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The Qero Project: Conservation and Science Collaboration Over Time

Emily Kaplan, Ellen Howe, Ellen Pearlstein, Judith Levinson
AIC OSG/RATS Session
9 May 2012

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The qero project – which feels to us like the longest running technical study ever - started as a collaboration in 1995 between conservators in four museums holding collections of ceremonial Andean drinking vessels called qeros. The conservators included Ellen Pearlstein, then at the Brooklyn Museum, Ellen Howe at the Metropolitan Museum of Art (MMA), Judith Levinson at the American Museum of Natural History (AMNH), and Emily Kaplan at the National Museum of the American Indian (NMAI). The impetus for the project was a serendipitous confluence of events: conservators at the Brooklyn Museum were preparing qeros for the 1996 exhibit “Converging Cultures”, the MMA had received a gift of 25 qeros, and Kaplan was a postgraduate fellow at NMAI which meant she had the opportunity and time to do a research project. All four conservators were in New York city when the project began and despite some location changes of conservators and collections, the collaboration continues. Here we report on the collaborative nature of this project, how it has changed over time, and focus on some significant recent results.

Left to Right: Images courtesy: Metropolitan Museum of Art 1994.35.12; Smithsonian National Museum of the American Indian 15/2412; Copyright American Museum of Natural History, 2012 ALL RIGHTS RESERVED 41.2/516
Exhibitions The long duration of this project has been of benefit. Several important exhibits and publications focusing on Inka and Colonial Andean culture featuring qeros were produced in the early years of the project: “Converging Cultures” at Brooklyn Museum, “The Colonial Andes: Tapestries and Silverwork 1530-1830” at the MMA in 2004, and more recently “The Arts in Latin America 1492-1820” organized by the Philadelphia Museum of Art in collaboration with the Antiguo Colegio de San Ildefonso, Mexico City, and the Los Angeles County Museum of Art (LACMA), and “Contested Visions in the Spanish Colonial World” at LACMA.

References:
Various qeros: Tiwanaku Tiwanaku (500-900 CE) ceramic qero, private collection; Sicán (750-1375 CE) gold qero, MMA; Tiwanaku wood qero, MMA; Sicán or Chimú (900-1470 CE) double-walled silver alloy, Denver Art Museum; Inka (1450-1532 CE), ceramic, Museo Inka, Cusco, Peru, after Flores 1998.

A brief background on qeros: Qeros are vessels that have been used in the Andean region for millennia and still used today for the ritual consumption of fermented beverages. They are made and used in pairs, reflecting the Andean concepts of duality and reciprocity but there are few pairs in museum collections as most are separated as they enter the art market. Qeros have been made from a variety of materials – gourd, ceramic, wood, gold, and silver and have been excavated from archaeological Inka and pre-Inka sites. [On the bottom right is a pair of ceramic Inka qeros.] Qero is a Quechua word – Quechua is the language of the Inkas – meaning both cup and wood, but is often applied to vessels from various materials and earlier cultures as seen here: including Chavin, Wari, Tiwanaku, and Chimú. Following the arrival of the Spanish in 1532, Andean artists continued to produce qeros for native use, mostly in wood as the use of gold and silver was restricted by the Spanish. Most Colonial qeros, which we focus on here, are unprovenienced and therefore difficult to date. They were handed down as heirlooms but, again, by now most have been dispersed on the art and antiquities market.

References:

Qeros described and illustrated in Colonial chronicles, decried in sermons, listed in legal documents

illustrations from colonial period chronicles: Qeros in Inka and Colonial society were described in the chronicles produced after the arrival of the Spanish in 1532, listed in wills and government documents and decried in iconoclastic sermons, but little is written about production methods, locations, or the artists who made them. On the left, the native Andean writer Guaman Pomo de Ayala illustrates the use of qeros in his 1615 letter to King Phillip III in which he describes Inka customs and the plight of the Andean people under Spanish rule. Here a native Andean woman pours chicha, the fermented corn beverage, into a pair of qeros while an Inka nobleman toasts the sun with a qero. On the right, Fray Diego de Ocaña also depicts an Inka noblewoman holding a decorated qero.

References:


**Contemporary use** Qeros are still used today. These images depict people using qeros in Sonqo, in the highlands of Peru where anthropologist and collaborator Catherine Allen has worked with community members over several decades. The tradition persists, with some changes in form, use, and meaning.

**References:**


Goals of the study

For years other scholars have studied the indigenous and European imagery depicted on qeros in an attempt to understand the convergence of Inka and Spanish cultures during the Colonial period. The unique brilliantly colored polychrome technique used to decorate qeros has been of some interest to these scholars, but of more interest to us as conservators. We suspected that much could be learned about the people who produced and used these vessels from a thorough examination and technical study. We hoped to find trends and groupings in our results which might illuminate questions about production and chronology. Although several attempts were made by others to characterize the materials and techniques, ours is the first comprehensive scientific investigation.

Image courtesy Smithsonian National Museum of the American Indian 15/2413
Collaborators: Scientists  A Mellon Foundation Curatorial-Conservation grant awarded through the Brooklyn Museum supported analysis of pigments and binding media by Richard Newman and collaboration with art historian Tom Cummins and anthropologist Catherine Allen. Further instrumental analysis was carried out at the MMA and AMNH by conservators and scientists to establish initial material identifications and refine pigment analysis. In these early stages of the project we identified a range of organic and inorganic pigments as common to polychrome wood qeros manufactured over a period of approximately three hundred years. Much of this was reported at an OSG session in 1999 and Newman and Derrick published their findings in 2001 (see citations below). As the project progressed, so did the number of collaborators as well as the scientific methods applied for characterization.

References:


Palette

The colorants include orpiment (As$_2$S$_3$) for yellows and browns, cinnabar or vermillion (HgS) and occasionally cochineal for reds and pinks, indigo for blues and combined with orpiment for some greens, copper-based materials for other greens, and carbon black. All of these materials have a potential source in the Andes, with known uses in the pre-Hispanic period as either textile dyestuffs or as mineral pigments on wood or other substrates. Open architecture instruments at the MMA have allowed us to analyze some pigments without sampling. However the majority of the colorant analysis was performed by the removal of samples for polarized light microscopy (PLM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD) and identification of organic colorants and medium was performed on samples with Fourier-transform infrared spectroscopy (FTIR) and high pressure liquid chromatography (HPLC). One of the benefits of the longevity of this project is that we are able to take fewer samples due to the relatively recent access to portable x-ray fluorescence spectroscopy instrumentation (pXRF). Since we established a palette with this early work on samples removed from qeros we feel comfortable using pXRF for non-destructive elemental analysis to identify and confirm pigments.

Image courtesy Smithsonian National Museum of the American Indian: NMAI 15/2412 with major elements identified with pXRF.
Curators and other collaborators

• Thomas Cummins, Art History Professor, Harvard University
• Diana Fane, Curator Emerita, Brooklyn Museum
• Julie Jones, Curator, Metropolitan Museum of Art
• Craig Morris, Curator, American Museum of Natural History
• Ramiro Matos, Curator, National Museum of the American Indian
• Nancy Rosoff, Curator, Brooklyn Museum of Art
• Catherine Allen, Anthropology Professor, George Washington University
• Jorge Flores Ochoa, Anthropology Professor, Universidad Nacional del Cuzco
• Charlotte Taylor, Botanist, Missouri Botanical Garden
• José María Obondo, Master Barnizadore, Pasto, Colombia
• Aparicio Quispe Amaru, Artist, Cuzco, Peru

Other collaborators During the course of this project we benefitted from a renewed scholarly interest in qeros, particularly the work of the art historian Tom Cummins, now at Harvard University, a valued collaborator who we met through then Brooklyn curator Diana Fane. Cummins studied qeros in museums and private collections world wide for his dissertation “Abstraction to narration: Kero imagery of Peru and the Colonial Alteration of Native Identity”, and in 2002 produced the authoritative book “Toasts with the Inka: Andean Abstraction and Colonial Images on Quero Vessels”. We include these titles here because they help convey the historical and cultural importance of these objects. Cummins further states (2002:3) that “the quero is one of the few pre-Columbian artistic expressions from either Mexico or Peru that transcends the trauma of the conquest and its subsequent cultural suppression.” Funding from the MMA and NMAI has enabled Howe and Kaplan to travel to the Andes to investigate modern craft production using materials and techniques found on Colonial qeros, and to study collections in Andean museums and to work with Andean artists and scholars.

Image courtesy Smithsonian National Museum of the American Indian 10/5635

References:


Ollantaytambo qeros. At the time of the conquest, it appears that artists were already using the complex polychrome inlay technique for decoration that we see on our group of Colonial qeros. The evidence for this is the only known excavated wooden qeros with polychromy. This pair of qeros, now in the collection of the Museo Inka in Cusco, was excavated from a tomb at the site of Ollantaytambo, near Cuzco, dated to 1537-39, just after initial contact between the Spanish and Inka (Llanos 1936). As you can see one of the pair is in much better condition than the other, but losses help reveal technique and the museum gave us permission to sample from deteriorated areas. This appears to be a transitional style: these qeros combine the incised geometric designs typical of wooden Inka qeros with repeated small figurative areas of inlaid color typical of Colonial qeros. Here six felines in profile are depicted on each qero. These were found with several other pairs decorated in Inka style - with no polychromy. The absence of known antecedents emphasizes the importance of the early date of these Ollantaytambo qeros; the technical skill demonstrated by the inlaid polychrome decoration implies an earlier existing tradition.

Images courtesy Museo Inka, Cuzco, Peru, MoMa 229, 230.

Reference:
Plant resin binder. Some earlier qero literature noted that the binding medium for the enamel-like inlaid polychromy might be derived from the resin of the plant *Elaeagia pastoensis*, sometimes known by the common name of mopa mopa and still used today in the Pasto region in southern Colombia for folk art called *barniz de pasto*. Sixteenth century chroniclers describe trade goods coming from the city of Pasto (the northernmost part of the Inka empire), through Quito, and into Inka centers in Peru. The implication is that this material was imported south from Pasto, perhaps at the end of the Inka period, and used for qero production. Richard Newman confirmed this identification using FTIR to compare botanical reference specimens with samples taken from qeros. We have no evidence of this species of *Elaeagia* anywhere else in the Andean region during the Inka and Colonial period, but today it is widespread. In an ongoing related project, Richard Newman has been analyzing resin obtained from plants from several areas and species for comparison and this may inform our understanding of production further.

Barniz de Pasto [www.barnizdepasto.com](http://www.barnizdepasto.com)

References:


Velasco, Juan de (1841-1844) Historia del reino de Quito en la América Meridional, escrita por el Presbítero de Juan de Velasco año de 1789. Quito: Imprenta del Gobierno.
Replication: cleaning

We made facsimiles using freshly obtained mopa mopa following some of the production procedures demonstrated to Ellen Howe during a study trip to Pasto. Now, of course, there are youtube videos of barnizadores in Pasto working with this material. This is a complex process involving repeated cleaning in hot water, picking out woody plant parts, and kneading. The resin can be stretched into thin sheets, which would then be laid into recesses carved into the wood. Experts can clean this resin so that it is nearly translucent.

Videos: “barniz de pasto”
http://www.youtube.com/watch?v=h-Hfx8C_PF
http://www.youtube.com/watch?v=s6ZjOB65krE

Photo credit: Odile Madden.
**Replication** Shown here: mixing pigment and oil with the resin and pulling the resin into long strings. Analytical results from qero samples indicated the presence of a semi-drying oil, which made sense when we tried kneading pigments into the cleaned resin. Some pigments could not be integrated into the medium without the addition of oil. These experiments informed our understanding of the surface of the qeros and of the analytical results identifying oil mixed in with the mopa mopa.

Photo credit: Odile Madden.
Inlay technique Replication work also helped us understand how the fine painterly details on the qeros were created: the resin can be pulled into long strings and then laid down with heat and pressure. Losses and imaging techniques help reveal the technology of the surface decoration: shallow recesses were carved into the wood and the pigmented resin was applied into these recesses, often in layers.

Images courtesy Smithsonian National Museum of the American Indian 16/3605.
Inlay technique: more examples of the fine details created with long strings of resin to create fluid lines.

Images courtesy of Smithsonian National Museum of the American Indian 16/3605
Chronology based on style and iconography. One of our principal goals has been to see if our data can be correlated with stylistic chronologies for Colonial period qeros proposed by others. Inka period wooden qeros were decorated with regular, repeated geometric designs created with incised lines. There are no known examples of Inka wooden qeros decorated with color of any sort. The polychrome decoration seems to have begun at the period of contact, typified by the Ollantaytambo qeros, and becomes a hallmark of the later Colonial period qeros. Several scholars, notably John Rowe (1961) and Tom Cummins (1998, 2002), proposed chronologies for qero production based on style and iconography. Rowe suggested a chronology based on the way human figures are rendered, suggesting a gradual change from simple to complex, with styles occurring simultaneously at the intersection. Cummins emphasized that stylistic developments were likely simultaneous and that synchronic production meant that the stiff isolated figures of the simpler style came into existence almost simultaneously with the complex, pictorial scenes of the later complex style. Nonetheless, after reviewing qeros in all four of our collections, Cummins assigned vessels to four categories: Inka period, early Colonial (1600-1650), middle Colonial (1650-1750), and late Colonial (late 18th century).

Images courtesy of Smithsonian National Museum of the American Indian 13/6899, 10/5635; Museo Inka, Cuzco, Peru MoMa 229; Metropolitan Museum of Art 1994.35.13.

References:
Chronology based on materials: white pigments correlate with stylistic chronologies. We have identified three types of white pigment, none of which have a known history in the pre-Columbian Andes. Investigation of these white pigments is the focus of our recent and continuing work. The first type is an unusual white pigment consisting of cristobalite, anatase and alpha quartz; this occurs on approximately 8% of the qeros in our study. The other two, found on the majority of surviving qeros, are varieties of white lead, or basic lead carbonate, which is also commonly found in Colonial Andean paintings.

Images courtesy of Metropolitan Museum of Art 1994.35.12, 1994.35.13; American Museum of Natural History 41.2/516.
The cristobalite-anatase pigment is an unusual finding and has, to our knowledge, not been previously reported. We have identified this on twelve qeros in our sample group, distinguishable from the rest of the corpus in iconography, design, and palette: these are Inka and early Colonial, and as such appear to represent the earliest white pigment used for qero decoration, pre-dating Spanish influence. This finding was surprising at first, given the association of TiO$_2$ with modern production and forgery, and some colleagues presumed these samples to derive from areas of restoration. Our SEM and XRD analyses found TiO$_2$ in anatase form with higher than trace content in two cases and with 30% Ti in another, prompting further investigation. This is where the conservator’s eye was critical in distinguishing original from restoration. Our observation was further supported by the presence of the diagnostic binder Elaeagia resin, and no other signs of restoration. When we started focusing on the Ti pigment we contacted numerous geologists and archaeologists working in the Andes. None knew of a possible source for this kind of pigment. However, a Google search turned up an occurrence of ore known as the “Giacomo Deposit” near Tacna in southern Peru which is currently being commercially mined for TiO$_2$ and SiO$_2$. Tacna is at the southern end of the Inka empire. We compared samples of this ore to samples removed from qeros, and results are similar.

Giacomo deposit http://8itc.com/giacomo_deposit_location.html

Lead white: LA-MC-ICP-MS isotopic analysis. We are currently collaborating with Javier Iñañez, now at University of Barcelona, who was performing lead isotope analysis at the University of Maryland for sourcing lead glazed ceramics during a post-doc at the Museum Conservation Institute (MCI) in 2010. He agreed to analyze samples taken from middle and late Colonial period qeros where lead had been previously identified as the primary element for white pigments. His results indicate two different sources for the lead white pigments used for qeros. Those vessels considered to be stylistically in the early to middle periods include lead white from European sources, while for a later group of qeros the pigment source is Andean. Though lead white has not been reported as a pigment in the pre-Colonial context, lead ore is common element throughout the Andes and metallic lead artifacts have been excavated from Late Intermediate 1000 CE – 1476 and Late Horizon AD 1476 – 1534 sites. There is evidence of the significance of lead for extractive metallurgy of silver in the prehispanic Andes in the Lake Titicaca Basin in the first century AD as lead ore was apparently used in complex regimes to smelt and refine silver-rich ores. Despite this familiarity with lead and its ores, however, prehispanic Andean artists do not appear to have used it to produce the lead-based pigments in any form. With the possible exception of a small percentage of white post-fire pigments on ceramics from Paracas on the south coast of Peru, it appears that most white pigments pre-dating the Spanish are calcium or clay-based. Lead white became a significant painting material in the Andes after the arrival of the Spanish in the mid 16th century. Of course, lead white as an artificially produced pigment has a long history of use in European painting traditions and even earlier applications in antiquity; it served as the most frequently used white colorant in the European style painting palette until the advent of synthesized titanium dioxide in the 1920’s. Recent studies (Siracusano 2011) of pigments used in Colonial painting and the relationship between indigenous and Colonial pigments indicate that lead white was a primary pigment in Colonial paintings as early as 1545. However, geological sources for the pigment – as well as the chemical nature of the lead – have not been identified.

Images courtesy of Metropolitan Museum of Art 1994.35.13; Smithsonian National Museum of the American
Indian 10/5635

References:


Continuing work. Organic reds – identification; Hg isotopic analysis – cinnabar sourcing; atomic mass spectrometry (AMS) radiocarbon dating; cristobalite-anatase ore source; colonial painting – pigment correlations; distribution of Elaeagia spp.; when, where, and how did polychromy begin: further archaeological data; imaging: reflectance transformation imaging (RTI); rollouts; development of online resource to share data.

The long duration of this project has been of benefit. Changes in technology and in conservation science have allowed us to take advantage of new documentation methods and analytical techniques, bringing us closer to addressing our original goals. Ways to organize, share, and store data have changed. We started with a paper-based survey to record our extensive observations, and later entered that data in a shared Access database created by Eugenie Milroy. When we began the project the internet was only beginning to be accessible or useful, now of course it is indispensable. Email, Skype, Flickr, and Dropbox are much better than faxing documents and duping and mailing slides. We are currently investigating ways to aggregate and share our data online using projects currently in production as models, for example the Mellon funded multi-institutional collaborative conservation/science/curatorial online resources. And our fascination with these remarkable objects only increases over time - the more we learn about them, the more there is to learn.

Images courtesy of Smithsonian National Museum of the American Indian 16/6131
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In Their True Colors: Developing New Methods for Recoloring Faded Taxidermy

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In 2011-12, the American Museum of Natural History (AMNH) undertook an ambitious program of renovation to the 45 habitat dioramas in the Hall of North American Mammals. Some of the earliest collections at the AMNH were mounted taxidermy specimens and the evolution of the habitat diorama was a natural development in the tradition of using art to teach science. Within the museum, dioramas were created to promote the awareness of wildlife and so-called ‘primitive cultures’ as finite, and to engender concern for the populations and habitats that were threatened by unregulated development and hunting.
Fusing art and science, these habitat dioramas depict specific geographic locations and house anatomically correct mounted specimens in their natural habitat.
On permanent display for over 70 years, with at least one known prior renovation campaign, many of the zoological specimens were faded to such an extent that they no longer reflected their accurate scientific appearance.
The original fabrication of the dioramas was a collaborative effort, combining the talents of artists and scientists to represent the complex inter-relationships between animals and their environment. Alongside the Museum’s curators, they conducted extensive research, visiting each site to assemble reference sketches, photographs, and specimens for exhibit. Once back at the museum, every detail of the scene was painstakingly recreated from the narrative moment implied in the postures of the taxidermy and the illusion created by the background painting, to the site-specific foreground materials. Each diorama is illuminated using a specific combination and placement of lights to create the illusion of a particular season and time of day in the depicted location.
The diorama at the American Museum, the ultimate mixed-media artifact, is composed of three elements: a background painting, foreground materials, and mounted taxidermy specimens.

The partial dome-shaped enclosure is constructed from vertical angle iron beams and heavy wire mesh that supports layers of plaster. The canvas for the background painting is adhered to the plaster surface with a lead white/oil mixture. The front face of the diorama consists of a large glass panel, which is angled slightly to prevent reflection. A separated light box with fixtures for interior illumination is located above the enclosure. Access to the dioramas is difficult and can only be achieved by removing the large front panes of glass or, in some cases, is attained by narrow ladders on the interior extending from the light box to the diorama floor.
The background paintings were examples of the highest form of wildlife artistry in their day and many consider those in the North American Mammal Hall to be the most accomplished of their kind. “The curved oil painting is essential to the overall illusion of space, distance and environment. It draws on Renaissance techniques such as under-painting, plotting perspective and transferring images with grids.” (S. Quinn, Windows on Nature: The Great Habitat Dioramas of the American Museum of Natural History)
Painters of note included James Perry Wilson, Frances Lee Jaques, and Charles S. Chapman. Wilson described his diorama work as “art to conceal art”, in other words, art intended to imitate nature so closely that the artist’s role is not visible.
The floor of the diorama was built up to the appropriate height with an underlying structure of wooden beams, over which wire screening was formed to simulate the desired topography.

Physical features of the landscape were constructed over the wire screening with a mixture composed of plaster, dextrin, whiting, and asbestos fibers. Plant materials were generally fabricated from painted cotton or paper, sometimes flocked or modeled with wax.
Broad leaves were made from vacu-formed acetate sheet. Snow was created using combinations of plaster, sand, cotton batting, and plastics. A limited number of real botanical specimens, such as grasses, evergreen branches, mosses, and leaves for ground litter, were collected, sometimes chemically treated with preservatives, and then installed.
The mammal specimens were mounted in the museum following procedures developed by Carl Akeley in earlier decades, which was reported on in detail at the 2005 OSG session (Uricheck, S.; Levinson, J. ‘A Survey of Carl Akeley’s Dioramas in the American Museum of Natural History’).
The general method involves sculpting an exact model of the animal in the pose to be presented out of water-based clay. A plaster mold is made of the sculpture and a hollow positive is formed within it from paper mache. An internal wood and metal support is placed within the hollow form, which is then assembled to create the mannequin. The skin is draped and stitched together, creating fabulously life-like figures. The larger taxidermy specimens are mounted into the diorama floors, and thus cannot be removed for treatment. Many of the smaller specimens, however, are able to be removed.
The original lighting scheme from the early 1940’s is known to have included large theatrical lights. Lighting revisions shortly thereafter, in the 1950s, resulted in a combination of fluorescent and incandescent fixtures. This scenario caused a number of unsurprising problems. Temperature inside the dioramas was elevated, often reaching the high 80’s °F. The relative humidity was low, with daily and seasonal fluctuations. Light levels were far higher than is recommended for museum collections and, until recently, were not screened for ultraviolet emissions. These conditions resulted in deterioration, desiccation, and fading of most exhibit materials.
Informed by a 2003 conservation survey of the dioramas in the Akeley Hall of African Mammals undertaken at the museum, testing had demonstrated that it was possible to reduce heat and light levels inside the dioramas while maintaining the desired visual appearance through the use of energy-efficient lamps.
In 2010, as a result of the American Museum’s participation in a citywide effort to decrease energy consumption, funding was provided to replace the diorama lights with more energy-efficient fixtures. The goal of the re-lamping project was to achieve a 50% reduction in electric power consumption. Retrofit fixtures were researched and chosen by an outside lighting design firm to reproduce the visual appearance of the original design, using a combination of energy efficient fluorescents for indirect lighting and LED flood lights and metal halide spot fixtures as accent lights. All new lighting fixtures are filtered for UV emissions.
The re-lamping project provided the impetus for a broader renovation of the North American Mammal dioramas. The renovation team began to explore possible methods of restoring naturalistic color to specimens that had become faded and desiccated in the previous damaging lighting environment in hopes of extending their exhibit life.
Just as the dioramas’ fabrication was necessarily achieved through collaboration, this conservation effort also involved a diverse team of participants, including curators, objects and paintings conservators, exhibition department staff, outside scientists, and a master taxidermist.
One of the most immediate difficulties was the short project timeline, which imposed limitations on the type and extent of materials investigation. The plan for renovation gained last minute approval after the relighting project was well underway, leaving one year for the work to take place from start to finish. A maximum of only 2 months within that year could be allotted for research and testing of possible colorants for the faded mammals.
Several important factors restricted the materials that could be considered for re-coloring. Even with the new energy efficient lights, the naturalistic lighting design in each diorama precluded reduction of light levels to those generally considered acceptable for museum collections.
The highest recorded light levels are 65 footcandles on the top of the Mountain goat and 50 fc at the head of the cow in Bison, whereas the recommended level for fur at the museum is 5 foot candles. Therefore, even with somewhat reduced light exposure, it was clear from the outset that any colorant considered for use would require high light-fastness ratings.
Because the larger taxidermy mounts had to be treated in situ, custom built platforms to avoid crushing fragile ground cover were required to provide safe access. Washing or rinsing excess coloring materials from the specimens would not be possible, consequently, ease of preparation, application, and clean up were all-important considerations in the choice of colorants.
The use of certain solvents was restricted because of the limited possibility of effective fume extraction within the dioramas. Furthermore, because half of the exhibition hall was required to remain open to the public over the duration of the project, control of solvent fumes was critical.
And finally, because the dioramas would probably not be renovated again for at least 25 years due to associated costs, favorable aging characteristics, reversibility and ease of future retreatment were critical factors in material choice. The substances selected should not cause the hairs to clump or matt, and if not fully reversible, the coloring agents chosen should not prevent future recoloring campaigns on these irreplaceable taxidermy mounts.

Investigation of the conservation literature on contemporary methods, revealed few references for recoloring faded taxidermy mounts. Through personal correspondence, the Canadian Museum of Nature reported success recoloring some of their taxidermy mounts using Clairol commercial hair dye, but their situation allowed for the removal of the specimens from the diorama for treatment.
A recent study investigated the use of fiber-reactive dyes for feather recoloring, but concerns about aqueous treatments having an adverse effect on the tanned hides, as well as the long-term effects of the acidic or basic dye residues, ruled out this approach.
Aqueous and solvent-based acrylic paints are commonly used among contemporary taxidermists. In this application, reversing acrylic paints for retreatment would be very problematic. Also, due to their low glass transition temperature, there is potential for the paints to soften in the heat of the diorama, entrapping dust and hindering future surface cleaning.
The project taxidermist’s familiarity with commercially available acrylic paints and his primary mode of application by airbrush played a tremendous factor in determining what alternative colorants would be considered.
His method for restoring faded specimens consisted of layered airbrush applications with constant grooming throughout the process in order to control the hue and intensity of the color. Any alternative colorant would need to be applied in a similar manner, in order to fully utilize the taxidermist’s skill in this method and to meet the tight project deadline.
Two colorants, Orasol® dyes and XSL pigments, showed initial promise as suitable alternatives to the acrylic paint. Orasol® dyes are commercially available 1:2 metal complex dyes that are soluble in organic solvents and require no rinsing after application. They are available in a palette of 17 colors - sufficient to mix the range of tones characteristic of the North American Mammals. Orasol® dyes are generally approved by the conservation community and are commonly used in furniture and wood stains, as well as for tinting epoxy and other resins used for fills.
Like other 1:2 metal complexed dyes, the manufacturer ranks the lightfastness of the Orasol dyes as moderate to high. However, the product literature indicates that these ratings are based on their use in printing ink, and the tests conducted with two different binders produced significantly different results. In order to assess the lightfastness of the Orasol® dyes in a manner more applicable to taxidermy restoration, it was necessary to design a customized course of analyses. More details about these dyes as well as their interactions with wool substrates can be found in the poster that accompanies this presentation in the poster session: “Developing New Methods for Recoloring Faded Taxidermy Specimens at the American Museum of Natural History”.
Water-dispersible micronized “XSL” pigments (from Kremer Pigments) was another material explored for recoloring. These pigments have an extremely fine particle size and are treated with dispersing agents, resulting in a suspension that will pass easily through an airbrush, giving it the potential to create naturalistic, lightfast color using a non-toxic system. The XSL pigments are available in a limited palette of 8 colors that lack brown tones. They are not soluble in organic solvents or solvent mixtures containing less than 15% water, so there is some potential for adverse effects on skin or other water-sensitive materials used in taxidermy preparation.
Having initially limited our colorant choices by working properties, a course of analysis was developed that focused on comparing the acrylic paints favored by the project taxidermist to the Orasol® dyes and XSL pigments. Conservators worked closely with the taxidermist and partnered with outside conservation scientists to assess the materials against these necessary criteria: minimal physical alteration to the hairs, retreatability/reversibility, and high lightfastness.
If an acceptable recoloring method could be found, the greatest and most convincing challenge would be its application in the iconic Bison diorama. It is one of the most visible and brightly lit scenes with a multitude of mounted specimens. Additionally examples of non-faded specimens are visible for direct comparison painted in the background. Swatches of bison hair colored with the acrylics, dyes, and pigments were prepared for testing. Due to time constraints, it was impossible to test all of the colorants on samples of all of the mammal species displayed in the hall. It was hoped that a successful outcome in the bison diorama would be applicable for use on other types of fur.
The physical appearance of the colored bison hairs was examined using optical light and scanning electron microscopy. At the macro level, all of the colored samples appeared somewhat similar.

The acrylic paints produced a matted and stiff feel, whereas the Orasol® dyes and XSL pigments produced a more natural look and feel. But touching caused some transfer of colorant, more so with the XSL pigments, which also had a somewhat duller appearance.
However, microscopic examination revealed, as expected, that the binder in the acrylic paints covered and obscured the hair cuticle unevenly creating a non-cohesive coating around the hair, with some visible peeling and lifting. The Orasol® dyes and XSL pigments were only just visible on the hair fibers and did not appear to cover or coat the hair shaft. We were not able to determine the level of dye penetration into the hair.
The taxidermist also found that the Orasol® dyes could be reduced or removed entirely when wiped or rinsed with ethanol. Although initially taken aback by this revelation, the team quickly recognized the potential for reversibility, as well as an expansion of the dye’s working properties, such as localized reduction or removal of color to achieve special effects.
With the Orasol® dyes having gained the approval of the taxidermist in terms of application, and the deadline for determining a conservation-approved colorant swiftly approaching, the lightfastness of the dyes was tested using microfadeometry and accelerated light-aging. Microfade testing was chosen because it could return results quickly. To compliment this work and broaden the range of dye samples tested, accelerated light aging was conducted following the ASTM D4303 Standard Test Methods for Lightfastness of Colorants Used in Artists’ Coloring Materials.
Test swatches for the Orasol® dye family were produced by airbrushing a 1% solution of dye dissolved in ethanol onto unbleached 100% wool. As a flat substrate comprised of keratin fibers, the wool textile was chosen as the most reasonable substrate for measurement of color changes using a colorimeter. One wool swatch was produced for each of the most relevant dye colors in each of three application weights: light, medium, and heavy.

A select number of colors was also applied to swatches of bleached bison fur. A customized palette of 8 dye mixtures was later developed for testing that replicate the natural color range of the American bison, referred to as ‘bison brown’ mixes.

Twenty-eight single color dye samples were sent to Dr. Paul Whitmore, Director and Research Professor at the Art Conservation Research Center at Carnegie Mellon University, who graciously agreed to conduct microfade testing on the wool and bison fur swatches.
Microfade testing indicated 9 of the 14 colors in the sample set had lightfastness values equivalent to ISO Blue Wool 4 or higher. Because the xenon light in the instrument was filtered to remove UV, it was not feasible to get higher than Blue Wool 4 equivalents without an extremely long exposure period. The lack of UV mimicked the new diorama lighting system, but left the longer term stability of the dyes in question. Further investigation into the parameters that define the BlueWool Scale and the estimated exposure time to “just perceptible fading” quickly illustrated that further testing was required.
The Blue Wool Scale is used to assess the relative lightfastness of materials, and the results are translated as “years to perceptible fading” based on a 50 lux per hour exposure, with a yearly exposure of 3000 hours - that’s roughly 8 hours a day, 365 days a year, for a total yearly exposure of 150,000 lux hours.

The higher the blue wool number, the more lightfast the material. As you can see, filtering ultraviolet radiation makes a large difference in projected lifespan. Most literature recommends using materials with a BlueWool rating of 4 or higher.
These parameters are easily applied to normal museum or gallery environments, but the most brightly-lit areas inside the bison diorama experience light levels of over 500 lux, 24 hours a day, 365 days a year, for a total yearly exposure of 4,380,000 lux hours.

At these light levels, it was essential for us to be able to determine whether the materials had a lightfastness rating equivalent to Blue Wool 6 or higher.
A second group of samples was sent to Dr. Cory Rogge at Buffalo State College to be exposed in a QSun Xenon light aging chamber according to ASTM D4303 testing procedures. This larger sample set included single color dye swatches and bison brown mixes applied to both wool and fur.

This test helped us characterize the dyes in more defined stability classes, as well as defining total lux-hours of exposure to "just perceptible fading" in terms of CIE deltaE* - details on the testing procedure can also be found on the associated poster.
In the QSun chamber, samples were exposed to a spectrum that included a UV component, causing them to fade more quickly than the initial set tested at Carnegie Mellon. This allowed determination of detailed lightfastness ratings above the threshold imposed by the microfader. Using a procedure that included an ultraviolet component also allowed a “worst-case scenario assessment” of the dyes. A material that tested well in the UV-rich chamber was projected to have a long lifespan inside the bright but UV-free bison diorama.
The lightfastness categories are defined by deltaE calculations with Lightfastness 1 having the least color change. Initial results from the Qsun testing indicated that of the 17 dyes on wool, the majority tested as lightfastness 1 or 3.
Of the Bison Brown mixtures applied to wool and fur, most were lightfastness category 2, and half of the dye mixtures showed the same lightfastness even on different substrates.
With multiple datasets from two instruments using different lightfastness scales – Blue Wool ratings and ASTM Lightfastness Categories – interpretation of the data was challenging.
The manufacturer lightfastness ratings are defined by the Blue Wool Scale and could be plotted against the microfade test results, though again it should be emphasized that substrate-dye interactions are known to play a role in lightfastness and therefore the manufacturer’s numbers cannot be directly extrapolated to yield the stability of binder-less dyes on keratin.
While the ASTM test characterizes materials according to its five categories of lightfastness, the standard does not attempt to correlate these categories to a projected material lifespan.
There are a number of references in conservation literature that characterize susceptible materials into variously named Classes of Photochemical Stability, which are often further refined with projections of “Intended Useful Lifetimes” and theoretical ties to Blue Wool ratings.
However, there is a growing body of research that supports the belief that while use of Blue Wool cards allows for a rough estimate of cumulative light exposure, they do not necessarily predict how a material will actually fade. While relied upon by many industries, the Blue Wool test is less precise at determining light levels, and fading is assessed more subjectively compared to more quantitative instrument-based tests. The fading rates of the dyes are temperature and relative humidity dependent, and furthermore, changes in the dye formulas used to create the cards cause batch-to-batch inconsistencies. The ASTM committee on lightfastness has tried to find connections between the delta E values measured in the ASTM test with the fading of the Blue Wool cards, but thus far has found no correlations of any significance between these two methods.
As all of our dioramas are now screened for UV emissions, and the majority of specimens are located in dioramas with low to medium light levels, this represents a worst-case scenario for assessing lightfastness.
Real time monitoring of cumulative light exposure is continuing with the strategic placement of dyed swatches and a blue wool card inside the Bison diorama, as well as covering sections of dyed bison to be able to directly compare to exposed hair.
The reversibility and retreatability of the dyes also played a major factor in its approval for use in those dioramas with higher light levels, with the acknowledged possibility that fading of the material may occur over time.
The AMNH conservation and exhibition team was able to successfully recolor the bison, and subsequently many more specimens in the North American Mammal Hall. The treatment protocol that was developed provided an acceptable visual solution within the given limitations of the project while meeting most of the key conservation criteria. Associated dye research has generated numerous new questions and will be a valuable starting point for work in support of future taxidermy restoration projects. It has also informed a better understanding of changes that should be made to the diorama environment to support the longevity of these treasured exhibits.
It is evident that the light levels in our most brightly lit dioramas must be lowered to retard fading of the dyes and specimens; and the project is currently continuing with screening down of the fixtures to achieve an acceptable visual appearance at the lowest levels possible.

The Museum is also investigating possibilities for turning off the lights for a portion of each night, while minimizing associated swings in relative humidity. While the hall is air-conditioned, full-climate control is not possible because the hall adjoins a museum entrance and requests for the installation of doors have not been approved. Installation of microclimate generators presents a host of other problems, making them impractical within our context.
Air exchange testing has been performed and installation of a positive pressure environment is being explored for increased dust mitigation in the bison and other dioramas.
Since the conclusion of the project and the reopening of the Hall, study of Orasol® dyes and re-coloring procedures has continued. The focus of recent work has been the lack of dye penetration into the keratin fibers. For this project, non-penetration worked in our favor, providing a ‘do no harm’ solution. It was advantageous, as it imparted reversibility and the ability to manipulate the dye colors on the specimen to achieve naturalistic effects. Nevertheless, it is important to better understand the factors that contribute to this state. Development of a means of improving penetration would extend the existing tool-kit of recoloring techniques in the service of future projects. Details on this research can also be found on the accompanying poster.
This investigation of the Orasol® dyes, as well as XSL pigments, has contributed to a better understanding of their aging properties and allowed for development of an acceptable solution for a specific challenge in a very short time frame.
This investigation of the Orasol® dyes, as well as XSL pigments, has contributed to a better understanding of their aging properties and allowed for development of an acceptable solution for a specific challenge in a very short time frame.

It has led to innovative re-coloring methods that prioritize long-term stability and retreatability.
It should be stressed, however, that the treatment applied to this group of mounted specimens at the American Museum would not be appropriate for all situations in which recoloring of taxidermy is desired. Its use must be confined to specimens housed in closed exhibit cases.
The dye is somewhat transferrable and vacuuming or cleaning could lead to its removal. Moreover, contact with the chemicals by unsuspecting people, such as in a historic house or private residence, is not advised.
In conclusion, this investigation has made stunningly clear the difficulties encountered when the published product data does not correlate with the information needed to solve the problem at hand. Testing data produced by industry cannot necessarily be adapted wholesale without thorough investigation of testing methods and conditions.
Collaboration among a variety of disciplines served to enrich this process, as well as the outcome of the project. In particular, the support of conservation scientists was critical to developing appropriate testing methods and to interpretation of data. This project has provided one means to solve the problem of faded taxidermy, and has suggested a number of avenues for further investigation.
A Comparative Study of Protective Coatings for Marble Sculpture

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AIC Annual Meeting, OSG/RATS Joint Session, May 9, 2012

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Presented at the RATS/OSG joint session
40th Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
Albuquerque, NM, May 8-11 2012
This paper presents the research that I carried out as a Postgraduate Fellow at the Smithsonian American Art Museum (American Art): a study to evaluate four protective coatings for use on marble sculptures in a museum environment.
The inspiration for this experiment came from two incidents I heard about at American Art, with these two marble sculptures Sleeping Children by William Henry Rinehart and Tennyson’s Princess by William Couper. They are both well loved sculptures in the collection at American Art...
...so well loved that in each case, on separate occasions, someone felt compelled to kiss them with bright lipstick on.
Additionally, a sculpture at the National Portrait Gallery, this copy of Houdon’s Marquis de Lafayette, had a mysterious sticky red liquid dripped onto it while on view. And while these are somewhat extreme examples, marble sculptures commonly develop yellowish grimy areas just from visitors touching them.

(Over all image of the sculpture originally included can be viewed by accessing the National Portrait Gallery website’s collection search, http://npgportraits.si.edu/eMuseumNPG/code/emuseum.asp?newpage=NPG.)
The problem is, as conservators know, marble is porous and easily stained. Staining material can wick into its pores and become impossible to remove. We also know that it is difficult to clean properly. Marble is soluble in water if the pH or ion content is not well-managed. Additionally, marble sculpture is often large and overall cleaning or poulticing with harmful solvents is not desirable and not practical, especially in gallery settings. With all of this in mind, it seemed that preventing damage is the best strategy and identifying a suitable coating for marble sculpture would be useful.

While I know from anecdotal evidence that marble sculpture has been coated frequently by artists, restorers and conservators, a literature search produced only two published accounts of protective coatings for marble in an indoor context and both sources were published in the 1970s. Because so many institutions have marble sculpture in their collection, this seemed like something useful to investigate and I proposed this experiment.
For my research I chose four coatings to evaluate:

The first is a wax resin mixture of Cosmolloid 80H wax and Ketone N resin, also known as Larapol K80, in Stoddard Solvent. While this material has some known problems, like questionable reversibility and yellowing, this was the only protective coating used in an indoor setting for which I could find literature references. I used a recipe from objects conservator Ginny Naude, who worked with Ken Hempel, the author of the articles that mention the material (Please add the references for these articles).

I also chose to evaluate Renaissance microcrystalline wax, a common coating for many materials, including marble that I’m sure most of you are familiar with. Anecdotal evidence points to microcrystalline wax being widely applied to marble sculpture for aesthetic and probably protective reasons.

The next material I chose to evaluate was methyl cellulose. After the kissing incident with Tennyson’s Princess, the sculpture mentioned earlier, Hugh Shockey one of the objects conservators at Smithsonian American Art Museum, applied methyl cellulose as a protective coating, after removing the lipstick. Methyl cellulose is commonly used in conservation as an adhesive, gelling agent and poultice material. But, I am unaware of published accounts using methyl cellulose as a protective coating for stone. Following Shockey’s procedure, I used a 2% solution in water that was conditioned with marble chips, so as to minimize the harm to the marble surface from the water.

The last material I chose was Avalure AC 315, an acrylic resin that was developed in the cosmetics industry for nail polish and mascara. It is reversible in polar organic solvents like ethanol and acetone, as well as in alkaline pH water, none of which will harm marble in good condition. Avalure has not been used widely in conservation, but has recently been applied as a masonry coating on the exterior of the National Building.
Museum by Richard Wolbers, and Masters and PhD students at the Winterthur/University of Delaware Program in Art Conservation, most recently Amanda Norbutus, have studied the material as a coating for outdoor murals and stone.
Here are some of my sample tiles. Each piece has four sample areas, and so constitutes four samples. Each tile has a polished and an unpolished side and every coating has been applied to unpolished and polished marble surfaces.

In this image, the top row shows polished tiles and the bottom row shows the unpolished surfaces. The control tiles, with no coating, as well as tiles coated with each test material are shown.

For each coating I made a set of tiles with one application of the coating and another set with two coats of the material. The one exception to this procedure was Avalure, which did not produce good results when a second coating was applied, so I used a 5% solution and one with a 7% solution instead. All of the coatings were applied with brushes.
To evaluate the success of the coatings, I wanted to take into account several factors: does it have the appropriate aesthetic properties, or are the color or gloss changed just by application of the coating? I also wanted to evaluate the effectiveness of each coating as a protective barrier: does the coating actually prevent staining? Can the coating be safely applied and removed without harming the substrate? How easily can each material be reversed? How does aging the coatings affect all of the above properties?
I used the colorimetry functions of this spectrophotometer and a gloss meter. Both instruments helped me evaluate the properties I just discussed by quantifying any visual change that occurred, as a change in gloss or color after the coatings have been reversed could indicate damage.
The SpectroEye spectrophotometer I used has an internal light source that the sample is exposed to and then the instrument detects the color reflected, giving measurements using the L* a* b* color system. When I take a reading with the colorimeter it reads one number each for the L*, a*, and b* channels. The L* value is a measurement of blackness to whiteness or another way to think of it is- how light or dark a color is. A value of 0 corresponds to black and 100 corresponds to white. The a* value indicates how red or green your sample is. A negative value indicates greenness and a positive value indicates redness. The b* channel measures how blue or yellow your sample is, with a negative value indicating blueness and a positive value indicating yellowness.

To calculate the overall color change I used the CIE 1976 equation seen here. The resulting number is known as ∆E. A just noticeable difference is reported to be 1 ∆E, however this is with a trained observer under standard conditions, so a normal viewer may have less acuity at detecting differences.

(Figure was a visual representation of the CIE L*a*b* color system from http://dba.med.sc.edu/price/irf/Adobe_tg/models/cielab.html.)
The gloss meter measures the glossiness of a surface in Gloss Units, which are used in industry standards testing. The gloss meter I used also has an internal light source. The light is shone onto the surface of the samples at 3 different angles: 20 degrees, 60 degrees and 85 degrees, and the amount light reflected at each angle is detected. Using this system, a 0 is a completely matte surface, and higher gloss units indicate glossier surfaces. The data recorded at 20 degrees was used to evaluate the polished tiles, while data recorded at 85 degrees was used for the unpolished tiles. It is also important to keep in mind that a change of about 5 GU is visible to most observers’ eyes, although with very matte surfaces, changes of 3 units may be visible.

(Image removed was a figure illustrating the measurement angles found at http://www.master.co.th/detail_editor.php?IDEditor=43.)
With both of the instruments it was essential that I take my readings on the same spot every time in order to ensure accurate detection of any change. To help with this, I made a jig out of matte board that had bumpers for both of my instruments built in so that I could place the instrument easily at the same spot each time.
Another component of the experiment was light-aging a small portion of the samples to see how aging affected the aesthetics, effectiveness and reversibility of the coatings. Because the coatings are for use indoors, I wanted the temperature and RH conditions in the chamber to stay near museum standards, about 70 degrees and about 50% RH. I also didn’t want softening of the coatings from heat or RH to alter the results.

I intended to use the weatherometer at the Smithsonian’s Museum Conservation Institute (MCI), but some technical difficulties last year prevented that. Luckily, the Image Permanence Institute (IPI) in Rochester New York had equipment that I was able to utilize. Their unit was custom built for them. They normally use it for light fading and their standard RH and temperature parameters matched the conditions I wanted.
The staining agents I chose to test were lipstick, red wine, and Sharpie marker. I chose red wine even though many museums have “no red wine” policies, because I thought it would be harder to determine whether white wine had penetrated the coating. I tried applying each stain in a manner that mimicked reality, by actually kissing the tiles (which I really do not recommend), splashing on the wine with a pipette, and drawing on the marker.
Here is the big picture view of my experimental process. First, I took gloss and color readings of all the samples before they were coated. Then I coated the samples, except of course for the control samples. Then I took color and gloss measurements again. Next a portion of the samples were sent to IPI for aging, and more color and gloss measurements were taken upon their return. Then I applied some staining agents to a subset of the unaged samples. Following that step, I reversed the coatings, and recorded color and gloss measurements again.
Now I will present my overall findings and then get into the details. All of the coatings provided some protection from soiling. However I would not recommend Renaissance Wax as a barrier, because it performed the worst against the wine and the Sharpie marker stains.

The Avalure really stood out because it was the only coating to prevent etching of polished surfaces by the wine. The only problem was that it did not look very good on the polished surfaces. I could see iridescence and it looked plasticy and reticulated in some areas. However, it looked invisible on the unpolished surfaces. The other coatings did very well aesthetically.

As for reversibility, the methyl cellulose and Avalure do not require toxic solvents to apply or reverse, which are benefits. I took some Fourier transform infrared spectroscopy (FTIR) data that Jennifer Giaccai, conservation scientist at MCI, helped me interpret that I don’t have time to discuss in detail, but it supported my observations that the methyl cellulose had the best reversibility, while traces of the other coatings remained, especially the microcrystalline wax.

With aging, the wax resin and the Avalure had some very small color changes that the other coatings didn’t have. There did not seem to be a chemical difference between the FTIR data for the aged or unaged samples.
As you just saw, the first step was to take color and gloss measurements before and after coating. Then, I reversed the coatings and recorded any changes.
When observing with my eye, I thought that microcrystalline wax and the wax resin mixture seemed to saturate the matte surfaces more than the other materials. This is a difference in appearance, but in some situations this could be a benefit. The methyl cellulose looked nice on the marble after it dried, but it seemed more easily abraded than the other coatings. The Avalure, as I mentioned before looked bad on the polished surfaces. It should be noted that my polished marble samples are extremely shiny, most above 90 gloss units, and most sculpture is not that shiny. I took some gloss readings of sculptures at Smithsonian American Art Museum and those sculptures gave readings between 12 and 40 gloss units. So this might not be a problem for the typical sculpture.
The calculations comparing the colorimetry data before and after coating are close to what I observed. (Note that \( s \) = standard deviation.) The most change, according to the data occurred in the unpolished wax resin samples. This is consistent with my observation that the wax resin saturated the samples. It is worth noting that most of the color change, occurred in the \( L^* \) channel of the data, indicating darkening, which makes sense if the color change is due to saturation.

### Color Change Data (\( \Delta E \)) – Coating Applied

**Most samples: \( \Delta E \) of less than 1**

1 = Just noticeable difference.

<table>
<thead>
<tr>
<th>Wax Resin Not Polished</th>
<th>Thick coat</th>
<th>Thin coat</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average ( \Delta E )</strong></td>
<td>4.36 ( (s=0.776) )</td>
<td>3.45 ( (s=0.983) )</td>
</tr>
<tr>
<td><strong>Average ( \Delta L )</strong></td>
<td>-4.34 ( (s=0.779) )</td>
<td>-3.43 ( (s=1.01) )</td>
</tr>
</tbody>
</table>
The Avalure also shows some color change, on average, on the unpolished samples, which I did not notice with my eye. The other samples performed pretty similarly to one another and none of the other coating types had an average ∆E that should have been noticeable.
When the coatings were removed, the microcrystalline wax coated samples had the most color change, on average, and again the change most often a decrease in the L* channel of the data, indicating darkening.

<table>
<thead>
<tr>
<th>Micro-crystalline Wax</th>
<th>Not Polished Thick coat</th>
<th>Not Polished Thin coat</th>
<th>Polished Thick coat</th>
<th>Polished Thin coat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average ΔE</td>
<td>1.00 (s= 0.969)</td>
<td>1.73 (s= 2.02)</td>
<td>3.09 (s=1.56)</td>
<td>1.49 (s=1.72)</td>
</tr>
<tr>
<td>Average ΔL</td>
<td>-0.51 (s= 1.3)</td>
<td>-0.72 (s= 1.9)</td>
<td>0.29 (s=3.35)</td>
<td>-1.41 (s=1.73)</td>
</tr>
</tbody>
</table>
The averaged data for the unpolished Avalure coated samples with thick coatings showed what should have been a just noticeable difference as well, although I did not notice it with my eye. None of the other samples exhibited significant color change on average.
This table shows the average change in gloss for the polished samples after the coatings were applied. None of the unpolished samples had a significant change in gloss. The data for the polished samples were much more variable and largely doesn’t match my observations, because I didn’t see the decrease in gloss indicated here, in most of the samples. However, you can see the standard deviations (s) are quite high. The change seen in the Avalure data, in the blue column, is not surprising, as those samples did not look good coated. It is interesting to note that the microcrystalline wax is the only coating that showed an increase in gloss.

<table>
<thead>
<tr>
<th>Units= GU</th>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
<th>Control (No coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished Thick coat</td>
<td>-11.43 (s= 8.61)</td>
<td>8.06 (s= 4.24)</td>
<td>-18.69 (s=4.46)</td>
<td>-35.12 (s=20.11)</td>
<td>-0.15 (s=0.39)</td>
</tr>
<tr>
<td>Polished Thin coat</td>
<td>-11.49 (s= 9.04)</td>
<td>6.24 (s= 4.77)</td>
<td>-14.13 (s=7.50)</td>
<td>-27.77 (s=10.36)</td>
<td></td>
</tr>
</tbody>
</table>

All unpolished samples changed less than 3 GU

Just Noticeable Difference = 3-5

Average Gloss Change - After Coating
When the coatings were removed, the general trend was no noticeable average change in the unpolished samples and an average decrease in gloss in the polished samples. The wax resin and Avalure had similar results. The decrease in gloss that is indicated for all the polished samples, even if not detectible by eye, could be due to scratching the very glossy surfaces of the tile via coating application and removal, or could signal incomplete removal of the coatings.

All unpolished samples changed less than 1 GU

Just Noticeable Difference = 3-5

Average Gloss Change- Coating Removed
The next data I will present is from the small subset of samples that was sent to the Image Permanence Institute (IPI) and the Rochester Institute of Technology for accelerated aging for 76 days. The samples were exposed at 50,000 lux, 24 hours per day. This is equal to fifty years of museum exposure, if you account for 10 hours of exposure over 365 days. Only 1 set of tiles could be sent, so the data sets for the aged samples only includes four samples of each type, which is a very small sample group, but I hoped it would be a good starting point.
After aging, the tiles looked very good to my eye and I could not detect a significant difference in color or gloss after the aging was complete.

<table>
<thead>
<tr>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• No color or gloss difference detected</td>
<td>• No color or gloss difference detected</td>
<td>• No color or gloss difference detected</td>
<td>• No color or gloss difference detected</td>
</tr>
<tr>
<td>• No apparent change in reversibility</td>
<td>• No apparent change in reversibility</td>
<td>• No apparent change in reversibility</td>
<td>• No apparent change in reversibility</td>
</tr>
</tbody>
</table>
According to the data, only thicker coatings exhibited what should have been a noticeable difference in color. In the unpolished samples with thicker coatings, the wax resin and Avalure samples seem to have had slightly more average color change after aging. Methyl cellulose had the least average change over all in the unpolished samples. For the polished samples all of the coatings performed very similarly to the control, even those that had an average ΔE of 1 or more.

The change in the control makes me think the changes in the polished samples may simply have been due to abrasion from being packed up and traveling to IPI in Rochester and back. Most change was in the L* channel, but this time the average ΔL* was positive, indicating lightening. This could be from abrasion or it could be bleaching or blanching, i.e. the beginning of light damage related change.
This table shows average gloss data from the aged samples. None of the unpolished samples showed a noticeable difference. All of the polished samples except the microcrystalline wax samples decreased significantly in gloss, on average. Again, it is likely that abrasion from travel and handling could be the culprit.

<table>
<thead>
<tr>
<th>Units = GU</th>
<th>Wax Resin</th>
<th>Microcrystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
<th>Control (No coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Not Polished</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thick coat</td>
<td>2.00 (s=1.30)</td>
<td>0.80 (s= 0.555)</td>
<td>0.10 (s=0.174)</td>
<td>1.47 (s=0.375)</td>
<td>-0.041 (s= 0.046)</td>
</tr>
<tr>
<td>Thin coat</td>
<td>0.48 (s=0.0298)</td>
<td>0.87 (s= 0.630)</td>
<td>0.20 (s=0.166)</td>
<td>0.64 (s=0.114)</td>
<td></td>
</tr>
<tr>
<td><strong>Polished</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thick coat</td>
<td>-12.40 (s=9.21)</td>
<td>6.47 (s= 3.22)</td>
<td>-14.71 (s=0.137)</td>
<td>-38.21 (s=13.92)</td>
<td>-2.01 (s=0.835)</td>
</tr>
<tr>
<td>Thin coat</td>
<td>-9.22 (s= 5.36)</td>
<td>8.08 (s= 8.11)</td>
<td>-2.76 (s=1.13)</td>
<td>-21.57 (s=2.32)</td>
<td></td>
</tr>
</tbody>
</table>

3-5 = Just noticeable difference
Next I will present the results from the soiled samples. Again the samples were a subset of the original tiles, so for each average that you see, there were 8 samples.
I will begin with the lipstick stained samples. After the lipstick was applied and stayed on for 24 hours, I wiped all of the samples with mineral spirits to remove the lipstick, including the controls, before removing the coatings.
After doing so, I observed that all of the samples actually looked quite good, especially compared with the controls. I did note some very tiny pink particles remaining in small divots in the tiles with micro crystalline wax and wax resin, but this was only with very close inspection by eye - not from normal viewing distance.

### Observations - Lipstick

<table>
<thead>
<tr>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Very small pink particles in divots on polished samples</td>
<td>• Very small pink particles in divots on polished samples</td>
<td>• No noticeable staining</td>
<td>• No noticeable staining</td>
</tr>
<tr>
<td>• Better result than control</td>
<td>• Better result than control</td>
<td>• Better result than control</td>
<td>• Better result than control</td>
</tr>
</tbody>
</table>
Here are some examples of the tiles after the lipstick and coating were removed. This photo doesn’t show very well that the control tiles actually looked worse than the others. The control is in the center in each photo and the left image shows polished tiles, while the image on the right shows unpolished tiles, the type of coating is indicated across the top of the image, and is the same for the bottom and top rows.
Here is the color change data comparing before coating and after the coatings were removed to see if staining could be detected. As you can see, each coating generally did better than the controls and they all performed very similarly, although the Avalure in the blue column seems to have done especially well with the polished samples.

<table>
<thead>
<tr>
<th>Not Polished</th>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
<th>Control (No coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick coat</td>
<td>1.07 (s= 0.77)</td>
<td>1.12 (s= 0.79)</td>
<td>0.93 (s=0.62)</td>
<td>1.29 (s=0.50)</td>
<td>1.84 (s= 1.17)</td>
</tr>
<tr>
<td>Thin coat</td>
<td>1.14 (s=0.49)</td>
<td>1.26 (s= 0.96)</td>
<td>1.77 (s=1.75)</td>
<td>1.98 (s=0.84)</td>
<td></td>
</tr>
<tr>
<td>Polished Thick coat</td>
<td>1.20 (s=1.18)</td>
<td>1.72 (s=1.39)</td>
<td>0.22 (s=0.16)</td>
<td>0.29 (s=0.41)</td>
<td>3.55 (s= 1.99)</td>
</tr>
<tr>
<td>Polished Thin coat</td>
<td>1.71 (s= 1.37)</td>
<td>1.74 (s= 1.49)</td>
<td>1.20 (s=1.45)</td>
<td>0.34 (s=0.43)</td>
<td></td>
</tr>
</tbody>
</table>

1 ΔE = Just noticeable difference

Average Color Change - Lipstick
But with gloss change the polished Avalure samples were the only ones to show an average difference that should be just noticeable. Over all, the coatings did well.
The wine staining provides much more drama than the lipstick staining. After the wine had been on for at least 24 hours, I wiped all of the tiles, including the controls, with water to remove excess wine before removing the coatings.
The staining was reduced on all of the tiles, even the controls. However some staining remained on all samples. The polished marble had more of a brownish haze, while the unpolished samples had darker, more discreet stain spots. None of the unpolished samples looked very good, but the microcrystalline wax samples looked the worst. One dramatic result was that on all of the polished samples, except those coated with Avalure, there was significant etching of the polished surfaces. This is an important piece of information because while more may be done to reduce the staining of the marble, the etching is irreversible, without repolishing the surface of the stone.

<table>
<thead>
<tr>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Staining on all, similar to control</td>
<td>• Worst performer on unpolished samples</td>
<td>• Staining on all, similar to control</td>
<td>• Staining on all, similar to control</td>
</tr>
<tr>
<td>• Etching of polished samples, similar to control</td>
<td>• Staining on all</td>
<td>• Etching of polished samples, similar to control</td>
<td>• No etching visible</td>
</tr>
</tbody>
</table>

The staining was reduced on all of the tiles, even the controls. However some staining remained on all samples. The polished marble had more of a brownish haze, while the unpolished samples had darker, more discreet stain spots. None of the unpolished samples looked very good, but the microcrystalline wax samples looked the worst. One dramatic result was that on all of the polished samples, except those coated with Avalure, there was significant etching of the polished surfaces. This is an important piece of information because while more may be done to reduce the staining of the marble, the etching is irreversible, without repolishing the surface of the stone.
Here is an image of some of the samples after the coating was removed.
And here is an image taken of the etching. The dark spots you see are etching. The tile in the top of the image with no spots, was the Avalure coated tile. (The square outline over all the tiles, is a light reflected in the surface.)
The color data for the unpolished samples is fairly consistent with my observations. The microcrystalline wax had the most average change of all the coatings. Much of the color change in the polished samples can actually be attributed to the gloss change, which gives a blanched appearance, and that is why so little change is reflected in the polished Avalure samples.

### Average Color Change – Wine

<table>
<thead>
<tr>
<th>ΔE</th>
<th>Wax Resin</th>
<th>Microcrystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
<th>Control (No coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Not Polished</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thick coat</td>
<td>1.26 (s= 0.67)</td>
<td>3.32 (s= 2.89)</td>
<td>1.87 (s=1.59)</td>
<td>3.82 (s=2.23)</td>
<td>2.78 (s= 2.24)</td>
</tr>
<tr>
<td>Thin coat</td>
<td>1.68 (s= 0.64)</td>
<td>5.47 (s= 3.17)</td>
<td>2.59 (s=1.38)</td>
<td>4.26 (s=2.63)</td>
<td></td>
</tr>
<tr>
<td><strong>Polished</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thick coat</td>
<td>2.34 (s=1.70)</td>
<td>2.39 (s=1.58)</td>
<td>1.33 (s=0.47)</td>
<td>0.58 (s=0.45)</td>
<td>3.16 (s=2.82)</td>
</tr>
<tr>
<td>Thin coat</td>
<td>3.08 (s= 1.77)</td>
<td>3.19 (s= 1.55)</td>
<td>1.91 (s=0.74)</td>
<td>0.55 (s=0.50)</td>
<td></td>
</tr>
</tbody>
</table>

1 ΔE = Just noticeable difference
The gloss data are also consistent with what I observed. The unpolished samples did not change in gloss, but all of the samples except the Avalure had significant etching, as you saw in the photograph.

<table>
<thead>
<tr>
<th>Units = GU</th>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
<th>Control (No coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polished</strong> Thick coat</td>
<td>-33.49 (s=10.05)</td>
<td>-17.83 (s=14.33)</td>
<td>-37.52 (s=14.58)</td>
<td>-1.53 (s=0.96)</td>
<td>-39.10 (s=7.11)</td>
</tr>
<tr>
<td><strong>Polished</strong> Thin coat</td>
<td>-29.67 (s= 31.78)</td>
<td>-15.39 (s=10.82)</td>
<td>-47.36 (s=20.62)</td>
<td>-0.53 (s=3.4)</td>
<td></td>
</tr>
</tbody>
</table>

**All unpolished samples changed less than 1 GU**

**Just Noticeable Difference = 3-5**
The last soil I applied was Sharpie marker. To remove the marker, I first poulticed each sample with acetone on cotton pads and then I removed the coatings.
Almost all of the polished tiles looked like new, except one of the wax resin tiles, which had very faint lines from the marker and looked very similar to the polished controls. The unpolished samples of all types did much worse and had a lot more staining in general, but there was significantly less staining if a coating was present. The wax resin seemed to do the best and the microcrystalline wax performed the worst. I did not notice any difference in gloss between the samples.

<table>
<thead>
<tr>
<th>Wax Resin</th>
<th>Microcrystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• One Polished tile that had one coat has very faint staining, similar to control</td>
<td>• Polished tiles looked like new</td>
<td>• Polished tiles looked like new</td>
<td>• Polished tiles looked like new</td>
</tr>
<tr>
<td>• <strong>Worst performer on unpolished tiles</strong></td>
<td>• Unpolished samples were better than control</td>
<td></td>
<td>• Unpolished samples were better than control</td>
</tr>
<tr>
<td>• <strong>Perform best on unpolished samples</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Here is an image of some of the tiles after the coatings were reversed. You can see the unpolished samples on the right are in rough shape. Having a thicker coating, as seen in the samples on the bottom of each image, definitely made a difference for the unpolished samples.
The average color change data reflects what I saw and confirms that the microcrystalline wax performed the worst in general.
The gloss data did not show an average change that should have been noticeable in any of the sample sets.

Gloss Change Data – Sharpie

All samples:
Average gloss change less than 1 GU
Similar results to control

Just noticeable difference = 3-5 GU
Here are my conclusions again for you as I wrap up.

This study really just broaches this topic and my results point to a few areas that could warrant more research. The methyl cellulose did surprisingly well, in my opinion, and since there are so many different types, it might be interesting to study them for this purpose and see if there is an even better type to use as a coating for marble. I also think further study of Avalure for use on stone indoors and outdoors would be useful, as it also performed well.

<table>
<thead>
<tr>
<th>Wax Resin</th>
<th>Micro-crystalline Wax</th>
<th>Methyl Cellulose</th>
<th>Avalure</th>
</tr>
</thead>
</table>
| • Provided some protection from all soils, especially lipstick  
  • Allowed wine to etch polished tiles  
  • Performed well aesthetically  
  • More matte than polished tiles, saturated unpolished tiles  
  • Perhaps some color change and loss of gloss with aging  
  • Toxic solvents needed to reverse | • Not recommended as a barrier  
  • Performed worst with wine and sharpie  
  • Performed well aesthetically  
  • Went on glossy  
  • Seemed least reversible, solvents needed to reverse | • Provided some protection from all soils, especially lipstick  
  • Allowed wine to etch polished tiles  
  • Performed well aesthetically  
  • More matte than polished tiles  
  • Did not change color before or after aging  
  • Best reversibility, but must be careful with aqueous solutions | • Provided some protection from all soils, especially lipstick  
  • Did NOT allow wine to etch polished tiles  
  • Mixed aesthetic results  
  • Iridescence on polished tiles  
  • Minimal change on unpolished tiles  
  • Reduced gloss on all tiles  
  • Perhaps some color change and loss of gloss with aging  
  • Alkaline water or ethanol removal |
I would like to thank all of the individuals and institutions listed on the screen, and thank you for your attention.
The Use of Agar as a Solvent Gel

Cindy Lee Scott
UCLA/ Getty Conservation of Archaeological and Ethnographic Materials
Conservation Intern - Museums of New Mexico
AIC Annual Meeting - May 9 2012

Cindy Lee Scott

Graduate Student, UCLA/ Getty Conservation of Archaeological and Ethnographic Materials
and Conservation Intern at the Museums of New Mexico

Presented at the RATS/OSG joint session
40th Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
Albuquerque, NM, May 8-11 2012
At a conference on cleaning held in Valencia in June 2010, Italian chemist, Paolo Cremonesi presented a paper on the use of rigid agar gels for the conservation and cleaning of outdoor plaster busts. I heard about this presentation second-hand during a summer internship at the National Museum of New Zealand – Te Papa Tongerawa, and I was immediately intrigued by the possibilities for my own research in shellac reversal from ceramic substrates. The research presented in Valencia by Cremonesi, and that was published in later months by him and his colleagues in Milan (vide infra) showed great promise in the use of agar gels as a cleaning material for three-dimensional objects. During their studies, they used the gel primarily with deionized water. Given their degree of success, I wondered if other cleaning agents, such as solvents, could be added to the gel to increase its versatility, and how the addition of such agents would affect the stability and working properties of the gel. None of my research, however, was able to answer these questions.
The studies published by Anzani et al. (2010) and Cremonesi (2010) explored the application of agar as a sol (colloidal solution, described in more detail on the next slide), which allowed its application on 3-dimensional materials (the rigid nature of the gel had previously restricted its use to 2-D or flat materials). Since this study was published, the applications and usage of agar gels in conservation has gained ground here in North America, as exemplified by an upcoming workshop sponsored by the Smithsonian Institute in June 2012.
Agar is a rigid gel derived from the cell walls of a species of red algae of the *Gelidium* or *Gracilaria* families (Davidson and Jaine 2006). Agar gels can be classified as reversible sol-gels or reversible hydrocolloid gels. A 'sol-gel' starts from a colloidal solution (the sol) that acts as the precursor for an integrated network of polymers (the gel) (http://en.wikipedia.org/wiki/Sol-gel). Herein, the warm, semi-solid form of agar will be referred to as the sol, while the cooled, more rigid form will be referred to as the gel.
According to the Lonza Bench Guide on the physical properties of agar, the gelation mechanism involves a “shift from a random coil in solution to a double helix in the initial stages of gelation, and then to bundles of double helices in the final stage” (Lonza Bench Guide online). Each stage of gelation is reversible and is reached by the addition or subtraction of heat.
At the molecular level, agar consists of two polysaccharides, agarose, which forms approximately 70% of the mixture and has the greatest gelling tendency, and agaropectin. The polymeric backbone structure of both of these molecules consists of alternating galactopyrose molecules, listed here, which form agarobiose units (FAO online/American Society for Microbiology 1981). The agarobiose units form long chains with an average molecular mass of 120 000 daltons, or roughly 400 agarobiose units (Lonza bench guide).
Agar powder can be purchased in a number of purities, ranging from highly purified agarose used in biological studies, to food grade agar. Both my own research, and that conducted by Anzani and Cremonesi showed little to no detectable differences between the FTIR spectra of food grade samples and those that were of analytical grade. Experiments conducted at UCLA were done using an analytical grade of agar powder ground to 80 mesh; those conducted at the Museums of New Mexico used a food grade agar purchased from Moor Agar Inc., also ground to 80 mesh. Some initial experiments at the Museums of New Mexico were also conducted using flake agar purchased from the local Whole Foods, and ground in a coffee grinder.
Dried agar, either as a powder or raw flakes, is insoluble in cold water, though it dissolves easily in boiling water. The minimum temperature at which the polymeric chains cross-link to cause gelation is 85°C. An agar sol needs to be cooled to below 40°C to form the gel. Once cooled, it is easily reheated to its sol state, a process that can be repeated multiple times without change to the working properties of the gel (though a loss of water through evaporation should be compensated for with each reheating) (Chaplin 2009; Anzani et al. 2010, 42).

Agar gels exhibit high gel strength even at concentrations < 6%. They are stable up to 65°C, and are not enzymatically degraded by most bacterial species. They are stable in both highly alkaline and acid conditions, and, prior to the addition of other cleaning agents, completely non-toxic and natural. It is an ideal gel matrix for biomedical applications because it is biologically inert with controlled ionic properties (FAO online).
The porosity of an agar gel is directly related to the concentration of agarose within the dispersion phase. Thus by altering the concentration, it is possible to manipulate viscosity, absorption, and dispersion as needed by a given treatment or experiment (http://en.wikipedia.org/wiki/Agar). The average pore size for a prepared gel between 2-7% w/v, is typically between 100 and 300nm (Lonza Bench Guide online).

Agar sol-gel in its sol phase at different concentrations from 0.5% to 7%. The agar was dyed using the same amount of alizarin dye to better illustrate the differences in opacity as the concentration of the gel increases. As alizarin is also a pH indicating dye, the pink colour visually demonstrates that the gel is at a neutral pH of around 7 (specifically, pH 6.7)
It is this porosity that allows an agar gel to act as a ‘molecular sponge’, though rather than adsorption, we are here, speaking of absorption by means of gradients of concentration, as well as osmosis (Anzani et al. 2010, 44).
The degree of absorption possible for a given solute is influenced by both the concentration of the agar gel, as well as by the particle size of the solute.

For example, in two instances of removing gouache paint from a plaster surface, a large particle sized blue pigment and a finer particle sized orange pigment, it was found that a 2% solution of agar gel was required to clean the blue gouache, while a 3% solution worked well for the orange gouache. While the binding medium was the same, as was the substrate, the particle size of the respective pigments differed and as such, a modified treatment approach was necessary.
Diffusion studies were carried out by Anzani et al. (Anzani et al. 2010, 48) on agar gels prepared using only water; their experiments found that after a period of twenty minutes, a 4% (w/v) agar gel will diffuse up to 2mm into a given porous substrate, in this case, gypsum, while a 2% (w/v) gel will diffuse to a depth of 4mm under the same conditions. In comparison, the researchers also applied a cotton poultice soaked in water and found that the water had diffused to a depth of 5-6mm after only 3 minutes. This study found a concentration of around 3-4% to be ideal, but for highly sensitive materials, I would recommend a higher concentration, sometimes up to 8%, which can be easily mixed. On highly textured or porous surfaces, I would advise against concentrations lower than 2%, as the dried residues can be exceedingly difficult to remove (they form a very thin film that can be removed mechanically, but with difficulty).
Preparing an agar gel is relatively simple:

Measured amounts of agar powder and cold water are mixed. The mixture is then heated to a temperature above 85°C. Heating can be done either in a microwave or on a hot plate, ensuring the solution is well mixed before, during, and after the heating process. After heating, a measured amount of solvent, chelating agent, oxidizer, or other cleaning agent is added to the agar sol and stirred in to achieve homogeneity.
Preparation

1. Mix measured amounts of agar/agarose powder and cold water (deionized or purified).
2. Heat the mixture to above 85°C either in the microwave or on a hot plate, stirring often
3. Add a measured amount of solvent/cleaning agent to the warm semi-solid gel.
4a. Apply the warm gel to a three-dimensional object to achieve the best contact.

OR

4b. Allow the gel to cool to a rigid gel, cut to size and apply to desired area.

The agar can be allowed to cool and applied as a gel, cut to the desired shape and size, or applied while warm as a sol with a brush or spatula to the desired area.

Given the combustible nature of most solvents habitually used by conservators, if the agar is to be applied warm, the solvent should be added after heating.
It is important to note that a colour change has been observed when agar sols are created using alkaline solutions. This darkening is not observed when the alkaline material is added to the warm sol after the initial dissolution and colloid formation has occurred. The nature of this colour change is not fully understood at this point, but can cause staining on some substrates and therefore discolored sol-gels should not be used on objects.
Removal of the gel after treatment is a simple matter: one need only lift an edge of the gel and peel it off. The softness and elasticity of the gel makes removal complete. Any small residues, particularly around edges, will tend to detach from the substrate and spontaneously flake off after drying (Anzani et al. 2010). The entire application process can be seen here, where a mixture of agar, ethanol and water were used for the removal of gouache overpainting on the plaster fills of a Gallina-Largo ceramic prior to soaking it to swell the PVA used to reassemble it.
Generally speaking, the gel is removed before it has dried out completely, but should the gel dry out, current evidence has not indicated increased risk of damage to the object. Anzani et al. even recommend allowing the gel to dry out completely if there is a need to remove deeply penetrating stains, or salts. This slide shows agar that has been allowed to dry in order to better remove acrylic overpaint from a plaster fill on a Rosa Grey ceramic.

The drying time of agar can be influenced by the thickness of its application. Even at thicknesses of less than 2mm at an ambient RH of 50%, the gel will stay moist for more than 8 hours without being covered. Covering the gel can extend the drying period over several days, though it should be noted that the risk of mould growth is increased with extended applications, and multiple applications should be considered instead.
My own experiments and research into agar gels occurred in two phases: the first was conducted as a component of my thesis research at UCLA; the second was conducted during my internship with the Museums of New Mexico.

During the first phase, I conducted experiments on ceramic test tiles created in the lab. In this instance, agar was being explored strictly as a support material for other chemicals in order to find alternative ways of reversing shellac from previously restored ceramics (for which the agar performed beyond expectation, whereas the other elements of my study were not quite as successful). The ceramic tiles used here were made of terracotta coated with a kaolinite-type slip and fired in a furnace at 900 degrees Celsius.

Ceramic test tiles made of terracotta with kaolinite slip. As a part of these experiments, the tiles were broken, mended with raw shellac and artificially aged before treating.
As a part of the first phase of study, I tested the agar sol-gels mixed with ethanol, acetone and 5M NaOH, and various combinations of these three materials. Evaluation of the efficacy of the agar gels in this context, including clearance, was conducted using visual analysis with binocular microscopy, UV-visible fluorescence imaging, and FTIR spectroscopy.

Preliminary results showed excellent working properties when the agar sol was mixed with both ethanol and NaOH, as well as good clearance after treatment. To increase clearance and ease of removal for lower concentration gels (to increase porosity), Japanese tissue paper was used as an intermediary layer; this additional layer did not seem to impede the absorption action of the gel in any way.
During the second phase, several classes of cleaning agents were tested for their use in agar gels with care taken to note the working properties of each mixture, colour changes that could potentially lead to staining, and the degree of miscibility. Given my limited access to some resources, each of these characteristics are observational qualities only, and require further research. The classes of cleaning agents explored in preparation for this paper include solvents, surfactants, chelating agents, oxidizers, and acids.
The best results here were achieved with ethanol, followed by Stoddard Solvents, then acetone, and finally xylenes, which, if added in too high a concentration, caused the gel to completely dissociate. None of the solvents caused colour changes that were concerning.

### Cleaning Agents - Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Misceability</th>
<th>Colour Changes?</th>
<th>Working Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Mixes readily</td>
<td>None</td>
<td>Excellent</td>
</tr>
<tr>
<td>Acetone</td>
<td>Destabilizes the colloid mixture&lt;br&gt; -Effect mitigated by the addition of EtOH</td>
<td>Becomes slightly opaque</td>
<td>Difficult-Good</td>
</tr>
<tr>
<td>Xylenes</td>
<td>Destabilizes the colloid mixture</td>
<td>Becomes opaque</td>
<td>Difficult</td>
</tr>
<tr>
<td>Stoddard's Solvent</td>
<td>Mixes well</td>
<td>Becomes slightly opaque</td>
<td>Medium-Good</td>
</tr>
</tbody>
</table>

All solvents were added to an 8% w/v agar gel after heating during sol-phase. Ratio of solvent to gel is 1:1 to create a 4% w/v gel.
With respect to other cleaning agents, excellent results were achieved for the chelating agent, oxidizer, acid and base tested. Additional testing should be done with other examples of these classes of materials in the future. Surfactants could not be mixed at all, causing complete dissociation of the gel, for reasons that will be discussed in greater detail below.

### Cleaning Agents – Other

<table>
<thead>
<tr>
<th>Cleaning Agent</th>
<th>Miscibility</th>
<th>Colour Changes?</th>
<th>Working Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton XL-8CN (1% w/v in H₂O) (Surfactant)</td>
<td>Gel dissociation</td>
<td>None</td>
<td>Gel dissociation</td>
</tr>
<tr>
<td>Orvus Paste (4% w/v in H₂O) (Surfactant)</td>
<td>Gel dissociation</td>
<td>None</td>
<td>Gel dissociation</td>
</tr>
<tr>
<td>Ammonium Citrate (3% w/v in H₂O) (Chelating Agent)</td>
<td>Excellent</td>
<td>None</td>
<td>Excellent</td>
</tr>
<tr>
<td>Hydrogen Peroxide (1% w/v in H₂O) (Oxidizer)</td>
<td>excellent</td>
<td>none</td>
<td>excellent</td>
</tr>
<tr>
<td>Phosphoric Acid (99% w/v)</td>
<td>Excellent</td>
<td>None</td>
<td>Excellent</td>
</tr>
<tr>
<td>Sodium Hydroxide (5M)</td>
<td>Excellent</td>
<td>Yellows slightly (temporary)</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

All agents were added to an 8% w/v agar gel after heating during sol-phase. Ratio of cleaning agent solutions to gel is 1:1 to create a 4% w/v gel.
In addition to the above tests, plaster tiles were cast in the labs at the Museum of New Mexico in order to further test the gel using these different cleaning agents in a number of cleaning challenges. The plaster tiles were coated with alizarin, shellac, watercolour, gouache, acrylic paint, PVA and soil/dirt.

After each of the tiles was ‘mis-treated’ with their respective cleaning challenges, they were artificially aged with cycles of heat and humidity for 14 days.

Using the most efficacious cleaning agent, as determined through solubility testing using a cotton swab, the agar gel was applied in its sol form and left in place for 15 minutes, after which time, it was removed. Generally, only one application was evaluated, though in the case of the blue gouache, a second application at a lower concentration was tested.

Each test was evaluated for the following:

1. Efficacy and efficiency of cleaning
2. Visible damage or morphological changes to the substrate
3. Working properties of the gel
4. Ease of removal/clearance
Solvent mixtures with agar gels were inadequate in the cleaning of either of these tiles, though some reduction is visible on the alizarin tile. On the shellac tile, clearance was achieved only through the addition of 5M NaOH, which did cause some slight pitting to the plaster.
All treatment efforts for removing the water colour from the tile were unsuccessful – I suspect due to the use of a pthalo green dye based water colour. I have already discussed the gouache, but as you can see, there is good success in the lower image, using a 2% agar.
Acetone on a cotton swab proved to be quite efficacious for the removal of the acrylic emulsion, whereas an acetone/agar mixture proved to be completely ineffective. Treatment of the PVA with agar was highly successful, though difficult to see in this image. The extended contact time with the adhesive has proven a very effective means to enhance removal.
A high degree of success was achieved using agar on the soiled tile. A single treatment showed significant cleaning, without damage to the surface (as was seen during the cotton swab cleaning test).
The results are summarized in this table.

It should go without saying that in any conservation treatment using an agar gel, the efficacy of treatment can only be as good as the suitability of the chosen cleaning agent. Beyond this element, efficacy can be enhanced by increasing or decreasing the respective concentrations of agar and solvent, the method of application (warm or cold), the length of application, and the number of applications.

Some other noteworthy results are as follows:

1. The addition of ethanol to the gel increases the efficacy of treatment through improved wettability. When trying to mix the gel with acetone, the addition of ethanol can increase the miscibility of the solution.

2. Chemically complexed materials, such as the alizarin, cannot be removed by solvation alone; additional steps must be taken to reverse the chemical complex; this can be accomplished by lowering the pH of the gel to create an acid environment.

3. Agents that disrupt hydrogen bond formation, such as chaotropic agents and some classes of surfactants, can significantly decrease melting and gelling temperatures, and can even inhibit the formation of the gel entirely; when adding such agents to the gel after gelation has occurred a disassociation of the gel has been observed, such as occurs upon the addition of surfactants.

<table>
<thead>
<tr>
<th>Tile</th>
<th>Solvent</th>
<th>Efficacy</th>
<th>Damage</th>
<th>Working Properties</th>
<th>Clearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alizarin Dye</td>
<td>Ethanol</td>
<td>Moderate</td>
<td>None</td>
<td>Excellent</td>
<td>Total</td>
</tr>
<tr>
<td>Garnet Shellac</td>
<td>1:1 EtOH and</td>
<td>Minimal</td>
<td>Lac Dye stains</td>
<td>Good</td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaOH and EtOH</td>
<td>Moderate</td>
<td>Lac Dye stains</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Water Colour</td>
<td>Water/EtOH</td>
<td>Minimal</td>
<td>None</td>
<td>Excellent</td>
<td>Total</td>
</tr>
<tr>
<td>Gouache</td>
<td>Water</td>
<td>Needs lower concentration</td>
<td>Tidelines</td>
<td>Excellent</td>
<td>Total</td>
</tr>
<tr>
<td>Acrylic Emulsion</td>
<td>Acetone</td>
<td>No change</td>
<td>None</td>
<td>Excellent</td>
<td>Total</td>
</tr>
<tr>
<td>PVA Adhesive</td>
<td>Water</td>
<td>Excellent</td>
<td>None</td>
<td>Excellent</td>
<td>Total</td>
</tr>
<tr>
<td>Soil</td>
<td>Water</td>
<td>Excellent</td>
<td>None</td>
<td>Excellent</td>
<td>Total</td>
</tr>
</tbody>
</table>
For the cleaning of heavily soiled or saturated substrates, the gel should be reapplied intermittently to avoid saturation of the gel and diffusion of the solubilised material back into the substrate. The more saturated the surface, the more often the gel should be changed.
Clearance methodologies for agar gels are as simple as they are effective; “the surface freed from the gel has suffered no [physical] manipulation” (Anzani et al. 2010, 48). This rigid gel is not ‘adhered’ to the object in any way, it is simply held in place by gravity, and depending on the texture and shape of the surface to which it is applied, physically. Such a methodology has many advantages, largely due to its simplicity.

This is in contrast to more traditional cleaning methodologies, which can involve a high degree of physical interaction with the surface in trying to clear post-cleaning gel residues. Further, the more complex mixtures of surfactants, solvents and other chemical gelling agents, such as polyacrylic and PVOH gels, can leave a greater variety of residues, particularly on porous or uneven surfaces; there is evidence that such residues can interact with the surface as they age.

One area of concern in using a natural gelling agent is that of biodeterioration in the event that full clearance is not achieved. Agar gels have found their major use as microbiological media “as it is not easy for microorganisms to metabolize” (Chaplin 2011). Thus, while agar gels have traditionally been used as a growth medium in petri dishes, it is not because they are a food source for microorganisms, but rather, because they are not.
FTIR spectra of dry agar powder showed characteristic polysaccharide bands that were not definitively detected on the treated ceramic tiles after treatment. FTIR analysis of the agar gel after it was removed was not able to determine if there had been undesired leaching of minerals from the ceramic substrate, and further analysis should be considered to better address this issue.
UV induced visible fluorescence, using a wavelength of 365 nm, did show some faintly fluorescent zones, particularly along the margins of treated areas, as seen on the above slide (Cremonesi 2010; Anzani et al. 2010; Scott 2012). Anzani noted a similar fluorescence when they inspected their treated gypsum tiles using UV induced visible fluorescence: further tests led them to believe that this halo was likely attributable more to the action of water on the surface, than to a dry, superficial residue of the gel itself (Anzani et al. 2010, 52). I have not yet confirmed or refuted either possibility.

Agar gels do not change the hygroscopicity of a porous substrate after treatment, and in fact, do not show any observable interaction with the treated surface including signs of erosion or etching either macroscopically or microscopically (Anzani et al. 2010, 35). SEM still has yet to be explored for verification.
To summarize, Agar based solvent gels show a number of important advantages and uses that can make them a more favourable treatment option for the cleaning of certain substrates. Conversely, there are a number of disadvantages that would preclude the use of an agar-based gel.

Such advantages include:

1. It is a simple compound; there is no question as to the active ingredient. The gel, on its own, is largely inert, and as such, it is only as effective as the cleaning agent that it’s carrying.

2. The absorption and diffusion qualities of the gel can be easily tailored to a given treatment of substrate by manipulating the concentration of agar in water.

3. The porosity of the gel allows it to act like a ‘molecular sponge’, therefore playing the dual role of both a solvent carrier and a poulticing material. It simultaneously solubilizes the solute while drawing it away from the surface and holding it within its gel matrix, minimising any physical interaction with the substrate.

4. It is easily removed without any special clearance methodologies. There is a reduced risk of differential clearance form one conservator to another. It also requires less training to learn how to use.

5. Agar shows a wide ranging stability to both temperature and pH fluctuations.

6. Agar as a dried powder has a long shelf-life, is inexpensive and widely available.

Conversely:

1. Agar gels must first be mixed with water. Though the diffusion of water can be minimised by using a higher concentration of agar, there will always be the diffusion of some water into the substrate. If the substrate is sensitive to water, another cleaning treatment should be considered.

2. Because of differences in polarity, some solvents, such as acetone, can be tricky to mix into the gel. The addition of a small amount of ethanol prior to mixing more polar solvents can mitigate this effect, but the presence of ethanol in a mixture is not always desirable. Further, the volatility of solvents, such as acetone, can have a rapid cooling effect on the gel, causing it to solidify before the solvent has been fully mixed. The use of a double boiler to heat the gel can help to mitigate this effect.

3. Currently, it is not possible to mix surfactants into the gel. The disruption of hydrogen bond formation causes the gel to dissociate and liquefy in the presence of the surfactants tested.
4. There is some risk, though minimal and improbable, of biological deterioration if full clearance is not achieved.

5. If using the gel as a carrier for flammable solvents, it is not possible to keep the agar solvent gel premixed as one does with Carbopol, unless it will only be used as a rigid gel and not reheated. If reheating is necessary, the solvents should be added only after heating, just prior to application.

6. If one wishes to apply agar as a sol, special equipment such as a hot plate or microwave will be necessary; these are not always available or practical in a field setting.
As with any material that one uses for conservation treatment, additional research into the aging, potential residues and interaction with different substrates is required before it can and should be used on other types of materials, but the properties seen within the scope of this study have shown it to be a promising material.

“Agar may be considered a substance capable of shaping itself perfectly to three-dimensional forms. It produces detachment/absorption action on particulate deposits, does not leave residue, leaves open the possibility to repeat the operation, and does not modify the surface of the support. It is better able than any other traditional material used until now to achieve successful, controlled, in-depth cleaning”

Anzani et al. (2010, 45)
I would like to acknowledge and thank the following people, without whom this project and my research could have never moved forward.

REFERENCES


SOME UNUSUAL, HIDDEN, SURPRISING, OR FORGOTTEN SOURCES OF (POSSIBLE) SULFUR CONTAMINATION IN MUSEUMS AND HISTORIC STRUCTURES

Presented by Paul L. Benson

AIC Annual Meeting, OSG/RATS Joint Session, May 9, 2012

Paul L. Benson

Associate Conservator of Objects
Nelson-Atkins Museum of Art

Presented at the RATS/OSG joint session
40th Annual Meeting of
The American Institute for Conservation of Historic and Artistic Works (AIC)
Albuquerque, NM, May 8-11 2012
This presentation discussed how and where sulfur can enter the museum. No discussion of corrosion mechanism, equations, charts, etc. will be presented. The use of the word ‘museum’ is meant to include purpose built museums buildings, re-purposed or converted industrial building (for example, the Tate Modern Museum in London), historic homes and out buildings, and converted collections storage buildings.

The first part of the presentation will introduce elemental sulfur as an adhesive/cement/grout. When used as an adhesive molten sulfur has many advantages over more conventional adhesives. It is quite cheap, it is easily obtainable, it melts at a low temperature, it sets quickly, and it expands upon cooling. It has been used to fix drills into the floors of mines, set heavy industrial equipment into concrete floors, affix metal railings into stone, repair gravestones, anchor bolts into stone, set survey markers into stone, lift stone quarry blocks, join pipes, etc.

Sulfur can also be used as a casting material and as decorative inlays in period wood furniture, guitars, rifles, ivory cane handles, a strengthening material in hollow gold jewelry, etc. It has also been combined with materials such as graphite, rubber, and gypsum to produce materials from which every day objects are made.

Sulfur has either been unidentified or misidentified in museum collections and in the fabric of museum buildings themselves. Locating the source of sulfur contamination can be costly and time consuming so it is hoped that by showing how it can enter the museum the task of tracing the source can be made easier. The final part of the presentation is a case study of how sulfur contamination affected a collection of bronze artifacts and where the source of the contamination was found.
I doubt that this type of artifact would ever make it into a museum but it could be encountered during consulting with law enforcement agencies. The only method to make casts of footprints in snow is to use molten sulfur as the casting material. When these casts are stored for long periods of time in an evidence storeroom, as required by law, they could cause corrosion on metals stored nearby. This could compromise evidence in future criminal cases and could corrode metals objects if these are ever displayed in some type of exhibition.
Sulfur melts at a relatively low temperature of 112.8 degrees Celsius so just about any type of container can be used to produce molten sulfur. This property is convenient for field applications such as setting survey markers in stone, repair of gravestones, or re-setting of iron railings in stone or concrete. It is particularly useful in cold climates where its setting is not affected by ambient temperatures.
Rock anchor for an aerial cableway using sulfur as the grouting material. Sulfur has also been used to anchor lifting bolts in slabs of rock in stone quarries. The bolts are very difficult to remove so they may be cut off leaving the sulfur behind.
Molten sulfur makes a cheap, quick adhesive. This weight is being used in a tower clock mechanism. Another clock weight in a New England church was also suspended by an iron hook set in sulfur and it failed after more than one hundred years due to a leaky roof. The weight fell into the church basement; no information was provided on any damage to the church or items stored in the basement. Sulfur does not react with water but iron does so it was probably the hook that failed and not the ‘adhesive’. The iron within the sulfur adhesive forms insoluble iron sulfides so it is not effected by water.

Molten sulfur has also been used as a strengthener in Roman and Byzantine hollow gold jewelry, particularly rings. The Thetford Treasure, late 4th century Roman jewelry found in England in 1997 and now in the British Museum, offers several examples of this application. Sulfur was also used in some of these rings to set stones and fill around those that were smaller than their settings. Sulfur in a plastic state (molten sulfur quenched in water) could also have been used as the filler in a hollow ring to offer resistance during the chasing or reposé process. As the sulfur hardened it would act as a strengthener for the hollow ring. The sulfur is most often hidden inside the jewelry where it would go undiscovered and possibly be the catalyst for corrosion to surrounding base metal objects. Romans also used sulfur to attach ivory to stone.
The substitution of sulfur for Portland cement in concrete has some financial benefits. Sulfur is less expensive than Portland cement and sulfur concrete cures in about half the time of traditional Portland cement based concrete. Sulfur cement is particularly non-reactive with chemicals so it has been used in areas where chemicals are processed or stored. While this type of concrete would never be specified for new museum construction it could be encountered in older buildings that have been converted into museum use space; i.e. exhibition or storage space.
This is an example of a cement block building that has been constructed with no mortar between the blocks. The structure has been stabilized by spraying molten sulfur on the blocks to act as a surface adhesive. It isn’t clear if the sulfur is applied just to the exterior or to the interior surface as well. This type of construction is popular in South America, Africa, and the Middle East. It is possible that this type of structure could be used locally for displays or artifact storage.
Chinese drywall was imported into the US between 2001 and 2009 but mainly from 2004 to 2006. The drywall had a higher than normal sulfur content which allegedly caused corrosion to electrical wiring and plumbing lines. The sulfur in this drywall is known to offgas into hydrogen sulfide, carbon disulfide, and carbonyl sulfide. This type of drywall is more likely to be found in repairs to historic structures that had suffered flood or wind damage during hurricane seasons than in museums proper.

Molten sulfur was also recommended as the adhesive to re-attach sagging plaster ceilings in texts from the 1920’s. It may be possible to trace a contamination problem to the hidden sulfur in plaster ceilings and walls of historic structures.
Sulfur makes a good casting material because it actually expands up to 3% upon cooling from a molten state.
This is an example of a sulfur inlaid piece of furniture. This type of inlay was done for a relatively short period of time, approximately 1785-1820, and produced from the relatively limited geographical area of eastern Pennsylvania. More than one hundred examples of this type of inlaid furniture are now known.

Sulfur inlays can actually be white in color and not the expected yellow color. These inlays can turn white due to a decrease in particle size in the sulfur resulting from fluctuations in temperature and relative humidity over long periods of time. The yellow color can also be dampened by the addition of calcite, gypsum or silica to the molten sulfur or by the application of a colored varnish layer on the inlays. White colored inlays have been mistaken for ivory and mother-of-pearl. Perhaps the best reference for the reason for this color change is an article by Jennifer L. Mass and Mark J. Anderson titled “Pennsylvania German sulfur-inlaid furniture: characterization, reproduction, and ageing phenomena of the inlays”, in Measurement Science and Technology, 14 (2003), p. 1598-1607.
An allotrope of sulfur that can be confused with other materials is Rosickyite, also known as mother-of-pearl sulfur. It is thought to be the inlay material in rifles, for example rifle #24 from the Kutztown Historical Society, and possibly guitars where it has been misidentified as real mother-of-pearl. It is worth noting that real gut strings for musical instruments are processed with sulfur to give them a white appearance but nothing has been found to suggest that any residual sulfur remains on the strings after they have been bleached by the sulfur.
Sulfur is the best known electrical insulator so its presence on an antique glass insulator is not surprising. This type of object is usually only found in industrial collections so it could easily be mis-identified.
This 1900-01 image illustrate the scale of production of two-part electrical insulators sealed with sulfur. The pot with the chimney in the center of the image is for melting the sulfur. These types of insulators were produced on a fairly large scale but only for a period of two years.
Collections of military equipment can contain materials not found in general art collections. These materials can incorporate substances that are not found in civilian equivalent objects. The sulfur here is acting as an adhesive along with the plaster cement. Its presence is not obvious but it could be a source for corrosion found on other metallic objects displayed or stored nearby.
No explanation for why this miniball is filled with sulfur could be found. It does illustrate that sulfur can be found in period munitions and its presence in military collections should be investigated further.
Spence’s metal is technically not a metal but a combination of metal sulphides. It was developed in England in 1880 as a replacement for lead and bronze castings. Its creator championed its properties of expanding on cooling, taking a high polish, and its ability to accept coloring agents. It was also good for joining water pipes, joining metal to stone, coating the holds of ships, and good for preserving fruit! Spence’s metal was only in vogue for approximately ten years so it was not widely used and it is not well documented so it can easily be mistaken for lead or bronze. If it is stored or displayed with other metals there is the possibility that it could initiate corrosion of the other metals.
The rubber erasers on pencils are processed with sulfur.
Good quality graphite for pencils was originally found only in England where the mines were carefully guarded against theft. German producers of pencils were forced to use lesser quality graphite mixed with sulfur to make their writing instruments. German pencils with this sulfur/graphite mixture were produced up to about 1790.
Ebonite is a form of rubber that was first made in 1839 and contains approximately 30-40% sulfur. It can be shaped into just about any form from bowling balls to buttons. Ebonite buttons can be found on military uniforms where it may be misidentified as a type of plastic. Black colored casters on furniture may be ebonite. Exposure to high heat, high light levels, and high humidity will cause the sulfur to migrate out of the rubber.
In the last few years attention has been given to the deterioration of the wood on this vessel and similar waterlogged wooden objects recovered from marine anaerobic environments. It was found that large quantities of elemental sulfur, sulfur salts, and sulfur acids are present in the wood. Without going into details of the mechanism of their formation it is sufficient to say that wood of any dimension recovered from similar marine conditions should be examined for the presence of sulfur and its related compounds. The sulfur is an immediate danger to the object itself and to surrounding objects.
This is an image of the famous Coin Cabinet at the Kunsthistorisches Museum in Vienna, Austria. A few years ago it was noticed that some of the gold coins were developing black spots on their surfaces. An investigation of this problem revealed that sulfur was emanating from the many plaster (calcium sulfate) casts in the room.
This is an example of the type of black spot corrosion that has been found in the Coin Cabinet of the Kunsthistorisches Museum. This coin is obviously not from that collection but it does illustrate the type of problem found in the Coin cabinet. It was determined that the corrosion on the coins in the Coin Cabinet was caused by the sulfur dioxide emitted from deteriorating gypsum casts. The literature source was not clear as to where the casts were located within the gallery, i.e. within the display cases or simply in the room but it should be assumed that the corrosive gas concentrated in the closed display cases.
This rather comical re-creation in Plasticine of a famous painting is just to a reminder that Plasticine does contain sulfur and any metals in contact with it could be corroded. Its presence in a closed environment like a display case could be the source of future corrosion.
The ancient art galleries at the Nelson-Atkins Museum of Art are lined with approximately 605 Italian black and gold colored marble panels. The heavily veined marble is inherently weak. Construction contracts from 1932 specify that these panels were to be reinforced on the back with pieces of either slate or sound marble. For some unexplained reason, the reinforcement was done differently. The method will be explained below.
The ancient galleries have several built-in wall cases that are lined with either travertine, as shown here, or with black colored marble. The travertine is exceptionally porous allowing air inside the cases to fully exchange with air from behind the false gallery walls. The example shown here is a typical case displaying two ancient bronze sculptures. The small Kneeling satyr will serve as an example for the deterioration occurring inside these cases.
This small bronze statuette shows the effects of a sulfur laden atmosphere concentrating inside a display case. The discoloration on the figure on the left began to appear just weeks after being placed inside the display case. The corrosion was superficial and easily removed (see the figure on the right) but only because the corrosion appeared in a very short period of time and was easily detected visually.
The image on the left is a detail of the corrosion on the Kneeling Satyr. Analysis revealed that the corrosion products were sulfides. Not all of the bronzes in the cases were effected to this extent. It appeared that there was a source of sulfur contamination in these galleries but after extensive investigations over several years the source could not be positively identified. Ten years after this problem was recognized the galleries were re-organized. One of the marble wall panels was removed in a test to see if it was possible to remove the panels without damaging them. It was then that the source of the sulfur contamination was discovered. It was found that the stone masons who constructed the galleries did not reinforce the panels as the contract called for but rather they used a technique know as ‘rodding’.

Detail of *Kneeling Satyr* Showing Sulfur Related Corrosion
Rodding involves cutting a shallow channel in the back side of a stone slab, placing a metal rod in the channel and filling the channel with an adhesive, usually an epoxy these days. In the case of the marble panels in our Ancient Art galleries the adhesive used to fill the channels was molten sulfur.
These are images of the backs of a marble panel and a panel fragment. There is an exposed surface area of sulfur of approximately sixteen square feet on the back surfaces of the panels in the two galleries. The estimated weight of the sulfur is 860 pounds. The backs of these panels are inaccessible so there is no way to either remove the sulfur or to coat it with a non-permeable material. The only viable solution to preventing the sulfurous air from entering the wall cases was to seal the backs of the wall case panels.
The wall cases were de-installed and Royco (type unknown), an aluminum and plastic laminate vapor barrier material developed for the military, was adhered to the back of each panel with Beva 371 film. Here one of our technicians is ironing the Beva and Royco onto the back of one of the case panels. After the wall cases were re-installed and sealed copper, lead, and silver coupons were placed in the cases to monitor for sulfur fumes. After fifteen years now the coupons do not display any signs of sulfur related corrosion.

In conclusion, sulfur can enter the museum through collections or be part of the building fabric itself. Most of the examples shown here have a very remote chance of causing corrosion except when the sulfur containing object is in a sealed display case or if sulfur laden air concentrates inside the case from an external source. Sources of sulfur within the building may be the hardest to track down as the since may be hidden behind wall, ceilings, or under the floor. If called upon to consult with foreign museums it should be remembered that building standards and construction materials used in other parts of the world may not be as strict they are in North America. Proper identification of all materials from which works of art are made is critical.
Quantitative X-ray Fluorescence Methodology for Examination of Cultural Heritage on Paper

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Quantitative vs. qualitative XRF—reasons to persist:

- Paper is a common denominator in terms of substrates in much of LC collections
- Paper-based materials have a similar matrix, i.e., cellulose (carbon) with trace metals derived from papermaking process and treatments
- Non-invasive XRF is often first line of analysis and desire to qualify results in terms of “a lot” or “a little” is very strong
Value of quantitative or semi-quantitative XRF results:

- determination of limit of detection (LOD)
- provenance/method of manufacture information
- treatment history information
- condition information
- treatment monitoring
Problems calibrating XRF spectra:

- differences in scattering of X-rays (baseline shape) caused by
  - material density
  - material thickness
- other matrix effects
  - inter-element interactions
  - element interferences (overlaps)
- sample non-homogeneity
Instrument and common instrumental parameters used in Preservation Research & Testing Laboratory at the Library of Congress.

- **Bruker TurboTracer**: SDD detector, Rh anode
- **Usual settings**: 
  - 15 kV, 55μA, Ti filter
  - OR 40 kV, 20μA, Ti filter
  - 180 s exposures; vacuum pumping
Approach:

- **Reference calibration samples**
  - Single and multi-element doped Whatman paper with ICP-MS metal concentration validation
  - XRF calibration standard films (Micromatter) + blank Whatman paper

- **Processing**
  - Bruker Calprocess program (interfaces with S1 PXRF operating software)
  - Excel calibration plots and calculations using regions of interest (ROI) and baseline subtraction defined in Artax software

These are the most feasible and practical methods that were found.
The overlaid XRF spectra of a blank piece of Whatman filter paper (black) and an historical 18th century paper from Fabriano, Italy (blue) show that, even without normalization, the scattering characteristics of the two samples are similar at the instrumental settings shown. This indicates that the Whatman filter paper has a suitable matrix for making reference materials.
The same two spectra are normalized to the Compton scattering hump here. This operation allows for minor adjustments in sample thickness before quantification of peak intensities.
The overlaid XRF spectra of the same blank piece of Whatman filter paper (black) and historic Fabriano paper (blue), show that scattering characteristics of the two samples remain similar at other instrumental settings, as shown. Calibration curves were constructed using Compton normalized spectra of the doped reference papers at both sets of conditions (15 kV/55 µA or 40 kV/20 µA with Ti filters).
The set of reference calibration papers used in this study were the first to be manufactured and were not optimal. Despite their flaws, the reference set has proved to be useful for method development and rough quantifications. The reference sample manufacture consisted of immersing the papers into salt solutions and air drying on a sheet of glass in the hood. The drying method was, however, too slow to avoid wicking of metals out to edges, resulting in non-homogeneous distribution. The papers were therefore analyzed only in the middle areas, which were found to be relatively homogeneous.
The Micromatter standard films have the obvious advantage of pre-certified concentrations. These were recommended for use by Dr. Michael Glascock.
The blank Micromatter films have a serious disadvantage for use as paper calibration standards due to significant scattering and intensification of peaks, presumably arising from the Mylar (red spectrum). As shown in comparison to the blank Whatman paper spectrum (black), intensification of peaks associated with the instrument materials (Ti, Ca, Cu and Zn) leaves artifacts after Compton normalization. Slightly better matrix matching can be achieved by placing a piece of blank Whatman filter paper onto the films, with the film lying closer to the detector (green spectrum). The filter paper appears to dampen, but not completely diminish, the scattering effects, as seen in the circled areas and the Ti peaks. An additional disadvantage of the films is that repeated use can lead to abrasion, so that certified values will eventually be incorrect.
Processing of data (creation of calibration curves)

- Advantage of Calprocess: can be used conveniently in S1 PXRF
- Disadvantage of Calprocess: complicated to use and cannot see the curves created
- Advantage of using ROI (Artax)/Excel method: easy and can evaluate every aspect of curves created
- Disadvantage of ROI/Excel: somewhat laborious and can make mistakes
The XRF spectrum of a multi-element doped paper sample (filled) is shown overlaid with that of a blank Whatman filter paper (black line), using Artax software (Bruker, Inc.). This software allows definition of regions of interest (ROIs), shown by wide areas superimposed on elemental peaks. The elemental table at the lower right lists potential interferences in any ROI and helps define appropriate start and end energies, as shown for Fe. The area of each ROI under any selected elemental peak is given for both gross and net counts after background (blue line) subtraction; the table (bottom left) can be copied and pasted into a spreadsheet. In this method, reference and sample spectra have been normalized as a group to the Compton peak of the blank Whatman paper or blank film + Whatman paper, and net counts have been used.
This slide shows two resulting calibration curves, where concentration is determined by ICP-MS and net ROI intensity values are given by Artax ROI definitions after background subtraction, as outlined in the previous slide. The curves are quite linear in these concentration ranges. It is important to limit the concentration ranges to those applicable to collection (i.e., sample) items, since a linear relationship may not be maintained at higher concentrations. Of the elements calibrated in this work, only potassium showed a second order relationship, rather than a linear one. The spread observed here in each concentration region represents both reading error, which is relatively small (as seen at low concentrations), and non-homogeneity in reference sample set, which is relatively large at high concentrations. As previously mentioned, these reference samples are not a final set. Production of better-quality samples in the future will tighten up clustering on the curves and the resulting precision. Additional validation of concentrations by other analytical techniques will correct slope accuracy.

Note that the curves are not forced through zero in order to account for the small Fe peak that is present due to steel parts in the instrument. Note also that the curves include data from multi-element samples, which fit nicely, indicating that any inter-element effects on Fe and Cu are low or negligible at these concentrations.
Initial Fe and Cu curves produced from the Micromatter films (with Whatman paper backing) show excellent correlation when forced through zero, which appears to partly compensate for scattering artifacts in these regions, as previously described. However, the total contribution of the film scattering effect is not well understood. Note that the limited data set shown here is a result of keeping readings for each film to a minimum, since reference films can easily be abraded through use.
Calibration of Ca using the doped papers (left) shows a linear relationship in the limited concentration range represented; this range is appropriate to historic materials encountered in collections. Note the spread of values at higher concentrations again, most likely arising from non-homogeneity in the reference samples. In addition, note that ICP-MS validation was only conducted on one set of samples, so that further validation both of more samples and in another laboratory is necessary for good accuracy in this case.

The initial Ca Micromatter (with Whatman paper backing) curve, in contrast, appears problematic, as is easily seen. Curves for Micromatter films of all elements produced using 40 kV and 20 µA appeared even worse, probably due to magnification of Ti, Rh, and other artifacts that occur at this higher power setting.
The papers shown are from a set of test papers used to see how well different calibration curves predict metal concentrations, which were determined for K, Ca, Fe, Cu, Zn and Pb by ICP-MS. These papers were collected by Sylvia Albro for her research into the history of papermaking in Fabriano, Italy from the 17th – 19th C. They are not part of the LC collections and can therefore be cut up.
This table shows concentrations calculated from different methods for select samples; in the case of multi-element doped papers, results are calculated from curves that were produced without those individual samples. The Fabriano paper results (Viterbo and Iesi papers) are produced from one reading only on each paper, so that the margin of error may be much greater here due to likely uneven distribution of the metals. Nevertheless, these initial results overall look quite good when calculated by the top two methods, as shown by error (percent difference from ICP-MS value) that is generally <20% above detection limits (LOD-see slide 23), with some exceptions. The most notable exception is the Viterbo 1876 paper, which shows error that is relatively high across the board by all three methods. This is due to altered scattering in the matrix caused by relatively large amounts of Zn, and is a good warning against trying to quantify results for any sample that is not well matrix matched to the calibration standards. The altered scattering is easily observed in the baseline of the raw spectrum of this sample (not shown). Note also that the Calprocess method utilized here benefited greatly from calibration curves that were plotted out in Excel from ROIs defined in Artax (the second method), which showed whether curves were linear or second order and therefore gave guidance for manipulations allowed in Calprocess.
Two papers were presented about the Ptolemy *Geographia* technical study at 2011 AIC meeting, and have also been published in the AIC's Book and Paper Annual:


A central aim of this study seeks to explain why only 7 out of 47 hand-colored maps in the Ptolemy Atlas, all containing verdigris pigment, are in poor condition. Note that identification of verdigris was confirmed by polarizing light microscopy and other means. For example, the Quinta Europa Map (left) is cream colored and in good condition. In contrast, the Septima Asiae Tabula (right) has verdigris pigment-induced offset and discoloration, and is now medium brown and in fairly poor condition. In addition, as shown in lower right inset, white accretion/particles are observable on this and other maps in poor condition.
Further inspection revealed that there are three types of paper in the volume in terms of watermark. Two of the three different types of paper in the volume are shown here in visible and transmitted light. The maps printed and colored on laid paper with a crown watermark (upper and lower left) are generally in very good condition and exhibit expert papermaking qualities: even fiber distribution and mould lines. In contrast, maps and text on the unwatermarked paper (upper and lower right) appear inferior in terms of condition, flexibility, fiber distribution and mould line regularity. This is described in more detail in: Albro, Sylvia, John Bertonaschi, Lynn Brostoff, Daniel De Simone, Fenella France, and Eliza Spaulding. Solving the Ptolemy Puzzle, *Book and Paper Annual* (2011): 5-8.
XRF analysis of maps in varying condition revealed distinct differences in elemental profiles that appear to correspond to these different papers and their respective conditions. As exemplified by overlaid spectra from multiple spots on the paper substrates (away from colorants) of the Quinta Europa and Septima Asiae maps, poor condition substrates are characterized by relatively larger amounts of S, K, Fe and Cu (red spectra) and good condition substrates are characterized by relatively higher levels of Ca (blue spectra).

Detection of K and S here suggests the presence of K-alum, which was also confirmed by Raman and FT-IR spectroscopy. Note that these elements are also present in the map in good condition, but at much lower levels, such as may be expected from K-alum that is added to harden gelatin sizing. However, UV imaging (upper right inset) and FT-IR analysis (not shown) strongly suggest that the quite high levels of K alum detected on this and the other six maps in poor condition are the result of a gelatin solution having being brushed onto their surfaces. The red spectra here also show relatively greater amounts of Fe and Cu, the latter possibly as a result of brushing the alum solution over the Cu-containing pigmented areas, thereby spreading Cu ions in the paper.

This example raises the question of whether the concentration of various elements affects longevity in the paper substrate. In this case, *quantitative* XRF data was applied as an aid to understand the condition of the artifact.
Quantitative XRF also allows us to define the limit of detection (LOD) in an XRF experiment, so that we understand what lack of detection for any element means. In this illustration, LOD is defined for Fe and Cu at 15 kV, 55 µA and with a Ti filter from samples of known concentration that were produced for a former LC study on the effect of trace metals on paper longevity conducted by C. Shahani (reference above), selected results of which are shown at right. For Cu (upper left inset), XRF spectra of a blank Whatman paper and the Shahani study control paper show indistinguishable peak intensity; i.e., 1-2 ppm Cu is <LOD. In the case of 185 ppm Cu, the peak intensity is near LOD, within experimental error. On the other hand, Shahani study control paper shows that 200 ppm Fe (below left inset) is easily distinguishable from a Whatman blank paper containing about 10 ppm Fe.

In relation to paper longevity and condition as described by the Shahani study, quantitative XRF thus allows a simple means of identifying artifacts on paper that contain levels of Fe and Cu that may be expected to compromise their aging behavior.
This table shows calculated concentrations of different elements by different calibration methods for the paper background in the same two maps from the Ptolemy Atlas. The relative standard deviation (RSD) shown is the variation of this element as detected in different spots on the sample.

In order to get some idea of the calculated concentration accuracy, we obviously cannot conduct destructive ICP-MS analysis here, but we can visually compare peak intensities in different regions that have a linear concentration relationship to papers of known concentration (normalized), as shown (insets on right), where: black = Whatman No. 1 and Shahani Cu-doped papers; purple-pink is Ptolemy Septima Asiae and lime green is Ptolemy Quinta Europa; blue is Fabriano paper Montefiascone; red is Fabriano paper Viterbo (Dazio); and green is Fabriano paper Iesi.

Results of visual inspection of the overlaid, normalized spectra indicate that Cu concentration in the selected maps should be <LOD (less than 60 ppm) in the Quinta Europa map and about 400-800 ppm in the Septima Asiae map. Fe concentration should be about 200 ppm or less in the Quinta Europa map and about 800 ppm in the Septima Asiae. K concentration is hard to judge visually, especially since it was shown not to be a linear function. Nevertheless, since the Montefiascone paper is known to contain 1227 ppm of K, it is not unreasonable that Quinta Europa could contain about half of this quantity and Septima Asiae could contain about 1/10 of this quantity. The Ca concentration in the Quinta Europa map should be quite a bit higher than the Viterbo (Dazio) paper, which is known to be 4300 ppm, and in the Septima Asiae map should be about the same as this value. Reasonable calculated values are marked in green or, when more speculative, in italics.

These visual comparisons indicate that the ROI-Excel calibration method, as well as the Calprocess method, appear to be reasonable methods for quantification of most of these elements at the stated instrumental settings. It is not clear, however, why the calculated values for Fe are somewhat high other than the non-homogeneous distribution of Fe in the paper substrates.
Quantitative XRF results for maps and text on different quality papers are shown above. We may conclude the following from these results:

1. Calculated Cu values appear fairly accurate, since visual comparison to known papers shows that the Text p.167 and Quinta Europa have Cu levels at about or below the Shahani control paper, which is 3 ppm, and the other papers are in between the Shahani Cu-doped IV and V study papers, i.e., between about 400 and 200 ppm. These values are close to those reported above and calculated by the ROI-Excel Method. In the Shahani study, the latter levels of Cu were shown to markedly compromise paper longevity. Therefore, we can conclude that the treatment intervention not only spread Cu around in the paper substrate, but contributed directly to acceleration of the paper’s aging behavior.

2. Nona Asiae, as well as Septima Asiae and Text p. 167, have Fe concentrations at about the same level as in the Shahani Fe-doped IV paper, i.e., closer to 500 ppm. Calculated Fe concentration for the Quinta Europa should be about 200 ppm Fe when compared visually with the Shahani papers. This difference in relative amounts of Fe appears to be another indicator of differences in inherent paper quality.

3. K and Ca: Text p167 should have K and Ca levels at about the same as in the Fabriano Roma and so are calculated approximately correctly. The comparison of Ca:Fe ratios lends support here for inherent differences in the original paper quality between the crown watermarked and unwatermarked papers, which could explain differences in condition apart from the evident treatment intervention at a later date.

Note that the Ca:Fe ratios may be best indicators for paper condition, in combination with the absolute values for Fe and Cu.
The application of this quantitative XRF analysis method has proved very useful for treatment planning and monitoring. This table shows elemental profiles in the paper substrates before and after blotter washing of Nona Asiae Tabula (after disbinding) with a 50:50 mixture of ethanol: water. Results show a diminishment of K after treatment, implying only partial removal of the K-alum coating. Since K levels in the Quinta Europa are about 2500 ppm, possibly due to added sizing before application of colorants, and these levels appear relatively benign in terms of an affect on the map condition, the decision was made to continue treatment to further reduce K to about that level. Note that the levels of Ca and Fe are essentially unchanged after blotter washing. Note also the apparent increase in RSD of K after treatment, which indicates that the treatment resulted in a non-uniform distribution of K.

<table>
<thead>
<tr>
<th>Map</th>
<th>Nona Asiae (no WM, treated) ave. ppm</th>
<th>variation (rSD)</th>
<th>Nona Asiae (blotter washed) ave. ppm</th>
<th>variation (rSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>11000</td>
<td>15%</td>
<td>7100</td>
<td>43%</td>
</tr>
<tr>
<td>Ca</td>
<td>4600</td>
<td>3%</td>
<td>4400</td>
<td>6%</td>
</tr>
<tr>
<td>Fe</td>
<td>810</td>
<td>5%</td>
<td>750</td>
<td>21%</td>
</tr>
<tr>
<td>Zn</td>
<td>80</td>
<td>4%</td>
<td>140</td>
<td>11%</td>
</tr>
<tr>
<td>Ca:Fe</td>
<td>6</td>
<td></td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
Summary

- Quantification of trace elements in paper is not impossible, just difficult
- Evaluation of scattering and matrix effects essential for any quantification
- The preferred method found so far for K, Ca, Fe, Cu and Zn calibration is use of lab-made doped Whatman filter paper and processing curves with ROI-Excel method – can achieve \( \leq 20\% \) accuracy
Future Work

- Workshop(s) to make improved set of reference papers to share with colleagues
- Reference standardization through multiple analyses for improved accuracy
- Calibration of more elements (S & Pb, Mn & Cl, photo-related)
- Application of quantification to routine analysis and treatment monitoring
- Evaluation of statistical-based processing methods
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Methods for Crude Oil Removal from Fort Livingston Grand Terre Island, Louisiana

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Methods for Crude Oil Removal from Fort Livingston Grand Terre Island, Louisiana

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Fort Livingston is located on Grand Terre Island in Jefferson Parish, Louisiana. The MS252 wellhead is located ~165 km (~100 statute miles or ~90 nautical miles) offshore to the southeast (location marked with circular yellow icon).

National Center for Preservation Technology and Training (NCPTT) staff made three visits -- the first at the request of the Louisiana (LA) Office of State Parks (June 2010), second in September 2010 at request of the Unified Area Command (UAC), the organization responsible for coordinating response to the Deepwater Horizon oil spill, and the third at the request of the LA Office of State Parks (July 2011).
Aerial view of Fort Livingston. Barataria Pass lies between Grand Isle and Grand Terre. The Gulf of Mexico is to the south. The southwest facing wall of the fort is partially submerged, and the southeast wall was destroyed in a hurricane in the early 20th Century. A concrete wave break was installed within the last two decades to protect the site from further weather damage. A portion of the former Louisiana Department of Wildlife and Fisheries marine lab is in the upper right in the photo.
Older photo of Fort Livingston looking west, from the National Register of Historic Places. Fort Livingston was listed in the register in 1974. Construction of the fort began in 1841. The fort was occupied during the American Civil War but had not been completed at that time. The site is managed by the Louisiana Office of State Parks as part of Grand Isle State Park. Erosion has been a problem at this site since the time construction began. Today portions of the fort are partially submerged, even during low tide.
The first several slides will give an idea of the setting, the materials at the fort, and the extent of oil contamination of the site. The National Register nomination and other documents indicate that the brick was produced in Mississippi or Florida. Lintels and stairs are made of a white, fine-grained granite.
Storm damage has exposed the tabby walls (tabby is a unique Southern coastal building material made from a mixture of lime, sand, and oyster shells). A bathtub ring of oil can be seen on the southern, partially submerged portions of the fort, and is obvious at the high water line on the beach to the left in the photo.
Brick facing covers tabby walls. Shells for the tabby were reportedly gathered from local middens.
The tabby is exposed in some of the interior spaces. Note the oil contamination at the base of the wall. Water enters this room (one of the casemates, or fortified gun emplacements) during high tide.
This is the same location as that shown in the previous slide. Note the oil at the base of the wall that remains from the June 2010 contamination of the site.
Looking west in the same room, June 2010, showing patches of oil stranded on the sand that has been deposited over the floor of this room over time.
Remaining oil in the same room, July 2011. The interior portions of the fort were not included in the beach and wetlands cleanup efforts.
Northwest (left) and southwest (right) facing walls of the fort. The site is now protected by a rip-rap (mixed rock rubble) wavebreak visible in the background to the right. Note the oil sheen and globules on the surface of the water, and the debris that has collected against the wall to the left.
This area was originally a “moat” that surrounded the fort. The wall to the right is the location of the cleaning tests in performed in July 2011.
Southwest facing wall showing the condition of the exterior brick walls and the oily “bathtub ring” at the base.
Crude oil in the moat area at Fort Livingston. The wall in the background is the location of the cleaning tests performed in July 2011. The lighter colored material in the foreground are portions of the boom that broke away and floated into this area. The pom-pom like texture is meant to increase the surface area and therefore to take up and trap more oil. The outer portions of the site (beaches and marshes) were cleaned by the response crews. The interior portions were not cleaned because Fort Livingston is also an archaeological site and a decision was made to not disturb the interior spaces. No large-scale cleaning of the structure itself has been undertaken. Contaminated trash and debris were removed during the beach cleanup.
Crude oil on the granite stair treads and on the surface of the water. This is in the south facing bay that now adjoins the courtyard of the fort. The stairs lead up to the terreplein, the top surface of the ramparts on which cannon would have been placed. Note the contamination of the stair treads from oil transferred from boots/shoes.
Looking southwest inside the fort, water intrudes into the fort during high tide. In the foreground is the corner of the interior courtyard. In the background is one of the casemates (fortified gun emplacements) that has been contaminated with oil.
Looking southeast from inside the fort.
Closeup of the tabby. Secondary contamination at the site occurred when unauthorized visitors transferred oil from their hands and shoes/boots to other areas of the fort.
These are the criteria used to select cleaners for testing. Because any products used have the potential to enter a waterway (the Gulf of Mexico), we considered cleaners that could be approved for use in this setting. These products are listed on the Environmental Protection Agency’s National Contingency Plan Product Schedule (NCP Product Schedule). During our tests, runoff from cleaning was collected using puppy training pads.
Cleaners were chosen based on their composition. Both solvent-based and surfactant-based cleaners were tested. In addition, a surfactant with enzymes was tested.

<table>
<thead>
<tr>
<th>Types of Cleaners</th>
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<tbody>
<tr>
<td><strong>Composition</strong></td>
</tr>
<tr>
<td>Solvent based</td>
</tr>
<tr>
<td>Surfactant based</td>
</tr>
<tr>
<td>Surfactant plus enzymes</td>
</tr>
<tr>
<td><strong>Delivery Method</strong></td>
</tr>
<tr>
<td>Spray/agitate</td>
</tr>
<tr>
<td>Poultice</td>
</tr>
</tbody>
</table>
Katherine Langdon performing the solubility test. She added 2-3 g crude oil to a test tube, then added 9-11 mL of a cleaner. She allowed the mixture to stand for 5 minutes and recorded initial observations. She then used the vortex mixer at low speed to stir the mixture for 1 minute and made additional observations 5 minutes after mixing. The sample was mixed again for 1 minute on high speed and additional observations were made 5 minutes after mixing. The samples were allowed to sit for 2 days, then additional observations were made.
Solubility testing done by Katherine Langdon. The products tested included some from Environmental Protection Agency’s (EPA) NCP Product Schedule, some that are readily available at hardware and grocery stores, some that are commonly used in conservation, and others that were simply available in our lab for comparison.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goo Gone Pro-Power</td>
<td>Gel</td>
</tr>
<tr>
<td>Gel</td>
<td>Resolve</td>
</tr>
<tr>
<td>Shout Advanced</td>
<td>Shout Triple-Acting</td>
</tr>
<tr>
<td>De-Solv-It Citrus Solution</td>
<td>Micro-90</td>
</tr>
<tr>
<td>Lysol Concentrate</td>
<td>Mr. Clean</td>
</tr>
<tr>
<td>Simple Green</td>
<td>Hy-top Glass Cleaner</td>
</tr>
<tr>
<td>VeruSolve Marine 200HP</td>
<td>Vulpex soap/water 1:10</td>
</tr>
<tr>
<td>100% mineral spirits</td>
<td>Vulpex/mineral spirits 1:6</td>
</tr>
<tr>
<td>Citrikleen XPC</td>
<td>Dawn classic detergent</td>
</tr>
<tr>
<td>Marine Green Clean</td>
<td>Biz Stain Fighter in water</td>
</tr>
</tbody>
</table>
The cleaners highlighted were used in field testing at Fort Livingston because they appeared to perform well in the lab.
Katherine Langdon selecting bricks for use in the study.
Katherine Langdon cutting bricks to size. The surface to be tested was the exterior (fire skin) of the brick.
Sample preparation and measurements. Samples were cleaned after cutting to eliminate cutting dust. Samples were photographed using a KODAK color card as a reference. Samples were equilibrated at 70% relative humidity in a humidity chamber before weighing. Analyses included FT-IR and colorimetry.
Crude oil samples were collected in June and September, 2010 from Fort Livingston, Grand Terre Island, Louisiana. Oil samples were collected in glass jars to minimize loss of volatiles.
Oiled samples, and unoiled control samples, were weathered in a Q-Labs QUV accelerated weathering tester.
Samples were photographed using a KODAK Color Card for reference. Sample number are indicated by the blue sticky notes. Shown here are a control sample (001N) and one of the test samples (A11Y). From left to right these show the test sample before oiling or weathering, after oiling but before weathering, and after weathering. The crude oil required warming in order to be spread across the surface of the sample. Note that the weathered oil appears to have been absorbed into the sample. As the sample was warmed in the QUV during weathering, some of the oil melted onto the sample holder, and any remaining volatiles were released from the sample. The remaining oil had little to no odor after weathering. The samples were weighed before and after oiling as well as before and after weathering.
June 2010 pre-cleaning.
June 2010 after cleaning. At this time it was relatively easy to remove the crude oil through standard cleaning techniques. We applied a surfactant-based cleaner by spraying, allowed it to dwell on the surface for 2 minutes, another small amount the cleaner was applied, the cleaner was agitated for 2 minutes with a soft brush, then the surface was rinsed with clean water. When we returned in September 2010, we performed some additional cleaning tests on an area that had not been cleaned previously. At this point the oil had lost much more of the volatile component and had become more sticky and tarry. We found that it was much more difficult to remove the crude oil after it had weathered for several months.
September 2010, softer brick (left face) and harder brick (right face). Both faces shown were cleaned in June 2010.
July 2011, softer brick (left face) and harder brick (right face). Both faces shown were cleaned in June 2010.
Northwest facing wall, within the “moat” at Fort Livingston, before the July 2011 cleaning tests.
Katherine Langdon using the standard cleaning method, in which the cleaner was applied by spraying, allowed to dwell on the surface for 2 minutes, another small amount was applied, the cleaner was agitated for 2 minutes with a soft brush, then the surface was rinsed with clean water.
Agitation for 1-2 minutes.
Erin White applying a poultice. A poultice method was also tested. A cleaner was mixed with a clay poultice to the consistency of peanut butter, applied, and allowed to dwell on the surface for approximately 16 hours. Once dry and beginning to crack, the poultice was flaked off and the surface was rinsed with clean water.
Poultice tests after approximately 16 hours. Test patches were covered with plastic overnight so they would dry slowly.
The clay poultice had dried slowly overnight. The cracked surface indicated that it was dry enough to remove. The piece that is being held shows some of the oil residue that was removed with the poultice.
Overview of the test area with labels indicating the cleaning method tested. The test patches on the left, indicated by the red arrows, were cleaned using a poultice. The patches on the right were cleaned by the standard spray application and agitated with a soft brush.
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NCPTT
Ed FitzGerald
Erin White
Atomic Layer Deposition Films as Protective Coatings for Silver

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4 Director of Conservation, The Walters Art Museum
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The American Institute for Conservation of Historic and Artistic Works (AIC)
Albuquerque, NM, May 8-11 2012
This project is part of a National Science Foundation (NSF) new direction for applications of nanotechnology initiative, and is one of first projects funded by SCIART, a NSF grant program with the focus of applying cutting edge scientific techniques to the field of art conservation.
The team members come from the University of Maryland and The Walters Art Museum with Beneq as an industrial partner.
Many cultural heritage institutions use mechanical polishing and the application of nitrocellulose lacquer to protect silver objects from oxidation/corrosion. The surface is reconditioned to remove the old nitrocellulose coatings and/or tarnish layers. Nitrocellulose (NC) is then sprayed, dipped, or brushed onto the silver surface. Depending on the size and complexity of the object, this can take between 3 to 40 or more hours per object. In the case of the walking lion sculpture shown here, the object is very detailed and complex so it may take even longer. The NC film last ~10-30 years depending on the museum environment – less for open air/dusty environments. For institutions (e.g. The Metropolitan Museum of art) with large silver collections of thousands of objects (~6000) with each object requires a minimum of 3 hours of reconditioning and coating, it would require ~8.5 years to coat all the objects. Given the lifetime of the film, the museum would be in a constant cycle of coating and recoating.
Pictured: Amy Marquardt in front of the University of Maryland’s (UMD’s) Beneq TFS 500 atomic layer deposition (ALD) machine. For experiments, we tend to coat small (square centimeters) of sterling silver or silver/copper that’s been coated on silicon wafers. This TFS 500 has been outfitted with an inner chamber where the ALD gases and samples to be coated are placed. This decreases deposition time and likely increases uniformity. The large barrel contains heating elements that are not exposed to the coating gases. The Beneq site shows photos with trays of jewelry in the same reactor, where no inner chamber is used. In that case, many more samples can be coated, and the entire chamber is exposed to the ALD gases. The complexity of the equipment resides in the gas flow and heat control system, which can be adapted to a chamber of any size and shape.
The ALD deposition process is a series of sequential self-limiting reactions such that the surface builds a sub-monolayer of alumina per cycle. For the deposition of alumina, the silver surface is exposed to trimethylaluminum (TMA – note that the cartoon is generic. TMA would be $M = \text{Al}$ and $L = \text{methyl}$ with only 3 methyl groups), which reacts with any surface hydroxyls. The chamber is purged of the TMA to avoid chemical vapor deposition. Water is introduced into the reactor, and the Al-methyl groups react to form Al-OH and methanol. The chamber is evacuated and the cycle repeated. This process provides incredible film uniformity and thickness over rough surface.
The left plot shows how the thickness is controllable by selecting the number of ALD cycles. The right plot shows the deposition into very thin (less than 100 nm wide) and deep (~1 micrometer) channels. The black lines are the ALD deposited coating. The deposition thickness into these trenches is incredibly uniform and unmatched by any other vacuum deposition technique.
For our experiments, we use these conditions to pre-treat samples prior to depositing. It is likely that fewer rinses in fewer solvents will also work, however, we go through this process to insure a uniform coating with as few surface defects as possible to allow for the evaluation of the physical properties of the films (rather than the properties of films with defects from underlying surface dust and oils).

Bulk sterling refers to sterling silver purchased from a foundry.

Lab deposited is a very thin film of sterling silver (100’s of nm) deposited using thermal evaporation onto a silicon wafer.
There are four main areas to address prior to implementing/recommending this method for use on cultural heritage objects.

Can ALD be used on art objects?

**Effectiveness**: Lifetime of ALD coatings vs. nitrocellulose films

**Reversibility**: Efficacy of removal techniques and the effect on the starting surface.

**Application acceptability**: Surface preparation and deposition conditions

**Appearance**: Visual effect on the way a coated object reads
Primary Research Paths:

**Effectiveness:** Use accelerated aging (elevated temperature or \( \text{H}_2\text{S} \) concentration) to compare tarnish rates of ALD and nitrocellulose coated sterling silver.
- Evaluate patterned silver
- Evaluate silver with embedded polish particles
Develop coatings with improved barrier properties

**Reversibility:** Assess mechanical polishing and chemical removal
- Evaluate the surface before and after deposition and removal (composition and topography)

This presentation focuses on the effectiveness and reversibility of this process.
To evaluate the effectiveness of the coatings, we exposed coated and uncoated silver to accelerated aging conditions. This slide shows the progression of techniques used and the years of implementation. The thioacetamide chamber was implemented in 2006 at the Metropolitan Museum of Art’s Department of Scientific Research by Eric Breitung under the supervision of Dr. Marco Leona. Eric found the levels of $H_2S$ produced to vary widely unless fresh batches of thioacetamide were introduced to the chamber before each experiment. This process produces large amounts of hazardous waste and is not recommended. Aging using elevated temperatures (2011) was performed at UMD and provides information about the relative effectiveness of coatings, diffusion coefficients, and activation energies. While difficult and more expensive to produce, a controlled chamber with known $H_2S$ and water levels at ambient temperatures was also produced and used to allow accelerated aging at temperatures just above ambient to best reflect the acceleration of ambient aging conditions and allow for the quantification of diffusion rates of known amounts of $H_2S$ through the deposited films. This system is a sealed chamber with gas inlet and outlets, $H_2S$, temperature, and humidity sensors. The sealed chamber is placed inside of an insulated, warmed, box to prevent the condensation of moisture and allow more precise control of humidity.
Preliminary tests were performed by aging coupons in a chamber containing thioacetamide + water (a chemical reaction forms H$_2$S). We used the standard procedure described earlier, but depending on the freshness of solution, the concentration of H$_2$S varied – bare silver was always included as a control.

The main conclusions from this study were that ALD films showed the potential to protect silver better than nitrocellulose – especially in the case of sterling silver, which tarnished more rapidly than fine.

This was a preliminary study. The results were used as a guide for the NSF SCIART funded research, where a more detailed investigation into the effectiveness of commercially available ALD coatings, development of improved coatings, and the reversibility of the most promising ALD coatings is underway at the UMD and Walters Museum laboratories.
This is a comparison of fine and sterling silver coupons that have been coated with 10 nm of alumina. Samples were aged in the ambient atmosphere on a hotplate at increasing temperatures for 19 hours each, and the sulfide film thickness was determined using optical methods.

The step change in sulfide thickness at 173 °C, based on an evaluation of the literature, has been attributed to a phase change in the silver sulfide layer from acanthite to argentite. The rate of reaction at the silver surface with sulfide appears to be more rapid when the high temperature phase is present (data not shown), and a thicker sulfide film results. This reaction with the argentite phase is self-limiting as the color/thickness is the same between 206 and 240 °C.

These results led us to limit the temperature to 150 °C for future hotplate tests to avoid sulfide phase conversion.
Using thicker films and the controlled flow H₂S chamber for aging, nitrocellulose was compared to ALD coated sterling silver using colorimetry as the evaluation method. Shown is an a* b* LAB space plot where the center (0,0) represents a white sample, and the positive a* axis indicates reddening and the positive b* axis indicates yellowing.

Nitrocellulose films were both brushed on (double coating) and flow coated (double coating). ALD films ranged in thickness from 20-100nm.

Results:
1) The initial color of the ALD films varies depending on the thickness due to optical interference effects. The 20nm film shows a slight yellowing relative to the 70 and 100nm films. The 70 and 100nm films are very close in color to the uncoated silver sample. Both nitrocellulose films show a yellowing of the surface prior to aging. On the LAB space scale, a change of 2 is supposed to be observable by the naked eye.

2) Upon aging, the uncoated bare silver film shows a yellowing and reddening over time. The ALD coated films, however, do not change color/show no tarnishing, whereas the nitrocellulose films – especially the brushed on sample shows significant yellowing and reddening over time.
These are the Ag/Cu coated silicon samples used in the experiment from the previous slide after 30 hours of H2S aging.
The results from this experiment can also be evaluated using the delta E* 1976 values per the LAB space colorimetric output. This incorporates not only color change, but the density of the color change (grayscale...).

It is clear that the ALD coated films not only outperform NC for its ability to initially match but also maintain the color of uncoated silver.
Before implementing this process on culturally relevant objects, it is necessary to determine if the coating is removable without affecting the surface. It is known that amorphous alumina is soluble in aqueous sodium hydroxide, so we evaluated three concentrations of sodium hydroxide for their ability to remove the film while at the same time evaluating the amount of silver and copper removed from the surface into those solutions using inductively coupled plasma mass spectrometry (ICP-MS).

This slide shows our method for determining the time required to remove the alumina. Following the cartoon from left to right, if the polysulfide solution tarnishes the lower right corner of the coupon, we determined that the remaining alumina film was less than 2 nm thick.
The removal rates of alumina are NaOH concentration dependent. All concentrations show the ability to remove the alumina coating.
To evaluate the effect on the underlying sterling silver, ICP-MS was used to evaluate the solutions used to remove alumina coated and uncoated samples. At the same time, polishing was evaluated to determine how much of both Ag and Cu are removed in a typical polishing of a silver coupon as well as whether polishing with those same materials is a possible method for removing the alumina film.

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### Does NaOH affect sterling the silver surface?

<table>
<thead>
<tr>
<th>NaOH</th>
<th>5% (13m30s)</th>
<th>5% (10m30s)</th>
<th>5% (6m46s)</th>
<th>0.5% (15m30s)</th>
<th>0.05% (53m54s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated sterling</td>
<td>X</td>
<td>X</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>70nm Al2O3 on sterling</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td>Solution only</td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>X</td>
</tr>
</tbody>
</table>

### How does mechanical polishing affect the silver surface?

<table>
<thead>
<tr>
<th>Polishing</th>
<th>0.3um α-alumina</th>
<th>0.04 um ppt chalk</th>
<th>0.05um γ-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated sterling</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>80nm Al2O3 on sterling</td>
<td>x</td>
<td>x</td>
<td>X</td>
</tr>
<tr>
<td>Powder + swab</td>
<td>x</td>
<td>x</td>
<td>X</td>
</tr>
</tbody>
</table>

### Evaluate amounts of Ag and Cu removed from surface using each process via ICP-MS
Does polishing uncoated samples remove more or the same amount of Ag and Cu than NaOH solutions?
- Ag – polishing removes much more silver
- Cu – polishing removes about the same amount of Cu as the 5% NaOH
  - polishing removes more than the lower concentrations of NaOH

Polishing of coated samples required 15 minutes for 2.5 cm x 2.5 cm sample – not practical

Do NaOH treatments of coated samples remove more or the same amount of Ag and Cu than polishing?
- Ag – NaOH removes almost no Ag
- Cu - Lower concentrations of NaOH remove almost no copper

For controls ICP-MS was used to evaluate the adventitious silver and copper concentrations found in the polishing materials/etchants used. Amounts of precipitated chalk only, γ-alumina only, 5% NaOH only, 0.5% NaOH only, and 0.05% NaOH equal to that used to treat samples were analyzed via ICP-MS. The resulting quantities of copper and silver were subtracted from the concentrations found in the solutions and polishing slurries used on the coated and uncoated samples.
We are also in the process of evaluating the surfaces of coated and uncoated samples using scanning electron microscopy (SEM) and atomic force microscopy (AFM). In this case, where γ-alumina was used to polish an ALD coated surface, we observe particles of the polish remaining in the surface. This is a note to conservators that polishing can leave metal objects altered from their original surface, and we will need to evaluate the ALD process on samples with embedded polishing particles to determine if the coating can successfully coat over the particles and proved a continuous barrier to oxidants.
Summary

ALD provides superior tarnish resistance
  – Colorimetry a useful tarnish monitor

Coating removable with minimal loss of surface copper and silver using NaOH(aq)
  – Further analysis needed into other trace metals (Hg, Pb, Zn, …)
  – Analysis of surfaces before and after needed (SEM, AFM)

Coating removable with polishing
  – Time consuming
  – Leaves embedded particles
Acknowledgements and Publications

- Dr. Shy-Hauh Guo, Materials Science and Engineering, University of Maryland
- Dr. Karen Gaskell, Surface Analysis Center, University of Maryland
- Dr. Sami Sneck, Beneq

Presentations:
ACS March 2011: SCIART: Protection of Silver Objects from Corrosion using Atomic Layer Deposited Barrier Coatings
APS Feb 2012: Atomic Layer Deposition Films as Diffusion Barriers for Silver Artifacts
AVS Oct 2012: Improved Barrier properties for Anti-Tarnish Coatings on Silver Artifacts

Publications:
2012 Submitting to Applied Physics Letters, Tarnish Kinetics through Atomic Layer Deposited Oxide Barriers for Silver Alloys
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Digital Imaging Analysis of Writing Material using “Photoshop® Assisted Spectroscopy”

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A presentation of ongoing research on potential digital alternatives to traditional scientific methods of analysis.
The idea for this project developed as a combination of several fields and specific techniques including those listed on this slide.
The initial motivation for developing this method was to create a way to analyze the level of degradation in ballpoint pen ink, which is known to be particularly sensitive to light and oxidation.

Significant color shift is evident in the artwork on the right. The areas with darker ink were created with a different pen than the areas with disappearing ink. According to accounts from both the curators and the artist, the ink color has shifted significantly while the document was stored in a “proper” environment. Detecting ink likely to exhibit changes at an early stage may enable conservators to take preventive measures based on the ink composition.

The scope of the problem is broad. Beginning in 1945 the ballpoint pen began to be produced and within a decade began to be used widely. Many different ink formulae, many of which are either undocumented or protected trade secrets, contribute to a wide range of components that must be considered.
The key to a ballpoint pen is the ball. This ball acts as a buffer between the material on which you are writing and the quick-drying ink inside the pen. The ball rotates freely and rolls out the ink as it is continuously fed from the ink reservoir. Ballpoint pen ink is very thick and quick-drying. It is thick so that it doesn't spill out of the reservoir, but it is thin enough so that it responds to gravity. That is why a normal ballpoint pen cannot write upside-down -- it needs gravity to pull the ink onto the ball.
Of course, analysis of ink on historic documents doesn’t start with a ‘fresh’ sample. As with most other objects, documents with ballpoint pen ink arrive in the conservation lab after degradation has begun. One of the problems conservators face is that the original color is not often documented, and therefore the degree of color shift is difficult to accurately determine.
The document which is a driving force in this project is Marshall Nirenberg’s Genetic Charts – a series of important documents in scientific history. The charts contain original data from experiments that determined how protein sequence was dictated by the sequence of precursor ribonucleic acids (RNAs).

James D. Watson and Francis Crick discovered that deoxyribonucleic acid (DNA) was in the shape of a double helix. Identifying the shape of DNA was a major breakthrough in genetic research and Watson, Crick, and Maurice Wilkins won the Nobel Prize in Physiology or Medicine in 1962. What was not known was nature’s genetic code; how a DNA sequence is translated into an RNA sequence that is in turn translated into a protein sequence. By 1965, Nirenberg, with help from his colleagues at the National Institutes of Health (NIH), had become the first to completely solve the sequencing of the code. The language of protein synthesis was understood. Once completely solved, the genetic code could be expressed in a chart. As a result of the work that was recorded on these charts, Marshall Nirenberg was awarded the 1968 Nobel Prize in Physiology or Medicine.

Nirenberg understood the far-reaching implications of his work, which provided the foundation for genetics research ranging from gene therapies to Dolly the cloned sheep to the Human Genome Project. Once scientists could read the code, the possibilities for genetics research expanded and continued to expand.

http://history.nih.gov/exhibits/nirenberg/index.htm
The Nirenberg chart consists of multiple sheets of 1950s Addison Wesley lined paper which has been joined with pressure sensitive tape. The tape is in an oxidized state, but the carrier is an important part of the chart because ink was applied over it during the creation of the chart.

The chart was professionally scanned at 500 ppi using a Cruse Synchron Light Scanner. The primary purpose of the scan was for the creation of high quality facsimiles. Conservators chose to use the scan for a secondary purpose as well – to attempt analysis of ink using Photoshop® Assisted Spectroscopy.
The final goal of this analysis is to determine the optimal storage and display environments for the charts. In order to do so, the ink must be analyzed to determine the best way to slow degradation. A comparison of different charts from the same period (all on the same substrate) is one step in this process.
National Library of Medicine staff at NIH are fortunate to be able to work with two of the original technicians that worked on the charts – Norma Zabriskie Heaton and Theresa Caryk. They have provided essential information to the project team regarding materials and practices during the period of chart creation. Additionally, they are cross-analyzing data from the chart with data in their lab notebooks and linking that information to journal publications in order to provide a degree of data validation that is rarely encountered.
There are many non-destructive analytical techniques available for ink analysis. Photoshop® Assisted Spectroscopy is one we would propose as a method of broad spectrum analysis of color shift. The technique can be performed using only a good quality scanner and a program that allows the user to monitor RGB values on a pixel-by-pixel basis. We found Photoshop® to be optimal for this purpose, but we recognize that other programs with this capability may exist either now or will exist in the future.
Many different factors affect color shift in ballpoint pen ink. Like most media, external factors in the environment such as light, temperature, oxygen content, and humidity are important. However, because of the nature of ballpoint ink there are other factors, too. During writing, friction created between the ball, substrate, and casing generates a lot of heat. Additionally, ink components added in order to make writing easier may contribute to color shift.
Today, the ballpoint pen industry is a large one in which consumers have a wide choice of material from which to choose. Unfortunately for conservators, this drives companies to produce materials that are price-competitive, a process which often involves reduction in the quality of materials and components. The focus is usually on the cost of the pen and the ease of writing, not on the longevity of the ink.
Some early ballpoint ink components can be determined based on the year the pen was manufactured. The ink formulae started out relatively simple, but have grown more complicated as the industry has grown.

For this reason, initial analysis in this project was done on dated material written in ballpoint ink from the 1950s and 1960s. The first phase of analysis was destructive in nature and performed on weeded documents. The current phase, Photoshop® Assisted Spectroscopy, is non-destructive and therefore may be performed on select collection items.
Using a camera capable of detecting heat, it is evident how the ink is subjected to temperature change during application. If a person is writing consecutively, then ink at the end of the document will be exposed to more heat than at the beginning of the document. This is something to take into consideration during document analysis.

The upper set of images shows the relative temperature of a ballpoint pen as a document is written. At the point the image is capture here, the ball area of the pen is already much warmer than the surrounding environment.

The lower set of images shows ink on a substrate under magnification. The left image is a close-up image of the ink resting on the substrate. The right image is focused on the paper fibers which have been crushed due to the pressure of the pen on the page.
A quick review of the characteristics of pigments vs. dyes, both which can be contained in ballpoint ink, reminds us of the broad range of media components that might be present in any given ink. Fortunately, due to these same properties, examination by determining light interaction of various kinds (such as done with spectroscopy or a scanner) can provide useful information regarding the ink components.
Here are some of the dyes and pigments found in blue and black ballpoint pen. Notice that some dyes are found in both ink colors – Blue Violet 1, for example, is often added to the black ink to make it appear ‘blacker.’
When the chromophore present in the ballpoint ink is exposed to light, it enters an excited state which is more prone to reaction with oxygen. When it begins, this oxidation results in color shift. This process is often begun with the initial application of the ink and continues throughout the life of the document.
The National Institutes of Health has been supplying its employees with the same type of pen for many years – a Skillcraft ballpoint pen that has had no ink formula changes. Analysis of this pen shows some differences between it and other ballpoint pens, but the pen provides one constant in a project that is overloaded with variables.
SEM images show the differences between a BIC brand pen ball (left) and the Skillcraft pen ball (right).

Note the difference in the shape of the ball’s housing. The ink can be seen emerging on the edges of both balls. The image on the right shows ink emerging in a relatively uneven pattern that could result in a less even application. Ink formulae are often changed in order to create quick drying inks that are easy to apply evenly.
This invoice from the Marshall W. Nirenberg papers held at the National Institutes of Health, National Library of Medicine, History of Medicine Division archives is written using a Skillcraft pen.
Under a VSU 6000 document scanner, differences in ink are evident. Black inks that appear to be the same under visible light show different levels of fluorescence when excited. Using the VSU 6000, we were able to confirm that the black ink on the invoice, seen in the lower left and right corners was, in fact, the Skillcraft pen. For comparison, the word “government” is also written in Skillcraft pen in the upper images.
FTIR analysis also shows distinct characteristics in different inks.
From upper left to lower right spectra for black, blue, red, and green ballpoint inks are shown. Note the variation in relative locations of the peaks with each spectrum.
One method that may be used to assist in validation of Photoshop Spectroscopy is FT-IR imaging. This method ‘samples’ an area, then provides an FT-IR spectrum for each point sampled.
Staff have also examined one of the most complicated charts using IR photography, using the IR to ‘remove’ layers from the image.

The image on the left is taken using IR photography whereas the image on the right is taken using visible light. Note the ‘disappearance’ of the red writing in the IR image.
One of the goals of Photoshop Assisted Spectroscopy is to enable conservators to analyze a larger area of a document, more than most micro-analytical techniques will allow.
Using Photoshop Assisted Spectroscopy, conservation staff will be able to examine a document more effectively as a whole rather than a sum of its parts.
As seen here, when compared, a visible spectrometer and photo-reproduction hardware are actually very similar.
It is important to remember that with Photoshop Assisted spectroscopy, the analysis is done using numbers that represent color. However, since color is directly linked to chemical properties, these numbers do have meaning. The simplest method allows the observer to pinpoint the exact location of each triplet group of numbers (red, green, and blue-RGB) on the object. However, in the future, it should be possible to link these numbers to the actual chemical properties they represent.
Of course, particularly in order to achieve accuracy across the board, it is imperative to have a properly calibrated scanner that can accurately represent the colors in the object. While it is also important to have a computer that can use imaging analysis software such as Photoshop, National Library of Medicine (NLM) conservation staff have determined that monitor calibration and computer hardware are largely irrelevant for analysis—though accurate calibration does assist the user in visual distinction of color. The reason for this is that Photoshop relies on the RGB values and, based on experiments performed by NLM conservation staff, these do not change (unless altered by the user) even if the image file is opened on distinctly different computers.
Some questions considered with this technique are whether we can relate color shift to degradation (and, subsequently, to the type of degradation), whether we can eventually have an accurate comparison of Photoshop and UV-Vis-IR spectroscopy, and whether it will be possible to assess material condition using Photoshop manipulation.
It is also possible to separate layers in Photoshop using the RGB values of each color. This allows the user to manipulate the image in order to determine the likely outcome of further degradation of an individual color on the item as a whole or, once the degradation pattern is fully understood, to determine what the object may have originally looked like.
In order to show the degree of color shift in an object, it is useful to graph color space on a 3D graph. The third dimension allows the viewer to understand to a greater degree the direction in which the color is moving. It is convenient that RGB values can correspond easily to an XYZ axes.
For example, as seen in this section of one of the Nirenberg Charts, with ballpoint pen inks, some blue inks will shift towards a point where they appear to be black. Additionally, since many black inks contain blue dyes (to make them appear ‘black’), a color shift in the blue component of the black ink will cause the degraded ink to appear different, potentially altering the overall viewing experience of the object.

In this image, it is possible that the inks originally appeared to be different. The right column may have been blue at one time, and the ink that currently appears blue may originally have been a different color blue. The black ink in the middle column may have lost some of its ‘depth’ as blue dyes in it shifted.
A comparison with UV-Vis absorption spectra may allow for a more accurate translation of RGB values to ink characteristics.
The next few slides show screenshots of the initial analysis phases NLM conservation staff have performed using Photoshop Spectroscopy.

The image above reflects an analysis of a color-checker card intended for color accuracy in photography. The color-checker card was scanned multiple times in a row in four different positions on a scanner and then analyzed in Photoshop in order to address several questions:

1) How much variation is present from pixel-to-pixel in the scanner (keeping in mind that the color should be even throughout)?
2) How much variation is present from a ‘cold’ scanner bulb to a ‘hot’ scanner bulb?
3) How much variation is present when different scanner quadrants are used?

The left side of the image shows an Excel file which was used to analyze individually recorded RGB values. The right side shows the image opened in Photoshop (and zoomed in to allow for easy visual distinction of individual pixels.

The RGB values were recorded for the same pixels across a series of images. The average of the pixel variation was compared to the RBG values provided by the company for that section of the chart and the degree of variation from pixel-to-pixel was also recorded.
Recording the RGB values in this way provides data which can easily be graphed on an XYZ axis. Here, 100 points of three different colors from the color-checker chart are graphed. Notice that the graphed colors appear as clusters in this situation. This is due to the evenness of color application and the lack of variation from pixel-to-pixel.
Hand-applied ink analyzed and graphed in the same way, however, shows a much different pattern. The linear nature of this graph can be attributed to several different factors. Among them are the variation in colors present in ballpoint ink and the variation due to the thickness of the media layer – something directly related to the application method (written by hand). The color shift in this instance reflects scans taken at three different levels of degradation via artificial aging under a UV light. The substrate was also graphed but is not shown in this screenshot.
Here, blue ink, black ink, and the substrate are graphed both immediately after application and after artificial aging. Notice the variations in color shift depending on the media type. Both inks were applied to the same substrate and aged under the exact same conditions.
Of course, the experiments graphed on the previous slides are done under ideal circumstances. NLM conservation staff created a document, scanned it, and documented the degradation as it was aged under known conditions. Accurately tracking this process on a collection item is likely to be a much different experience and one that staff hope to address in the next phase of the project.
In summary, it is possible to track color shift using Photoshop. At this point, linking RGB values displayed in Photoshop to distinct media components requires further study and validation. It is the hope of NLM staff that this tool will be considered as one way in which color shift can be documented in an item without the need to use analytical equipment which may not be practical or accessible in all situations.