and somewhat stubborn conservator, I decided to see if there was anything I could do to change this gloomy forecast.
After studying the material for some time I concluded there were gaps in our understanding of this material. I decided that in order to figure out a treatment protocol, I needed to understand how the material was falling apart, and to do this I needed to better understand the chemistry and microstructures of the material. Over the following year I improved my understanding of bark materials through library study of plant biology, and by attending workshops like the NMAI bark materials workshop led by conservation scientist Dr. Mary-Lou Florian, pictured here. The technical approach was complemented with field work undertaken in Sitka, Alaska, and supervised by Tlingit artist Teri Rofkar.

I should confess at the start of the presentation that whilst I have not figured out how to treat the material, I know a lot more about why it falls apart than I did when I started.
The Western Red Cedar is an evergreen tree from the Cupressaceae (Cypress) family. Trees range from about 65-70 meters tall, and 3-4 meters in diameter with the oldest known tree calculated at 1460 years old.
The natural range of the tree is in the Pacific Northwest Coast and some inland areas - British Columbia, Washington, Oregon, Northern California, Idaho and Montana. Cultural material made from cedar bark can be found in almost all of the cultures associated with these geographical areas.
Western Red Cedar is a little unusual in that it doesn’t have a true bark at maturity. The tree has a bark layer in the first few years of growth, but the wood growth rate exceeds that of bark growth rate to such an extent that it practically ‘bursts out of its clothing’ as the tree increases in girth.

The material that we see on the outside of the mature tree is actually part of the ‘secondary phloem’ layer, normally involved in the movement of nutrients around the tree, that has undergone mechanical and chemical changes to help protect the tree from the outside world.
Cells produced at a thin layer called the vascular cambium differentiate toward the outside of the tree to become phloem cells, whilst other cells differentiate toward the inside of the tree to become xylem (wood) cells (Beck 2010).

The secondary phloem layer can range between about 1/2 and 1 inch in thickness (Dallimore and Jackson 1967).
Looking at Western Red Cedar phloem under the microscope can be a little confusing, but the basic tissue structure is beautifully simple. The 480x scanning electron microscope (SEM) image above shows a small section of phloem viewed in the transverse plane.
Elongated fibers with thick cell walls form the structural scaffold of the phloem. The cross sectional shape of these cells varies from thick, almost square cells, to flattened oblong cells, arranged in axially aligned rows.
Sieve cells are distributed in rows on either side of the fiber cells. These thinner walled cells serve as the pipe work for distribution of the nutrients and metabolites, moved through pores concentrated in the overlapping ends of these long slender cells.
Thin-walled parenchyma cells are distributed between the rows of sieve cells. Cedar phloem parenchyma cells play a role in storage of nutrients in the form of starch grains visible as small round balls in the SEM image, but may also contain phenolic compounds responsible for regulation of growth, signaling, pigmentation, UV radiation screening, and defense against herbivores depending on the stage of phloem development.
When we look at cedar phloem in three dimensions, we can see that in addition to the structural arrangement described previously, nutrients are also stored and distributed through ribbon like clusters of conducting ‘ray’ cells arranged radially in the tissue.
In this image, we are looking at a small section of what would be a continuous ring around the outside of the tree. The large green section represents the wood, the red section the cambium (where new cells are produced) and the yellow, brown and orange squares the fiber, sieve, and parenchyma cells. As new phloem cells are produced at the vascular cambium layer, older phloem cells get moved toward the outside of the tree...
The relatively fast growth rate of the wood parts of the tree exerts pressure on the phloem tissue, (imagine the phloem layer as a elastic band around the increasing girth of the tree) to such an extent that the thin walled sieve and parenchyma cells in the outer phloem layers are crushed and distorted (Beck 2010). Whilst the phloem fiber cells become increasingly lignified and therefore tougher during this process, the crushed sieve cells are no longer able to move nutrients around the tree (Barton and MacDonald 1971). Some of the parenchyma cells resist compression and become filled with phenolic compounds.

These chemical and mechanical changes contribute to the tissue’s function in providing protection against UV radiation, weathering, grazing from animals, and attack from insects and other forms of bio deterioration (Esau 1977, Franceschi et al., 1998). Cedar bark objects made from phloem tissue near the outside of the tree will have stronger fibres, more crushed cells between these fibres, potentially making it come apart more easily, and increased levels of phenols, potentially making them more resistant to UV and bio deterioration.
One of the better understood mechanisms of deterioration for Western Red Cedar phloem is related to the close association of the thick-walled fibre cells and the thin-walled, more delicate parenchyma and sieve cells. Fractures in one or more of the less robust parenchyma or sieve cells contribute to stress concentrations that, as the cell wall fails...
... are transmitted axially along the row of cells, eventually contributing to portions of tissue cleaving away. This arrangement of weak and strong cells is also the reason why cedar splits easily along the width of the tissue, a trait useful for preparing the material for production of cultural material.
My early research also examined the role of pectin in deterioration of culturally processed phloem tissue. Pectic materials exist as a gel like polysaccharide distributed in some cell walls and throughout the intercellular spaces in Western Red Cedar phloem. Pectin in the living plant is negatively charged and tends to attract Ca2+ and other positively charged ions (Cooper 1997) such that it is sometimes referred to as calcium pectate (more on this later).

While little has been written about the role of pectin in culturally processed cedar bark, empirical observation indicates that pectin gels of different concentration eventually recrystallise under ambient museum conditions.

The image on the screen shows the extent of crystallisation of small gel disks after about one month in the climatically controlled NMAI conservation lab. It seems likely therefore that the dehydration of pectic materials in dry cedar bark will impact cellular cohesion to some extent. In other words, the cellular ‘glue’ has dried out.
I wanted to visualise the changes that occur across the width of the phloem, but given the disrupted nature of some cells in this tissue, found that physical preparation of consistent optical microscopy slides was extremely difficult.

The Western Red Cedar phloem photomicrograph above, given to me by Dr. Mary-Lou Florian, is one of the best images I have seen of how swollen cells impact the surrounding tissue. In this extremely well prepared slide, the swollen cell (possibly a radially arranged parenchyma cell) has disrupted what would have been at one time a continuous row of fiber cells.
Some of my NMAI colleagues had been experimenting with computed tomography (CT) scanning as a means to better understand what goes on in the visually inaccessible parts of objects. I felt that this non-destructive technique had potential for allowing me to more accurately understand what was going on within the phloem structure.

The resolution on the Smithsonian Institutes medical scale CT scanner was much too low to resolve the small tissue structures I was interested in. This led me to Micro Photonics, a commercial imaging lab in Allentown Pennsylvania.
The micro CT scanner used in this study is the Bruker Skyscan 1172, pictured here in the Micro Photonics lab. The sample requires no special preparation before being mounted by gently clamping on a spindle in the scanning chamber.

I won’t go into too much detail about how CT scanning works in this paper as I’m sure many of you already understand this, but essentially the scanning device produces hundreds of two-dimensional ‘slices’ though the sample, and collates these using computer software to produce a three dimensional model. The model can then be used to analyse the two and three-dimensional morphological parameters of the specimen.
The video above is a three-dimensional rendering of the cedar bark sample, composed from two-dimensional X-ray images, stacked and arranged using Bruker Skyscan CT Vol software.

The sample can be virtually sectioned in any plane, and while this is useful for visualising the sample shape and volume, the 1172 MicroCT can’t resolve the extremely fine cellular structure of the phloem tissue in any useful detail.
A second piece of software, *Skyscan Dataviewer*, was used to produce this video.

Here, we are looking at a cross sectional view of the phloem structure, oriented with the inner phloem near the top of the screen, and the outer phloem toward the bottom. The software allows the user to cycle through hundreds of two-dimensional cross section images produced by the scanner, revealing tissue structure patterns.

The large bright spot that appears in the tissue closest to the vascular cambium (near the top of the screen) at about 30 seconds was somewhat unexpected but interesting none the less. This bright speck, and others like it, were identified as bio-mineral crystals, but I will expand on this later.

As the video progresses, we see that the tissue in the lower section of the screen is disrupted at various points throughout. I believe that these disruptions are a result of compression of the outer phloem and swelling of phenol filled parenchyma cells described previously.

The video illustrates that even across a very narrow cross section of phloem tissue, we see considerable variation between relatively well-organised tissue near the vascular cambium, and the disrupted tissue less than 5 mm toward the outside of the phloem layer.

This video helps us visualise how objects made from more disrupted Western Red Cedar outer phloem might be less stable during handling and treatment than inner phloem objects.
I wanted to see if I could put some numbers to the visual patterns I was seeing in these videos, and asked the team at Micro Photonics to run some analysis. Analysis was performed using BRUker CT Analyzer software which uses built-in algorithms to calculate various morphometric parameters.

Four regions of interest were defined by virtually ‘shrink wrapping’ four naturally occurring sections of the sample labeled in the image above. The cell wall thickness, and volume of negative space within each region were calculated using built-in algorithms under the software 3D Analysis function, and are compared in the following tables.
This table shows the results of measurements of average cell wall thickness across the 4 regions shown on the previous slide.

<table>
<thead>
<tr>
<th></th>
<th>Region 1</th>
<th>Region 2</th>
<th>Region 3</th>
<th>Region 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bark Structure Volume (excluding air space):</td>
<td>3.45717 mm³</td>
<td>2.23383 mm³</td>
<td>2.7576 mm³</td>
<td>2.63842 mm³</td>
</tr>
<tr>
<td>Average Cell Wall Thickness:</td>
<td>0.01523 mm ± 0.00538 mm</td>
<td>0.01442 mm ± 0.00476 mm</td>
<td>0.01434 mm ± 0.00471 mm</td>
<td>0.02152 mm ± 0.01113 mm</td>
</tr>
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As we can see from the table, there is little detectible variation in the average cell wall thickness between regions 1-3.

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The cells in region 4, (the area closest to the vascular cambium) have a significantly higher average thickness than those in regions 1-3. This is most likely influenced by the high number of cells in this region with not yet fully developed intracellular spaces.
This table shows the results from measurements of negative spaces within the four phloem regions.

<table>
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<tr>
<td>Total Structure Volume</td>
<td>7.25978 mm$^3$</td>
<td>4.53243 mm$^3$</td>
<td>5.74543 mm$^3$</td>
<td>4.35312 mm$^3$</td>
</tr>
<tr>
<td>Negative Space Volume</td>
<td>3.50052 mm$^3$</td>
<td>2.11017 mm$^3$</td>
<td>2.771 mm$^3$</td>
<td>1.51355 mm$^3$</td>
</tr>
<tr>
<td>Negative Space Percent</td>
<td>48.22 %</td>
<td>46.56 %</td>
<td>48.23 %</td>
<td>34.77 %</td>
</tr>
<tr>
<td>Average Width of Tissue</td>
<td>0.01950 mm</td>
<td>0.01817 mm</td>
<td>0.01835 mm</td>
<td>0.01691 mm</td>
</tr>
<tr>
<td>Negative Spaces:</td>
<td>± 0.00863 mm</td>
<td>± 0.00664 mm</td>
<td>± 0.00631 mm</td>
<td>± 0.00593 mm</td>
</tr>
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The table shows that, although regions 1-3 have very similar amounts of negative space as a percentage of the total tissue volume...
...the average size of each discreet area of negative space in region 1 is larger...

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...than in regions 2 and 3, and significantly larger than in region 4.

The larger areas of negative space within region 1 may make this material less suitable for the production of fine grade cultural material than that in regions 2-4. In simple terms the bark in region 1 has bigger holes in it.
One of the more unexpected results of CT scanning this material was the visualisation of relatively dense material distributed throughout the bark.

The model above has been produced using the same *Skyscan CT Vol* software described previously, with the settings adjusted to represent only the most dense material within the tissue.

The video on this slide goes some way to illustrating the number and distribution of dense materials (represented by white specks), which turn out to be bio-minerals, within the bark structure. Bio-mineralization is the precipitation of minerals as a result of the metabolic functioning of a living organism, and is widely practiced by plants. Plant-tissue biominerals are overwhelmingly of three chemical types: calcium oxalate, silica, and calcium carbonate. Of these types, calcium oxalate is thought to be the most prevalent and widespread.
This video was produced using the *Skyscan Data Viewer* software described previously.

In this video we are looking at a transverse view of the phloem tissue with colours assigned to the different pixel density values. In this case, blue and white pixels represent the most dense material within the tissue, while yellow and red colours the least dense material.

As we cycle through the two-dimensional images, distributions of blue/white coloured dense material appear to flow from the tissue nearest the vascular cambium toward to the tissue closer to the outside of the tree, giving us a much clearer idea of how the bio-minerals are distributed throughout the phloem. Of course the material is not ‘flowing’, but if we translate this into a three-dimensional volume, it would be distributed in gently sloping radially-arranged channels (running from the inside to the outside of the plant) in much the same orientation as the phloem rays.

The video also indicates flushes of dense material in association with areas of disruption. It is unclear, but interesting to speculate about whether this material is contributing to dehiscence in these areas (splitting at maturity along a built-in line of weakness in a plant structure in order to release its contents).
The sample material was examined using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) to help characterise the relatively dense material within the phloem structure.

As we can see in the series of images above, white specks of material in the intercellular spaces agree with the distribution of dense material observed in the previous video.
Using EDS mapping, we see calcium detected in correlation with the white material. The association of Ca2+ ions with negatively charged pectin makes it difficult to distinguish between the distribution of calcium pectate and calcium oxalate using EDS mapping alone.
When we look at the white material in more detail we can see that what appear to be amorphous globs are in fact made up of clusters of small shard-like crystals. The individual crystals in this image measure in the region of 1-2 microns in diameter. Again using EDS mapping, we can see that the rhombohedral and tetragonal crystals map closely for calcium and oxygen, suggesting that they are likely calcium oxalate.

A 2003 study that examined distribution of calcium oxalate in different conifers (Hudgins et al 2003) agrees with the distribution in our sample, with calcium oxalate most abundant between radial walls of all cell types, and generally embedded in and enveloped by cell wall material. The study also concludes that there are higher concentrations of crystals in the middle and outer phloem than in the inner phloem tissue, and that some members of the Cupressaceae family have 10-20 times the amount of CaOx as are found in other conifers.

The large volume and widespread distribution of calcium oxalate in Western Red Cedar phloem may well be a contributing factor in the deterioration by cell wall abrasion of cultural material made from this tissue. Some of the abrasive action is likely mitigated in the living plant as the crystals are distributed within a pectic gel matrix, but as the pectic material crystallises in harvested and processed phloem, the lubricating action of the pectin is greatly reduced. The higher distribution in middle and outer phloem tissue may indicate increased abrasive action in cultural material made from these parts of the phloem.
When we look at the more well-defined crystals using the SEM we can see that these crystals are much larger -- between 10 and 20 microns in diameter -- and have a less regular shape than the smaller calcium oxalate crystals. Using EDS we can see that the crystals are formed from aluminum (green), titanium (yellow), potassium (purple) and silicon (blue) and are likely silicate biominerals formed in combination with metal ions absorbed from the surrounding soil.

While these crystals are much less abundant than the calcium oxalate crystals, their relatively large size could be enough to induce localised stresses necessary to initiate the axial cleavage mechanism described previously, contributing to delimitation of layers of phloem tissue.
I had hoped to use the Bruker analytical software to map the number and distribution of crystals within the phloem tissue. While this ‘bright speck analysis’ functionality exists within the software, the resolution of the scans was too low to accurately detect the extremely small individual calcium oxalate crystals. The 1-2 micron diameter crystals are smaller than the individual 3.77 micron pixels size selected for these scans.

I am currently making arrangements to have cedar sample analysed at Skyscans Laboratory in Belgium where they have a relatively new unit -- the 2011 x-ray nanotomograph -- with spatial resolution in the range of hundreds of nanometers (1 million nm = 1 mm).

Some research into the size and scale of pertinent features of sample material can be helpful in selecting the appropriate scanning technique- CT, Micro-CT, to Nano-CT.
Whilst some of these findings may seem abstract, they have implications for the conservation of Western Red Cedar bark material objects. Hilary Stewart (Stewart 1984) mentions a process of ‘grading’ cedar bark after harvest by splitting the thickness of the harvested phloem. Further investigation of this process may help refine the currently used terms ‘inner’ and ‘outer’ phloem.

Cedar bark objects in the collection of NMAI range from material that appears to be made from very fine, well ordered phloem consistent with that observed near the cambium, while other objects appear to be made from a ‘rougner’ grade of phloem material.

Further research is required to gain a better understanding of how much of the phloem harvested from the tree is used to produce cultural material. How do harvesters and makers determine the inner/outer tissue boundaries? How are different parts of the phloem tissue used for different applications?
This research concludes that cultural material made from phloem tissue close to the cambium in the living tree may have quite different properties to material formed from phloem tissue in relatively close proximity (Hudgins et al 2003). Disruption of sieve and parenchyma cells, observed in the outer but not the inner phloem, will likely impact the structural stability of cultural materials made from these tissues. Likewise abrasion associated with increased accumulation of calcium oxalate crystals in outer phloem tissue may result in increased cell wall damage during manipulation of some bark objects during treatment and handling for exhibit and storage. The higher concentration of extractable phenols in Western Red Cedar outer bark versus inner bark indicate that inner bark material objects may be more susceptible to damage from UV and biological deterioration than those made from outer bark tissue (Franceschi et al., 1998, Lattanzio et al., 2006). This needs to be considered in relation to storage and display of these types of objects.

Whilst I agree that these conclusions do not necessarily solve the problems that I initially set out to, I believe they bring us one step closer to understanding where to begin. Beyond my current research commitments, I would like to correlate what I have learned about this unique material with condition issues observed in museum collections, and eventually draw up a list diagnostic features and treatment protocols for the different types of phloem tissue.
Thank You!

My sincere thanks to the following people, all of whom have been invaluable in putting this research together.

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Susan Heald
Lauren Horelick
Mary-Lou Florian
Terri Rofkar
Michelle Austin Dennehy

and

The Smithsonian Institute
The National Museum of the American Indian
The Andrew W. Mellon Foundation
The Margaret A. Cargill Foundation
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Elemental Identification Of Pigments Used In Traditional Bark Paintings In The Northern Territory of Australia

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Elemental Identification Of Pigments Used In Traditional Bark Paintings In The Northern Territory of Australia

AIC Annual Meeting

Georgina Rayner
Andrew W. Mellon Postdoctoral Fellow in Conservation Science
This paper is split into five sections. We will begin with an introduction to the project, followed by a discussion about sample collection, preparation and analysis. The paper concludes with a summary of results.
Two examples of traditional bark paintings are shown at the top of this slide. These were sampled as part of this project.

The description of the project has been split into three questions: What this project about? Why are we undertaking this project? How we are going to complete the project?

What: Harvard Art museums is conducting a major study into traditional bark paintings created in the Northern Territory of Australia. There are two projects underway; this project which focuses on characterizing the pigments and a second project focusing on the binders.

Why: In early 2016 Harvard Art Museums will host ‘Everywhen: The Eternal Present in Indigenous Art from Australia’ curated by Stephen Gilcrest. With our research we aim to determine whether or not it is possible to trace the provenance of ochre based on its elemental composition, with our work contributing to an ochre atlas that may be used to trace trade routes locally and across the continent. Previous research conducted at the University of Western Australia demonstrated that an ochre’s elemental composition varies across the continent. In our study we are focusing on a narrower geographical location to see if there are local differences.

How: As part of a trip to the Northern Territory of Australia we were able to collect samples from traditional bark paintings held in galleries and museums across south-east Australia. The paintings date from the late 19th through the 20th century and used only traditional methods and materials. For the majority of the paintings their place of origin is documented. We are using a variety of scientific techniques together to help us characterize these materials using previous research as a guide.
The Northern Territory of Australia is highlighted on the first map by the red circle.

During this presentation four questions will be addressed:

1. Are samples prepared in different ways comparable? Previous research used pellets of crushed ochre for their work. By preparing both ochre pellets and paint samples from our ochres we hope to be able to determine whether or not different sample preparations are comparable. If big differences are observed it would not be appropriate to use pellets as references when studying chips of paint.

2. Are Yirrkala ochre samples the same? As part of our natural ochre collection we have the most reference samples from Yirrkala, highlighted in the second map by the blue circle. Having a large number of samples from one area means we can see if they all have the same elemental composition. If samples of the same color from the same location are found to be different it would make tracing ochres much more difficult as there would not be a distinctive element or elemental pattern we could use to identify them based on an area.

3. Are ochres from Yirrkala different to others from across Arnhem Land? This will inform us whether or not it is possible to separate ochres from nearby locations based on their elemental composition.

4. Are Northern Territory ochres different to those from Western Australia? With this question we want to investigate whether samples from different regions, in this case the Northern Territory and Western Australia, are as easily identifiable as previous research suggests.
Further examples of traditional bark paintings sampled as part of this project are pictured on this slide.

The art of bark painting has played an integral part of aboriginal life and culture. Many depict scenes such as hunting or camping while others illustrate the legendary time of creation known as Dreamtime. The palette is typically limited to just four ochre colors; red, yellow, black and white. The colors often have symbolic meaning; red may represent blood, yellow fat, white bone and black aboriginal skin. Red and yellow ochres are typically iron oxides. Black ochres are either carbon or manganese oxides. White ochres vary and could be kaolin, gypsum, chalk or huntite.
The tradition of bark painting is still performed across Arnhem Land and in the north of Western Australia. The process of bark painting begins with sourcing the bark. A stringy bark, which is from a type of eucalyptus tree, is carefully chosen, ensuring that it is tall and knot-free to create a good painting surface. The bark is prised from the tree after making 2 horizontal cuts and one vertical cut. The bark is placed in a fire to drive out the moisture and make it pliable. The bark is then weighted down for a long time to flatten it. Before painting, the surface can be primed by rubbing with plant juices such as those from an orchid, as demonstrated in the images by Mulkin Wirrpanda, a Yirrkala based artist. Orchid juice can also be used as a pigment binder along with other plant gums and resins, wax, honey, egg, animal fat and saliva.
These pictures show Nyapanyapa Unupingu preparing and using a yellow paint. The paint is prepared by grinding the ochre rock on a stone (or in these pictures a breeze block) with water and/or the addition of binder, seen in the photographs as the white liquid in the water bottle. Traditionally the paint is applied using special brushes made from animal or plant derived materials such as bark fibers, feathers and hair. Commercial brushes are now used where available.
Working in collaboration with the museums and galleries listed in the slide, we were able to collect samples from traditional bark paintings known to have originated in the Northern Territory.

The map of the Northern Territory marks with a red star where bark paintings that have been sampled originated. A yellow star marks the location of where samples of natural ochre have been collected.
Here is a close-up of one of the paintings that was sampled; one sample of each color present was taken. This painting dates from the 1930s and is a good example of how bark paintings are prone to degradation. The bark is very sensitive to humidity and mechanical damage. While the pigments are generally stable, they often powder and flake. A situation not helped when only a minimal amount of binder, if any, has been used in the paint preparation.
The ochres used in this project were collected from known, natural sources. Some form naturally along the coastline, while others are found in important dreamtime locations.
The natural ochre collection we have at Harvard Art Museums to use for this project are pictured on this slide. The four ochres pictured on the left were donated by Museum Victoria, Melbourne. We also have a sample of stringy bark, highlighted in the main picture by the red circle.
A selection of our ochres were collected from the same location and are grouped as such in this image. It is possible to get multiple colors from one site, and that may suggest that they should have a similar basic elemental composition.
We have a large reference set of ochres from Yirrkala, highlighted by the red circles and pictured individually on the sides of the slide. In theory we would expect all Yirrkala samples of the same color to be similar. However, looking at the images of the two yellow ochres highlighted in green it can be seen that the two ochres have a very different texture and appearance.
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As part of our study we wanted to investigate whether or not it is possible to compare samples prepared in different forms. For our study we are analyzing three forms of the natural ochres; the ochre rock itself and a paint and pellet prepared from the same ochre rock.

To prepare our paint samples the rock was ground on or between glass, depending on the hardness of the rock, with water.
The ground ochre was placed on a microscope slide to dry before being mixed with PVA and painted onto a sheet of Mylar.
When preparing the paints it was interesting to see the different textures of paint that different rocks produced, with softer ochres producing a smoother paint (highlighted in red). We mixed pigments following a traditional aboriginal method (green) and produced layered paint samples (blue) to enable us to investigate how the elemental composition of the paint would be affected compared to the individual ochres. It is also interesting to note that contaminants in an ochre can have a significant effect on the color of the paint produced. In the example here (orange), the white ochre contains very small red particles and produces a vibrant pink paint.
Pellets were made by crushing the ochre into a fine powder using a mortar and pestle before being compressed into a mould.
During this project we are using a combination of analytical techniques to identify our ochres. Using microscopy we can identify what other contributing pigments are present. FTIR and Raman spectroscopy are being used to identify the mineral compounds present in the ochres, and SEM-EDX provides us with some basic information about the elemental composition.

Finally, we are using laser ablation inductively coupled mass spectrometry (LA-ICP MS) to look at the trace elemental composition of our samples. This technique was used in previous research and is the main focus for the rest of the presentation.
Inductively coupled plasma mass spectrometry is capable of detecting metals and some non-metals in concentrations as low as one part per trillion. The first step in the analysis is the introduction of the sample into the system and for our research we are using laser ablation. The laser is focused on the surface of the sample creating a plume of ablated material which can be swept into the plasma by a carrier gas. The plasma’s extreme temperature causes the sample to split into individual atoms which are then ionized and detected by the mass spectrometer. The system used in this work is located at Cranfield University in the UK.

Images of paint chips taken from bark paintings are shown at the bottom of the slide. The ablation crater is highlighted by the red arrow. The laser creates a hole only about 250 μm wide as it scans across a samples surface. Sample size has been a reoccurring issue when using this technique. If the samples are sufficiently small they can be completely destroyed by the laser.
Another problem encountered is the issue of ablation volume. The ablation volume is a measure of the amount of sample ablated by the laser and is important for quantitative analysis. In a good sample that is thick with a uniform surface, illustrated in the schematic by the blue hatching, a uniform amount of sample is ablated as the laser scans across the surface. All of the samples that we studied, with the exception of the ochre pellets, were thin with an uneven surface. As a result, the ablation volume varies as the laser scans across the sample’s surface, illustrated in the schematic with the yellow hatching.

As an extra difficulty, due to the samples being so thin, we also encountered the laser penetrating through the samples and hitting the mount underneath leading to contamination of our results. This can be seen in the images at the bottom of the slide where a glint of silver from the SEM stub can be seen in the ablation crater.
Aside from sample size there are other issues when dealing with samples taken directly from bark paintings. We have often found that the samples contain one or even two additional layers of paint, the paint itself can be contaminated with other pigment particles and the paint may still be on the bark support.
This slide serves as a reminder of the questions we aim to answer as we discuss the results of the LA-ICP MS analysis in the following slides.
The LA-ICP MS results for the three forms (rock, paint and pellet) of ochre 8 are plotted. All three forms have the same major elements, sodium, aluminium and iron, although there is a little variation in the observed counts.
By removing the major elements from the plot, it is possible to study the trace elements present. As observed with the major elements, the same minor elements are observed between the three sample forms again with a slight variation in observed counts.

The ratios of selected elements are included in the table. A little variation is observed and it was decided that overall it would be best to use paint samples prepared from the ochres as they are the most similar to the samples of interest – paint chips from bark paintings.
As previously mentioned, four ochre colors are traditionally used in bark paintings: red, yellow, black and white. White and black ochres will be discussed in the remaining slides as they provide a good representation of what we have seen during this work.

The white ochres from our reference collection are pictured here alongside microscope images to show the contaminant particles present. We also have also been given a sample of huntite sourced from inside Arnhem Land (ochre 25).
Using ternary plots we are looking at the relationship between three elements in a sample. Depending on the elements chosen it has been possible to separate samples by region. When plotting the relationship between sodium, magnesium and silicon we can see that three samples sit apart from the rest. One is the sample of huntite, known to be high in magnesium, and a sample from the Western Australia/Northern Territory border which also displays a high magnesium value. The third sample is uniquely high in silicon and originated in the Kimberley region of Western Australia. In the plot of cobalt, nickel and zinc the Yirrkala samples group together and away from the other samples.
The Yirrkala ochres continue to group together when looking at other elemental relationships and samples from Bathurst Island (which includes Cape Fourcroy) are also seen to group together. This analysis shows that Yirrkala ochre whites are similar to one another and different to the other ochres we have in our reference collection suggesting that is possible to group ochres together based on their elemental composition and location depending on the elements you chose to plot.
We have four black ochres from Yirrkala and one from the Western Australia/Northern Territory border. The sample from the WA/NT border is a charred bark and is expected to be different to the Yirrkala mineral blacks. When plotting the ternary diagrams this is exactly what we see. The same plots also show that there is a good degree of variation in our Yirrkala samples as well.
Depending on the elements chosen it is possible to group two of the Yirrkala blacks (ochres 13 and 23) together, however, this is not always the case. These results suggest that all four Yirrkala blacks are different.
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From the ternary plots we were able to determine that Yirrkala white ochres are similar to each other and different to other ochres from nearby locations. Blacks, as well as reds and yellows although not discussed here, are more complicated.

The questions proposed at the start of the presentation have been answered. Samples prepared by different methods are comparable but it is best to use the sample form which most closely represents the samples you are interested in. In general Yirrkala ochres were not found to be the same within their color groups. Whites were the only exception observed in this study. There is a difference observed between Yirrkala ochres and those from nearby locations but the variation within locations makes interpretation difficult. Samples from Western Australia appear to be significantly different to those from the Northern Territory so it may be possible to distinguish between samples across the continent.

Overall we found LA-ICP MS to be a very difficult technique to use with this type of material. In general the samples are too small for this type of analysis and due to the inhomogeneous nature of the material it is very difficult to get consistent results for the same sample. The amount of variation that we have seen within one location such as Yirrkala, and across Arnhem Land as a whole, will make it difficult to determine local trade routes.

This work will continue by looking at the samples taken directly from bark paintings for comparison with the ochre references.
Elemental Identification of Pigments Used in Traditional Bark Paintings in the Northern Territory of Australia

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Background image adapted from Mawalan Marika, Djang’kawu story, 1959, natural pigments on bark, Art Gallery of New South Wales IA53.1959

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