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Abstracts

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Micro-Raman and ATR-FTIR for the study of modern paints containing synthetic organic pigments (SOPs): characterization of the photodegradation processes

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In the 20th century, especially between the thirties and the sixties, new classes of synthetic organic pigments (SOPs) were synthesized and introduced into the market. They were mainly employed in the dyeing and coating industry [1]. During the same years new binding media e. g. acrylics and alkyd resins were made available on the market. Soon these materials became of popular use as art materials and dedicated products were developed and widespread.

These products had the advantages of being easily accessible and to combine excellent tinctorial properties and faster drying times together with an overall lowering of costs.

The characterization, the stability and the performances of such materials are studied and investigated since many years [2]. In the commercial paint formulations, pigments and organic binders are mixed with fillers and various additives, in order to improve the characteristics of the paint, to obtain different saturation of the colours, and, eventually, to lower the production costs [3].

The chemical stability of paint formulations depends not only on the components themselves, but it is also strongly affected by the environmental conditions the artworks are exposed to. Especially the electromagnetic radiation in the UV range plays an important role in causing chemical changes and photo-degradation processes in synthetic organic materials.

Among different analytical techniques that can be employed for the characterization of such materials, vibrational spectroscopies are probably the most used ones, especially in the field of conservation science [4]. Raman and infrared spectroscopy indeed give us the possibility of being used in a non-invasive (or micro-invasive) and non-destructive way. Moreover, these techniques, used with a complementary approach, allow us to characterise the pigments and the binding media, as well as to obtain useful information about degradation and interaction processes occurring between the components present in artworks.

In particular, in the last decades, Raman spectroscopy has been widely used for the identification of SOPs [5], while infrared spectroscopy is particularly suitable to obtain information about organic binders [6]. Photo-oxidative reactions that can cause degradation of organic materials occur due to the combination of absorption of radiation, mostly in the UV range, and oxygen diffusion into the paint layer. The penetration depth of oxygen, thus of the photo-degradative processes affecting the paint layers, are considered to be around 5-10 μm [7]. Therefore, the surface area analysed by ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared) and Raman spectroscopy can be considered as representative of photo-degradation phenomena, allowing us to investigate the effect of the SOPs on the binding media during ageing.

Thus, in the frame of a bigger project*, ATR-FTIR and micro-Raman spectroscopy were used to characterize paints containing synthetic organic pigments mixed with modern binders and exposed to accelerated UV ageing. In particular, copper phthalocyanine (PB15:1), metal free phthalocyanine (PB16), chlorinated phthalocyanine (PG7), brominated phthalocyanine (PG36) and monoazo yellows (PY3 and PY74) were selected. Each pigment was mixed with the acrylic emulsion of p(nBA/MMA), Plextol D498 (Kremer), and with an alkyd resin (Lukas Medium 4) in order to obtain two-components paints, without using additives. Subsequently, commercial paints containing the same pigments and class of binders (acrylics and alkyd) were selected and analysed. Self-made and commercial paints were used to prepare mock-ups, casting a 150 μm (wet) layer of paint on glass slides. The UV ageing was performed in a Dr. Hönle UV chamber Xenon Arc Simulator with a constant illumination of ca. 910 W/m^2, using an exposure range almost comparable with the outdoor conditions (295-4000 nm). This parameter wants to consider that in contemporary art, the artists may conceive their creative works, properly or improperly, for outdoor spaces (e. g. painting such as graffiti, sculptures etc.). In the exposure chamber temperature and relative humidity were not user-adjustable.

The sets of self-made and commercial paints were subjected to accelerated ageing for two and four months in the UV chamber, and material characterization was carried out periodically.

Micro-Raman analyses were performed testing and comparing three different lasers (532, 632.8, and 785 nm). Thus, the best measuring parameters for each pigment and paint could be selected taking advantage of resonance and pre-resonance effects.

The use of different lasers allowed us to evaluate the way different excitation wavelengths affect the results and how the fluorescence in the Raman spectra could be conditioned by the ageing of the samples [8].

In particular, the blue and green phthalocyanines (Pc's) PB15:1, PB16 and PG7 showed better signal-to-noise ratios and resonance effects using 532 nm laser [9]; for the PG36 the 632.8 nm laser gave better results, while the 785 nm laser was particularly suitable for both the monoazo yellow pigments, PY3 and PY74 [10].

By means of Raman spectroscopy a correct identification of the SOPs contained in the mock-ups was possible, even after four months of continuous UV exposure. As far as the characterization of the photo-degradation process is concerned, this is affecting mainly the organic binding media and not the pigment itself. Due to the instrument setup, it was not possible to detect Raman bands assignable to the binder, nor to degradation processes, even if using acquisition range 150-3500 cm^{-1}, in order to include the C-H stretching bands at ca. 3000 cm^{-1}. Of interest was the detection of the Raman band at 485 cm^{-1} present in the phthalocyanine (Pc) samples, e.g. PG7 (Figure 1), which was disappearing after the first two months of exposure. This band is assigned to twisting motions in the five membered ring of Pc and it is likely activated by a lowering of symmetry in the structure of the pigment [11]. Finally, in the Raman spectra acquired on commercial paint mock-ups, it was possible to detect the presence of fillers, e.g. $BaSO_4$ at ca. 1100 cm^{-1}, but this capability was not observed systematically on all the samples considered.

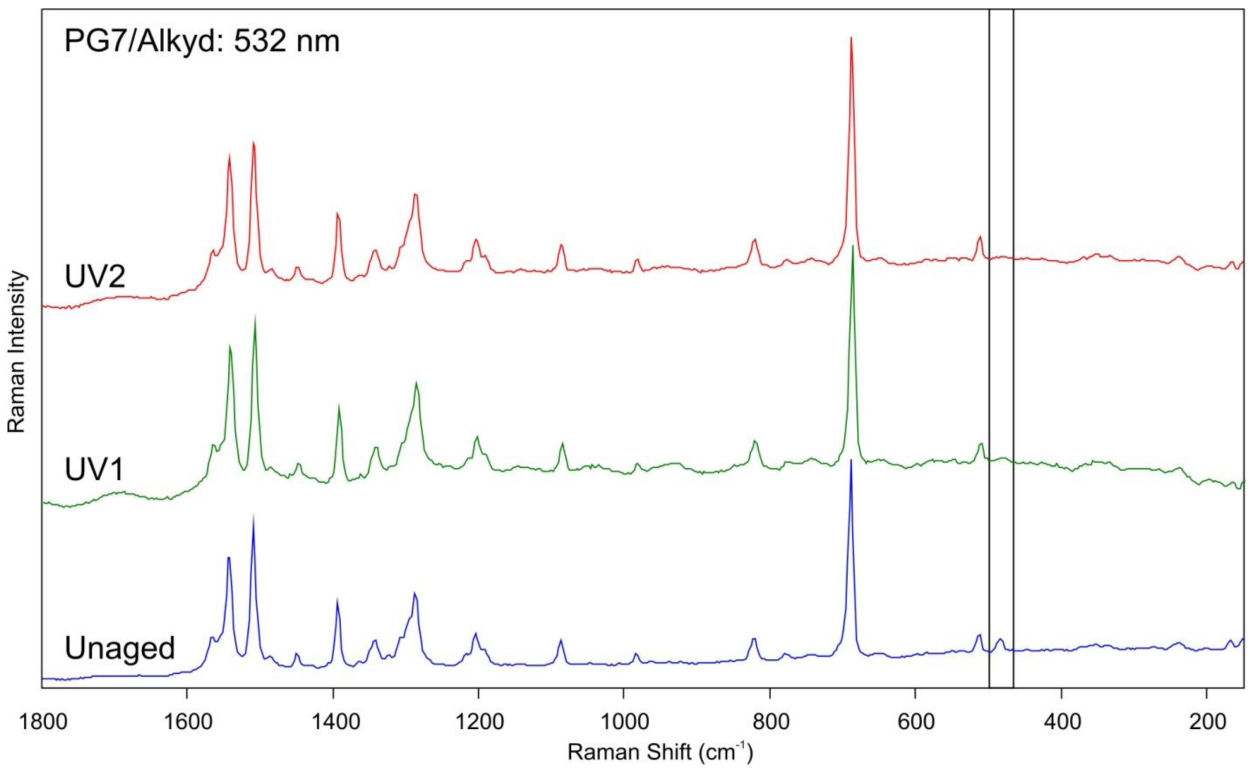

Figure 1: Raman spectra acquired with 532 nm laser of PG7 mixed with alkyd resin and exposed for two (UV1) and four (UV2) months in UV chamber. The symmetry in the pigment structure is increasing by UV ageing (see Raman band at 485 cm^{-1}).

On the other hand, ATR-FTIR analyses allowed us to identify the binding media, the fillers and other additives, e.g. surfactant, in the commercial paint tubes.

Moreover, by using this technique, it was possible to characterize the photo-degradation processes involving the binding media in both, self-made and commercial paint mock-ups.

An example is shown in Figure 2, where the ATR spectra do not present any contribution of the pigment, while the bands are assignable to the binding medium p(*n*BA/MMA), and to a PEG surfactant present in the Plextol D498, especially visible at 2890, 1455, 1343, 1110, 963 and 842 cm^{-1}.

The ageing caused a general increment in surface roughness, which led to the broadening of the bands in the ATR-FTIR spectra. Nevertheless, the identification of monoazo yellow pigments (PY3 and PY74) was achieved in unaged and aged mock-ups.

As far as the ageing processes of acrylics are concerned, after two months of UV exposure, one could notice that the surfactant bands (Figure 2) completely disappeared. In addition, the broadening of the C=O stretching band due to the formation of lactones at ca. 1773 cm^{-1}, and formation of ketones and other products of polymer chain scission at lower wavenumbers, and a general loss of volatile, e. g. butyl units, can be determined [12].

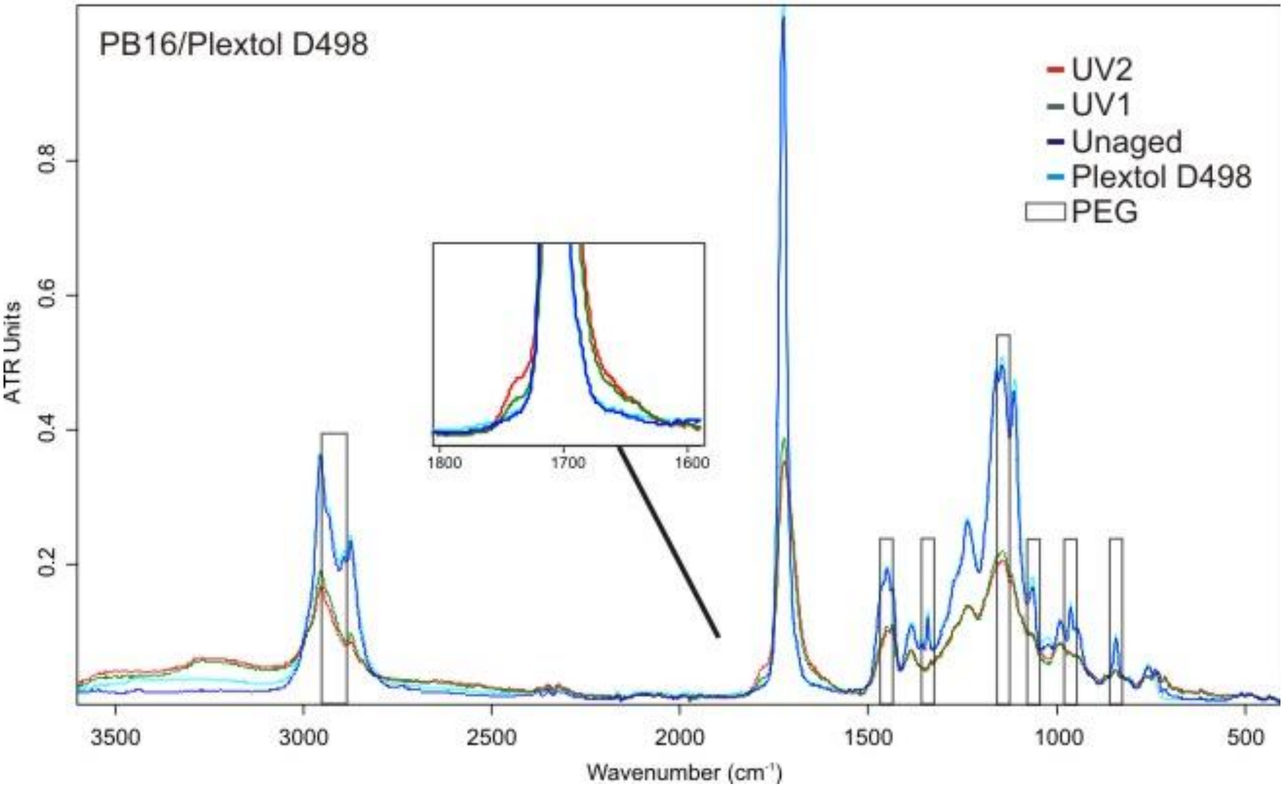

Figure 2: ATR-FTIR spectra of p(*n*BA/MMA) Plextol D498, and of the same mixed with metal free blue phthalocyanine PB16 and aged for two (UV1) and four (UV2) months. In the detail, photo-degradation products are highlighted.

For the alkyd resin containing mock-ups, it was evident a stiffening of the paint layer, and the appearance of a dusty surface, resulting in a change of the mechanical properties. Besides, by ATR-FTIR, typical features of oxidative degradation were identified, such as broadening of O-H and C=O stretching bands, respectively at 3500-3200 cm^{-1} and at 1713 cm^{-1}.

The changes observed due to ageing processes were detectable in all the samples, independently from the type of pigment contained in the mock-ups.

By comparing the mock-ups of self-made paint and the commercial ones, a stronger colour change concerned the latter.

Evident was the case of Lukas Acryl paint containing PB16. After two months of UV ageing, the surface of the paint became lighter and with a chalky texture, while after four months it got completely white. In the unaged mock-up, ATR-FTIR measurements allowed us to detect the presence of baryte, $BaSO_4$, (bands at 1000-1200, 980 and 610 cm^{-1}) and of China clay (band at ca. 3600 cm^{-1}), both used in the paint as fillers. The binding medium was found to be p(EA/MMA), according to the position and shape of the C-H and C=O stretching bands, at 2860, 2888, 2949 cm^{-1}, and 1723 cm^{-1}, respectively. Moreover, features of PEG were clearly detectable (Figure 3).

In both, ATR-FTIR and Raman spectra acquired on the surface of Lukas Acryl PB16 aged mock-ups, the bands assigned to the presence of baryte increased with the ageing of the paint, suggesting a relative enrichment of

$BaSO_4$ on the surface. The disappearance of the PEG bands from the ATR-FTIR spectra, indicates a loss of surfactant. Such strong changes were not observed on any of the self-made paint mock-ups.

In conclusion, by means of Raman spectroscopy SOPs were characterized, while by ATR-FTIR it was possible to identify acrylic and alkyd binding media, fillers, additives, and monoazo yellows present in the paints. In addition, the photo-degradation products occurring after UV ageing were determined.

Overall, the results proved that the presence of additives in the commercial paint tubes, can compromise the stability of the paint systems, additionally to the interaction pigment-binder. Moreover, among the pigments used to prepare the self-made mock-ups, the blue phthalocyanines seemed to be the less prone to photo-degradation processes under continuous UV light exposure. Thus, they can be considered particularly suitable for outdoor use.

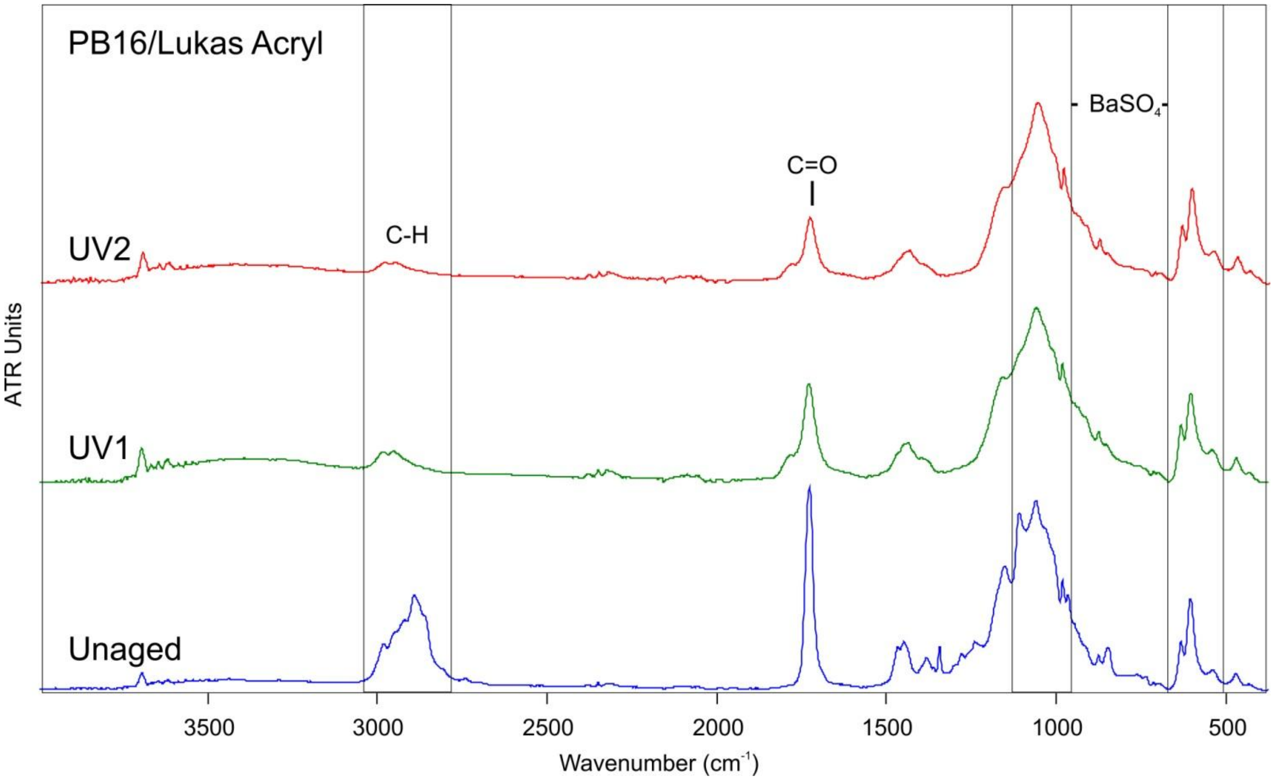

Figure 3: ATR-FTIR spectra of a commercial paint tube Lukas Acryl, containing PB16, after UV ageing for two (UV1) and four (UV2) months. Bands of $BaSO_4$ are highlighted.

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Characterization of unprocessed historic platinum photographic papers by Raman, FTIR, and XRF

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ABSTRACT

The technique for making platinum photographs was patented by William Willis in 1873, who called the prints 'Platinotypes.' The most typical Platinotype photographs have a neutral black image material dispersed among the paper fibers of the substrate creating a rich, matte surface. By the 1890s, the Platinotype Company sold a small selection of paper types and, by the early twentieth century, the variety of papers blossomed and photographers could choose from a multitude of tones, textures, and surface sheens [1] [2]. In 1906, the Platinotype Company introduced 'Japine' papers [3], that had glossier or 'semi-matte' surface. Based on their glossy appearance, photographs made on Japine papers could easily be misidentified as prints with gelatin or albumen binder layers. It was proposed in 1916 [4], and more recently hypothesized by Mike Ware, that the manufacture of Japine may involve a parchmentization process using concentrated sulfuric acid applied to the paper's surface that would generate a modified layer in which the sensitizer would be applied.

For the present study, a set of unprocessed historic platinum photographic papers were characterized by a combination of Raman, FTIR and XRF spectroscopies to gain insight into their manufacturing processes and obtain information that can help identify the use of similar papers in works of art in a non-invasive manner. The analysis of one of these papers, 'Japine Platinotype for Sepia Tones,' showed a sensitized surface layer in the recto consistent with the use of a parchmentization process of the paper substrate, composed mainly of amorphous cellulose, and a slightly modified surface in the verso. No gelatin or other surface coatings were identified in Japine. In the rest of the papers studied, the sensitizer was found to have been applied directly onto the paper fibers and no gelatin or gums were observed as sizings [5]. The combined use of Raman and XRF provides information that can help discriminate platinum photographic processes involving parchmentization in works of art in a non-invasive manner.

This study is part of a collaborative project among scientists and conservators at the National Gallery of Art, Washington D.C., and at the MMA to study the platinum and palladium photographic processes used at the turn of the 20th century [3, 6].

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‘Green’ plastics in modern and contemporary art, what’s the deal?
The identification of ‘green’ plastics using Fourier Transform Infrared spectroscopy

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INTRODUCTION

Modern and contemporary artists working during the 1990s like Andreas Slominski and Paul de Reus incorporated everyday plastics in their works. They found plastic carrier bags in local stores and these bags form an important part of the work. In the 1990s plastic bags were primarily composed of polyethylene (PE). Photo-oxidation can cause degradation of the thin layers of the PE bag and in combination with mechanical stress, tears may appear and in some cases even totally crumbling of the bag[1].

What if Slominski and de Reus would shop for plastic carrier bags in 2014, what kind of plastic bags would they encounter?

Figure 1: ‚Bicycle’ (1991), Andreas Slominski, Waitz Collection, photo K. Haider

Figure 2: ‘Mijn oma als Louise B.’ (1993), Paul de Reus, Collection Stedelijk Museum Amsterdam, photo Lydia Beerkens

Living ‘green’ has become a popular trend in the last twenty years, and reducing oil consumption remains an important goal for the sustainably-minded of today. One of the top uses of crude oil is the production of plastics. For example, in 2010, 191 million barrels of liquid petroleum gases and natural gas liquids were used to make plastic products in the United States[2]. These plastics finally end up in landfills, where they take years to break down. Petroleum-based plastics are becoming more expensive as oil prices continue to increase, and plastic accumulation in landfills takes up valuable space and threatens the environment.

In the attempt of reducing oil consumption different plastic manufacturers are now using recycled plastics and they produce plastics using renewable sources.

There are two types of recycling: mechanical and chemical recycling. Mechanical recycling involves the melting, shredding or granulation of waste plastics. The plastic is either melted down directly and moulded into a new shape, or melted down after being shredded into flakes and then processed into granules. Chemical recycling breaks down polymers into their constituent monomers, which in turn can be used again in refineries, or petrochemical and chemical production.

The use of renewable sources for plastic production has resulted in plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch or pea starch.

In the case of thermoplastic starch (TPS) and the cellulose esters these renewable sources are used for the production of the plastic directly. In case of polylactic acid (PLA) and bio-derived polyethylene the renewable sources are used for producing the monomers for the end product.

In order to reduce plastic pollution, bio-degradable plastics have been developed. Biodegradable plastics are plastics that are capable of being decomposed by bacteria or other living organisms, examples are: polyhydroxybutyrate (PHB), polylactic acid (PLA), polybutylene succinate (PBS), polycaprolactone (PCL) and starch derivatives.

PLASTIC CARRIER BAGS

The modern types of plastic bags are noted in Table 1[3].

Type of plastic bag	Notes	Biodegradable?	Renewable?
Ordinary plastic bags	Made from oil based plastics	No	No
Recycled plastic bags	Made from recycled oil based plastics	No	No
Degradable plastic bags	Made from oil based plastics: will break down into small fragments in the environment	No	No
Plant based biodegradable plastic bags	Made from plant based plastics that are compostable to the European standard EN13432	Yes	Yes
Plant based non-degradable plastic bags	Made from plant based plastics that are durable	No	Yes

Table 1.

Ordinary plastic bags

The ordinary plastic bags are, like the plastic bags from the 1990s, made from polyethylene which is made from non-renewable sources. The polyethylene is produced by the addition polymerisation of ethylene[4].

Polyethylene bags are produced through a blown-film extrusion process; during this process small PE pellets are melted down under controlled conditions so that they become molten and pliable. They are then pressed (extruded) through a circular die gap to form a continuous tube of plastic. While it is still in this molten state, the tube is pinched off at one end and then inflated and stretched to the size and thickness of the desired finished product.

Recycled plastic bags

HDPE is accepted at most recycling centres in the world, as it is one of the easiest plastic polymers to recycle. Most recycling companies will collect HDPE[5] products and take these to large facilities to be processed.

First, the plastic is sorted and cleaned, to remove any unwanted debris. The plastic then needs to homogenised, so that only HDPE will be processed. If there are other plastic polymers in the batch, this can ruin the recycled end-product.

HDPE has a specific density of 0.93 to 0.97 g/cm3. This is much lower than that of PET which is 1.43-1.45 g/cm3, meaning that these plastic polymers can be separated by using sink-float separation. However, HDPE has a similar specific density to PP, which means the sink-float separation cannot be used. In this case, Near Infrared Radiation (NIR) techniques can be used. HDPE is then shredded and melted down to further refine the polymer. The plastic is then cooled into pellets which can be used in manufacturing[4]. Chain lengths of the recycled polyethylene may be shorter due to the 'second life' of the material.

Degradable plastic bags

The term 'degradable' broadly describes a material which breaks down into smaller pieces or particles; the use of "oxo-degradable" additives can speed up this process.

The "oxo-degradable" additives are typically incorporated in conventional plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephtalate (PET) and sometimes also polyvinylchloride (PVC) at the moment of conversion into final products. These additives are based on chemical catalysts, containing transition metals such as cobalt, manganese, iron, etc., which cause fragmentation as a result of a chemical oxidation of the plastics' polymer chains triggered by UV irradiation or heat exposure. In a second phase, the resulting fragments are claimed to eventually undergo biodegradation.

In addition to additives that trigger the fragmentation process, the "oxo-degradables" include stabilizers, which are added to limit the unwanted fragmentation of the polymer chains whilst the plastic is still used by consumers.

However, the stabilizing effect of the additives is limited. Research studies have concluded that "even with some content of stabilizing additives, PE film (with "oxo-biodegradable" additives) loses its mechanical properties rather fast, especially when exposed to sun-light." For this reason, different storage conditions would be required in order to prevent premature ageing and loss of mechanical properties.

Fragmentation of oxo-fragmentable plastics is not the result of a biodegradation process but rather the result of a chemical reaction. The resulting fragments will remain in the environment**.** Oxo-fragmentable products can hamper recycling of post-consumer plastics[6].

Plant-based biodegradable plastic bags

Biodegradation is the consumption of smaller pieces or particles by micro-organisms, resulting in water, carbon dioxide and organic matter. The 'biodegradability' of plastics is dependent on the chemical structure of the material and on the constitution of the final product, not just on the raw materials used for its production.

Therefore, biodegradable plastics can be based on natural or synthetic resins. Natural biodegradable plastics are based primarily on renewable resources (such as starch) and can be either naturally produced or synthesized from renewable resources. Non-renewable synthetic biodegradable plastics are petroleum-based. As any marketable plastic product must meet the performance requirements of its intended function, many natural biodegradable plastics are blended with synthetic polymers to produce plastics which meet these functional requirements.

Blends of starch and biodegradable synthetic aliphatic polyesters are often used to produce high quality sheets and films for packaging by flat-film extrusion using chill-roll casting or by blown film methods since it is difficult to cast films from 100% starch in a melted state. Approximately 50% of the synthetic polyester can be replaced with natural polymers such as starch, leading to a significant reduction in cost. Furthermore, the polyesters can be modified by incorporating a functional group capable of reacting with natural starch polymers. One of the biodegradable synthetic aliphatic polyesters used in starch blends is polybutylene adipate/terephthalate (PBAT) it is polyethylene terephthalate (PET) which has been modified to be biodegradable.

Polylactic acid (PLA) is a linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group. Lactic acid is produced (via starch fermentation) as a co-product of corn wet milling. The ester linkages in PLA are sensitive to both chemical hydrolysis and enzymatic chain cleavage. PLA is often blended with starch to increase biodegradability and reduce costs. However, the brittleness of the starch PLA blend is a major drawback in many applications. To remedy this limitation, a number of low molecular weight plasticisers such as glycerol, sorbitol and triethyl citrate are used [7,8,9].

Plant-based non-degradable plastic bags
Biopolyethylene (also known as renewable polyethylene) is a plastic produced from a renewable raw material such as sugar cane, sugar beet, wheat grain, sugar cane or corn. Via a fermentation process ethanol is formed which is then dehydrated into ethylene. Finally, the ethylene is polymerized to form polyethylene. The final product is identical to naphtha- or gas-based polyethylene, therefore maintaining the physical properties for conversion into plastics products and also maintaining its recycling properties. Biopolyethylene is available in many grades, including high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and low density polyethylene (LDPE).

INSTRUMENTAL

FTIR spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer combined with a Golden Gate single reflection diamond ATR unit (sample size 0.6 mm^2). Spectra were recorded from 4000 to 450 cm^{-1}. The infrared spectra of the samples were compared with spectra of reference materials.

For artificially light ageing a Xenotest Alpha High Energy (Atlas®) with a filtered Xenon Arc lamp (105 Klx, 50°C, 40% RH) was used. Ageing experiments using elevated temperature and changing relative humidity (70°C and 30-80% RH) were carried out in a Vötsch Vc 0200 climate chamber.

RESEARCH

Several modern plastic bags were collected, they included bio-degradable bags, oxo-degradable bags, bags made from recycled plastics and bags produced from plant based plastics. Using Fourier Transform Infrared Spectroscopy (FTIR) the composition of the modern plastic carrier bags was investigated.

To study the ageing behaviour of the identified plastics in museum environment, selected plastic bags were artificially aged using an elevated temperature of 70°C in combination with a changing relative humidity between 30-80%. To induce photo-oxidation, the bags were aged in the Xenotest. For comparison traditional PE, recycled PE and PET films were included in the ageing tests. During the ageing process the effects on the plastics were studied: changes in mechanical properties and appearance were noted and changes in the polymers were followed using FTIR.

RESULTS

One biodegradable bag was identified as a starch-polyethylene blend using FTIR. Other biodegradable bags were identified as a starch-polybutylene terephthalate blend. Using Pyrolysis Gas Chromatography Mass Spectrometry (py-GC/MS) the biodegradable polyester in the blend could be identified as polybutylene adipate/terephthalate (PBAT). Bags used for packaging organic vegetables and magazines were identified as polylactic acid (PLA). Bags with the following composition were selected for artificial ageing: PE, PET, recycled PE, PLA, starch-PE blend, starch-PBAT blend.

The selected bags were aged for up to 630 hours in the Xenotest to induce photo-oxidation. Four hour Xenotest is equivalent to one year’s exposure to museum conditions at 200 lux. Ergo 630-hour Xenotest is equivalent to 158 years of museum ageing at 200 lux.

The starch-PBAT blend showed signs of mechanical degradation, as in loss of tearing resistance, after 488 hours of ageing, at which point PE and PET showed no change at all and PLA and starch-PE only slight changes. After 560 hours of ageing also PE shows loss of strength and after 630 hours only PET shows no signs of mechanical degradation.

The FTIR spectrum of the starch-PBAT blend aged for 488 hours shows an increase of the O-H-stretching vibration absorption band at 3349 cm^{-1}, the absorption bands at 1102 and 1163 cm^{-1} have decreased in intensity.

After 7 days of ageing at 70°C and 30-80% RH, the transparent PLA bag shows opaque patches, after 14 days it has turned opaque totally, showing severe mechanical degradation, and after 35 days it has lost its integrity completely.

The starch-PBAT bag started to show loss in mechanical strength after 21 days. After 35 days the PLA and the starch-PBAT have become very brittle, the other bags (PE, PET, recycled PE, starch-PE blend and oxo-degradable PE show no signs of degradation.

The FTIR spectrum of the PLA aged for 14 days shows an increase of the absorption band at 1359 cm^{-1}, the absorption band at 1267 cm^{-1} has decreased in intensity.

The FTIR spectrum of the starch-PBAT blend aged for 21 days shows an increase of the O-H-stretching vibration at 3349 cm^{-1}.

CONCLUSION

Compared to the traditional material used for the production of carrier bags, polyethylene, the ‘green’ plastics PLA and starch-PBAT blend were more susceptible to hydrolyses in performed ageing experiments (70°C and 30-80% RH).

During the light ageing experiments the starch-PBAT blend showed signs of degradation at an earlier stage then PE, indicating the starch-PBAT blend is more susceptible to photo-oxidation then the traditional PE. The starch-PE blend showed the same ageing characteristics as traditional PE.

Differences in ageing behaviour between the ‘green’ plastic bags and the traditional plastics bags have been established. How the ‘green’ plastics will act in a museum environment and what implications these materials have on the conservation remains to be seen. During this ongoing research more artificial ageing experiments will be performed and results will be compared to the natural ageing of the materials.

In the meantime, for the exhibition of works of art containing ‘green’ plastics, the requirements for paper objects concerning light exposure, temperature and relative humidity can be applied.

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Development and application of a high spectral/spatial NIR hyperspectral imaging camera for the identification and mapping of organic artists' materials such as paint binders and fillers

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Near-infrared (750 to 2500 nm) reflectance imaging spectroscopy has been recently shown to be a useful tool to map and identify various artists' pigments. This approach has utilized both electronic transitions (color) and vibrational overtones from hydroxyl (-OH) and carbonate groups (-CO_3). Here we report on further efforts to extend this methodology to map and identify organic artists' materials such as paint binders and some fillers. Imaging spectroscopy, the collection of hundreds of contiguous narrow-band images, offers an improvement over site-specific fiber optic reflectance measurements by combining both spatial and spectral information. Currently we have developed a portable, high sensitivity NIR hyperspectral camera that operates from 1000 to 2500 nm with a spectral sampling of 2.7 nm and a spectral response of 9 nm (FWHM), with a spatial sampling of 0.1mm at the artwork. The camera consists of a scan mirror, fore optic, transmission grating spectrometer, relay lens, and indium antimonide 1024 by 1280 pixel array operating at 67K with a sterling cooler. The camera operates at the low light level conditions necessary to examine both paintings and works on paper. Near infrared chemical signatures include overtone and combination vibrational features associated with amide bonds, CH_2, OH, and CO_3 groups, and these spectral features can be used to identify and map the spatial distribution of organic materials. The instrument's performance is being verified using test panels and paintings in the National Gallery's collection whose composition is known by GC-MS and FTIR analysis. Case studies will be presented showing the utility and challenge of this approach, for example: (1) mapping of egg yolk and animal skin glue paint binders in an Early Renaissance painting by Cosimo Tura entitled "The Annunciation with Saint Francis and Saint Louis of Toulouse (ca. 1475)", and (2) identification and mapping of sub-surface microcrystalline wax filler in the conservation of Edward Steichen's "Study for "Le Tournesol"" c. 1920. The knowledge gleaned from NIR imaging spectroscopy will help both art historians and conservators better understand and preserve works of art.

Comparing spectral features of paint binders in the Near- and Mid-Infrared and the effect of pigment interference

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As part of our research to construct a near-infrared (1000 to 2500 nm) diffuse reflectance hyperspectral camera for identifying and mapping paint binders in situ, we are constructing a spectral database of the most commonly used binders for reference. The database consists of near- and mid-infrared (2500 to 15,385 nm or 4000 to 650 cm^{-1}) spectra of paints made with historical and contemporary paint binders. Test panels are being made using various artist pigments to determine their effects on the diffuse reflection and absorption spectra of the binders and whether spectral interference from the pigment precludes identification of the media present. Some of the paint binders of interest include egg yolk, egg glair, gum arabic, animal skin glue, drying oils, alkyds, and acrylic. In the mid-IR, carbonates usually interfere with the identification of proteins, and sulfates and silicates interfere with the identification of gums. In the near-IR, the absorption region of proteins and gums is relatively free from interference. This presentation will focus on new findings on contemporary media, including oils, alkyds, and acrylics. Briefly, the most distinguishing spectral features in the near-IR of a lipid-containing binder like oil are due to a combination of methylenic stretching and bending [$\nu(CH_2) + \delta(CH_2)$] and the first overtone of CH_2 stretching. In the mid-IR, C-H and C=O stretching are indicative of a lipid-containing binder. Carbonate and hydroxyl groups present in some artist pigments may interfere with the CH_2 combination band in the near-IR, but the CH_2 overtone features are usually still visible and identification of the binding media is still possible. In the mid-IR, a lipid containing medium can usually be identified in the presence of those molecular groups because the lipid features are found in a different spectral region. Near- and mid-IR spectra of oil and alkyd media are similar, but alkyds can generally be identified by additional absorption features due to aromatic C-H stretching. For acrylic media in the near-IR, C-H stretching occurs in a slightly different spectral region than that for oil or alkyd binders, and the features are generally broader due to a mix of copolymers. In the mid-IR, acrylics are often identified by characteristic C-O stretching patterns, but identification of the media may be hindered if sulfates and silicates are present. The ability to use these band assignments to map binding media will be validated on painting mock-ups.

Binders used in metallic paints investigated by micro-FTIR and synchrotron-sourced FTIR

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INTRODUCTION

This paper investigates the binders found in several historic cans of metallic paints and in a collection of German and Australian-made metallic paint-kits from an artist's box dating from the 1930s. A number of paintings by Australian artists that incorporate metallic paints dating from the late nineteenth to the mid-twentieth century were also examined. Characterisation of the binders from the artist's box and cans of paint were undertaken with micro-Fourier Transform Infrared (FTIR) spectroscopy in transmission mode. Analysis of the binders in paint samples from artworks is challenged by the opacity of the metallic flakes preventing conventional transmission FTIR. Attenuated Total Reflectance (ATR) FTIR of samples is also unsuccessful as many of these paints have little binder present at the surface. This is particularly the case with aluminium paints in which the metal flakes typically "leaf" by floating to the top of the paint film forming a continuous layer of aluminium metal. In these samples, synchrotron-sourced transmission FTIR can be a useful technique when cross sections are further cut as thin-sections and measured in transmission mode. The high lateral resolution provided by the synchrotron source ensure the spectra are measured only from the binder layer surrounding the metal flakes. FTIR mapping of these samples in 5 micron step sizes also reveals some phase separation within the binder layer.

ANALYSIS OF BINDERS FROM HISTORIC PAINTS

Metallic paints are made from flakes of copper, brass or aluminium suspended in a quick-drying, transparent medium. Gold-coloured metallic flakes were called 'bronze powders', but this is a misnomer as they were usually made from flakes of brass (copper and zinc alloys) and silver-coloured powders were made from flakes of aluminium. The primary use for metallic paint in the nineteenth century was for craftwork, sign-writing and coach-painting. Initially, metallic paints were supplied as separate liquids and powders to be mixed just prior to use but by the 1930s a number of pre-mixed metallic paints had become widely available and were popular for renovating leather goods and painting home appliances.

A collection of Australian and German-made metallic paint-kits dating from the 1930s were examined as a case study of typical metallic paint binders from the period. The four different metallic paint kits are part of a painter's box including pencils, crayons and watercolours (Gift of Caroline and Lee Cass 2013, Artists' Materials Archive, Art Gallery of NSW). A number of the pencils in the box are labeled "FIZ" and another "Crowley". Rah Fizelle (1891-1964) and Grace Crowley (1890-1979) were Sydney artists active in the 1930s. Neither artist is associated with the use of metallic paints. However, their close artist friend, Ralph Balson (1890-1964) painted a number of abstract paintings in 1941 using aluminium, copper and brass paints alongside conventional oil paints. It is possible that the metallic paint kits in the artist's box were those belonging to Ralph Balson. Made by Meteor, Benda and Genuine Supreme (German) and Taubmans (Australia) they are all packaged with the metallic powders and binder liquids separate to be mixed just prior to use in a small metal pan with a brush provided (Fig 1.). A display case has been made out of the collection of materials and the exact association of each metallic powder and binder liquid with each manufacturer's box has been lost. Never-the-less, they provide a useful survey of the types of binders that were used with metallic paints of the period. Two additional cans of ready-mixed metallic paints manufactured by Taubmans called Silvafros™ (circa 1940s-50s) and Sovro™ (circa 1930s), dated by their labels in comparison with advertised images of the cans, were also examined for this study.

The metallic paints from the artist's box were prepared for examination by sampling the residue in the four pans, the liquids in one small glass bottle and the dry paint residue on the paper envelope containing Taubmans bronze powder. The dried paint samples from the pans were separated from the metal flakes by solubilising the binder with acetone and the soluble extract scraped and placed on a diamond platform. Liquids from the bottle of binder and two cans of paint were extracted and dried on a glass slide before placement on the diamond platform. Transmission micro-FTIR was performed on the samples in the range from 4000-550 cm^{-1} in 100 scans at a resolution of 4 cm^{-1}. FTIR spectra were distinctive and diagnostic for each sample and the results are shown in Table 1.

Sample source	Sample site	Sample preparation	FTIR spectra match
Fizelle box	Oval pan silver paint	Dry mixed paint sample extracted with acetone	Nitrocellulose
	Oval pan bronze paint	Dry mixed paint sample extracted with acetone	Nitrocellulose
	Oval pan dark bronze paint	Dry mixed paint sample extracted with acetone	Nitrocellulose
	Circular pan bronze paint	Dry mixed paint sample extracted with acetone	Calcium resinate/limed rosin/gloss oil?
	Square glass jar	Liquid medium touch dry	Calcium resinate/limed rosin/gloss oil?
	Residue on Taubmans bronze powder envelope	Dry mixed paint sample on envelope	Drying oil
Ready-mixed tins	Taubmans Sovro™ bronze paint	Liquid medium touch dry	Tung oil
	Taubmans Silvafros™ silver paint	Liquid medium touch dry	Coumarone/indene resin and oil

Table 1. Metallic paint from historic samples

Three samples of dried paint from the mixing pans for both 'bronze' (brass) and 'silver' (aluminium) gave spectra consistent with documented nitrocellulose peaks at 1651, 1281, 1057 and 849 cm^{-1} (Learner, 2005). The samples from the bottle of mixing liquids and the circular pan of 'bronze' gave similar FTIR spectrum to each other suggesting the pan of mixed paint was made from the bottle of liquids. No FTIR library match could be found for the spectra but there are some similarities with documented rosin spectra (Derrick, Stulik, & Landry, 1999) suggesting it may be a derivative, although the large broad carboxylate peak 1620-1495 cm^{-1} is not typical for unprocessed rosin. X-ray fluorescence spectroscopy of the sample from the liquid bottle gave high spectral peaks for the presence of calcium. It is likely that this is calcium resinate commonly called limed rosin or gloss oil, a popular binder for gloss paints in the 1920s and early 1930s (Barry, 1969). The paint on the envelope of Taubmans bronze powder was consistent with spectra for drying oils. Typically the type of drying oil is not identified by FTIR in an aged and dry sample, however the sample of still liquid contents from the can of Sovro™, a ready-mixed bronze paint also manufactured by Taubmans, gave distinctive peaks at 993 and 966 cm^{-1} associated with fresh tung oil (Schöenemann & Edwards, 2011). This is an unexpected finding as although tung oil is described in the paint industry journals of the 1920s and 1930s as a popular quick-drying oil type in gloss paints (Standeven, 2011), these absorbance peaks are not found in FTIR spectra of dry and oxidised samples. However, the oil binder aged over 80 years in the can of Sovro™ has retained the unsaturated CH=CH bonds which give rise to the 993 and 966 cm^{-1} peaks. FTIR spectra of the dried sample of Sovro™ liquids taken at 24 hours and two days after drying, demonstrate the quick oxidising of these bonds and the subsequent disappearance of the identifying tung oil peaks (Fig 2). The sample of dry liquids from the can of Silvafros™ gave FTIR spectral peaks aligned with coumarone/indene resin, a coal-tar derivative, mixed with a drying oil.

ANALYSIS OF SAMPLES FROM PAINTINGS

A number of paintings by Australian artists dating from the late nineteenth to the first half of the twentieth century have been identified as making use of brass, copper or aluminium paints alongside standard oil paints (Table 2.). The appearance of metallic paint films on the paintings varies from dull and roughly textured to smooth, even surfaces with high reflectance. The light scattering and reflection effects are enhanced by the alignment of the metal flakes within the paint film and this is determined by the type of binder, the manufacturing technique of the metal flakes and the method of application of the paint (Allen, Dredge, Sawicki, Puskar, & Wuhrer, 2014). The selection of binder was principally for fast drying and ideally to promote alignment of the metal flakes while providing a non-corrosive environment for the metal.

Two paint samples from a selection of four paintings prepared as cross-sections demonstrated alignment of the metallic flakes leaving areas of the metallic paint layer with binder only, suggested that they may be good candidates for synchrotron-sourced transmission FTIR (Table 2). Samples from Roy de Maistre *Magnolias and path,* early 1930s (oil and metallic paint on canvas, 202 x 251 cm, Art Gallery of NSW) and Ralph Balson *Painting,* 1941 (oil and metallic paint on cardboard, 47 x 79 cm, private collection), that had been embedded in polyester resin and examined in Scanning Electron Microscopy were successfully prepared as 5-10 micron thin-sections cut by microtome on a tungsten blade. When prepared for analysis by placing the thin-sections on the diamond platform, the samples dropped out of the polyester resin and were, in these instances, clear of interference from the embedding resin.

The sample of paint from the de Maistre *Magnolias and path* demonstrated a clear chemical layer structure that was successfully mapped with synchrotron-sourced FTIR (Fig. 3). Two ground layers were identified, the lowest being rich in kaolin (clays) identified by the double peaks 3694 and 3620 cm^{-1} and the second layer of barium sulphate (1183, 1125 and 1080 cm^{-1}). Above the two ground layers the metallic aluminium flakes exhibited leafing towards the top of the paint layer, leaving an area approximately 20 microns thick of nitrocellulose and oil identified by the nitrate group at 1652, 1275 and 843 cm^{-1}, and the oil associated with a carbonyl peak at 1732 cm^{-1} and in the finger print region at 1240, 1168, 1009 and 725 cm^{-1}. Typically nitrocellulose lacquers manufactured as paints and varnishes in the 1930s and 1940s contained oils as plasticisers and spreading agents (Todd, 1990) and this multicomponent feature is seen in the standard nitrocellulose lacquer FTIR spectrum shown in figure 3. When the FTIR map of the de Maistre *Magnolias and path* sample is integrated on the nitrocellulose peak at 1278cm^{-1}, the separation of the oil and nitrocellulose phases of the nitrocellulose lacquer is apparent with the nitrocellulose being more concentrated towards the top and the oil settling lower in the layer (Fig. 3). This two phase separation is also apparent on the sample from the Balson *Painting* which was identified by synchrotron-sourced FTIR as nitrocellulose lacquer.

Painting	**Type of metallic paint**	**Physical characteristics of metallic paint**	**FTIR identification**
Charles Conder, *An impressionist* 1889	Copper paint	Flakes unaligned	Not identified
Roy de Maistre, *Magnolias and path* early 1930s	Aluminium paint	Flakes aligned	Nitrocellulose lacquer
Ralph Balson *Painting* 1941	Copper, aluminium and brass paints	Flakes aligned	Nitrocellulose lacquer
Eric Wilson, *Abstract (kitchen stove)*, 1942	Aluminium paint	Flakes unaligned	Not identified

Table 2. Metallic paint from painting samples

CONCLUSION

The analytical findings suggest that the type of binders that might be found in metallic paints used on paintings from the 1920s and 1930s could be some of the earliest examples of artist use of semi-synthetic (nitrocellulose and calcium resinate) and synthetic resins (coumarone/indene). The identification of tung oil is also an unusual finding as, although described as a common oil used in commercial paints of the period, its identification on paintings from the period is not possible due to the rapid oxidation of the distinguishing FTIR peaks. Synchtrotron-sourced FTIR of samples from paintings prepared as thin-sections of cross-sections gave excellent results in those instances in which the metallic flakes in the paint aligned parallel to the surface leaving areas clear of metal for infrared transmission using a beam size of 5 microns. FTIR mapping also demonstrated the phase separation of the oil and nitrocellulose components within the binding medium. The presence of resins vulnerable to solubilisation, such as those identified in the case studies presented, may have implications for the solvent treatment of paintings containing metallic paint.

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Figures:

Figure 1: Metallic paint kits from artist's box (Collection: Artists' Materials Archive, Art Gallery of New South Wales)

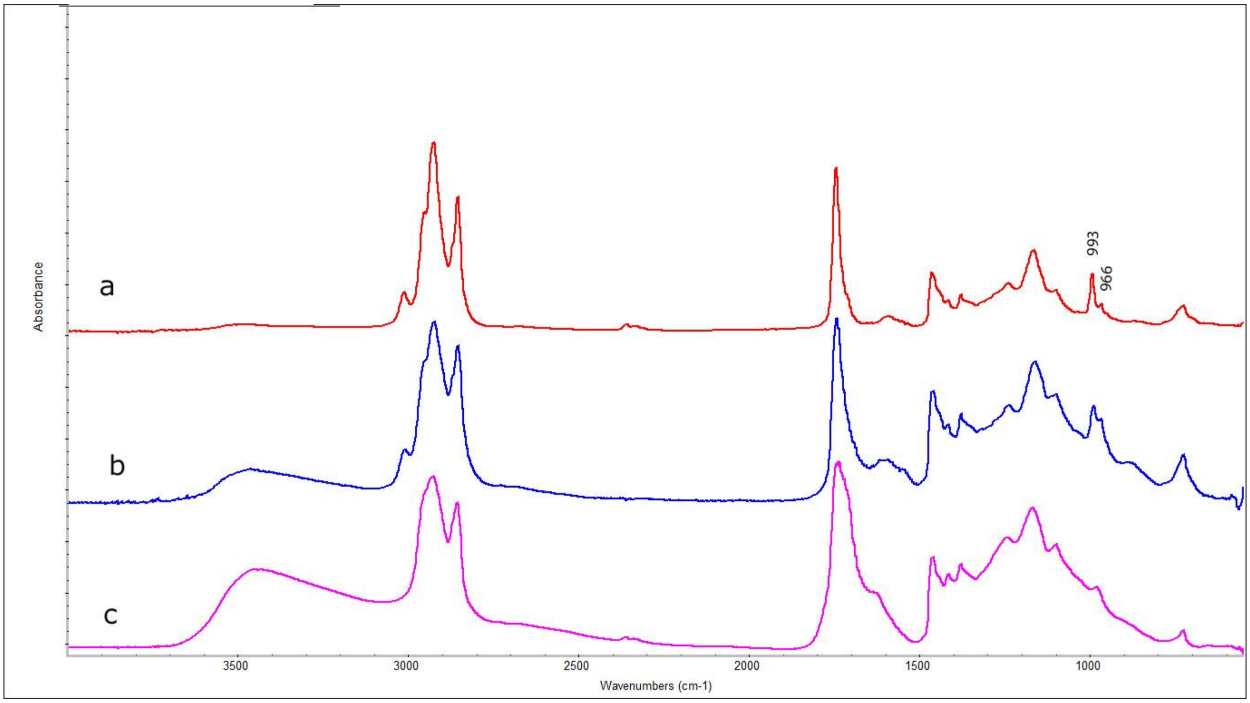

Figure 2: FTIR spectra of liquids decanted from can of Taubmans Sovro gold enamel after air drying at; a) one hour b) 24 hours and c) one month with gradual loss of identifying tung oil absorption peaks 993 and 966 cm-1.

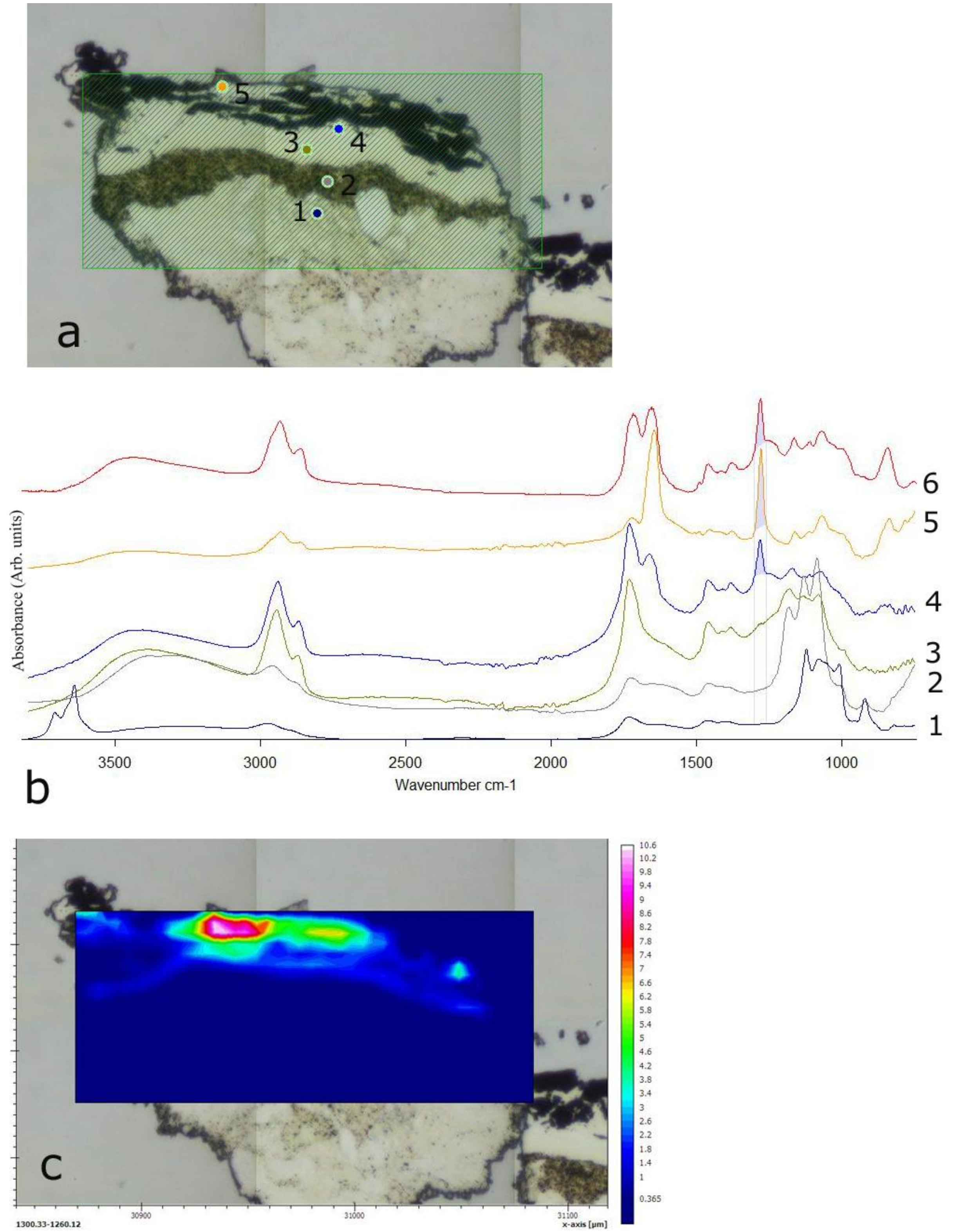

Figure 3: Cross section from Roy de Maistre *Magnolias and path* prepared as thin-section showing; a) area mapped with synchrotron-sourced FTIR in green; b) representative spectra from 1. lower ground (kaolin), 2. upper ground (barytes) 3. lower part of metallic paint binder (oil rich), 4. mid part of metallic paint binder (nitrocellulose & oil), 5. upper part of metallic paint binder (nitrocellulose rich), and reference spectrum of aged nitrocellulose lacquer containing both oil and nitrocellulose; c) integration map of nitrocellulose peak 1278cm^{-1} showing more intense absorptions related to nitrocellulose towards top of metallic paint binder layer.

Shadows from the Chat Noir theater: exploring the artist's materials and techniques

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This year, a set of 17 paper shadows from the *Chat Noir* theater (Fig.1) was being restored by a student. These artworks dated at the end of the XIXth century, belong to the Gadagne museum in Lyon (France) and represent portraits or scenes of all kinds. A note of origin certifies that these shadows were removed from a collection devoted to the *Chat Noir* but their historical background is not clearly defined.

It is admitted that the earliest origin of the shadow theater comes from Asia; the most common legend places it in China in the second century BC. This art spread in Europe in the seventeenth century by being commonly called "Chinese shadows". Moreover, it should be noted that the European shadow theater is directly influenced by the art of the silhouette due to the appearance of his black cut-out figures.

Shadow theater thus arrived in France around 1770 with François Dominique Seraphin and achieved first popular success. Thirty years later, this success became a real artistic infatuation with the Henri Rivière theater at the Chat Noir Cabaret. Founded in 1881 by Rodolphe Salis to welcome poets, novelists and bohemian musicians of the time, several hypotheses are explaining the origin of the name of the cabaret, among which the "Chat Noir" is a tribute to Edgar Allan Poe's black cat. The first shadow performances began in 1885 when the cabaret became a worldly place and a successful theater where people used to come for fun in the same way as the Moulin Rouge or the Elysée Montmartre.

The Gadagne museum’s shadows are cut in very thin paper and covered with black ink on one side only. They are between 7 and 20 cm height. Moreover, they are made of pieces of paper all glued together on a paper support. If the viewer is not aware of the cutting, he can easily confuse the works with a simple drawing in China ink. The silhouettes of the shadow theaters are traditionally carried out in zinc plates cut. These artworks could be preparatory studies for the production of larger parts. But this seems compromised

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[1] The Institut national du patrimoine (Inp) is an institution of higher education from the French Ministry of Culture. The institute trains conservators in different specialties (painting, sculpture, photography, textile, paper, furniture, metal objects and ceramic).

The Inp laboratory welcomes students for experimentations and analyses and provides them educational tools. Performing analyses and writing scientific reports in order to complete the objects’ documentation are some of its missions, as well as expanding applied research to the field of conservation.

The Inp laboratory has a scientific imaging equipment and several techniques of microanalysis adapted to the characterization of cultural heritage materials. Much of the analyses performed are based on infrared spectroscopy, specifically dedicated to hybrid materials. This technique allows the identification of a variety of materials, ancient or modern, degraded or not, natural or synthetic. This involves the continuous increment of the spectral database and the development of collaboration and network.

because the shadows do not match with none of the pieces made for the Chat Noir, from an iconographic and practical point of view.

More specifically, the papers that compose the shadows differ in their surface aspect: some are shiny whereas others, less glossy, have instead a matte finish (Fig. 1-b). The characterization of used materials should help to explain their heterogeneous surface appearance and to better understand these objects.

They are very delicate objects and some little pieces of fragments are torn and peeled off. Thus, a completely non-destructive analytical approach was conducted on some of the free fragments. This approach was necessary in order to reposition them during the conservation treatment.

Except the glossy aspect, both types of paper are quite similar according to the observations of the conservator. They are very thin and have the same light beige color on the back. The fiber composition could not be determined because it was impossible to take the amount of material needed. At first sight, there is no difference in color in the black inks. The color intensity leads to believe that it is a China ink. Observations with a binocular microscope highlight the mechanical treatment of some of the surfaces and a subtle difference of tint. The slight shine of matte papers is explained by a smoothing operation, usually performed by means of a hard stone [Fontenelle et Poisson, 1828]. Moreover, it is also clear that the tint of these samples is verging on the brown. The really shiny papers underwent a surface brushing too. Streaks are perceptible under an optical microscope, what suggests the use of a stiff brush. The ink layer is very thick and intensely black. The shiny black papers have also the particularity to generate an impress on the back of the paper support with which they had a prolonged contact, when the shadows were stacked on each others. The presence of a fatty substance deposited on the surface or incorporated in the ink is then supposed.

In order to identify the used materials and characterize the differences between shiny and matte inks, several non-invasive and non-destructive techniques were chosen. First, micro X-ray Fluorescence Spectrometry (µ-XRF) was implemented for the analysis of inorganic compounds (Bruker ARTAX 800, molybdenum X-Ray tube). That enabled to show the presence of iron on all the black surfaces. The significant difference is the presence of calcium and titanium on the shiny areas and the presence of barium on the matte areas.

Then, Infrared and Raman spectroscopies were used complementarily on the free fragments to determinate the ink composition and the potential presence of a surface coating.

The first tests performed with a macro ATR (Smart Endurance, Nicolet 6700,Thermo Scientific) were not conclusive because the fragility of the samples did not allow a good contact and the shiny surfaces reflected the signal of the diamond crystal. It was therefore necessary to consider using a micro-ATR spectrometer (iN10, Thermo Scientific) to realize punctual measurements on the heterogeneous surfaces with a 350 µm contact area, and to work with a germanium crystal to avoid the diamond artifact signal in the 2000 cm^{-1} region. Spectra were recorded between 4000 and 500 cm^{-1} with a resolution of 8 cm^{-1} and 64 scans are accumulated.

Working under this microscope configuration allowed localizing blue grains on the black surface of the shiny fragments. Figure 2 presents the IR spectra obtained on the samples. The spectrum of these blue grains (Fig.2-c) shows an intense band at 2088 cm^{-1} attributed to the stretching vibration of the CN triple bonds in Prussian blue [Kuckova, 2005]. Two others characteristic bands, 1636 and 1540 cm^{-1} are attributed to the amide I and amide II bands and therefore confirm the presence of protein (Fig2-a and c). The region between 1200 and 900 cm^{-1} is related to cellulose (paper).

The IR spectrum obtained for the matte samples (Fig. 2-b) is rather different. The peak at 2088 cm^{-1} is absent and the fingerprint region does not show the same profile. However, the two bands characteristics of the presence of protein, at 1636 and 1540 cm^{-1}, are also visible.

The second part of the vibrational analysis was performed by micro-Raman spectroscopy with a 780 nm excitation wavelength (DXR, Thermo Scientific). Laser power at the sample was reduced to 200µW for a non-invasive analysis of the fragments. The Raman signal was collected with a spectral resolution of 4 cm^{-1} over the range 100-3200 cm^{-1} using x50 microscope objective.

The shiny fragments spectrum show two broad bands at 1320 ($\delta_{C\text{-}C}$) and 1578 cm^{-1} ($\nu_{C\text{-}C}$) (Fig.3-a) that reveal the presence of amorphous carbon [Pitarch, 2012]. The bands position and morphology could indicate a combustion black like carbon black ink or lamp-black ink [Pagès-Camagna, 2004]. Despite a very weak intensity, another Raman band was visible at 2150 cm^{-1}. It seems to be attributed to the Prussian blue grains [Castro, 2005; Tavenska, 2014].

The spectra obtained for the matte samples show much more Raman bands, and no signal of the amorphous carbon is observed (Fig.3-b). The most notable bands are the region between 490 and 640 cm^{-1} with combined bands (here 493, 577 and 626 cm^{-1}), between 1310 and 1350 cm^{-1} (1341 cm^{-1} here) and finally around 1500 cm^{-1}. Given all the information already collected (the presence of iron and the color of the fragments) the bands position and morphology can be correlated with an iron -based ink [Lee, 2008; Pintanida, 2013] and probably iron and logwood [Bicchieri, 2008]. The ink composition and/or a mixture with other organic materials can induce a band shift on the spectra [Lee, 2008].

Although iron was present on both types of fragments, matte and shiny, the performed analyzes proved that the applied inks are not of the same nature.

The shiny fragments were covered with a combustion black ink, based on carbon black or lamp-black. A bone black ink cannot be considered because of the absence of phosphorus in the µ-XRF data. This ink was enriched with Prussian blue, which is a common practice for combustion black [Knipe, 1999]. It corrects their slightly brown tone to intensify the black coloring [Perego, 2005]. Calcium carbonate could be used as filler during the phase of surface paper brushing to give a satiny appearance, what justify the presence of Ca in the µ-XRF data. The presence of titanium cannot be clearly explained, but titanium dioxide is sometimes added as a filler in the ink in order to increase its covering power, but this practice did not start until 1922 [Perego, 2005], which seems a bit late compared to the creation of the shadows.

The matte fragments were colored with iron based ink, alone or mixed with logwood. Since the first half of the 19th century, logwood was found mixed with iron gall inks in the graphic arts field. [Perego, 2005]. The presence of barium revealed with µ-XRF could not be clearly explained although there is a strong probability that it comes from the filler in the paper.

For both types of fragment, the presence of proteins was highlighted by the IR analyses. Both inks may have been prepared using a proteinaceous binder such as animal glue.

The initial suggestion of the presence of an organic coating leading to imprints on the back of the stacked shadows could not be confirmed. This may be because it could not be detected using vibrational spectroscopies, or because its bands are hidden or mixed up with those of the other mixture constituents.

The shadows setting-up using shiny and matte papers was made randomly with no define or specific outline. The observations and the performed analyses show that the used papers were covered with inks from different chemical compositions, highlighting a probable different origin. A hypothesis would be that these two types of paper have been collected by the artist and reprocessed in order to obtain these particularly unique shadows.

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Figures:

Fig. 1: Examples of analyzed shadows, Musée Gadagne, before conservation treatment. a) *[Chien poursuivant une poule], inv. (9)55.198.13;* b) *[Chasseur et son chien], inv. (9)55.198.14* ; c) *[Homme fumant sa pipe, coiffé d'un bonnet de nuit], inv. (9).55.198.10. ©Inp/G.Vanneste and ©Inp/C. Kasprzak*

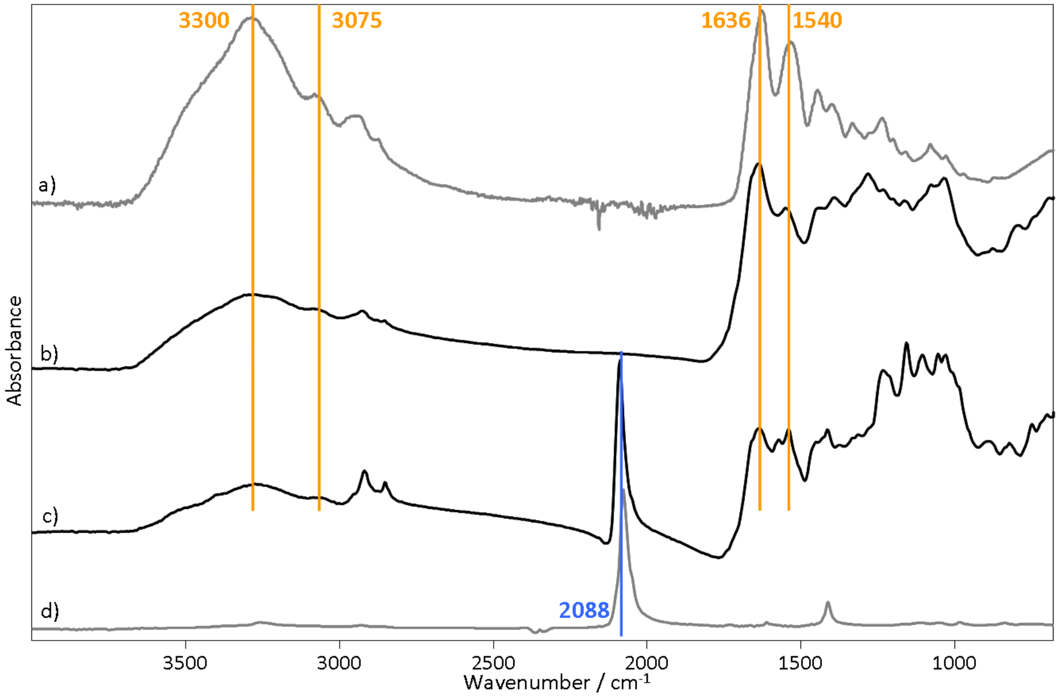

Fig. 2: IR-ATR spectra of two historical samples (black line) and references (gray line). a) Reference of rabbit skin glue (Sennelier, Paris), b) fragment (2013-154-P01) from the shadow entitled *[Homme fumant sa pipe, coiffé d'un bonnet de nuit], inv. (9).55.198.10*; c) fragment (2013-158-P02) from the shadow entitled *[Chasseur et son chien], inv. (9)55.198.14*; and d) reference of Prussian Blue. The indicated bands are discussed in the text.

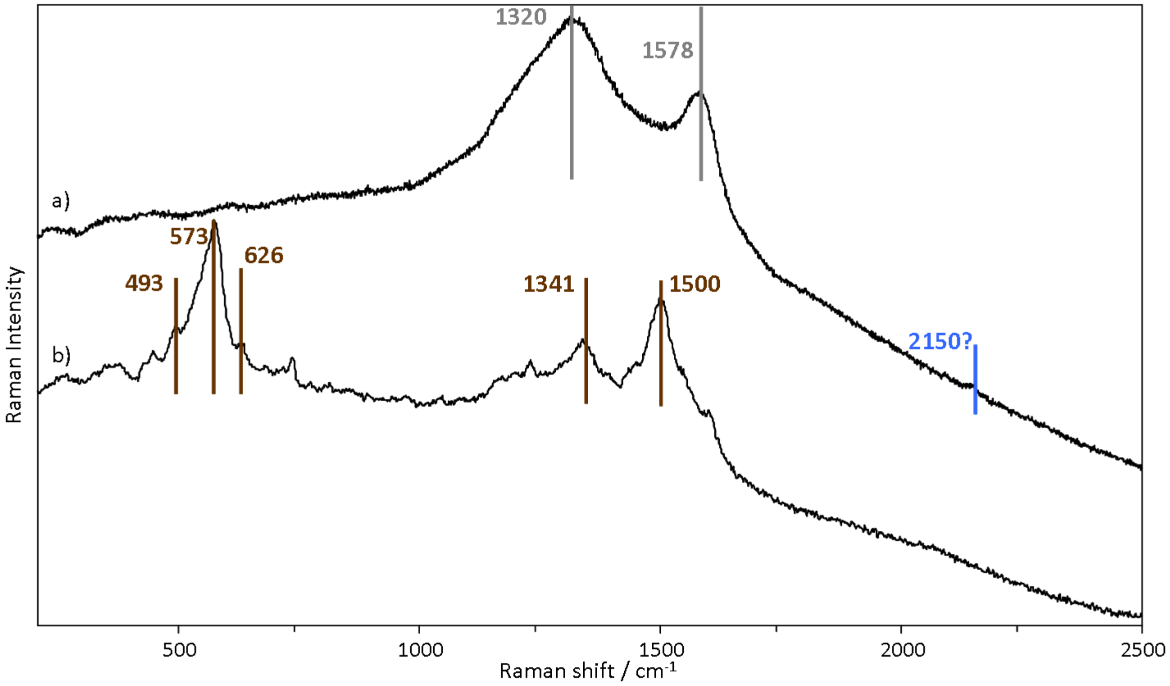

Fig. 3: Raman spectrum of a) the fragment (2013-158-P02) from the shadow entitled *[Chasseur et son chien], inv. (9)55.198.14* and b) fragment (2013-154-P01) from the shadow entitled *[Homme fumant sa pipe, coiffé d'un bonnet de nuit], inv. (9).55.198.10.* The indicated bands are discussed in the text.

Fifty shades of green in Islamic manuscripts

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The recent exhibition of the Calderwood collection of Islamic art and preparations for the new displays at the renovated Harvard Art Museums have focused attention on the range of pigments and materials used in Islamic manuscripts. Although a number of recent studies have looked at the palette employed by Islamic illuminators and artists, the absolute number of works examined is still relatively small and not all of the examples can be definitively ascribed to a particular city and/or closely dated. This makes it hard to distinguish any geographical or chronological patterns in the materials used. The Harvard Art Museums have an extensive collection of Islamic manuscripts and folios, with works of art produced across the Islamic world from the 13th to 19th century. Many of these can be assigned to a particular town or region and are well dated. A comprehensive analytical project was hence initiated to compare the materials and techniques used in a variety of locations from the 13th to 18th century. The current phase of analysis has included manuscripts from Iraq, Egypt, Iran, Turkey and India and includes most of the main production centers.

The initial phases of the project consisted of careful examination with visible, ultraviolet and infrared radiation and detailed photography of areas of interest. Following this, non-destructive x-ray florescence (XRF) and Raman spectroscopy were undertaken in multiple areas of each manuscript. Selected areas were sampled where appropriate after discussion with the curator if the material identification remained uncertain after non-destructive analysis. Samples were analyzed by Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy with energy dispersive microanalysis (SEM-EDX). All colors present on each manuscript were analyzed to assess the full range of materials used.

Although not all manuscripts or folios have been fully analyzed, the current results and comparison with other studies indicate a wide palette with some chronological and regional variation. The most variable of the pigments is green, which is hence the main focus of this paper.

In the 13th and 14th centuries, the main green employed was a mixture of yellow orpiment (arsenic trisulfide) and blue indigo. In the manuscripts studied, copper greens were used sparingly for decoration and highlights in the 14th century only. From the 15th century on, copper greens were used more extensively in parallel with the mixed orpiment-indigo green. Many manuscripts contained multiple different shades of a given color, which were created by mixing or layering pigments. The specific colorants used to produce a green were often related to the subject depicted, implying a deliberate choice by the artist. For example, the copper greens were employed mainly for architecture, clothing (as seen in figure 1a and 1b), decoration or highlights on a background of a contrasting color (often gold), with orpiment-indigo mixtures used more extensively for plants, foliage (as seen in figure 1a and 1c) and backgrounds.

The specific copper green employed was frequently hard to identify even with when sampling was possible. Varieties identified included malachite (copper carbonate), brochantite (tribasic copper sulfate), antlerite (dibasic copper sulfate), verdigris (basic copper acetate) and atacamite (copper oxychloride). In most cases, lead white was also present which complicates the spectra. Although malachite and verdigris are the green pigments most often quoted for Persian works on paper, neither of these was particularly common in this study. In fact, the only manuscript in this study which relied heavily on the use of malachite was a late 18th century painting of *Asavari Ragini* from India. The term verdigris seems to be used generically in the historic literature to refer to copper greens.

In terms of the presence of different copper greens signifies, it may be as simple as small variations in recipes that are, in fact, purely accidental. As mentioned, the artist often sought two greens, a soft greenish-yellow for foliage and landscapes made by mixing orpiment and indigo, and a green appropriate for architecture, some costumes and decoration. This latter green was made with copper using an inexact approach in varying physical environments creating greens that were slightly different from each other chemically. Whether artists knew that these copper greens were deleterious to paper and prone to flaking could have been a motivation for some of the variants. It should be noted that two later suites of paintings contained only indigo-orpiment greens.[i] The former, an Ottoman copy of European portrait prints dating from 1566-74, has little need for green because of subject matter and only uses the mix in the background where the orpiment chunks may, in fact, be used to mimic gold flecks from a hand-colored original. The other three paintings are from an anonymous Shahnama from Shiraz dated to about 1575-90. The lack of any copper greens in these pages is not understood but it corresponds with the study of another Shahnama by Mīrzā Kāsim dating to 1541 that also lacks any copper greens.[ii]

In most manuscripts, only a single copper green was identified. However, some manuscripts from Tabriz, dated to the early 16th century, contain more than one copper green phase. One such manuscript folio (shown in figure 2a) from Tabriz, dated to 1520-40, actually contained three different copper greens in different areas. The main green in the illustration of *The Embrace of Afrasiyab and Siyavush* was the copper sulfate antlerite, the main green in the illuminated text at the top of the image was the copper carbonate malachite (mixed with calcite), and the main green in the outer border was the copper chloride atacamite. Assuming these are contemporary, this suggests that the exact form of the copper green was not important, provided it could be ground or mixed to produce the desired shade. This manuscript folio was also unusual in that it did not contain any of the greens produced by mixing orpiment and indigo. A mixture of copper green pigments was also found in an Ikhanid manuscript from Isfahan, with both copper chloride and copper sulfate identified by SEM-EDX in a sample. Unfortunately this failed to produce a clear Raman or FTIR signal and the exact form of the chloride and sulfate could not be determined.

There was also some chronological and regional variation observed in the pigments used to produce blue and yellow/red. The main material used for blue areas was lazurite (ultramarine) which was found in the majority of the manuscripts studied. The exceptions all occurred in the 14th century but from diverse locations. In two early 14th century Ilkhanid manuscripts, one attributed to Maraga, Iran, and the other to Isfahan, Iran, azurite was the main blue pigment used. In contrast, Ilkhanid manuscripts of a similar date attributed to Tabriz and Bagdad contained ultramarine rather than azurite. Indigo was also identified in most manuscripts but was used mainly to highlight or outline features, for borders, or mixed with other colors. However, in one manuscript dated to the mid-14th century from Cairo, Egypt, the indigo appears to have been the only blue used and is mixed with lead white to create an unusual mid-blue shade. A darker blue in another manuscript from the same folio was found to consist of a mixture of azurite and ultramarine, indicating that all three blue options were available when this folio was produced.

A range of arsenic sulfides were employed and yellow orpiment and pararealgar and occasional red realgar were all identified. Although orpiment was the main phase used from the 15th century onwards, pararealgar occurs in several 13th and 14th century manuscripts and again in some 16th century Ottoman manuscripts. It is normally assumed that when pararealgar is identified, the original pigment was the red realgar and that this has altered subsequently to produce yellow pararealgar. The presence of occasional grains of red realgar within the yellow pararealgar certainly confirms that the latter was derived from the former. However, this implies a deliberate avoidance of the use of yellow within these particular manuscripts, despite the use of yellow orpiment in green areas. Careful consideration of the art historical interpretations of the original color scheme is required to confirm this. Certainly the avoidance of yellows is not the norm observed in this study.

The current project has identified a number of regional and chronological variations but further work is required to assess the materials used in each of the main production centers. This necessitates analysis and study of well dated and attributed works of art in order to build up a comprehensive database of the materials and techniques used across the Islamic world.

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Figures:

Figure 1a: *Timur Celebrates His Conquest of Delhi*, illustrated folio from the Zafarnama (Book of Victory) of Sharaf al-Din 'Ali Yazdi, 1436; Harvard Art Museums 1960.198.

Figure 1b: detail of the copper green robe.

Figure 1c: detail of the tree painted with orpiment and indigo.

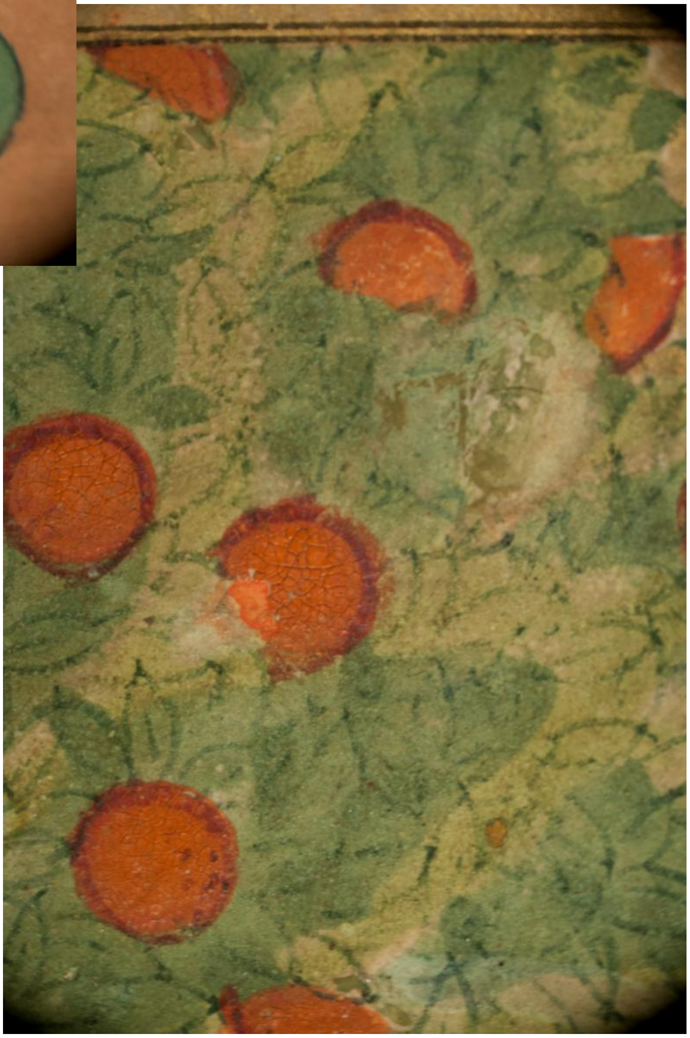

Figure 2a: *Afrasiyab and Siyavush Embrace*, illustrated folio from a manuscript of the Shahnama by Firdawsi, 1520–40; Harvard Art Museums 2002.50.13.

Characterization of daylight fluorescent pigments in contemporary artists' paints by Raman spectroscopy

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INTRODUCTION

Pigments, the coloring matter of paints, exist in every possible color tone and hue. Whereas most ancient pigments have natural sources - earths, minerals or extracts from plants and insects - many of the pigments in present-day paint formulations are synthesized, either inorganic or organic. Both ancient and modern pigments are extensively documented and can readily be identified by, for example, Raman spectroscopy. However, on one specific class of pigments little is known: the daylight fluorescent pigments [1]. Post-WWII, daylight fluorescent pigments slowly emerged on the artists' palette. Nowadays, due to their poor lightfastness, characterization of daylight fluorescent pigments has become of utmost importance prior to conservation and restoration.

The handful of manufacturers of these pigments supply only frugal information on their composition. In most cases commercial daylight fluorescent pigments are made admixing one or multiple fluorescent colorants (1-5%) in a transparent resin. To this, anti-foam agents, UV-stabilizers and optical whiteners can be added. The stained resin, often a copolymer of toluene sulfonamide, melamine and formaldehyde in varying proportions, is hammered and ground into small, insoluble flakes (3-5µm) that can be used as pigments for many applications, including artists' paints.

A series of over 60 daylight fluorescent pigments from different manufacturers and suppliers were collected and analyzed with micro-Raman spectroscopy (MRS) and to a lesser extent pyrolysis gas chromatography mass spectrometry (py-GC/MS) to study the composition of these pigments. A Raman spectral library was built to facilitate the identification of daylight fluorescent pigments in artists' paints. This library was applied on several contemporary works of art.

EXPERIMENTAL

Radiant Color donated samples of the complete PS, JST and PC series. The PS series has a lower concentration of colorants (2-3%), has improved heat and solvent fastness; a UV absorber is present. The JST and PC series have a higher pigment concentration (5%); the former is for aqueous usage, while the latter shows an improved solvent fastness. Finally, Radiant Color supplied a sample of pure toluene sulfonamide/melamine/formaldehyde resin. From DayGlo Color the complete AX series (thermoplastic, not solvent resistant), two samples from the A series (analogue but lower color strength) and three pigments of the T series (thermoset, solvent resistant) were donated by the University of Melbourne. Kremer Pigmente also distributes fluorescent pigments (donated by the Straus Center for Conservation and Technical Studies), but the actual manufacturer of those is unclear.

The S.M.A.K. museum has several contemporary art objects in its collections or on loan from the Flemish Community collections in which daylight fluorescent pigments have been used. Small samples were taken from several works of art (figure 1).

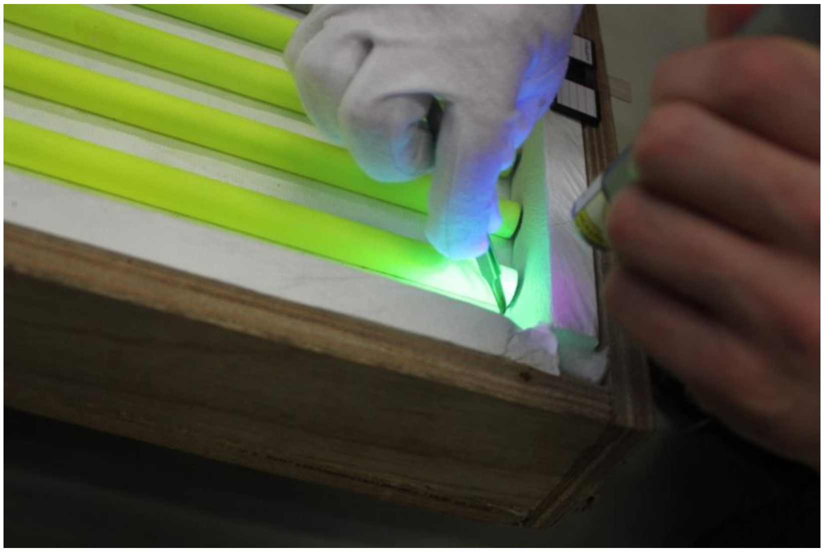

Figure 1. Sampling yellow daylight fluorescent paint from Kristjan Gudmundsson's *Yellow spaces and red channels* (Collection of the Flemish Community/SMAK)

The samples were analyzed with a Renishaw InVia dispersive MRS instrument using a 785 nm diode laser excitation source (laser power at the sample up to 20 mW) and a direct-coupled microscope with 50x long working distance objective lens. The py-GC/MS setup consists of a GSG Curie-point pyrolyzer using 625°C wires, coupled to a Thermo Trace Ultra gas chromatograph and a Thermo PolarisQ ion trap mass spectrometer. The py-GC/MS analyses were done without and with tetramethylammonium hydroxide (TMAH). A Supelco SLB-5ms column (20 m, I.D. 0.18 mm, film thickness 0.18 µm) was used with the following temperature program: 1 min on 50°C, heating to 100°C at a rate of 50°C/min, next to 180°C at 5°C/min and to 320°C at 10°C/min. Finally, this temperature is held for 5 min.

THE RESIN: A COPOLYMER OF TOLUENE SULFONAMIDE, MELAMINE AND FORMALDEHYDE

The toluene sulfonamide/melamine/formaldehyde resin is easily identifiable using MRS and py-GC/MS analysis of the pure resin sample. Although its Raman signal is relatively low, the peaks are in the same order of magnitude with those of the fluorescent colorants (figure 2): the Raman bands corresponding with the resin are marked with *. In case of the fluorescent blue and green samples, however, the intense Raman signals of the phthalocyanine blue (Pigment Blue 15:x) and green pigments (Pigment Green 7) are concealing those of the resin. Yet, the presence of the copolymer of toluene sulfonamide, melamine and formaldehyde, also in these blue and green pigments, is clearly recognizable with py-GC/MS. With this technique, the toluene sulfonamide monomer and related compounds can be identified and in presence of TMAH, also methyl esters of melamine become apparent. On the other hand, no traces of the colorants could be detected by py-GC/MS.

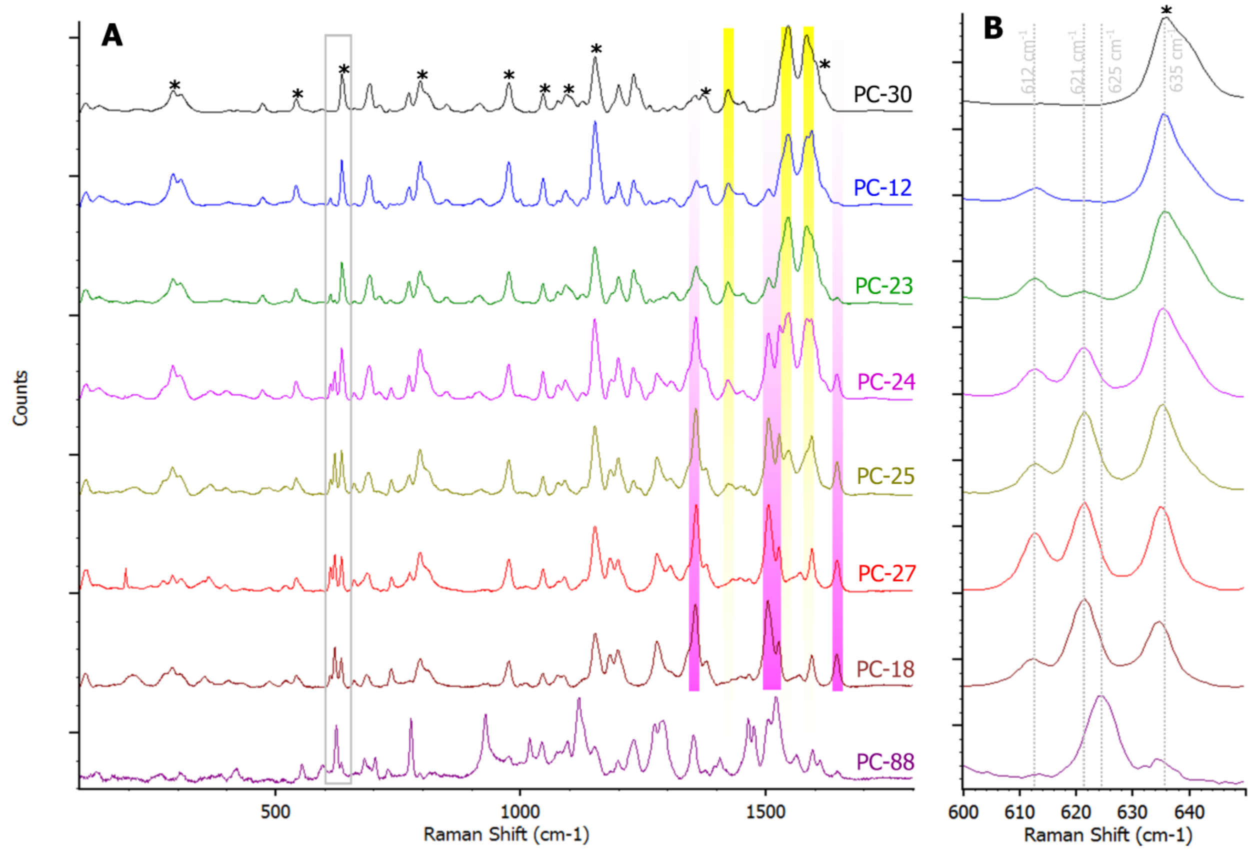

Figure 2. The Raman spectra of Radglo PC series by Radiant Color, from yellow (PC-30) over different shades of orange and red to purple (PC-88). (A) complete spectra, (B) detail. The Raman bands caused by the copolymer resin are marked with *.

DISTINGUISHING BETWEEN THE HUES IN THE SAME SERIES

The MRS spectra of the daylight fluorescent pigments composed spectra of one or more fluorescent colorants and the resin. There might also be a contribution of additives, such as UV-stabilizers, although this could not be identified in any of the samples. The pigment series exist in many fluorescent hues; these are made with only few different fluorescent dyes.

This is demonstrated for the PC series of Radiant Color (figure 2). The spectrum of the yellow PC-30 only contains Raman bands from the resin and a fluorescent yellow dye, characterized by an intense Raman band at 1530 cm^{-1}. This peak decreases gradually in the orange and red tones. In contrast, a band at 1500 cm^{-1} emerges and increases. Orange is thus made as a blend of fluorescent yellow and red dyes. The variance in the relative heights of the 612 and 621 cm^{-1} suggests that two different fluorescent reddish dyes were used, but always blended. The purple pigment is composed of a fourth fluorescent dye, most likely with a small proportion of one of the red dyes. Within a series, a careful study of the relative band heights allows the approximate identification of the daylight fluorescent pigment.

DISTINGUISHING BETWEEN THE DIFFERENT SERIES

Apart from some color tones that are only available for on brand, the daylight fluorescent pigments from DayGlo, Radiant Color and Kremer Pigmente seem to contain exactly the same fluorescent dyes. Similar hues from different series and even from different manufacturers are made using more or less equal ratios of those dyes. The differences between the series lay mostly in specific characteristics for a specific application, and thus rather in differences in the resin, in the resin/colorant ratio or in the presence or absence of additives. Figure 3 shows the ratio of two Raman bands for the yellow daylight fluorescent pigments: 1549 cm^{-1} assigned to the fluorescent yellow dye and 1154 cm^{-1} assigned to the toluene sulfonamide/melamine/formaldehyde copolymer. As was expected, this ratio was significantly lower for the DayGlo T and the Radiant Color PS series, which contain more or less half the amount of colorants of their counterparts with higher color strength. The DayGlo pigments contain slightly lower amounts of the colorants compared with the Radiant Color pigments. The differences between the Radiant Color JST and PC series are much smaller and it may prove impossible to distinguish between these. We found no other spectral features that would allow us to do so, neither could we see any differences in the py-GC/MS analyses.

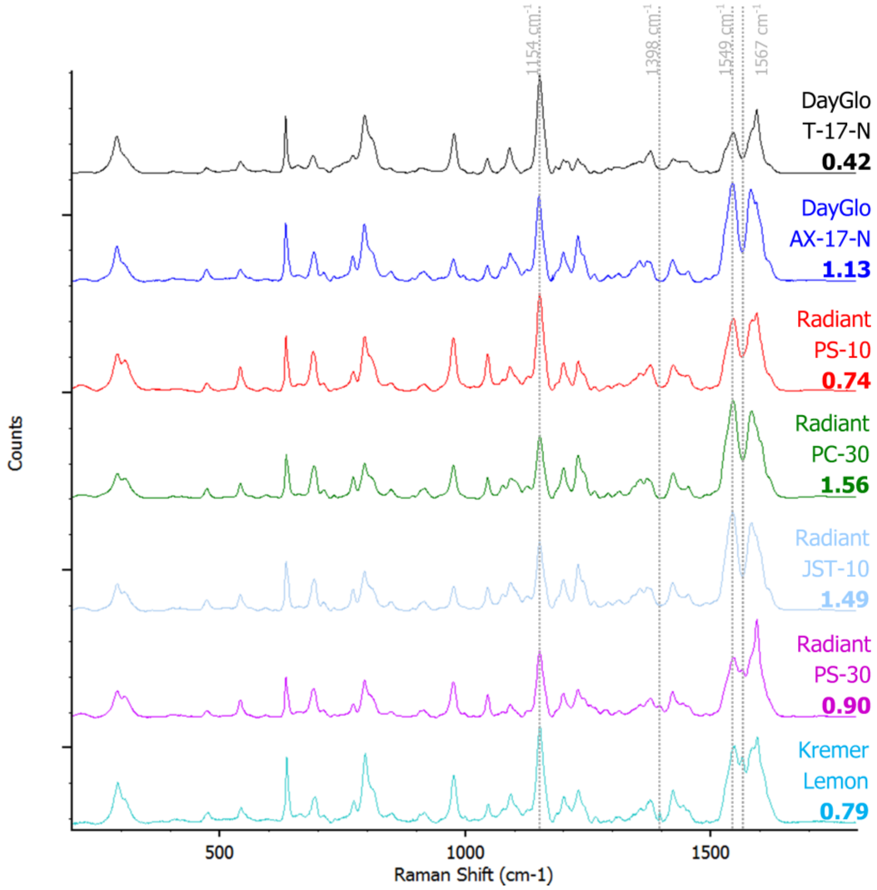

Figure 3. The Raman spectra of the yellow daylight fluorescent pigments by Radiant Color, displaying the resin/colorant ratio (1549 cm^{-1} : 1154 cm^{-1}).

Kremer's Lemon yellow pigment and Radiant Color's PS-30 have two minor spectral features at 1398 cm^{-1} and 1567 cm^{-1} that are not present in any of the other yellow pigments. The origin of these small Raman bands is unclear and might indicate the presence of a second fluorescent yellow dye. Because of the small difference in their 1549 cm^{-1} : 1154 cm^{-1} ratios, it is possible that Kremer's Lemon yellow is a rebranded PS-30.

Analogous results were obtained for the other hues, for example the fluorescent orange and red hues, for which 1507 cm^{-1} was chosen as the marker Raman band. Together with the 1549 cm^{-1} and 1154 cm^{-1}, a complete overview of the fluorescent yellow to red pigments is achieved.

CHARACTERIZATION OF THE FLUORESCENT COLORANTS

Overwhelming the Raman signal of the resin, the blue and green daylight fluorescent pigments are easily identified as Pigment Blue 15:x (according to DayGlo's MSDS files PB15:3) and Pigment Green 7. The eventual presence of optical brighteners or other fluorescence-inducing components could not be demonstrated.

The identification of the colorants in other color tones are less straightforward because their MRS spectra are composite spectra. Using spectral subtraction methods, approximate spectra of the pure colorants could be reconstructed. This way the fluorescent purple in Radiant Color's Radglo PC-88 was identified as (or closely related to) the rhodamine-type Pigment Violet 2 using our spectral library of synthetic organic pigments [2]. The yellow and red fluorescent colorants could (yet) not be unambiguously identified, but DayGlo's product MSDS files specify the coumarin-type Solvent Yellow 135 ("Alberta yellow") and rhodamine-type Basic Violet 11:1, amongst others.

IDENTIFICATION IN PRACTICE

The S.M.A.K. has several works of art with daylight fluorescent paints in its collections. Microsamples were taken from five objects to evaluate the methodology that was developed: *Your Portrait-May* (Tetsumi Kudo, 1966), *Pythagoras* (Jef Verheyen, 1967), *La flèche de Zénon* (Jef Verheyen, 1971), *Yellow spaces and red channels* (Kristjan Gudmundsson, 1996), *Encerreados* (Juan Uslé, 1997).

In some cases a very detailed identification was possible, while in other cases the identification failed. It is unclear to what extent the composition of the daylight fluorescent pigments has evolved during the past 50 years and thus if older formulations have to be added to this study of the present-day pigments. The exhibition prescriptions of some of these works also require blacklight illumination. The poor lightfastness of these pigments, especially under UV-illumination, is well known and might have implications on the colorants and resin ratios.

CONCLUSION

The combination of MRS and py-GC/MS allows the detailed study of daylight fluorescent pigments used in arts. Both the copolymer of toluene sulfonamide, melamine and formaldehyde and the different fluorescent colorants can be observed with MRS. Through comparison of the main Raman bands of the colorants and the resin, it is in most cases possible to determine exactly which brand, series and color tone was used.

Acknowledgements:

The authors wish to thank André Smeets and Koen Paesmans from Radiant Color (Houthalen, Belgium), Petronella Nel and Robyn Joyce Sloggett from the University of Melbourne and Daniel Kirby from the Straus Center for Conservation and Technical Studies (Harvard Art Museums) for kindly sharing their collections of daylight fluorescent pigments, and Marieke Verboven and Claudia Kramer from the S.M.A.K. (Ghent, Belgium) for access to their collection of contemporary art. This research is funded by the Belgian Science Policy in the framework of the project 'Modern and Contemporary Art in the laboratory: Analytical study of 20th century paint' (grant MO-39-010).

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Investigation of zinc carboxylate reaction products in several 20th-century Canadian paintings using FTIR spectroscopy[1]

Kate Helwig, Jennifer Poulin, Marie-Claude Corbeil, Elizabeth Moffatt, Dominique Duguay

Zinc carboxylate reaction products have led to conservation issues in a number of 20th-century Canadian paintings. Deterioration phenomena include: zinc soap protrusions, cracking and lifting paint, and disfiguring surface layers. Characterization of the compounds present in deterioration phenomena such as these is an important step in understanding their formation and in the design of appropriate conservation treatments.

In two oil paintings dating from the 1930s, one by Lawren Harris and the other by Carl Schaefer, zinc fatty acid salts (zinc soaps) have aggregated and formed protrusions that have broken through the paint surface. The FTIR spectra of the protrusions were compared with those of a series of synthetic zinc fatty acid salts (zinc palmitate, stearate, azelate, oleate and binary palmitate-stearate). Combined GC-MS and FTIR results indicate that the protrusions contain primarily zinc palmitate and stearate, with small amounts of oil and free fatty acid. The FTIR spectra of the zinc soaps in the protrusions, however, showed peak splitting of the carboxylate bands (ν_aCOO and ν_sCOO) and the strong CH_2 deformation band (δCH_2) that were not observed in the synthetic zinc palmitate, stearate or binary palmitate-stearate salts. The observed peak splitting is likely due to structural distortion. It is significant in the interpretation of the FTIR spectra that zinc soaps containing primarily saturated fatty acids can exhibit peak splitting when they form naturally in paint layers.

Cracking and lifting paint related to zinc white underlayers has also been noted on a number of 20th-century Canadian paintings. *Rouge sur blanc*, a 1954 oil painting by Jean McEwen, has a thick zinc white underlayer showing fragility and lack of cohesion due to an elevated concentration of zinc soaps. *Lake Superior Village*, an oil painting by Charles Comfort from 1927, has had a long history of structural problems, with the paint cracking and lifting from the white ground. The problematic ground has a waxy texture and was found to be a mixture of lead white and zinc white with a very high concentration of metallic soaps.

As well as producing zinc fatty acid salts within the paint, zinc white can also react with low molecular weight carboxylic acids. FTIR analysis of a disfiguring surface accretion on an oil painting from 1952-54 by Andor Weininger showed that it was composed primarily of zinc 2-hydroxypropanoate (zinc lactate). Low molecular weight carboxylic acids, such as lactic acid, form a major class of atmospheric pollutants and can be immobilised on the surface of the paint by reaction with zinc. Similarly, in a mixed oil-alkyd painting by Jack Chambers from the 1960s, reaction of formic acid with zinc white produced zinc formate in the paint; in this case, the source of the formic acid could be off-gassing from the wooden support or the degradation of the alkyd paint medium.

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[1] This presentation is based in part on the following: Kate Helwig, Jennifer Poulin, Marie-Claude Corbeil, Elizabeth Moffatt and Dominique Duguay. "Conservation Issues in Several 20th-Century Canadian Oil Paintings: The Role of Zinc Carboxylate Reaction Products." in *Issues in Contemporary Oil Paints (ICOP), Proceedings of the Symposium, 28 and 29 March 2013, Amersfoort, The Netherlands* (edited by K.J. van den Berg, A. Burnstock, A. de Tagle, M. de Keijzer, G. Heydenreich, J. Krueger and T. Learner). Switzerland: Springer International Publishing, 2014. **In Press.**

Natural resins and balsams from an 18th century pharmaceutical collection characterized by Fourier-Transform Infrared Microspectroscopy

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INTRODUCTION AND EXPERIMENTAL

Natural resins commonly are classified based on the connection between nomenclature and chemical composition. However, resin chemistry is connected to the botanical classification of source plants as well. Investigation of natural resins therefore can be enhanced by adding taxonomy. This approach successfully was applied to the Vigani Cabinet, a collection of 300-year-old pharmaceutical and chemical materials owned by Queens' College, Cambridge (UK). [1] This cabinet was compiled by John Francis Vigani, who held the first Chair for Chemistry in Cambridge UK, in 1703-04. In a previous comprehensive study the cabinet was described as a whole. [2] Among around 570 samples of natural raw material it contains 35 natural resins and balsams in an almost untouched condition, with their original labels still attached. Together with the cabinet, the invoices of the materials and lecture manuscripts associated with J. F. Vigani are preserved. It has to be stressed out that this collection contains natural materials that have undergone more than 300 years of natural aging in bulk and in the dark, which are very different conditions to exposed painting materials such as varnishes.

In an earlier work, botanical specimens, reference materials and 23 natural resins from the Vigani Cabinet have been analyzed with gas chromatography-mass spectrometry (GC-MS) with and without methylation. [1, 3] This technique provided detailed molecular compositions of the studied materials which is not discussed here. By correlating the GC-MS data profiles to those of related reference materials from botanical sources and recent collections it has been possible to clarify both composition and nomenclature of the aged resins sampled from Vigani's Cabinet. Unfortunately, reliable botanic reference material has been was available so far only from Pinaceae and one Pistacia sample. Based on the GC-MS analytical data, nomenclature and/or botanical source the investigated resins were classified in five groups: Conifer resins, Sapindales resins, Fabales resins (balms), fossil resins, and shellacs.

This knowledge served as a basis for the interpretation of the infrared spectra presented in this study. Generally, it is difficult to identify natural resins only on the basis of their infrared spectra. [4] The aim of this investigation was to establish to what extent it is possible to distinguish natural resins and balsam by their infrared spectra. The samples were applied in a diamond anvil cell (HPDO). Mid-infrared Spectra were recorded in transmission mode using an infrared microscope (Bruker Hyperion) connected to a FTIR-spectrometer (Bruker Tensor 27).

CONIFER RESINS

Vigani's Cabinet contains various materials labeled as "Turpentine" or "Terebinthina". Turpentine in this meaning refers to the resinous exudations of certain trees and today commonly is designated as "resin". According to the labels and historic sources these can be assigned either to resins from *Pinaceae* species (conifers) or *Pistacia* species which differ from each other in chemical composition. Conifer resins contain diterpenoids while *Pistacia* resins are composed of triterpenoids. [5] The biggest group of conifer resins originates from a broad range of species among Pinaceae family, from the genera of *Pinus* (pine), *Abies* (fir), *Picea* (spruce), and *Larix* (larch).

Infrared spectroscopy applied to most of these turpentines („Venice Turpentine“, „Terebintina Strasbourg“, Terebinthina Communis“) revealed similar spectra. They exhibit typical features both of natural resins in general and for diterpeniod resins. They are also in accordance to respective reference IRUG spectra (eg. NR00114 „rosin“). GC-MS analysis has revealed different *Pinaceae* sources (eg *Pinus* sp., *Larix* sp. *Abies* sp.) for the single specimens which do not reflect in different infrared spectra, because they are mainly distinguished by isomers of diterpenoid carboxylic acids and by presence of resin alcohols such as larixol or abienols . [1] Furthermore, specific ageing characteristics of conifer resins as uncovered by GC-MS analysis obviously do not reflect in infrared spectra. Infrared absorptions of the diterpenoid conifer resins from Vigani's Cabinet investigated in this study do not meet the flow chart for natural resins published by Derrick (1998) in [4]. In Vigani's Cabinet, there is one specimen labeled as „Oil of Turpentine“ which, according to Vigani's records, is a distillation product of Venetian Turpentine. [2] The infrared spectrum generally is similar to those of diterpenoid (conifer) resins except the carbonyl stretching band which lays at higher wavenumbers. Nevertheless the spectrum very closely fits that of a turpentine from the IRUG database (NR00119), thus suggesting the presence of a diterpenoid product.

In Vigani's Cabinet one sample is labeled "Pix Burgundica". It consists of one bigger lump that obviously has solidified as cast after thermal treatment. In the time of its origin there was some confusion about the botanical source of „Burgundy pitch“, especially in England. Very likely it has been obtained from the "Pitch-Tree" (*Picea abies*) or from the pine (*Pinus sylvestris*) by distillation or melting. [1] For GC-MS analysis and FTIR spectroscopy different samples were taken from the brown, hard outer crust as well as from the sticky interior of the lump. According to GC-MS analysis a fir resin had been used for the production of this material [1]. The sticky inner layer (A/23a) was very similar in composition to a not aged coniferous resin, while the black crust (A/23b) contained more oxidation products. The black crust (A/23b), in contrary to it appearance, has aged only to the same degree as the dried-up "turpentines" according to GC-MS-analysis. Under FTIR spectroscopy the inner layer of „Pix Burgundica“ indeed resulted in a spectrum that is very similar to that of conifer resin (eg. Venetian turpentine). The infrared spectrum of the black crust showed a bigger difference than GC-MS data supposed. Although generally representing a diterpenoid resin spectrum, the absorption in the carbonyl stretching region (1712…1600 cm^{-1}) is enhanced and much broader as compared to the inner layer, with a distinct band at c. 1602 cm^{-1}, indicating a high level of oxidation. Surprisingly, a sharp band of medium intensity at 1515 cm^{-1} might indicate a carboxylate but requires further investigation.

Another diterpenoid conifer resin type is „Sandarac“, which was gained from different species of the Cupressaceae familiy (*Juniperus spp., Tetraclinis sp.).* [3] The specimen from Vigani's Cabinet labeled "Sandaracha" was identified by GC-MS as a resin from *Tetraclinis articulata*, i.e. „true Sandarac". Its infrared spectrum shows typical features of diterpenoid conifer resin. There are minor spectral features that might be characteristic for true Sandarac, as they appear in the IRUG reference spectra for Tetraclinis a. (eg. NR0141) as well.

SAPINDALES

Numerous genera from the plant order of Sapindales produce well known triterpenoid resins. [5] The Vigani Cabinet contains three specimens which by their name can be attributed to the *Pistacia* resins from the

Anacardiaceae family („Terebinthina e Chio“, „Terebinthina e Cypri“ and „Mastic“). Although being of great interest, Vigani’s Cabinet does not contain any resin of “Dammar” type, because these have not been on the market at Vigani’s time. According to GC-MS analysis the specimen “Terebinthina e Cypri” from Vigani’s Cabinet was obtained from a *Pistacia* species, presumably *P. terebinthu*s L. During the 17th century, this resin from this “Terebinthus tree” usually was called “Cyprus Turpentine” and therefore represents the other type of products designated „Turpentine“, as mentioned above. The infrared spectrum of “Terebinthina e Cypri” is very similar to that of diterpenoid conifer resins, although containing triterpenoids. A slight difference is the generally broader appearance of the absorption bands. This feature could be verified by means of the IRUG reference spectrum for Pistacia terebinthus (INR000157). The specimen “Terebinthina e Chio” from Vigani’s Cabinet showed a very similar spectrum, apparently in accordance to its name. Surprisingly, in GC-MS analysis this specimen proved to be of diterpene composition and originating from a conifer (*Pinus* sp.). It can be stated that this product is a counterfeit and was sold for an even higher price than true turpentine. [1] In this case, the drawback of using infrared spectroscopy today for the characterization of a resin is obvious.

Mastic is a resin harvested from *Pistacia lentiscus* L.. It has a ychemical composition very similar to that of true turpentine (*Pistacia terebinthus* L.). [3] Consequently, the infrared spectrum of the single specimen “Mastiche” present in Vigani’s cabinet is almost identical to that of „Terebinthina e Cypri“ (from *Pistacia* sp.) as well as to the IRUG reference spectrum (INR00223). These findings coincide with the general difficulty to distinguish *Pistacia* resins by GC-MS either.

Another group of triterpenoid resins is produced by species of the Burseraceae family. These resins generally contain pentacyclic, unsaturated alcohols, but no aromatic compounds. [1] The specimens “Gum Elemi” and “Gum Copal” from Vigani’s Cabinet were characterized by GC-MS analysis as similar products from either *Protium* or *Canarium* genera. Their infrared spectra are very similar to each other, but also closely related to those of the *Pistacia* resins mentioned above. There are also two specimens labeled as “Tacamahaca” contained in Vigani’s Cabinet. This today nearly unknown product originated until the end of the 17th century only from American trees. By GC-MS-analysis it could be shown that the specimens were gained from *Bursera* species, a genus connected to “American copals" today. The composition of *Bursera* resins differs slightly from other American triterpenoid resins (eg. from *Protium* species). [1] The infrared spectra of both of these samples are very similar to each other as well as to the spectra from the other Burseraceae resins presented above. A more detailed inspection of the spectra of all Burseraceae revealed minor spectral features in the range of 1095…990 cm^{-1} (alcoholic stretching vibrations) that might be characteristic for this type of triterpenoid resins, as they were verified by the respective IRUG reference data for American copals (eg. INR00329, INR00342). It has to be mentioned briefly, that "Copal" in the modern sense is a generic name for different resins from Africa, Asia and America. Contemporary to Vigani it was used only for resins from America, even though "oriental copal" may originate from other parts of the world. [1]

FABACEAE

The term „balsam“ is used for different types of plant products. In a very general sense it describes all types of resinous exudates from trees and shrubs. More precisely, Copaiba balsams are gained from several *Copaifera* species of *Fabaceae* family growing in South America. They are chemically characterized by labdane diterpenoids. [5] The Cabinet contains two materials clearly attributed to „Copaiba“ („Balsamum Cipivi“ and „B. Capivi“) which are of different appearance. The specimen „Balsamum Cipivi“ could be characterized by GC-MS analysis as a certain type of balsam from *Copaifera* sp. Its infrared spectrum generally represents the type of a conifer resin spectrum, but with generally broader bands and a very strong and broad absorption in the carbonyl stretching region (1715 cm^{-1}). These features can be found in the IRUG reference spectra as well (eg. INR00140). Therefore, also Copaiba balsam cannot be distinguished from other di- or triterpenoid resins by means of FTIR spectroscopy. There is a specimen labeled as „Balsamum e Gilead" in Vigani's Cabinet, that shows a similar infrared spectrum. GC-MS analysis revealed a triterpenoid resin related to *Pistacia* sp., probably mixed with linseed oil. Another specimen in Vigani's Cabinet is labeled as „Gum Anime". This term is used today for American resins from *Hymenaea* sp. or *Protium* sp. However, through GC-MS analysis this specimen from the cabinet could be attributed to African *Fabaceae* resins of *Daniella* sp. or *Guibourtia* sp. [3] Its infrared spectrum is related to that of Copaiba balsam but shows sharper absorption bands in the fingerprint region (particularly at 1031 and 888 cm^{-1}). These features are in accordance with the only IRUG reference spectrum of anime (INR00052).

Another group of so-called „Balsamic resins" may origin from different botanic and geographic origins. The South American balsams are called Peru or Tolu balsams. Their main components are not terpenoids but aromatic acids (benzoic, cinnamic acid) and corresponding aromatic alcohols (benzyl- and cinnamic alcohols). [5] The two specimens from Vigani's Cabinet labeled "Balsamum Peruvianum" show infrared spectra that are different to all other natural resins described in this study. The spectra are clearly dominated by features typical for aromatic compounds (C-H-stretching, C-C-aromatic stretching, C-H-out-of plane deformation absorptions in a complicated pattern indicating mono- and di-substituted rings) together with a high number of other sharp bands of medium intensity in the fingerprint region. The carbonyl stretching absorption lays at c. 1712 cm^{-1}. The spectra of both Peru balsams from the cabinet are in close accordance to the IRUG reference spectrum (INR00118). GC-MS analysis of both resins confirmed the origin from *Myroxylon balsamum* Harms plant as followed from the content of benzylbenzoate, -cinnamate, cin-namylbenzoate, -cinnamate, benzoic, and cinnamic acids. Another specimen in Vigani's Cabinet labeled "Balsamum Americanum" shows an infrared spectrum very similar to the Peru balsams. GC-MS analysis showed mainly unidentified phenylpropanoids and their esters as well as small amounts of diterpene and triterpene acids, indicating probably a mixture as mentioned in historical sources.

The specimen labeled "Balsamum Tolutanum" from Vigani's Cabinet appeared as a *Myroxylon* sp. balsam as well in GC-MS analysis. However, its infrared spectrum is slightly different to those of the Peru balsams, mostly in the C-H-out-of plane deformation region which is less complicated. The spectrum is almost identical to the IRUG reference spectrum of Tolu balsam, explicitly from *Myroxylon balsamum* Harms plant (INR00124). Even a better correlation, however, exists to the IRUG reference spectrum of Benzoin gum (INR00224). It turned out that the infrared reference spectra of Benzoin (IRUG INR0037, INR0084, INR0138, INR0224) are very similar to those of Tolu balsam as well the results from GC-MS analysis are. However, the identity of Tolu specimen from the cabinet with Benzoin can be ruled out due the different appearance of the related resins. There still seems to be confusion between Peru, Tolu, and Benzoe balsams. Whether this is caused by a variation in the composition of the *Myroxylon* resins, by different botanical sources, or just by incorrect terms, could not yet clarified based on the available data. The specimen „Balsamum Capivi" from Vigani's cabinet shows an infrared spectrum similar to the spectra of Tolu balsams and benzoins, in contrary to its designation which would suggest a non-aromatic Copaiba balsam (see above). Only the carbonyl stretching absorption lays in the range of esters (1732 cm^{-1}) instead of carboxyl carbonyl absorption at c. 1700 cm^{-1}. GC-MS analysis indicates eugenol, which explains the similarity to benzoe resins, and probably guaiacyl derivatives.

FOSSIL RESINS

Three amber samples (“Succinum citrinum”, “S. flavan”, “S. albam”) from Vigani’s Cabinet exhibit similar infrared spectra typical for fossil amber, including the “Baltic shoulder” at 1235...1175 cm^{-1}. The spectra are in accordance to several IRUG Baltic amber reference spectra as well. By GC-MS analysis of the fraction which was soluble in methanol-trichloromethane mixture (50/50) characteristic markers of Baltic amber (succinic acid, succinates, isopimaranes, abietanes) could be detected [3]. The infrared spectrum of the specimen labeled „Succinum nigram“ (black amber) rather resembles the infrared spectrum of bitumen with almost no carbonyl stretching band. However, in GC-MS analysis the soluble fraction still gave results characteristic for amber. That sample is somewhat similar to the spectrum of a sample labeled „L[apis] Gagatis“ as well as to IRUG reference spectra of this kind of natural material (eg. spectrum NR000146, Dead Sea pitch). Thus, both of these original samples most possible are fossil mixtures of hydrocarbons including aromatics.

SHELLAC

The Vigani Cabinet contains four samples that can be identified as shellac already from the labels („Gum Lacca in Granis“; „Gum Lacca in Massis“, „Seedlack & Shellack“ „Shel Lac“). Infrared spectra were recorded from three of them which identified these materials as true shellac without doubt. GC-MS analysis was not carried out on samples from this group.

CONCLUSION

As a general conclusion, the potential and limits of FTIR spectroscopy in the field of natural resins are:

- Natural resins based on terpenoid hydrocarbons, both diterpenoid and triterpenoid, cannot be clearly distinguished by infrared spectroscopy in general. However, there are indications of minor spectral features of diagnostic value for Sandarac, Burseraceae resins, and Anime.
- Ageing and oxidation state of processes conifer resins (eg. “Pix Burgundica”) may be detected from the intensity and shape of the carbonyl stretching band
- The balsams based on aromatic compounds (Peru, Tolu, and probably Benzoe) easily can be distinguished from other natural resins by infrared spectroscopy.
- Among the fossil resins ambers as well as bitumen clearly can be defined by FTIR spectroscopy.
- Shellac clearly can be identified by FTIR spectroscopy

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Microextraction for the spectroscopic identification of binding media in early 20th century matte paint

Lauren Klein

As part of an ongoing investigation into the materiality of early 20th century commercial paint, a method was developed for the enhanced analysis of binder using FTIR. This method, although applicable to any type of paint, is particularly useful for matte commercial paints, which can be difficult to identify. One major complication arises from a common way that matte paints are typically made: a low binder to pigment ratio. Therefore, matte paints can be particularly difficult to identify with FTIR because a low binder concentration produces a weak binder signal, which are then often obstructed by pigment and filler peaks. In response, this research demonstrates a method to augment the identification of matte commercial paint by releasing the binder from the pigmented matrix and concentrating it onto an IR reflective substrate. This research especially hopes to provide valuable information on the use of early 20th century matte paints, as during this time artists began to demonstrate an interest in a matte appearance while commercial matte paints started to become widely available.

By 1915, trade journals like The Painter and Decorator were declaring that flat wall paints had "grown up like mushrooms in five or six years."[1] This new availability of matte commercial paints coincided with artists' interest in creating different degrees of sheen on the same painting as they experimented with unvarnished paints. And while much investigation has been done on the historical and scientific study of enamel commercial paints that proves commercial paint was integrated into works of this period, little scientific research has been done on the use of matte commercial paints.[2] This may be because, in addition to the subtleties distinguishing commercial from artists paint, matte paints also have the challenge of a low binder concentration.

A microextraction technique for FTIR was chosen to address the low concentration of binder in the samples to take advantage of the method's unique ability to separate and concentrate while also detecting very small amounts. Subsequently, the microextraction technique was customized for matte commercial paint by utilizing samples from commercial paint brochures and then applying the technique to samples from works in MoMA's collection that were created by various designers who more likely would have applied paint directly, without manipulation. Other sources of potential contamination were eliminated in the experiments by selecting works with no history of conservation.

The microextraction technique was first developed for an oil binder. First the paint was screened for an oil binder using a diamond cell and FTIR in transmission. Then, a 5-10 microgram sample of the paint was placed on a texturized aluminum foil surface. The sample and a control section of the aluminum were both treated with 1 microliter of alkaline solution. After evaporation of the alkaline solution, 6 microliters of an organic solvent was applied to both the sample and the control area. Deposits were spot analyzed using a Thermo Nicolet Continuum microscope with an MCT-A detector attached to a Nexus 670 spectrometer bench using a Happ-Genzel apodization. The microscope was fitted with UV fluorescence to permit examination of samples under UV and this helped to inform collection of data (Figure 1). Spectra were collected in reflectance mode between 4000 and 650 cm^{-1} using 256 scans and a corresponding background and 4 cm^{-1} resolution. The spectra were viewed and analyzed by Omnic spectroscopy software. Later, a Bruker Hyperion series FTIR with a Focal Plane Array detector was used for its mapping capabilities to help more easily identify where the deposits of extracted material appeared on the aluminum foil.

Because this method is a destructive technique, utilizing paint samples from brochures was essential for the development of the technique because the samples closely mimicked the age and composition of commercial paint potentially used in artwork. Sampling from these sources also allowed for the development of further improvements to the technique to give confidence to the interpretation that oil was present in the sample and was not contributed from an extraneous source. The further improvements include adding a control section to the method to check for contamination, utilizing a microbeaker to decrease the interactions with the sample matrix while also increasing the effectiveness of the benzene, and creating a texturized surface to concentrate the extracted binder.

The technique produced was one that successfully and consistently gave a confirmation of oil binder when present. Using FTIR, the presence of oil binder is an interpretation that can be difficult to make with a matte paint pre-separation, especially when the inorganic peaks obscure the binder peaks. An example can be seen in Figure 2. The top spectrum shows the transmission, pre-extraction sample where the peaks in the region below the carbonyl are obscured by inorganic peaks. The bottom spectrum shows the reflectance, post-extraction sample where only the oil, and perhaps a natural resin, is present.

The technique was then applied on a number of works including *St. Mark's Tower* by Frank Lloyd Wright. The method was also effective in confirming the presence of oil. The binder was even more ambiguous than the paint chip samples to interpret from the transmission spectrum as the carbonyl was very weak. In this case, the technique is even more important to the interpretation of oil as the binder.

Although this technique is not outright novel, it is innovative in that it draws inspiration from several different areas, including microextraction for FTIR proposed by several articles and books in the field of cultural heritage, as well as derivatization methods for GC-MS. The technique developed not only presented a successful extraction method for oil binder using FTIR, but also was successful at identifying the presence of an oil binder when applied to matte paint of various architectural models and works on paper in MoMA's collection. Additionally, the method utilizes readily available materials and could be easily applied in any conservation science lab. Although the binder identification of matte paint alone does not distinguish commercial from artist-made paints, this research hopes to draw attention to the analysis of early 20th century matte paints and add to the discussion about the use of commercial paints in early 20th century works.

Further research is being done to test the limits of detection and to improve the sensitivity of this technique. FTIR with FPA mapping may help achieve this by increasing the ability to locate and analyze very small amounts of extracted material. Additionally, the method is currently being developed for another common binder in early commercial matte paints, protein—e.g. casein, glue. Looking ahead, quantitative analysis, in the form of GC-MS, might be helpful in predicting the amount of binder, and thus the amount of extracted material, one would expect in a certain sized particle.

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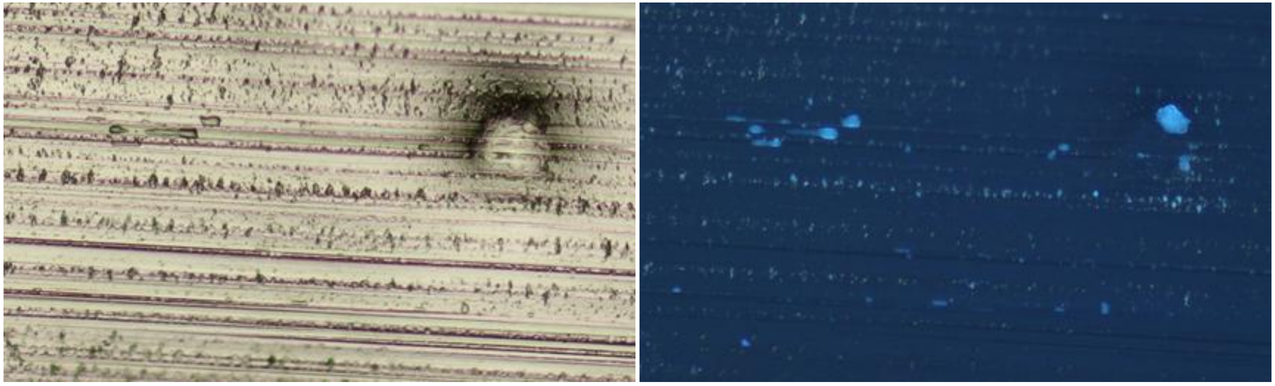

Figure 1. UV light helps to inform on location of deposits of extracted material

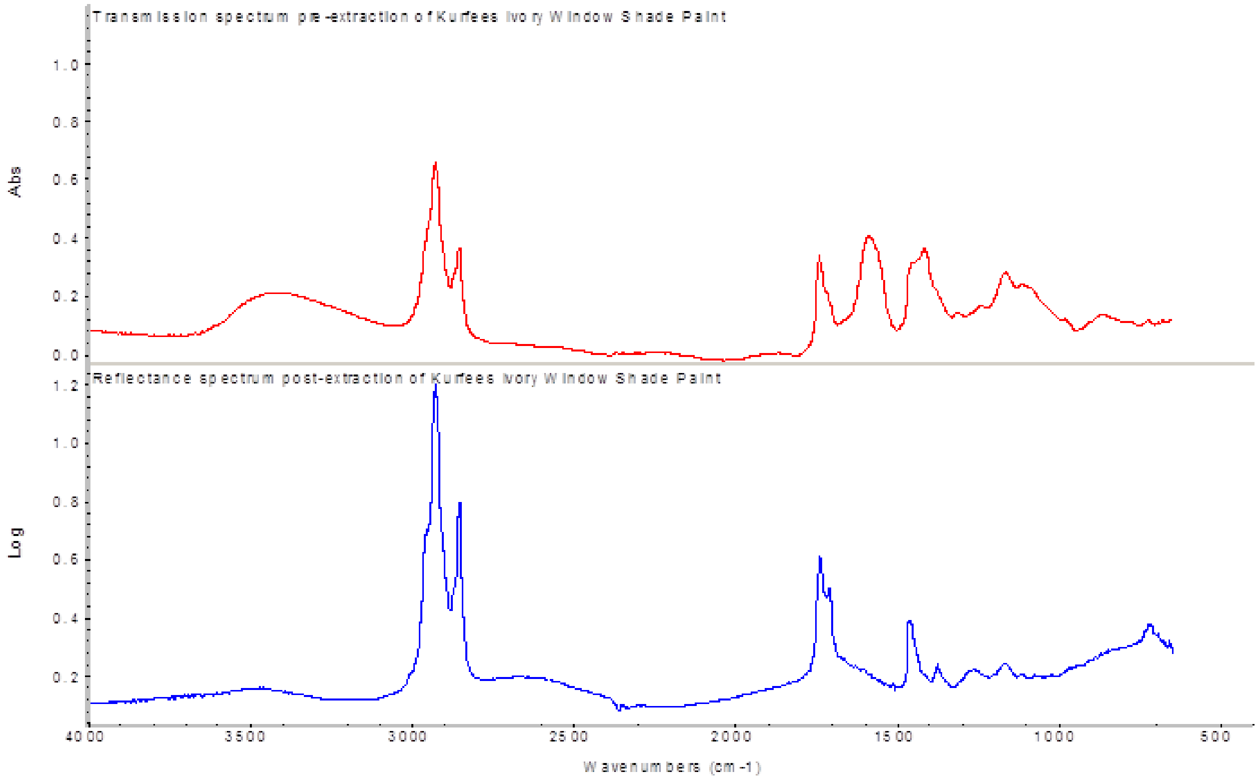

Figure 2. Comparison of pre and post extraction of a commercial house paint

Forensic applications of FTIR and Raman Microspectroscopy in studies of age, attribution, and authenticity

James Martin

FTIR and Raman microspectroscopy are powerful, versatile methods for characterization and identification of materials used to create, restore, and preserve works of art and other cultural property – as evidenced by the more than twenty year history of the Infrared & Raman Users Group.

Identification of materials helps conservators diagnose and treat works in their care, helps art historians research materials and technologies used to produce works from the same or different sources, and – together with stylistic analysis and provenance research – plays an essential role in studies of age, attribution, and authenticity.

FTIR and Raman microspectroscopy also are common analytical tools used in forensic laboratories for examination of trace evidence – such as paint binders and pigment, tapes, fibers, illicit drugs, explosives, and other materials that produce unique and characteristic spectra.

The principal uses of FTIR and Raman microspectroscopy in forensic laboratories are to assess whether a known and questioned material match – for example, traces of paint found on clothing worn by a hit-and-run victim and paint on a suspect vehicle – and to provide investigative leads.

Most trace forensic evidence involves current, recent, or modern materials, whereas materials found in works of art and other cultural property may also have originated in past centuries or millennia. Nonetheless, many of the same basic materials are represented in traditional trace forensic evidence and works of art and other cultural property – such as polymers, pigments, and fillers found in paints, plastics, and adhesives.

This presentation will discuss and illustrate forensic applications of FTIR and Raman microspectroscopy for analysis of trace evidence materials found in works of art, using as case studies investigations related the criminal and proceedings conducted since 1994 for the Federal Bureau of Investigation, U.S. Marshals Service, and collectors and law firms.

The terracotta sculptures of Palazzo Venezia in Rome. Investigation on the constituent materials for the knowledge and the conservation project.

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This work presents the results of the investigation carried out on a group of terracotta sculptures (16th-19th century) belonging to the extraordinary collection of Palazzo Venezia in Rome. The study, the diagnostic analysis and the conservation work were possible thanks to the grant supplied by the Getty Foundation of Los Angeles and by the bank Intesa San Paolo [1-4].

The terracotta sculptures had a practical function as they were of great use as sketches to the creation of the final masterpieces. As a consequence, the terracotta sketches allow reconstructing the creative process of the artists and for this reason they are fundamental to outline the ancient workshop production.

The analysis was performed to support the conservation work aimed at removing the surface dirt, soot or carbonaceous deposits but also non original layers applied subsequently the creation of the artworks. So, the analysis was focused at solving specific problems arising during the conservation process. In particular, X-ray spectroscopy (XRF), internal micro-stratigraphic investigation, Fourier Transform Infrared (FT-IR) and micro-Raman spectroscopy were chosen as useful techniques to study the morphology and composition of the surface layers. The cleaning work was performed mainly with laser under different conditions of energy, spot diameter, and fluence [3-4].

In the present work the results of the analysis on fourteen sculptures, restored within the research project, will be presented and discussed (Table 1).

Often the terracotta models were covered by coloured patinas simulating the materials of the corresponding sculptures, i.e. white for marble, green for bronze, etc. A peculiarity can be found in the sculpture representing *The Virgin with the Child, Saint Enrich, and an Angel* by Ubaldo Gandolfi (1728-1781). In fact, this terracotta was painted with different colours because it was created probably as model for a painting and not for a sculpture [5].

The characterization of the surface layer composition was fundamental in some cases to decide the removal of the layer itself. For example in the model sculpture representing *Olindo and Sofronia* (half of the 17th century), by a Roman sculptor of the 17th century, the analysis revealed the presence of a red surface layer made of crystalline hematite mixed with an organic synthetic dye (Figure 1), certainly non-original (Figure 2a). The removal of this red painting, that obscured the original surface, restored the sculpture's shaping to its ancient beauty (Figure 2b).

Another interesting case was the represented by the model *Saint Nicola from Tolentino* by Alessandro Algardi (1595-1654). The removal of the non-original surface layer made of gypsum setting and *bolo* gilding or thick painting based on zinc white, allowed to reveal the date (1652) carved by Algardi on the terracotta. This is the only known sculpture model on which Algardi carved the date (Figure 3).

The removal of the non-original patina by laser cleaning was useful also in the case of *Saint John the Baptist* by Mechiorre Cafà (1636-1667). The cleaning, in fact, revealed the number "102" corresponding to the inventory of the collection belonging to the restorer Bartolomeo Cavaceppi. The inventory was made in 1802 by Vincenzo Pacetti on the occasion of the sale of the collection to the marquis Giovanni Torlonia [1].

Zinc white was found also in the collar of *Pope Benedetto XIII* by Giuseppe Mazzuoli (1644-1725) and Bartolomeo Mazzuoli (1674-1748) in correspondence of a re-painting. The collar, in fact, was painted with lead white, zinc white was found only in a restored area of the collar.

The sculpture models were often created taking great care in the details and in the choice of the materials. For example, the *Nile* model by Gaspare Sibilla (1725-1782) was created for the restoration of the homonymous marble sculpture in the Vatican Museums. So the terracotta model was moulded with care and the firing defects were repaired by the artist himself who covered the sculpture with different painting layers in order to make uniform the surface (setting layer made of Naples yellow mixed with hematite) and to finally simulate the marble (two layers applied on the setting and made of white lead in oil binder) [3].

The *Virgin with the Child* that in 1954 was attributed to Benedetto from Maiano (1441-1497) by Antonino Santangelo, art historian and director of the Museum of Palazzo Venezia, has been recognized as a replica made in painted plaster, thanks to the careful investigation carried out on the occasion of the recent conservative intervention. Other replicas can be found in the Figdor collection in Vienna, in the Museum of Fine Arts in Budapest and in the Museum of *Spedale degli Innocenti* in Florence. In particular, this last one exhibits similar characteristics to that of Palazzo Venezia. The replicas were probably created during the 19th century for the requirements of the antique trade.

In conclusion, the conservative intervention has been an important occasion to deepen the knowledge of the investigated artworks both from an historical and scientific point of view. The close observation of the sculptures combined with the analysis of the materials allowed to better define the chronology and in some cases also to attribute correctly the artwork to an artist.

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Figures:

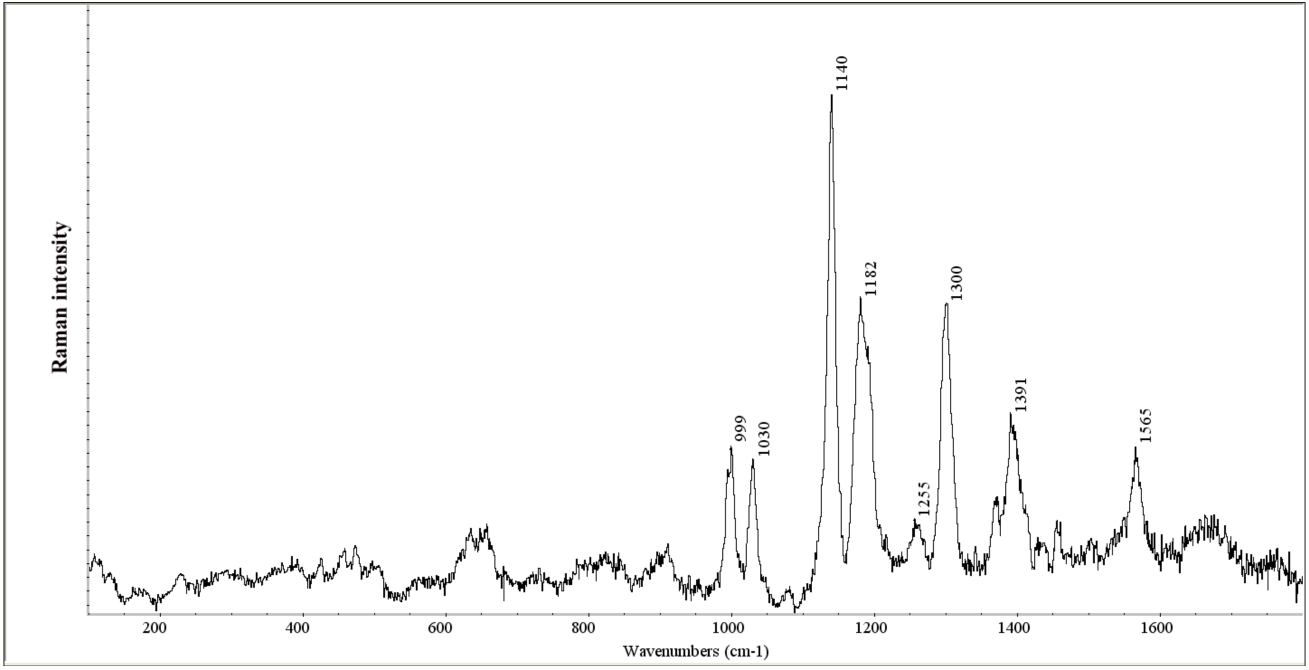

Figure 1. Raman spectrum of the brilliant red on the surface of the sculpture *Olindo and Sofronia* by a sculptor operating at Rome in the second half of the 17th century

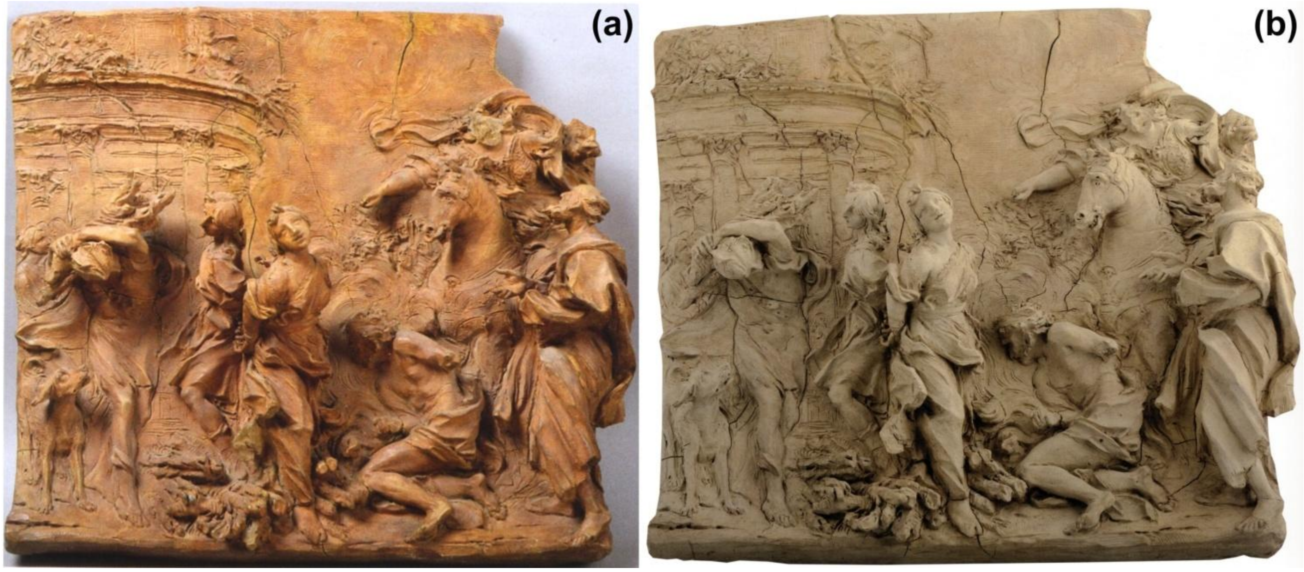

Figure 2. The sculpture *Olindo and Sofronia* before (a) and after (b) the cleaning intervention

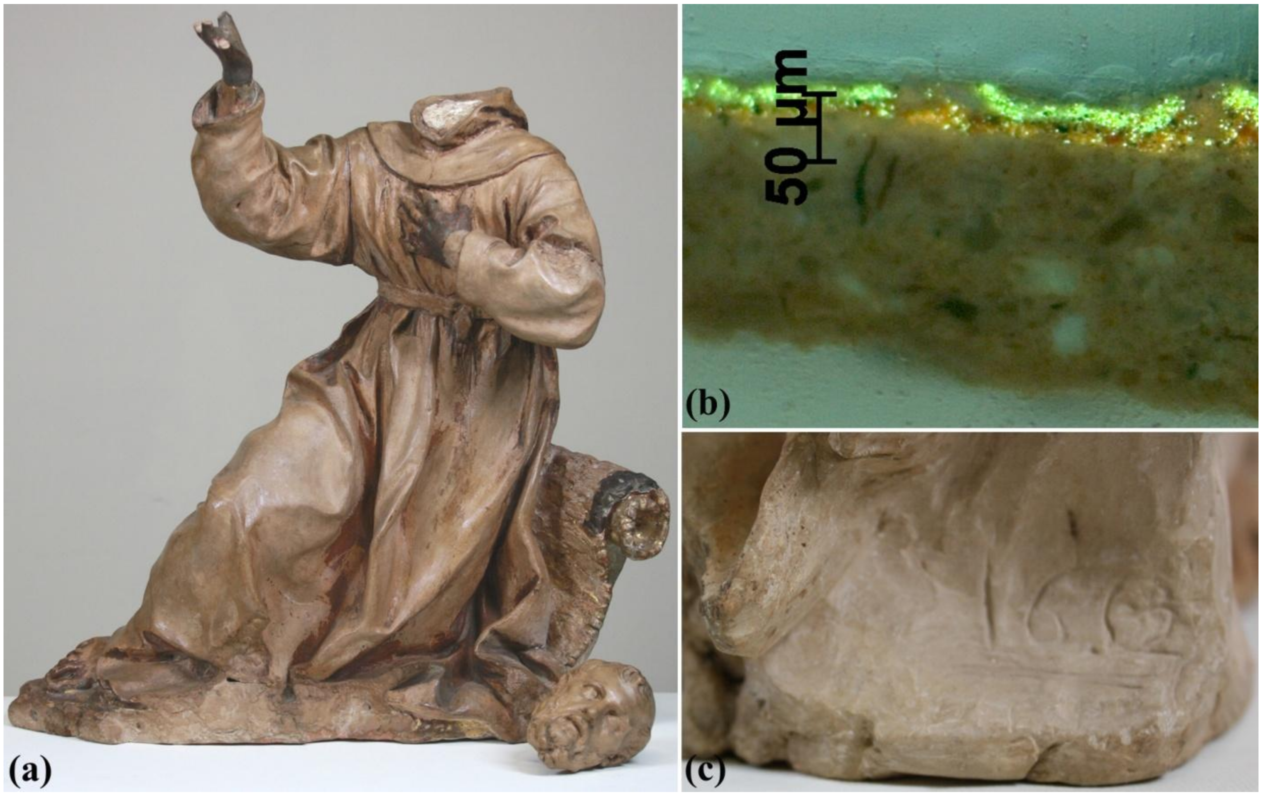

Figure 3. The sculpture representing *Saint Nicola from Tolentino* by Alessandro Algardi. (a) the sculpture before the cleaning, (b) the cross-section under UV fluorescence with the zinc white layer on the surface characterized by an intense lemon-yellow fluorescence, and (c) the detail of the sculpture after the cleaning intervention that revealed the date (1652) carved by Algardi.

Sculpture	Author	Date	Analysis	Results
Saint John the Baptist, height 35.5 cm	Florence or Venetian sculptor	1550-1560	XRF, cross section, micro-Raman, FT-IR	Red patina made of vermilion and lead based pigments (probably red lead); gilding applied by *missione*
Saints and Blessed souls of Society of Jesus, 29x51 cm	Alessandro Algardi (1595-1654)	1629	XRF, cross section, micro-Raman	Gilding applied by *missione*; setting layer containing calcite and lead based pigment
Bust of the Pope Innocenzo X 85x82 cm	Alessandro Algardi (1595-1654)	1650	Cross and thin sections, FT-IR and micro-Raman	Lead white applied by oil binder; natural resins used in previous restorations
Saint Nicola from Tolentino, height 36.2 cm	Alessandro Algardi (1595-1654)	1652	XRF, cross section, micro-Raman, FT-IR	Red lead covered by zinc white; gilding applied by *bolo* on a gypsum setting
Head of the Moor, cm 11.5x10.8	Gian Lorenzo Bernini (1598-1680)	1653	Cross section, micro-Raman, FT-IR	Light green patina made of green earth and orpiment
Saint John the Baptist, height 42.5 cm	Melchiorre Cafà (1635/1638-1667)	1661-1667	XRF, cross sections, micro-Raman	False bronze patina made of copper based pigments and /or metallic copper; lead white; calcite; gypsum
Cembalo model musical instrument, 30x100x30 cm [6]	Ludovico Gimignani (1634 - 1697) and Giacomo Reyff (1627–1700)	1665	Cross sections, micro-Raman, FT-IR	Indigo, Prussian blue, lead white, goethite, massicot, hematite, carbon black, gypsum, oil binder, shellac, proteins.
Cupid and Psyche, 31x26 cm	Giulio Cartari (1641-1699)	1679-1680	XRF, cross section, FT-IR and micro-Raman	Vermilion and red lead in oil binder; copper based pigments and/or metallic copper; acrylic resin as surface protective
Olindo and Sofronia, 49.5x53.5 cm	Sculptor operating at Rome	17th century (second half)	Cross section, micro-Raman, FT-IR	Crystalline hematite; mono-azo dye with acrylic /vinyl binder; presence of oxalates
Pope Benedetto XIII, 41x33 cm	Giuseppe (1644-1725) and Bartolomeo Mazzuoli (1674-1748)	1724-1725	XRF, cross-sections, micro-Raman, FT-IR	Vermilion; lead white, carbon black; oil binder; gypsum; zinc white
Ocean (from Pietro Bracci, 1700-1773)	Roman sculptor	Post 1759	XRF, cross sections, micro-Raman, FT-IR	Lead white, Prussian blue, goethite, zinc white, lead chromate, barium sulphate, gypsum, oil binder, proteins
The Virgin with the Child, Saint Enrich, and an Angel, 44.5x28.5x17.5 cm	Ubaldo Gandolfi (1728-1781)	1760-1770	Cross and thin sections, FT-IR, micro-Raman	Indigo, lead white, red lead, litharge, hematite, goethite, barium white, oil binder, proteins
The *Nile* model, 86x76 cm [3]	Gaspare Sibilla (1725-1782)	1773	Cross and thin sections, FT-IR, micro-Raman	Goethite, lithopone, hematite, Naples yellow, gypsum, lead white, oil binder, ultramarine blue, carbon black, sarandac
The Virgin with the Child (from Benedetto from Maiano), Ø 54 cm	Anonymous sculptor	19th century (second half)	XRF, cross sections, micro-Raman, FT-IR	Stucco painted with: indigo, carbon black, zinc white, chrome yellow, lead white, azurite, tin leaf, vermilion, oil binder

Table 1 – List of the investigated sculptures and main results of the analysis.

The colors of Keith Haring: a spectroscopic study on the materials of his mural painting *Tuttomondo*

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INTRODUCTION

The present study was carried out on the large mural painting *Tuttomondo* (Fig. 1), made in 1989 by Keith Haring (1958-1990) and located on the wall of the Church of Sant'Antonio Abate in Pisa (Italy)[1]. Painted to evoke and depict peace and harmony for humanity, it is one of the few pieces of outdoor public art that the artist intended as a permanent installation. The paint company Caparol Italy GmbH & Co. supplied the materials and an exterior insulation and finishing system (EIFS), which is a building exterior wall cladding system that provides exterior walls with an insulated finished surface and waterproofing in an integrated composite material system. The EIFS was used for supporting the mural to ensure the long term durability of the artwork. Caparol craftsmen as well as young people from the Church of Sant'Antonio and B-boys from Pisa assisted the artist in painting the mural.

The conservation treatment of *Tuttomondo* done in 2011-12 gave the authors the possibility to study its materials and follow the cleaning procedures. The results on the paints on the mural were reported in previous studies [2, 3] in which in situ and non-invasive UV-Vis-IR Fiber Optic Reflectance Spectroscopy (FORS) and laboratory Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) analyses were used. The presence of kaolinite as inorganic filler and an acrylic copolymer styrene-n-butylcrilate as binder was observed in all the paints. Concerning the pigments/dyes the following compounds were identified: rutile TiO_2 (white paint), *quinacridone red* PR122 (red paint), *Hansa® yellow* PY3 (yellow paint), tetracene (orange used in the pink areas of the mural), phthalocyanine blue (blue paint), carbazole dioxazine violet PV23 (violet paint).

This study is mainly focused on the characterization -by using FT-IR, dispersive and FT-Raman spectroscopies- of some acrylic paints, which are still produced by Caparol, of the same color and which were supposed to have chemical compositions similar to those used by Haring in 1989.

MATERIALS AND METHODS

Caparol provided seven different samples of paint: white, red, yellow, orange, blue, violet, and Capatect-Putz 622 Silacryl substrate. Painted mock-ups were prepared on glass microscope slides, using the paints as supplied by the producer.

Raman Microspectroscopy

A Jobin Yvon Horiba Labram 300 confocal Raman microscope was used, equipped with Andor multichannel Peltier cooled open electrode charge-coupled device (CCD) detector (Andor DV420-OE322; 1024x256), BXFM open microscope frame (Olympus), holographic notch filter, and a dispersive grating with 1800 grooves/mm. The excitation line of a solid state diode laser (l_0=785.7 nm), was focused through a 100x objective on to the samples and Raman scattering was back collected through the same microscope objective. Power at the samples was kept very low (about 0.2 mW) by a series of neutral density filters in order to avoid any thermal damage.

FT-Raman Spectroscopy

A Bruker high resolution (0.4 cm^{-1}) Fourier Transform Infrared Spectrometer (VERTEX 70-BS) coupled with a macro-FT-Raman module (RAMII-1063) and Ramscope III FT-Raman Microscope was used. The instrument is equipped with a (D418-T/R) high-sensitivity Ge detector and Nd3+/YAG laser, with excitation wavelength at 1064 nm. The nominal laser power used was 100 mW, and a microscope objective of 10x was employed.

FT-IR Spectroscopy

FT-IR spectra were recorded in transmittance mode on paint samples dispersed in KBr matrix (13-mm diameter KBr pellet, 64 scans, 4 cm^{-1} resolution, 4000–400 cm^{-1} range), using a purged Thermo Scientific Nicolet Protégé 460 E.S.P. Fourier transform spectrometer equipped with a DTGS detector.

In most cases, due to the extremely low percentage of pigment/dye in the formulation of the paints, the FT-IR spectra allowed to identify only the fillers and gave information about the binder. In order to maximize the content in pigment/dye of the analyzed samples, the paints were diluted with distilled water and acidified to pH 4-5 with diluted HCl (0.5-1%) in order to remove some inorganic fillers (such as calcite, $CaCO_3$). After filtration the insoluble materials were washed with ethyl acetate in order to solubilise as much as possible the organic resin.

RESULTS AND DISCUSSION

Raman Spectroscopy

Raman analyses were applied on the red, yellow, orange, blue and violet paints in order to recognize the organic compounds contained in each paint, and to identify the dyes and some of the fillers used by Caparol in the formulation of the paints. Both dispersive and Fourier Transform techniques have proved to be effective in recognizing the dyes and some of the inorganic materials used as fillers, and gave similar results.

All the spectra acquired on the mock-ups showed the presence of calcite ($CaCO_3$) and barite ($BaSO_4$) as fillers. With regards to the red paint, the spectra showed bands around 1650 cm^{-1}, 1598 cm^{-1} and 1568 cm^{-1} characteristic of the organic dye *Quinacridone Red* PR122 [4]. The Raman bands around 820 cm^{-1}, 713 cm^{-1}, 360 cm^{-1} and 330 cm^{-1} in the spectra obtained on the yellow paint revealed the presence of bismuth vanadate pigment PY184 [5] and the orange dye was identified as *Pyrazoloquinazolone* PO67 (bands at 1602 cm^{-1}, 1556 cm^{-1}, 1255 cm^{-1} and 1010 cm^{-1}) [6]. Concerning the blue paint, Raman analyses allowed to recognize the β-polymorph of copper phthalocyanine, blue pigment PB15:3 [4]. This attribution is due to the presence of four Raman bands around 1530 cm^{-1}, 746 cm^{-1}, 680 cm^{-1} and 257 cm^{-1}, and the absence of the band at 1190 cm^{-1}, which is present in copper phthalocyanines but not in the β-polymorph (Fig. 2). Finally, the bands at 1393 cm^{-1}, 1348 cm^{-1}, 1207 cm^{-1} and 530 cm^{-1}, observed in the spectra acquired on the violet paint showed the presence of *carbazole dioxazine violet* PV23 [4].

FT-IR Spectroscopy
FT-IR analyses made it possible to identify the inorganic fillers in the paints and provided some information about the binder. All FT-IR spectra showed absorption bands at 3700 cm^{-1} and 3624 cm^{-1} attributable to the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) as filler [7, 8]. Moreover, bands at 2515 cm^{-1}, 1795 cm^{-1} and 1412 cm^{-1}, characteristic of calcite [9, 10], and three bands attributable to barite between 1200 and 1050 cm^{-1} [8, 9] were observed, thus confirming the Raman identification. Concerning the binder identification, four bands between 3100 and 3000 cm^{-1} were observed, due to the aromatic C-H stretching, and a very strong band at 1735 cm^{-1} attributable to the ester C=O stretching [11]. Although these absorption bands can be attributed to the binder, they did not allow identification of the synthetic resin.

As already mentioned identification of the pigments/dyes was difficult by using FT-IR, because of the minimum amount of coloring compounds in the formulation of paints. After the chemical treatment previously described, only red and blue paint dyes were identified as *Quinacridone Red* PR122 (Fig. 3) and phthalocyanine blue, respectively, confirming the attribution obtained by using Raman.

CONCLUSIONS

Data obtained with Raman and FT-IR techniques confirmed that the paints supplied by Caparol in 2011 had the same compositions of the ones used by Haring for the mural *Tuttomondo* in 1989. Only the yellow paint showed a different composition when compared with the original one: the yellow arylide dye PY3 was substituted by bismuth vanadate pigment PY184. The analyses rendered also possible to recognize the orange dye *Pyrazoloquinazolone* PO67, and to hypothesize the presence of this compound in the pink areas of the mural, instead of tetracene. Furthermore, Raman spectroscopy resulted crucial for the identification of the pigments/dyes, while FT-IR analyses, in addition to giving information concerning the binder, allowed to unequivocally identify the fillers, thus demonstrating the potential of the combined use of these techniques. This study contributes to a deeper understanding of the materials used in the creation of contemporary artworks and provides useful information on the tailoring of analytical approaches to address their complex composition and the predominant use of modern synthetic colored pigments.

Acknowledgements:
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Keywords: mural paintings, Tuttomondo, Keith Haring, Raman, FT-Raman, FT-IR, acrylic paint

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Figures:

Figure 1 - *Tuttomondo* after the conservation treatment.

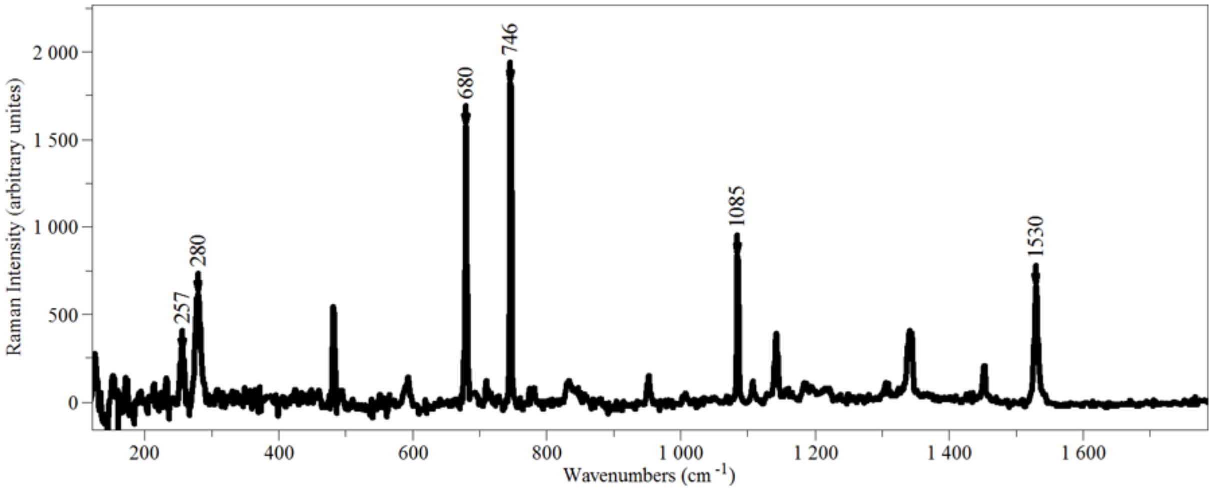

Figure 2 - Dispersive Raman spectrum of the blue paint.

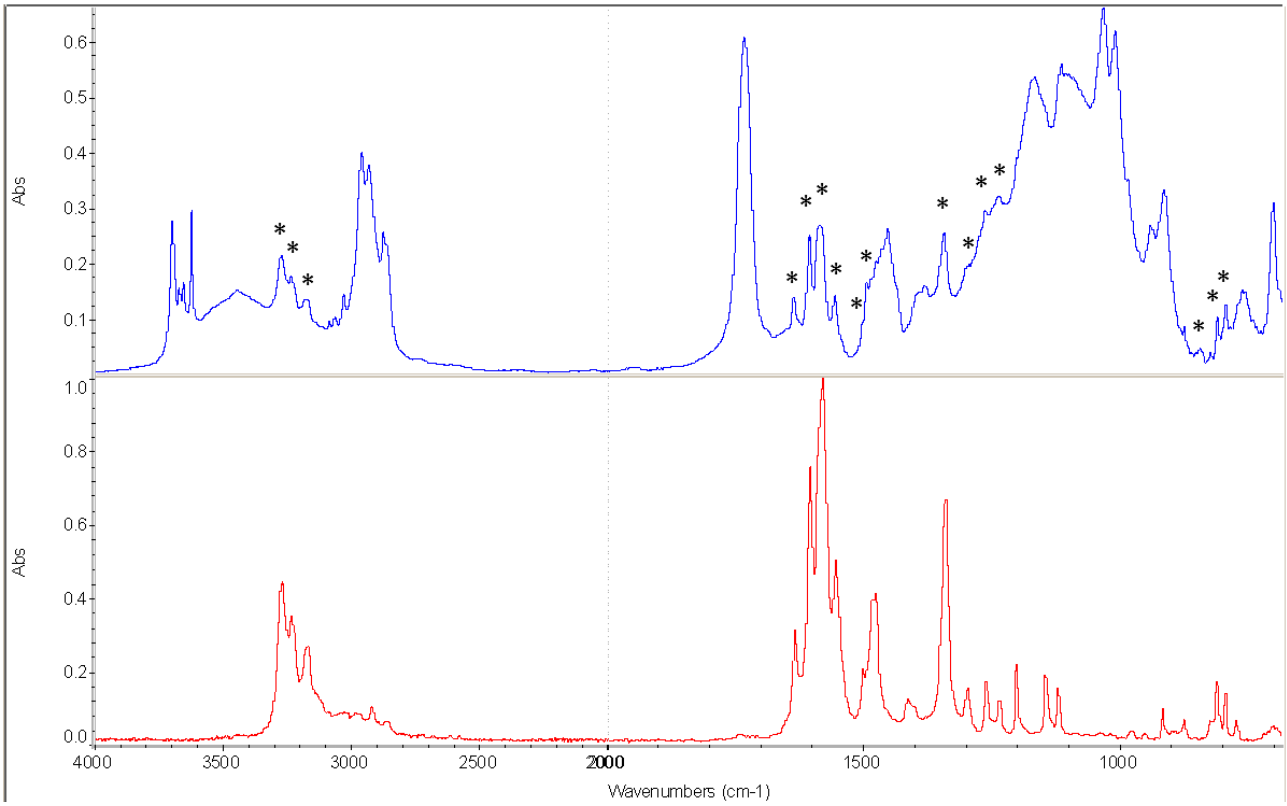

Figure 3 - FT-IR spectrum of PR122 (red line, from IRUG Database IOD00248) and the one collected on the red paint (blue line).

Dürer's metalpoint drawings: examining materials and techniques using Raman spectroscopy and technical imaging

Joanna Russell, Judith Rayner and Jenny Bescoby, The British Museum

The technical examination of all works of art is challenging, but that of works of art on paper presents particular difficulties; the quantities of applied materials present are vanishingly small, the paper support itself is delicate and vulnerable, and sampling is almost always impossible. A non-invasive research methodology for the examination of such works, relying heavily on the use of Raman spectroscopy and technical imaging, has been developed at the British Museum and was first applied to the study of a selection of Italian Renaissance drawings [1]. This same methodology is now being used for a research project focusing on metalpoint drawings from a wider region and over a much broader time period, supported by funding from the Andrew W. Mellon Foundation. This research is being carried out in anticipation of the exhibition 'Drawing in Silver and Gold' which will be held at the National Gallery of Art, Washington DC and at the British Museum, London in 2015 [2].

The technical examination of drawings can be used to increase knowledge of an artist's technique and provide new insights into how a work was made. Information from the paper support, the pigments and drawing materials and the ways in which they have been applied can all provide clues about a drawing's production and its relationship to other works, both to similar drawings and to work in other media. This type of study is well established for the examination of paintings, but with the increasing availability and sophistication of non-destructive methods of analysis, a similar process can be applied to the study of drawings. In this presentation the investigation of five metalpoint drawings by Albrecht Dürer will be discussed, focusing particularly on the advantages of using Raman spectroscopy for such studies and also on the problems encountered in the practical application of this technique on these works.

AN INTRODUCTION TO METALPOINT

Metalpoint as a drawing material was at its height of popularity during the Renaissance. It was used to great effect by artists including Leonardo, Raphael and Dürer, but gradually fell out of favour during the 16th century, although some artists have continued to use it up to the present day [3]. Most metalpoint drawings are made using a metal stylus to draw on a surface that has been prepared with an abrasive ground layer; the one exception to this is leadpoint, which is sufficiently soft to be used on unprepared paper. Metal styli composed principally of silver or lead appear to be the most common, but others based on gold or copper can be used in a similar manner.

Lead leaves a dark grey mark, which can be easily erased and was often used as an underdrawing material for drawings on paper, before working in a more permanent medium such as ink. Its appearance is not unlike that of a soft graphite pencil line, but leadpoint was in use long before graphite first gained popularity as a drawing material in the 16th century. Silver leaves a much finer line and lends itself to a very linear style of drawing using hatching to achieve shading, as it cannot easily be blended or erased, and is traditionally thought to be a difficult medium to master. The silver lines tarnish on ageing, becoming a warm grey-brown colour. The support is typically prepared with a ground containing bone white.

METHODOLOGY

The project methodology used three main stages of investigation. The drawings were first examined visually, at a range of magnifications and with the aid of transmitted and raking light. This was followed by technical imaging, including infrared reflectography, ultraviolet reflected and ultraviolet-induced luminescence imaging, in order to further distinguish materials, sometimes revealing elements of the drawing not usually apparent. The third stage was *in situ* chemical analysis with micro-Raman and X-ray fluorescence (XRF) spectroscopy, the analysis being guided by the results from the first two stages. Imaging provided an overview of the distribution of the different components, whereas the analytical methods were used for spot analyses. This combination of broad and spot techniques meant that it was possible to gain an idea of materials employed throughout the drawing from relatively few measurements. Raman spectroscopy was particularly useful for the identification of pigments in the preparation layers, while XRF was used to identify the elemental composition of metalpoint lines.

XRF analyses were carried out using a Brüker Artax spectroscope with a molybdenum X-ray tube and an analytical spot size of *c*.0.65 mm. The applied layers on the drawings are generally thin when compared with the depth of penetration of the spectrometer X-ray beam, so that each analysis reflects the elements present in both applied materials and support. Spectra from areas of grounded paper were compared with those from drawn lines in order to identify the elements present in the drawing materials.

RAMAN SPECTROSCOPY

Micro-Raman spectroscopy was carried out using a Jobin-Yvon LabRam Infinity spectroscope with green (532 nm) and near infrared (785 nm) lasers, a liquid nitrogen cooled CCD detector and an Olympus microscope system. This allowed tiny areas containing one or two grains of material to be targeted for analysis. Both lasers were used for the analyses; the red laser was generally more effective for identifying red and white pigments, while the green laser was useful for the identification of carbon-based blacks.

The use of micro-Raman spectroscopy has been particularly important for this project as it allowed the specific identification of pigments on the drawings *in situ*, since sampling was not possible. The drawing could be placed directly under the Raman microscope to make measurements of individual particles. The Raman instrument at the British Museum is equipped with a horizontally mounted objective that can be used to make measurements on larger drawings or those in wide mounts, while they are held on an easel, thus allowing access to all parts of the surface. The technique can also be used through the Perspex acrylic sheet used in the mounts of some drawings.

In addition to its obvious advantages, there were also various practical difficulties encountered with the analysis of these types of works using Raman spectroscopy. The primary concern when carrying out such analyses is the risk of damage to the drawing. To avoid any chance of burning, melting or altering the materials low laser powers and short exposure times must be used, making it difficult to get a clear spectrum. Fluorescence can also be a problem, especially if adhesives or consolidants are present on the surface.

Another major difficulty is maintaining focus on the area under analysis. A light and delicate object such as a drawing very easily moves out of focus during analysis as the paper is disturbed by air currents, or moves in response to relative humidity changes. Weighting down the surface, if possible, helps to overcome this problem, but is only practical when working on a drawing held horizontally. Even greater difficulties with focus were experienced when analysing a drawing held vertically on an easel, as the surface cannot easily be restrained.

One further consideration when carrying out this type of analysis is that micro-Raman is inherently a very focused technique, meaning care is needed with interpretation. On the relatively large surface area of a drawing, only a tiny fraction of the particles present can be analysed, and it is more likely that pigments that give a strong Raman signal, for example vermilion, will be identified even if these represent minor components. This is where the complementary techniques of examination, imaging and XRF are particularly helpful, to ensure that materials are not missed and to confirm that all the methods employed give the same broad picture.

THE DRAWINGS

Albrecht Dürer was born in Nuremberg in 1471 and was a very prolific draughtsman, painter and printmaker, using a wide variety of materials and techniques. He made an early attempt at silverpoint drawing in his self-portrait at the age of 13, and continued to revisit the technique throughout his career. Five metalpoint drawings by Dürer were examined using the methodology described above. Three of the works appear to be fairly simple examples of metalpoint drawing on a pale pink prepared ground, two of which have drawings on both recto and verso. These works were acquired by the Museum at different times, but are all believed to be from a sketchbook used during Dürer's travels in the Netherlands in 1520–21. Further pages thought to be from the same book exist in other collections, some of which have also been subjected to analysis [4].

The same pigment mixture, consisting of bone white, hematite and a carbon-based black was identified in the preparation layers on all five sides of these three drawings using Raman, supporting the belief that these were originally part of a single sketchbook, and could have been prepared at the same time. Using XRF analysis all the drawings were found to be in a silverpoint with a small copper content.

Infrared imaging of *Study of a dog* (1848,1125.3) showed a faint underdrawing was present, outlining the contours of the body. Silverpoint lines usually appear very faintly or not at all in infrared reflected images [5], allowing the underdrawing to be seen clearly in isolation. Although microscopic examination showed the underdrawing lines to consist of dark shiny particles, initially thought to be leadpoint, Raman spectroscopy identified this material as a carbon-based black, probably charcoal.

The remaining two drawings, *Head of a woman* (1895,0915.978) and *Head of a boy* (SL,5218.41) both use a more complicated technique in which metalpoint is combined with white highlights against a mid-tone provided by the coloured ground, a method probably influenced by Dürer's travels in Italy, although neither work can be securely dated. Examination of these works showed that the same type of paper has been used for both, bearing a crown watermark that has also been observed in other works by Dürer from the early 16th century.

The technical imaging of *Head of a woman* demonstrates how the different aspects of a drawing can be highlighted using the particular imaging methods (Figure 1). Raman spectroscopy identified vermilion in the ground, with bone white and a little carbon-based black. The highlights are in lead white with a carbon-based black used in the shadows. XRF analysis showed that a stylus of silver with a little copper was used for the main drawing. On *Head of a boy* the same pigments were identified in the ground, used in rather different proportions. Lead white is again used for the highlights but has become discoloured in some areas. The stylus used for this drawing appears to be different from that used for the other works discussed, containing zinc as well as silver and copper. In previous analyses of 12 Dürer works a silver-copper stylus was thought to have been used for all except one drawing which appeared to use a stylus with higher zinc content [4].

CONCLUSIONS

This research shows the type of information that may be revealed from a systematic imaging and analytical approach, and how this can be used to make connections between works, shedding new light on existing art historical information. The consistency in materials on three of the drawings provides further evidence to link them together as pages from the same sketchbook. The two portrait drawings also appear to be more closely associated than previously thought, showing similarity not only in technique but also in the paper type and pigments used.

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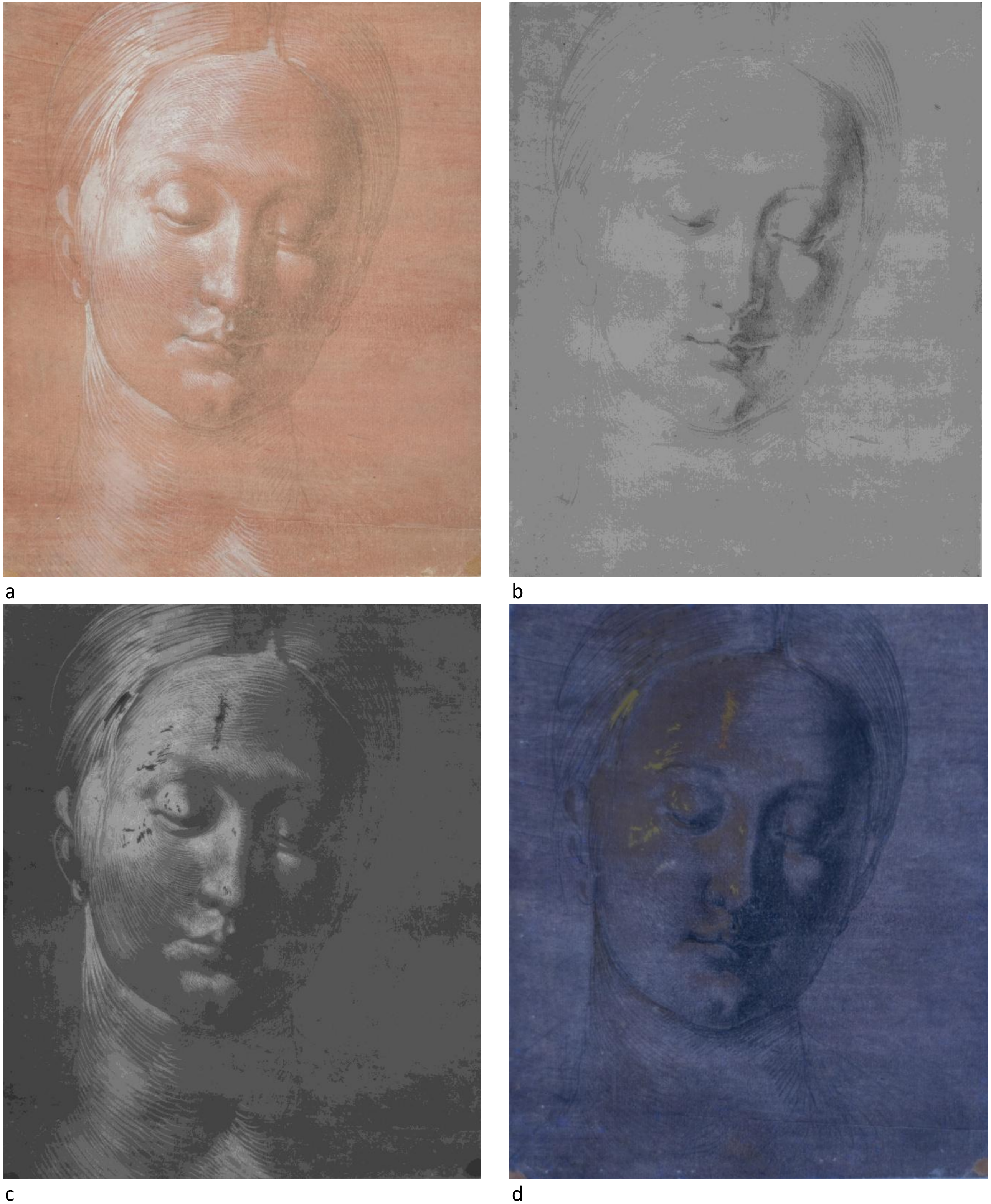

Figure 1. Technical imaging reveals the different materials used in *Head of a woman,* Albrecht Dürer, (1895,0915.978). a. normal illumination; b. infrared reflectogram (800-1700nm) showing a carbon-based black used in the shadows; c. ultraviolet reflected image showing white highlights; d. ultraviolet-induced luminescence image showing distinct silverpoint lines, for example in the hair and neck, and areas of retouching which appear yellow in this image. © Trustees of the British Museum.

Disappearing ink! Unraveling the fading of a modern design object

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INTRODUCTION

Painting a Fresco with Giotto #3 (Figure 1, Indianapolis Museum of Art, #2009.466) by contemporary Portuguese designer Fernando Brízio comprises a white faience vase pierced with Italian *Giotto*-brand felt tip markers. The bleeding of the pen inks creates a playful polka dot surface of solid circles or concentric dye rings around each marker. Part of the Conceptual Design movement, Brizio's piece has been compared to earlier works by Hella Jongerius where function is surpassed by experimentation in color and form [1]. Brizio has continued this theme in a series of colorful marker-stained artworks including other ceramics, but also textiles and furniture.

Figure 1. IMA design object *Painting a Fresco with Giotto #3* following exhibition. The detail image shows significant fading of some inks.

The vase, manufactured in 2005 as the eleventh in an edition of 20, was acquired by the museum in 2009 and immediately embarked on a three venue touring exhibition, *European Design Since 1985: Shaping the New*

Century [1]. Unfortunately, the object returned to the museum badly faded, with some of the ink dots, particularly the lighter pinks and purples, having nearly vanished (see Figure 1). Condition reports after each of the venues noted change only following the last installation. The total exhibition time was calculated to be approximately 282 days, roughly evenly divided amongst the three venues. The IMA conservation scientists were asked to explore the cause of the fading and to prepare future exhibition and handling guidelines based on the object's current measured lightfastness.

IN-SITU MICROFADEOMETRY FOR LIGHTFASTNESS ASSESSMENT

In-situ fade testing of the ink dots on the vase was accomplished using an Oriel microfade tester (MFT). Many of the colorants were found to be prone to continued rapid color loss, i.e. having the measured lightfastness equivalency of ISO blue wools #1-3. Communication with the manufacturer of the markers confirmed suspicions that these water-soluble pens are student-grade, and that they are not intended to have high lightfastness, but rather to be non-toxic and easily cleanable. Of the 30 colored pens, 10% fell below BW2 in lightfastness, placing them in the most restrictive category of light exposure and predicting noticeable fading from their current color in only a couple of years of exposure at 5 footcandles [2].

IN-SITU RAMAN ANALYSIS OF ARTWORK

The identification of the inks from the pen nibs and from the surface of the vase by Raman microspectroscopy proved challenging initially. Direct analysis of the color-stained faience surface was problematic due to the presence of a surface coating and the tendency of some of the dyes to fluoresce. Despite acquiring high quality data from the dried ink on several of the pens' nibs using a near-infrared excitation source, Figure 2, only two dyes - tartrazine and erthyrosine - could be positively identified based on current Raman spectral databases.

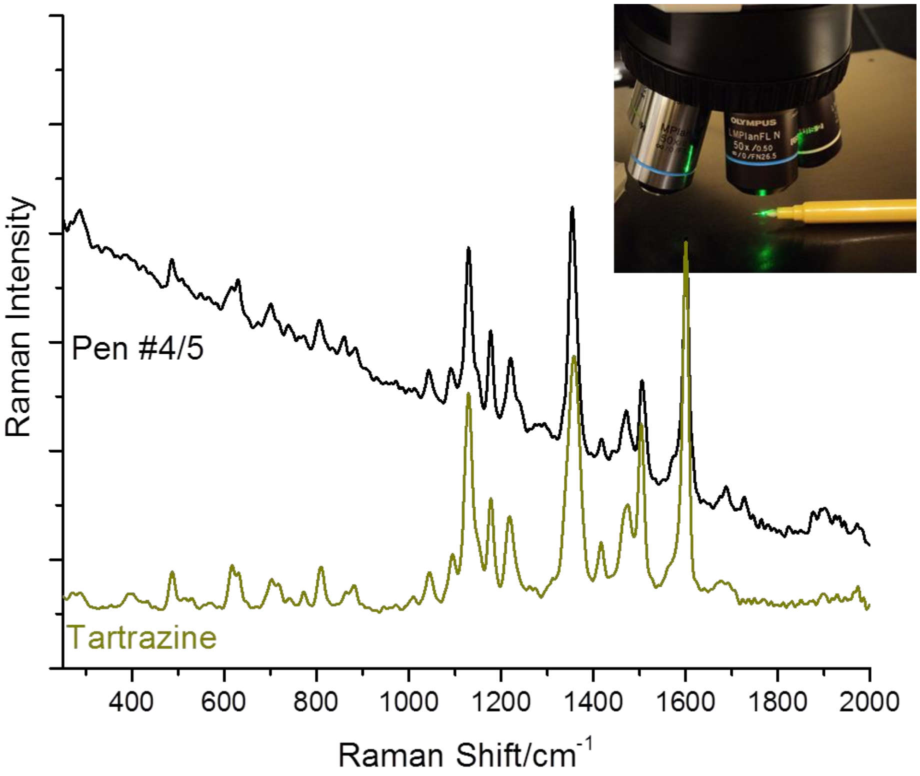

Figure 2. Raman spectrum of the mustard colored pen #4/e taken using 785nm excitation on residue from the dried nib compared to a reference spectrum of tartrazine. Inset shows analysis trials on the pen nib using 532nm excitation.

INK SEPARATION AND DYE IDENTIFICATION BY HPLC-ESI-MS

To assist in the identification of the dyes, new examples of 96 Giotto 'Turbocolor' pens were acquired for destructive analysis. The inks were extracted into methanol for the 28 pens that matched exactly the 30 colored pens used on the vase. One pen (Teal) was used twice by the artist, and one marker (Pink) appears to be no longer available in the Giotto Turbocolor line. These samples were analyzed by high pressure liquid chromatography-photodiode array-electrospray ionization-mass spectrometry (HPLC-PDA-ESI-MS). Based on the visible spectra and molecular weights, possible ink components were identified using the Color Index and then verified by comparison of their fragmentation patterns with the literature [3,4]. This approach led to the positive identification of 8 of 9 dyes detected in the 28 different pen colors: Acid Violet 17, Acid Blue 47, Acid Red 18, Acid Red 14, Acid Red 52, Food Yellow 3, tartrazine, and erthyrosine. Most of the identified compounds are widely considered non-toxic and safe to use as food colorings [3]. Structural elucidation by mass spectrometry of the unknown colorant has generated a plausible molecular formula, but this compound has so far not been located in the dye literature or the Colour Index.

Many of the pens utilize mixtures of these dyes to achieve a wide variety of shades, a fact demonstrated dramatically by the colorful spots on the vase itself, which often form concentric color rings resulting from chromatographic separation of the bleeding ink on the silicate body, Figure 1. Genuine examples of the individual dyes were next characterized by Raman spectroscopy. This data confirmed that indeed the dyes in the pens from the artwork and the surrogate pens used for the LC-MS analysis contained the same formulations. These reference Raman spectra further expand the in-house library of synthetic dyes used to identify colorants in museum artworks. A list of the pens from the artwork, and the dyes identified in the matching surrogate pen, are shown in Table 1.

CONCLUSION

Based on the severely faded appearance of the vase and its continued susceptibility to rapid color loss, doubts exist about the future exhibition potential of the object or its ability to communicate the artist's vision. The artist was contacted regarding the fading issue, about which he was already aware. Future interviews will record Brizio's material choices, his thoughts on the status of the IMA artwork, whether it still achieves his artistic intent, and how he views the longevity of his work in general. This project highlights the urgency of characterizing the fading rate of potentially fugitive artworks or directly identifying the colorants used by artists prior to exhibition of new works. The expansion of current spectral libraries to cover inherently unstable colorants will assist in identifying fugitive dyes in artworks by rapid, non-destructive means like Raman spectroscopy.

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Table 1. Giotto pens from the artwork, their color description, and the dyes identified by HPLC-MS and Raman spectroscopy

Row / Pen	Color	Dyes Identified
4 / e	Mustard	Tartrazine / Acid Red 18
4 / d	Green	Brilliant Blue FCF
4 / c	Peach	Acid Red 18
4 / b	Sky Blue	Brilliant Blue FCF / Acid Violet 17 / Unknown
4 / a	Red	Acid Red 14 / Acid Red 18
3 / e	Lt. Yellow	Tartrazine
3 / d	Dk. Yellow	Sunset Yellow / Tartrazine
3 / c	Purple	Acid Violet 17/ Acid Violet 49
3 / b	Mint Green	Brilliant Blue FCF
3 / a	Tangerine	Acid Red 18
2 / j	Lavender	Acid Red 52/ Acid Violet 17
2 / I	Mauve	Acid Violet 17/ Erythrosine
2 / h	Orange	Acid Red 18 / Sunset Yellow
2 / g	Lime Green	Acid Violet 17 / Brilliant Blue FCF
2 / f	Baby Blue	Brilliant Blue FCF / Acid Violet 17
2 / e	Pink	No Match in the Surrogate Pens
2 / d	Lt. Brown	Acid Red 18 / Brilliant Blue FCF
2 /c	Dk. Red	Acid Red 18/ Acid Red 14
2 / b	Lt. Gray	Tartrazine / Brilliant Blue FCF
2 / a	Powder Blue	Brilliant Blue FCF / Unknown
1 / j	Brown	Acid Red 18/ Brilliant Blue FCF / Tartrazine
1 / i	Black	Acid Red 18 / Brilliant Blue FCF / Acid Red 52
1 / h	Teal	Sunset Yellow / Brilliant Blue FCF
1 / g	Forest Green	Sunset Yellow / Brilliant Blue FCF / Tartrazine
1 / f	Gray	Sunset Yellow / Brilliant Blue FCF / Tartrazine
1 / e	Dk. Green	Brilliant Blue FCF/ Acid Violet 17
1 / d	Teal	Sunset Yellow / Brilliant Blue FCF
1 / c	Lt. Black	Tartrazine / Brilliant Blue FCF / Acid Violet 17
1 / b	Lt. Green	Tartrazine / Brilliant Blue FCF
1 / a	Royal Blue	Brilliant Blue FCF / Acid Violet 17

Infrared imaging of art objects: Is it as easy as it sounds?

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The non-invasive *in-situ* infrared analysis of art objects was first accomplished with single point portable analysis systems.[1] A small FTIR spectrometer could be brought to the object of interest and a quick analysis performed. This allowed objects to be analyzed without the need of removal from the gallery or removal of small samples from the object. The analysis is accomplished by illuminating the sample with infrared light and collecting the signal reflected by the sample. A natural extension of this method would be the replacement of the single detector element with a many pixel array detector such as a Photovoltaic Mercury Cadmium Telluride (PV-MCT) focal-plane array (FPA). FPA's have been used for many years in the remote sensing of airborne chemicals, hazardous material, and spilled liquids .[2-5] The conventional remote sensing infrared spectrometer with a single detector records the spectrum from a single field of view in seconds, and in contrast imaging spectrometers acquire thousands of spectra per second. As the pixels from state-of-the-art FPA detectors are small, microscopic data can be collected at high magnification over small areas or larger areas can be analyzed with less resolution. Such analyses can be accomplished in passive or active modes of analysis. Spatial and spectral information may be combined in order to improve the determination of chemical distribution.

Art objects present unique challenges to the remote measurement concept. The objects typically do not emit a signal strong enough for passive detection and the introduction of a high temperature source could potentially damage the object in question. Also, traditional SiC sources were designed to illuminate small areas and had too low a power output to be useful for large fields of interest. Objects can also be irregular in shape. A preliminary study of a variety of art objects has been performed to determine the feasibility of applying full-field middle infrared imaging to objects of interest. The large depth-of-field of a stand-off imaging system like the HI90 allows almost any object to be analyzed quickly and easily.

The hyperspectral imager HI 90 is based on the combination of a Michelson interferometer and a FPA detector and is shown in **Figure 1**. A spectrum is calculated for each pixel of the array. The spectrum contains the infrared signature of the scene that can be used to analyze gases, liquids, and solids. The interferometer of the HI 90 has been designed specifically for highest throughput, maximum imaging performance, and excellent quality of the spectra. A successful quantification requires Lorenzian band shape and a linear response over the dynamic range of detection system. The moving mirror of the Michelson interferometer is actively aligned while changing the optical path difference at the same time. This interferometric system is highly efficient and results in hyperspectral image cubes that contain high quality spectra with outstanding signal-to-noise ratios. Detection of the signal is accomplished using a multipixel focal-plane PV-MCT detector, which in this investigation contains 256x256 elements. The readout of the signal is performed using four channel 14-bit digitizers. The acquisition is undersampled at 900-1,450 cm^{-1} resulting in a data collection rate of approximately 8,000 spectra/s. The spectral range is limited to keep the readout rate within the limits of the digitizers. The spectral range can be changed to reflect the requirements of the investigation. For example, if it was desired to collect data from 1900-900 cm^{-1} (full fingerprint region), the data collection rate would be decreased by a factor of two. Each pixel is 40x40 microns before projection to the field of view (FOV).

There are unique challenges to analyzing art objects remotely. In order to obtain a strong signal from the object, a high power source that can be projected over a large area is needed. A new source has been developed for this purpose. A large SiC source is projected to the FOV using a large spherical mirror. The source is software controlled to expose the object to illumination ONLY when data is collected. A large iris is used for this purpose. Additionally, many objects may undergo changes with induced temperature increases. The temperature of the objects is constantly monitored to permit only those excursions that would not alter the object in anyway. Even objects that are black can be analyzed with lower power illumination and longer scanning times.

The HI90 is positioned using simple positoning software, where little to no user expertise is required. The angle of instrument panning as well as tilt are easily selected in the software. This is important for odd shaped objects. For flat objects of interest, an eisle is ideal for securing the object. For odd shaped objects, more creative mounting schemes may be needed. The easel can remain at a secure angle and the HI90 tilted to accommodate the object angle. Because the FOV is fairly deep, odd shaped objects with curved surfaces can still be analyzed. Objects with significant depth such as large bracelets, porcelain doves, sculptures, and even musical instruments have been characterized using this simple positioning method.

The data resulting from the analysis typically exhibit specular reflection distortions or diffuse reflection characteristics. Specular distortions occur when the sample reflectivity is greater than about 6% and results in a derivatization of the bandshape. The derivatization is due to the refractive index approaching infinity on one side of an absorption band and negative infinity on the other side resulting in a moment of discontinuity. The software can readily transform the data set to remove the contribution of the refractive index leaving the desired absorption spectrum. If the sample has reflectance less than about 5%, diffuse reflectance distortions can result that preclude successful quantification. A Kubelka-Munk correction on the data yields data that obeys Beer‘s Law and yields data that is typically absorbance like in nature and easily interpreted. **Figure 2** shows a color panel image collected from a reference panel of barn paints. The high contrast indicated is due to the integrated area of the cellulose band around 1030 cm^{-1} as shown in **Figure 3**. The resulting speactra are typically compared to reference data previously collected by ATR, reflectance, or transmittance for identification. The relative quantification is readily elucidated from the area image. An absolute quantification can also be determined by developing a quantification model using univariate (band integrations) or multivariate (partial least squares) analysis. Factor analysis can also be performed on the data to determine the number of unique species present and their distribution. Simple clicking on the high intensity area of the unknown component followed by a quick library search allows for ready identification of each unknown. Other advanced analysis methods are also available, such as neural networking, functional group profiling, quick comparison with many spectra, etc.

In conclusion, it is relatively easy to perform standoff FTIR based chemical imaging of art objects with active illumination by an external SiC source. However, careful consideration must be given to the objects in question. Dark objects must be illuminated at low power and be monitored, where highly reflective light objects can be analyzed more freely. The only downside to the arrayed analysis is the cost of the system detector. FPA’s are still costly, which may limit their ultimate use to larger museums and institutes.

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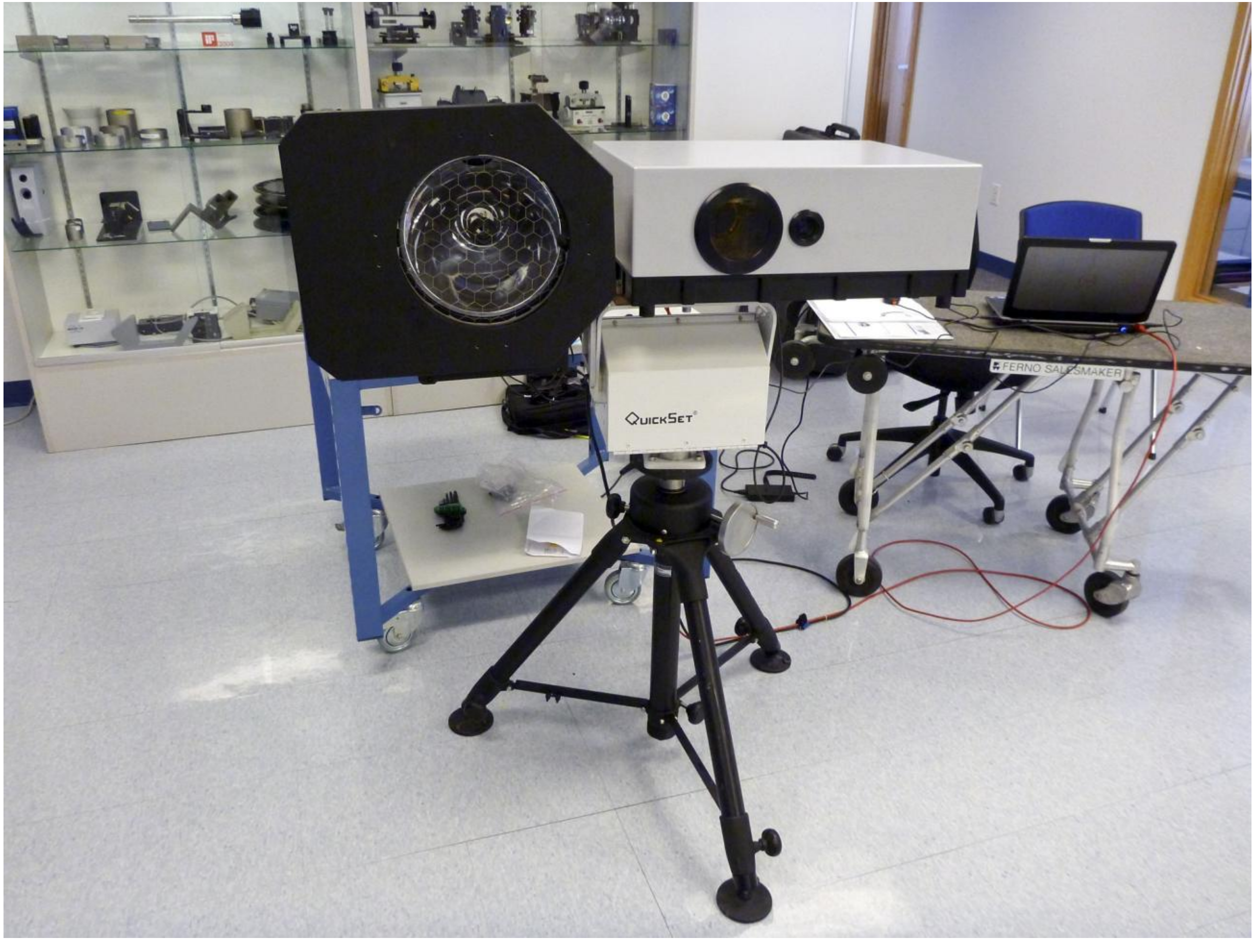

Figure 1 - The HI 90 with the external SiC source.

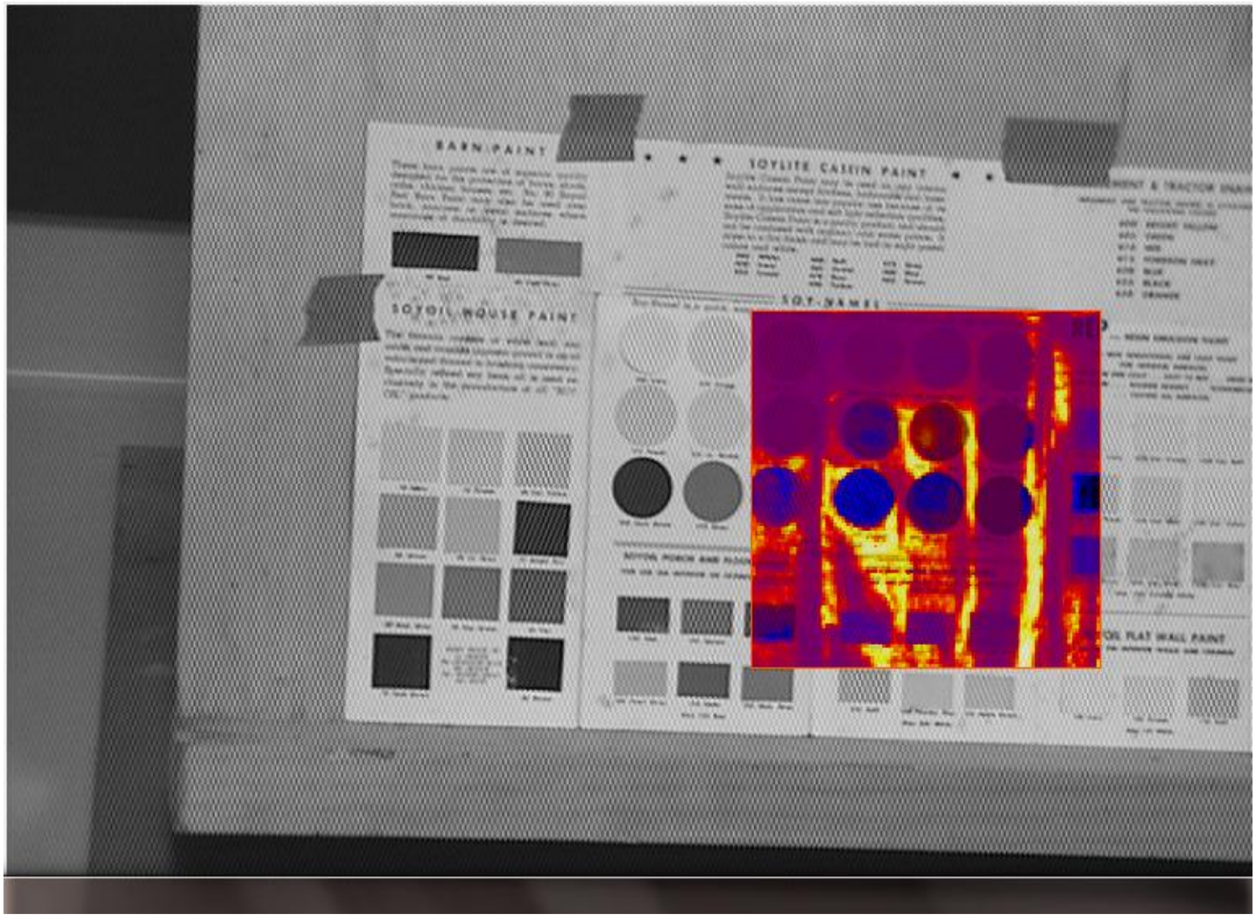

Figure 2 - Reference color panel with superimposed chemical image resulting from the integration of the infrared band at 1030 cm^{-1}.

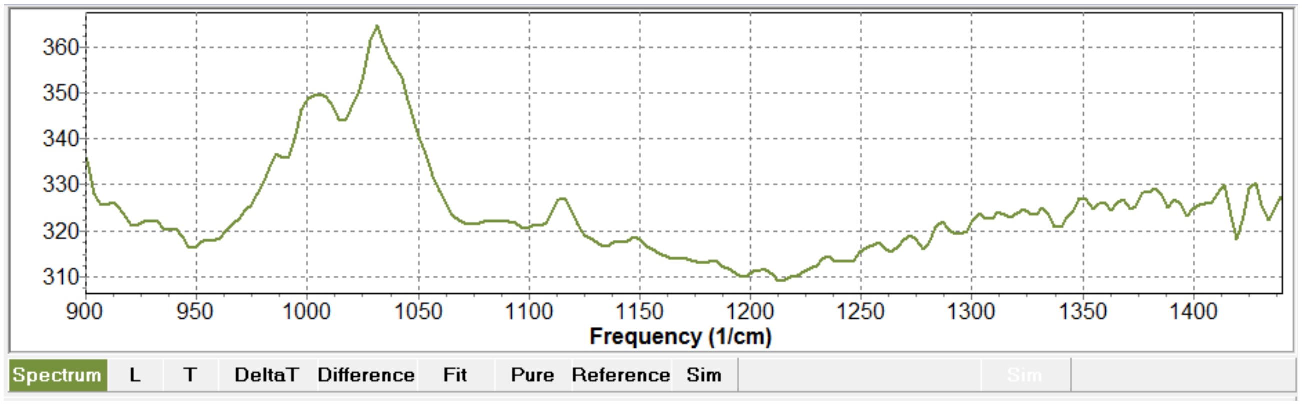

Figure 3 - Representative infrared spectrum collected from the color panel.

Identification of inorganic pigments by use of non-invasive reflection-FTIR with particular attention to the region from 900-375 cm^{-1}

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INTRODUCTION

FTIR has been used extensively for the identification of materials in the fields of art and cultural heritage, often along with complementary methods such as XRF, Raman or UV/Vis spectroscopy. As for all compound specific techniques, a successful identification of materials by FTIR strongly depends on adequate reference databases. Most of the FTIR spectrometers currently used allow an evaluation in the range of about 4000-600 cm^{-1} and hence, most of the IRUG database spectra cover this range. Since several years, reflection-FTIR instruments became available which allow non-invasive investigations of objects. Although reflection-FTIR spectra usually strongly differ from spectra measured in transmission, we found in previous studies[1] that the calculation of absorption index spectra by Kramers-Kronig transformation often enabled a match with IRUG database spectra and thus an identification of inorganic pigments particularly containing oxyanions (e.g. lead white, barium sulfate, malachite, brochantite, emerald green, bone black) or aluminium silicates (e.g. ultramarine, kaolinite).

In our work presented here, we discuss several reflection spectra of inorganic pigments which did not allow an adequate Kramers-Kronig transformation, but partially showed similar spectral features to absorption spectra (azurite, chrome yellow, zinc yellow) or transmission spectra (Prussian blue, lapis lazuli, bone black). Furthermore, we want to highlight several inorganic pigments mainly showing characteristic absorptions in the spectral range of 900-375 cm^{-1}, which cannot be evaluated with fiber optic instruments (e.g. barium yellow, iron (III) oxide-hydroxide, viridian, cobalt blue). In addition, a comparison of the results to reference spectra from a self-built reflection-FTIR database will be presented.

EXPERIMENTAL

The experiments on paintings, illuminated manuscripts and painting materials were carried out by use of a mobile reflection-FTIR instrument with DTGS-detector which allowed non-invasive analysis in the range of 4000-375 cm^{-1} with a resolution of 4 cm^{-1}. The beam diameter was approximately 4 mm. Compared to fiber optic devices, which are not transparent below 900 cm^{-1}, the use of mirrors in the beam path enabled the evaluation of this extended range. Depending on the surface properties of the analyzed objects, 32-256 scans were collected for a spectrum. Complementary XRF and (in some cases) reflection-UV/Vis spectroscopy were used to obtain reliable results. According to the particular requirements of the objects analyzed, measurements were carried out either in vertical or horizontal position of the instrument, using several supports (studio stand, tripod, tetrapod or laboratory lifting platform). Spectra were evaluated using IRUG 2007 and Hummel Industrial Polymers Vol. 3 (Wiley-VCH) databases as well as a self-built reflection-FTIR database of watercolor tablets and watercolors on paper.

RESULTS

Azurite ($Cu_3(CO_3)_2(OH)_2$) has been used as blue pigment since antiquity. We were able to identify it in an illuminated manuscript by Oswald von Wolkenstein (1377-1445) in the Library of the Federal State Tyrol and of the University of Innsbruck, Austria (MS B, 1432). The main bands in the reflection spectrum (Fig.1) were found at similar wavenumbers to azurite IRUG IMP00001 (3429 cm^{-1} – OH stretching, 1465 and 1425 cm^{-1} – CO_3^{2-} stretching, 956 and 838 cm^{-1}). The bands were inverted as a result of the reststrahlen effect, resulting in a similar shape as in the reference absorption spectrum. In contrary, the combination band ($\nu_1+\nu_3$) in the region of ca. 2500 cm^{-1} was not inverted and much stronger compared to the reference spectrum. Moreover, the spectrum showed two peaks at 3878 and 3837 cm^{-1} which are characteristic for azurite, but did not show up in the absorption reference spectrum, or more precisely, were too small for being noticed. Whereas the characteristic bands further matched with the reflection reference spectrum of azurite obtained from a watercolor tablet (Kremer 102078), the calculation of an absorption index spectrum by Kramers-Kronig transformation did not yield a satisfactory result. The main elements detected by XRF were Cu and Ba, which indicated a mixture of azurite and barium sulfate. However, no bands characteristic for barium sulfate were found in the reflection-FTIR spectrum.

We further observed inverted bands at wavenumbers relatively similar to absorption reference spectra in case of chrome yellow ($PbCrO_4/PbSO_4$, 1033, 808 and 625 cm^{-1}, reference IRUG IMP00503) and zinc yellow ($ZnCrO_4$, 944, 846 and 802 cm^{-1}, reference IRUG IMP00187), which were identified on 19th century watercolor paintings by Moritz M. Daffinger (1790-1849). As in case of azurite, Kramers-Kronig transform only provided absorption index spectra which did not match with the respective absorption reference spectra. In contrast, Kramers-Kronig transform was applied successfully in case of barium yellow ($BaCrO_4$), which also was identified on the watercolor paintings mentioned before. We could observe a good match between the absorption index spectrum and the absorption reference spectrum IRUG IMP00296, in particular for two strong bands at 897 and 859 cm^{-1} and three weak bands at 1139, 1113 and 1090 cm^{-1} (Fig.2). Additionally, two peaks at 419 and 392 cm^{-1}, which also have been observed by other autors[2], enabled a reliable identification of the material along with XRF detection of Pb and Cr and the results of reflection-UV/Vis spectroscopy. As all maxima of the main bands were detected below 900 cm^{-1}, the identification of barium yellow would not have been possible by use of fiber optic reflection-FTIR.

Lapis lazuli ($Na_{8\ldots10}Al_6Si_6O_{24}S_{2\ldots4}$) could be detected in manuscripts on parchment (Codex Millenarius Minor, Benedictine Stift Kremsmünster, Austria, 9th century) as well as on paper (Ottoman manuscript, Benedictine Stift Göttweig, Austria, 17th century). The results were confirmed by XRF detection of Si and S and in case of the Ottoman manuscript by reflection-UV/Vis spectroscopy. The main bands in the region between 1100-900 cm^{-1} with a maximum at ca. 1010 cm^{-1} (Si-O-Si and Si-O-Al stretching) were inverted and interfered with bands from the paper support in case of the Ottoman fragment (shoulders at 1104 and 1053 cm^{-1}, C-O-C and C-O stretching from pyranose ring structure). A comparison of the measured spectra with the reflection reference spectrum of lapis lazuli (Kremer 105608) showed a good agreement, whereas Kramers-Kronig transform did not yield evaluable absorption index spectra. The reflection spectrum further showed a peak at 2340 cm^{-1}, which is much more indicative for lapis lazuli than the alumosilicate vibrations mentioned before. It derives from entrapped CO_2 and appears similar as in the transmission reference spectrum IRUG IMP00048. This similarity probably indicates a contribution of diffuse reflectance, as both transmission and diffuse reflection spectra base on absorption processes. It is not surprising therefore, that application of the Kubelka-Munk function led to a proper match with the respective peak in the reference absorption spectrum, whereas Kramers-Kronig transformation, which is adequate in case of mainly regular reflection, did not. Additional detection of Cu and Co in the Ottoman fragment suggested that lapis lazuli was mixed with azurite and smalt (potassium glass containing CoO). A similar combination was also used in Byzantine manuscripts[3], most probably due to the high costs of lapis lazuli. However, no evidence for both materials could be obtained from the reflection-FTIR spectrum, while reflection-UV/Vis spectroscopy argued for a combination of lapis lazuli and azurite. This example clearly shows the advantages of the combined use of complementary techniques.

We were able to detect bone black (carbonated hydroxyapatite) in a 19th century oil painting by Alfons Walde (1891-1958). The reflection spectrum showed a sharp peak similar as in the transmission reference spectrum at 2016 cm^{-1}, resulting from cyanamide contents (NCN^{2-}). This peak is of high diagnostic value as it is characteristic for bone black and almost no other artist material shows absorption in this spectral range. The measured reflection spectrum excellently matched the reflection reference spectrum of ivory black (Kremer 120008) and, after Kramers-Kronig transformation, the absorption reference spectrum IRUG IMP00297 with maxima at 1655, 1456, 1038, 878 and 604 cm^{-1} (Fig.3). The transformation led to a distortion of the cyanamide vibration. Additionally, bands from a drying oil (2920, 2850 and 1739 cm^{-1}, reference IRUG IOF00001) and iron (III) oxide-hydroxide (573 and 473 cm^{-1}, reference Hummel HIP31376) were found in the absorption index spectrum. As in case of barium yellow, only the spectral range with wavenumbers lower than 900 cm^{-1} enabled the identification of iron (III) oxide-hydroxide.

Prussian blue ($Fe_4[Fe(CN)_6]_3$) was detected as a component of Hooker´s green together with gamboge (yellow gum-resin pigment) on several watercolor paintings from Moritz M. Daffinger. The main CN stretching vibration at 2094 cm^{-1} was similar to the corresponding band in the transmission reference spectrum IRUG IMP00049 and thus, a contribution of diffuse reflection can be assumed also in this case. Considering that the particle size of Prussian blue usually is lower than the wavelength of the used MIR-radiation, diffuse reflection has to be expected[4]. A mixture of Hooker´s green and viridian was identified on the painting "Solanum dulcamara L.". Kramers-Kronig transformation yielded an absorption index spectrum matching the absorption reference spectrum of gamboge IRUG IOD00007, whereas the CN stretching band of Prussian blue was distorted after transformation. Although the bands of viridian adversely interfered with gamboge in the range between 1400 and 700 cm^{-1}, two bands at 559 and 491 cm^{-1} enabled its identification according to a reference spectrum published by S. Vahur[2]. The FTIR results were confirmed by XRF detection of Cr and Fe.

The IRUG database spectrum of cobalt blue ($CoAl_2O_4$, IMP00103) only shows a single broad absorption band with maximum at ca. 665 cm^{-1}. Although the absorption index spectrum obtained from an original painting material (violet watercolor tablet) of Moritz M. Daffinger matched with the reference, an unambiguous identification was not possible as other pigments also show a similar band, e.g. anatase IRUG IMP00229. However, the detection of Co by XRF and the results of reflection-UV/Vis spectroscopy allowed the conclusion that the watercolor tablet contains cobalt blue. Moreover, Arabic gum (reference IRUG ICB00012) and calcium stearate (reference IRUG IOF00108) could be identified from the absorption index spectrum, whereas the red colorant could not be identified. Additional analyses on a small sample from the bulk material by FTIR microscopy showed that calcium stearate derived from a surface contamination.

CONCLUSION

We conclude from our results that reflection-FTIR is a useful tool for the non-invasive identification of inorganic pigments with characteristic absorptions in the range of 4000-375 cm^{-1} in paintings and painting materials. The use of the IRUG database allowed the identification of all inorganic pigments mentioned before except viridian and cobalt blue. Thus, the specific reflection database only offered few advantages considering that these pigments also can be identified by XRF and reflection-UV/Vis spectroscopy. Compared to fiber optic instruments, a mirror guided beam path offered an extended spectral range which provided useful analytical information in many cases, particularly in the region from 900 to 400 cm^{-1}.

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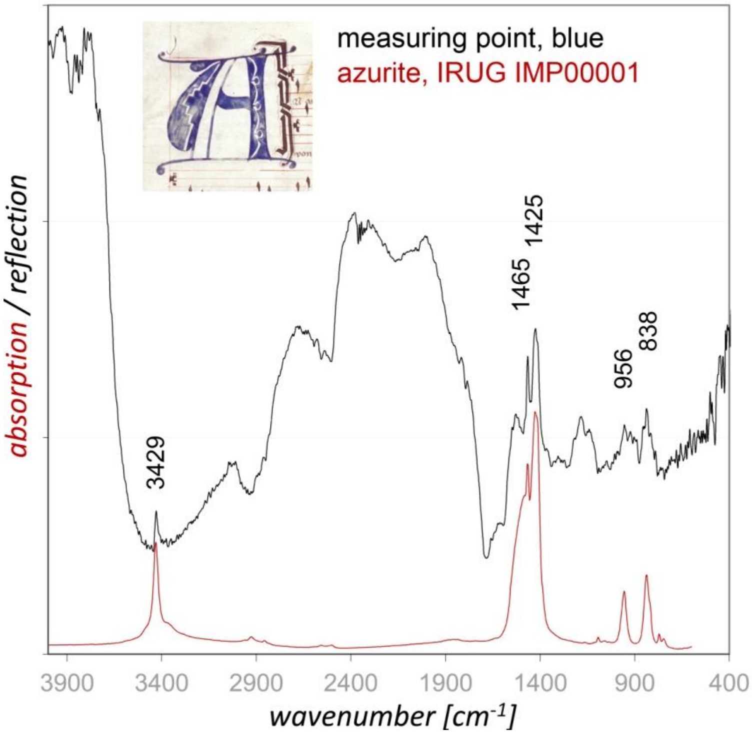

Fig.1: The reflection spectrum from a measuring point in a blue area (black curve) shows spectral features similar to the absorption reference spectrum of azurite (red curve).

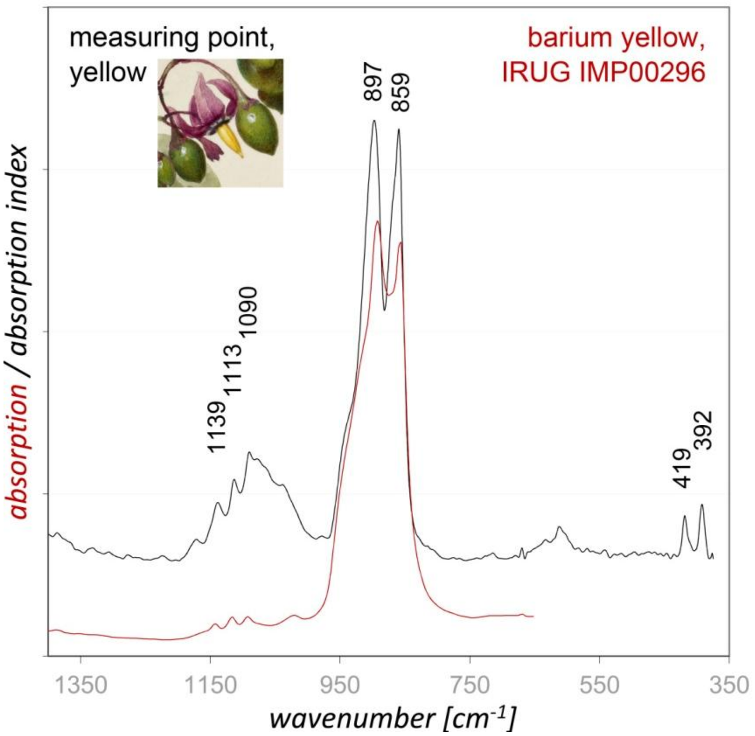

Fig.2: Kramers-Kronig transform of the reflection spectrum from a measuring point in a yellow area yielded an absorption index spectrum (black curve) which matched with the absorption reference spectrum of barium yellow (red curve).

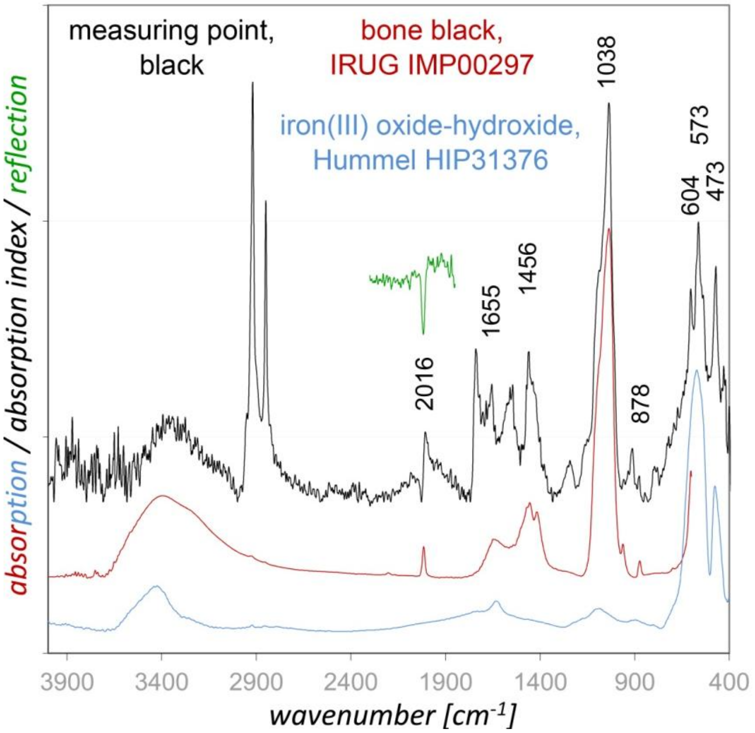

Fig.3: The absorption index spectrum from a measuring point in a black area (black curve) matched with the absorption reference spectra of bone black (red curve) and iron(III) oxide-hydroxide (blue curve). The peak deriving from cyanamide (NCN^{2-}, 2016 cm^{-1}) was distorted due to the transformation of the reflection spectrum (green curve).

Derivatisation strategies for micro-FTIR and chemical imaging FTIR-FPA - fluorination reagents to discriminate spectral interferences in paint samples

Stefan Zumbühl, Nadim C. Scherrer

INTRODUCTION

Fourier Transform Infrared Spectroscopy (FTIR) is a well-established analytical technique for paint samples and materials in conservation science. With the development of Focal Plane Array (FPA) detectors in the past 15 years, FTIR spectroscopic imaging has emerged as a powerful tool for chemical imaging [Salzer 2009]. ATR (attenuated total reflectance) technology allows the localisation and identification of organic and inorganic compounds in micro-samples at higher spatial resolution, beyond the optical diffraction limit. There are, however, limitations to the technique when analysing chemically complex multi-component materials. Paints are complex systems containing organic binding media, colorants, mineral fillers and several system- or production-relevant additives and ageing products. As most of these compounds are infrared-active, spectral interferences hinder the full characterisation of the binding media, with minor components remaining undetected. Thus it is of interest to discriminate overlapping signals and achieve signal enhancements on superimposed compounds. For standard analytical procedures using FTIR-FPA imaging, the signal separation in multi-compound systems is essential to derive chemical maps, as signal integration is only possible on isolated spectral bands.

THEORY OF DERIVATISATION

In order to improve the selectivity of the infrared spectroscopy, two preparation techniques were used to eliminate signal interferences in paint samples. Either the organic components are separated by micro-extractions from the insoluble solids, or the filler is chemically converted into a non-IR-active compound [Jönnson 2004]. The second method is largely restricted to the elimination of calcium carbonate with dilute hydrochloric acid. Both methods are destructive and have major drawbacks as they are only applicable to micro-samples, and they lead to the loss of the morphological context of the sample material. For these reasons they are not suited to FTIR-FPA imaging. Thus, spectral discrimination in solids by selective chemical modification of functional groups in gas phase delivers an interesting alternative to the above-mentioned approaches.

Different derivatisation concepts rely on either selective shifting of IR-bands resulting in splitting of overlapping bands, or by eliminating interfering signals. These effects are achieved by conversion of chemical bonds, since IR absorption and the resulting vibrational frequencies are dependent on bond force constant, atomic masses and molecular geometry [Socrates 1998]. The mid-infrared absorption of an individual bond is mainly dependant on the change in dipole moment, the steric orientation of the functional group within a molecule, as well as its sensitivity to neighbouring group effects [Stuart 2004]. In inorganic materials, the crystalline structure has a decisive influence on the IR-activity of an inorganic material [Farmer 1974]. If the vibration has zero change in its dipole moment, what is true for cubic crystals, it does not absorb IR light. Contrary to highly symmetric crystals, all minerals containing polyatomic ions exhibit strong IR signals, since the anions themselves have several internal vibration modes [Farmer 1974]. Derivatisation techniques aim at modifying IR-absorption selectively by characteristic alteration of the binding modes. The aim of derivatisation is to achieve a controlled, characteristic and reproducible functional group modification. Thus, based on the theory of infrared spectroscopy we can deduct 4 principle strategies to eliminate spectral interferences from organic and inorganic materials. The following principles are of practical relevance in this context: I) Single atom substitution within functional groups, II) Substitution of entire functional groups, III) Modification of the neighbouring groups of an IR absorbing bond, and IV) Modification of the crystal structure by ionic exchange.

FLUORINATION REACTIONS

Within this context of infrared spectroscopy, derivatisation of organic and inorganic materials by fluorination reactions is of interest, since various exchange reactions are possible due to the small mass of the fluorine. Furthermore, organic fluorine compounds show characteristic and narrow IR bands [Socrates 1998], which are specifically suited to FTIR analysis. The fluorination of an organic molecule can influence both, the absorption of the hydrocarbon backbone as well as of the functional groups. Due to the strong coupling of C-C and C-F stretching, fluorinated compounds can show specific absorption of the halogenated group [Socrates 1998]. Adjacent atoms, such as halogens, furthermore increase the intensity of weakly absorbing vibrations such as CH wagging, twisting and bending [Vandeberg 1980]. In functional groups the change in position of a vibration mode can be attributed to the mass effect, but is also due to the change in electron distribution, brought about by the substituted atom. It has been observed, for example, that inductive and resonance effects have the greatest influence on the shift in the carbonyl stretching frequencies [Vandeberg 1980].

There is a wide range of materials being modified by fluorination in industrial applications and there are a great number of specific reagents applied in different processes [Baasner 1999; Furin 1991]. In practice, however, the options to apply selective fluorination in combination with a spectroscopic technique are strongly limited since most fluorination reactants are either liquids or, their reaction proceeds in solution [Paquette 2007; Furin 1991]. Of the gaseous reagents, elemental Fluorine F_2, anhydrous hydrogen fluoride HF, and sulphur tetrafluoride SF_4 play an important role. To achieve the chemical modification of the hydrocarbon backbone, elemental fluorine F_2 is often used in industrial applications. Besides applying it for the total substitution of hydrogen, it is also used for the selective replacement of specific hydrogens in aliphatic and aromatic molecules, and for the addition of fluorine to various types of double bonds [Baasner et al. 1999]. Among these, anhydrous hydrogen fluoride HF is the currently most widely used industrial fluorinating agent for selective processes. But it has a major drawback, however, namely a number of secondary reactions that are due to its high acidity [Baasner et al. 1999]. Therefore, the weakly acidic sulfur tetrafluoride SF_4 attracts more practical interest for the analysis of paint samples and materials in conservation science. It is a corrosive gas at standard temperature and humidity conditions, forms hydrogen fluoride HF upon exposure to moisture (Reaction 1) and, it is a precursor to many organofluorine compounds. It converts hydroxyl, carbonyl, and carboxylic acid groups into mono-, di-, and trifluorinated functionalities, respectively [Wang 2004]. For each class of functional groups, different reactions take place under variable reaction conditions [Paquette 2007; Wang, 2004]. This reagent was recently tested for practical application to investigate oil, alkyde and tempera paint samples [Zumbühl 2014].

DERIVATISATION REACTIONS IN PAINT MATERIALS

The initial application of sulfur tetrafluorid SF_4 to paint samples has revealed different selective derivatisation reactions of *I) organic components, II) various organometallics* and *III) inorganic materials*, which may be exploited by IR spectroscopy. The application of this technique enabled the chemical characterisation and localisation of the different functional groups with clear signal discrimination:

I) Derivatisation of organic materials:

The gaseous sulfur tetrafluoride SF_4 treatment was chosen to achieve the distinction of carbonyl bands from ketones and carboxylic acids and esters, which is one of the main difficulties identifying material mixtures made from organic compounds and characterising of the oxidation state of a material. The principle of this technique is the selective conversion of carboxylic acids R(O)OH into an acyl fluoride R(O)F (Reaction 2) [Wilhelm 1994]:

(1) $SF_4 + 2\ H_2O \rightarrow SO_2 + 4\ HF$
(2) $C(O)OH + HF \rightarrow C(O)F + H_2O$.

Since fluorine has a high electronegativity, the highly inductive effect of this neighboring atom raises the frequency of the ν(C=O) vibrational mode of the modified acid carbonyl group. This derivatisation product shows characteristic IR vibrations at 1841cm^{-1} (Wilhelm, 1994), while ketones ν(C=O) at $\approx$1720cm^{-1} and ester groups ν(C=O) at $\approx$1740cm^{-1} remain intact. IR spectra after SF_4 treatment of such samples show the characteristic splitting of the carbonyl band, allowing the distinction of the individual functional groups **(Figure 1)**. Moreover, the elimination of the carboxylic νO-H signal makes it possible to detect alcoholic hydroxyls selectively.

II) Derivatisation of organometallic materials:

In the field of art conservation science, the combination of IR absorption of the organic, organometallic and inorganic compounds make it rather difficult to study the binder components in curing oil paint. Research on old oil paint samples has shown that it is possible to derivatise not only carboxylic acids, but also their salts R(O)OM into an acyl fluoride R(O)F:

(3) $C(O)OM + HF \rightarrow C(O)F + MOH$
$MOH + HF \rightarrow MF + H_2O$.

This is of interest for the investigation of oil-based paints. Following derivatisation treatment, the broad signals of carboxylates at around $\approx$1600cm^{-1} ν_a (C(O)O$^-$) [s], $\approx$1450cm^{-1} ν_s (C(O)O$^-$) [m-s] and $\approx$850cm^{-1} sci (C(O)O$^-$) [m] [Socrates, 1998] are no longer present **(Figure 2)**. The conversion of the strongly IR-absorbing ageing products such as zinc or lead soaps is of great interest, since it allows to explore the different superimposed C-H deformation and wagging vibrations [Zumbühl 2014].

III) Derivatisation of inorganic materials:

The conversion reaction of inorganic compounds is of particular interest in this context in order to eliminate the broad overlapping bands of some strongly IR-absorbing mineral fillers or pigments, as some have shown to be transformed into a non-IR active components. So far this reaction has only been investigated in detail for carbonates such as calcite $CaCO_3$, cerussite $2PbCO_3$ and hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$. The pigment conversion of basic lead carbonate is of great interest, as it was very popular and widely applied in paint manufacturing. The strong and broad ν_3 carbonate bands of the CO_3^{-2} ion at $\approx$1410cm^{-1} generally strongly limit FTIR analyses on binding media. Upon derivatisation using SF_4, all carbonate absorption bands are eliminated **(Figure 2b)**, since the pigment is converted into the non-IR active cubic lead(II)fluoride β-PbF_2 [Zumbühl 2014]:

(4) $Pb(OH)_2 + 2\ HF \rightarrow PbF_2 + 2\ H_2O$
$PbCO_3 + 2\ HF \rightarrow PbF_2 + H_2O + CO_2$.

DISCUSSION AND CONCLUSION

A major drawback of infrared spectroscopy is the poor selectivity in complex material systems due to signal interferences of different functional groups within similar spectral ranges, causing the minor components to remain undetected. This is of great limitation, in particular to the study of binding media analysis on artwork. A pre-treatment with gaseous sulfur tetrafluoride SF_4 to derivatise certain compounds substantially increases the selectivity of the FTIR technique by eliminating signal overlaps. As example this reagent was recently applied to investigate the protein content in tempera paint [Zumbühl 2014] (Figure 3). Furthermore, signal discrimination is also of interest for chemical imaging using the focal plane array technology FTIR-FPA. Besides the derivatisation of micro-samples, this pre-treatment can also be applied to polished cross-sections or surfaces. The technique allows research on the interrelationships of such complex material systems within the original stratigraphic structure [Zumbühl 2014] (Figure 1b,3b). The application of the SF_4 derivatisation technique on embedded and polished samples shows that the extent of the reaction with gaseous SF_4 is only superficial, yet deep enough for successful attenuated total reflectance ATR measurements. The IR penetration depth using ATR technology in organic layers using a germanium crystal is in the range of 0.2-0.7 µm [Salzer 2009], meaning that a reaction depth of 1µm during derivatisation is sufficient for the method to work successfully. The standard reaction time of 24h was sufficient to achieve an ubiquitous and homogenous derivatisation across the polished surface in all cases. The reaction products were found to remain stable for several weeks and can easily be removed by repolishing. It can be concluded, that a derivatisation pre-treatment with reactive fluorine gases has great potential to increase the selectivity of infrared spectroscopy in conservation science. The applicability of the technique in combination with 2D FTIR-FPA imaging at a spatial resolution of 1-1.5µm opens a new level of information when researching aged paint layer stratigraphies.

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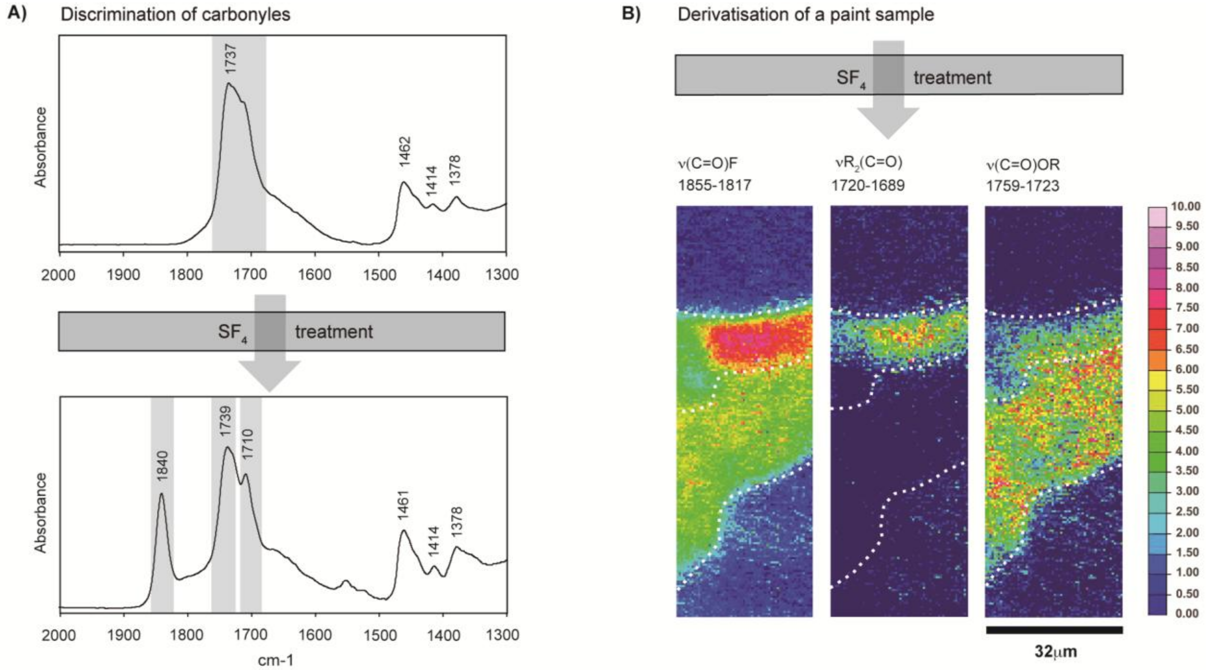

Figure 1 A) Micro-FTIR spectra before (upper) and after SF_4 treatment (lower). Focus is on the splitting of the carbonyl band upon SF4 treatment, which permits the distinction of acids (as acyl fluoride) ≈1740cm^{-1}, ketones ≈1710cm^{-1}, and esters ≈1740cm^{-1}. B) FTIR-FPA imaging on a cross-section: SF_4 derivatisation enables the localisation of the various carbonyls within very thin layers of about 10 Microns.

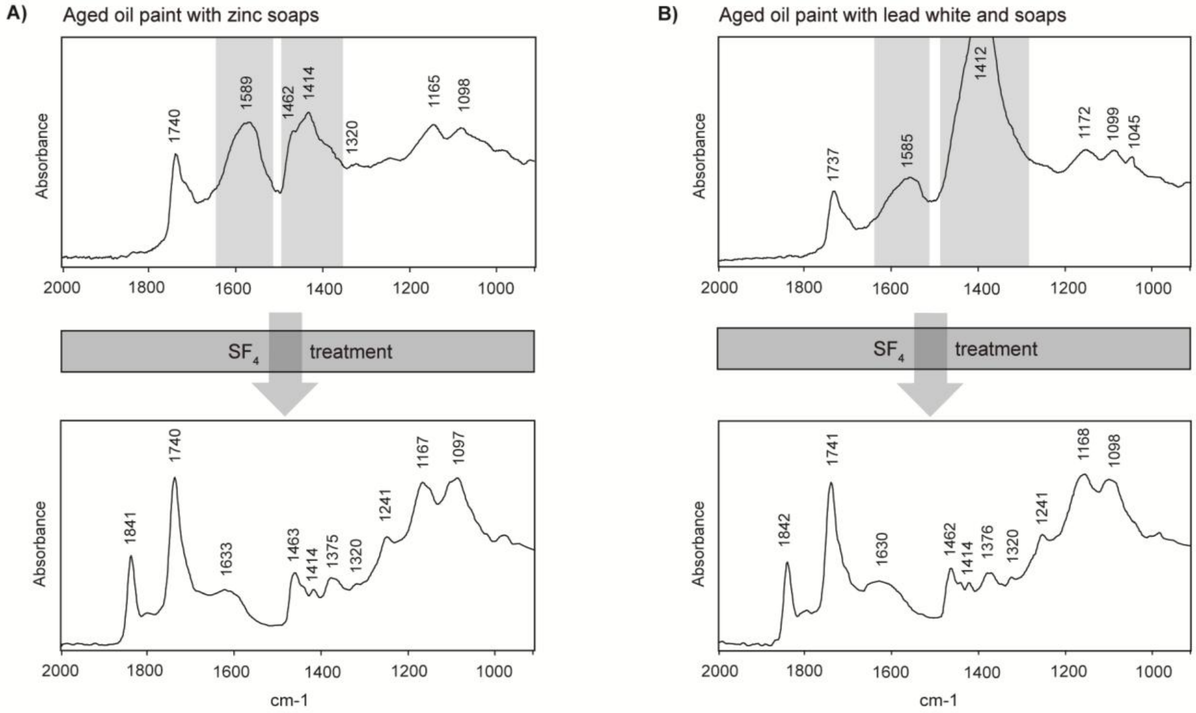

Figure 2 A) Derivatisation of 60-year old oil paint films containing zinc soaps (and zinc white), and B) a 60-year old oil paint film containing lead white and lead soaps (upper) and after SF_4 treatment (lower). After the elimination of the signals from the organometallic and inorganic compounds, the C-H signals at 1463cm^{-1}, 1414cm^{-1} and 1375cm^{-1} of the oil binder are uncovered.

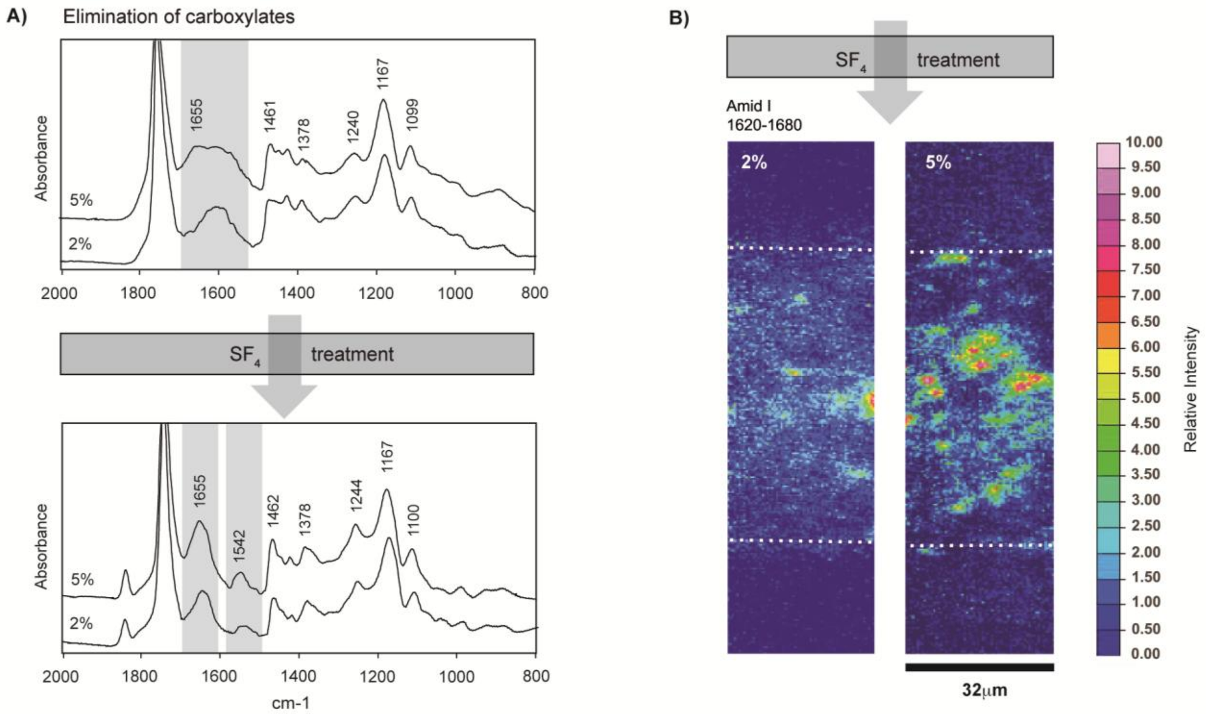

Figure 3 A) Micro FTIR: Derivatisation of tempera paint made of zinc white with variable protein content of 2% and 5% (protein/oil ratio) before (upper) and after (lower) derivatisation with SF_4. B) FTIR-FPA images: The SF_4 pre-treatment enables the localisation of the protein inclusions within a paint film. This is not possible without the elimination of the carboxylate signals in aged paint.

Poster Presentation

An investigation of the Tibetan book covers from the collections of the Bayerische Staatsbibliothek Munich by FTIR and Raman spectroscopy

Simon Mindermann, Thorsten Allscher*

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Tibetan books consist of a text block which could additionally be wrapped up in a woven fabric and two loose wooden book covers. Unfortunately, quite often the text and the covers were separated and only one of the two covers has been preserved. These book covers could be carved and/or painted often showing the beginning of the book's story.

Inner face of a Tibetan book cover, Bayerische Staatsbibliothek, Munich, Cod.sanscr. 423.

The Tibetan collection of the Bayerische Staatsbibliothek contains more than 100 Tibetan book covers from Tibet, Nepal and India ranging from the 12th to the 20th century. As the book covers are barely investigated and the tradition of manufacture was continued over a long period, dating only by iconographic and art historic characteristics seems to be a very imperfect method. Now, within a project "Digitization and Cataloguing of Book Covers as autonomous objects d'art" which is funded by the Deutsche Forschungsgemeinschaft (DFG) the Tibetan book covers will be investigated by spectroscopic techniques.

Therefore, FTIR and Raman spectroscopic investigations of the dyestuff, the binding material and the varnish can identify the individual compounds and discover the historical background of manufacture and provenience. Additionally, the knowledge of the used materials can be a valuable source for the dating of book covers, e.g. is the detection of titanium white a clear hint for a book cover from the 20th century.

For a contactless non-destructive investigation of the book covers reflection FTIR spectroscopy was carried out with a Bruker Alpha FTIR spectrometer equipped with an external reflection module. The reflection module focuses the beam via mirrors to the sample resulting in a beam diameter of about 5 mm. The reflected radiation is collected also by mirrors and directed to a detector. Total reflection spectra were collected in-situ in the range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1} over 24 scans. The background was acquired using a gold mirror/surface as reference sample. Raman spectroscopy was carried out with an Enwave Optronics ProRaman-L spectrometer with a 532 nm green laser which could be coupled into a Leica microscope with a 10x magnification.

By these two methods various pigments could be identified which were also found in Buddhistic thangka scroll paintings. Thick layers of varnish which could be original or added in later times overlay the pigments' spectral information and raise difficulties to obtain explicit spectral information.

The poster should inform about the possibilities and limitations of the methods of contactless FTIR Reflection and Raman spectroscopy used to investigate the Tibetan book covers of the Bayerische Staatsbibliothek and should present the actual results of the project.

Poster Presentation

Artificial aging of neutral verdigris: new evidence by Raman Spectroscopy and X-ray Diffraction

Lynn B. Brostoff,[1] Cindy Connelly-Ryan,[1] Gwénaëlle Kavich,[2] Alessa Gambardella[3]

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From antiquity through the 19th century, the synthetic pigment called verdigris offered artists an important alternative to natural green ores, dyes or mixtures of blues and yellows. Verdigris was particularly favored by book colorists, who required transparent color washes that would not obscure printed lines. It is not well understood why this copper-based pigment often, but not always, causes degradation of paper supports, or how this degradation may be related to chemical and physical properties of the pigment in its various forms. Therefore, verdigris remains an important area of investigation, both in terms of its specific identification and preservation. This study focuses on tracing the path of verdigris alteration under different conditions in order to better understanding both its historical use and relative stability.

Historical recipes provide evidence that verdigris could be made from numerous methods involving corrosion of copper with acetic acid from fermented materials such as wine products. When reproduced, these recipes result in permutations of two distinct types of copper(II) acetate salts: (1) the neutral copper acetate monohydrate, or (2) basic salts, which take on a baffling array of stoichiometric and hydrated forms [1,2,3]. While the former is invariably a bright teal-blue color, basic verdigris is usually more bluish-green in color. We have confirmed that re-precipitated or “distilled” verdigris, which was available commercially to artists early on, would have been neutral verdigris; this form of the pigment is also likely to have been produced by the famous French commercial industry [4]. While it is well known that verdigris will convert from teal-blue to green over several months, there is conflicting information in the literature about color variation and conversion in both forms of the salt [5]. Thus, it has not been well understood whether artists favored basic verdigris or tended to admix yellow colorants in neutral verdigris to achieve their desired hue from the outset.

The Library of Congress has undertaken a study into verdigris identification and deterioration mechanisms. For this purpose, verdigris pigment obtained from Kremer Pigments, Inc. or synthesized in-house was painted in gum arabic or glair on various paper substrates and exposed to artificial aging at 50 °C and 65% RH. This poster presents select results from study of the neutral verdigris samples by Raman and UV-Vis spectroscopy, with complementary X-ray diffraction (XRD). Results yield new evidence that points to early alteration paths of neutral verdigris, and clarifies some conflicting information in the literature, including: 1) verdigris from Kremer, Cornelissen and Sinopia suppliers is neutral, not basic; 2) neutral verdigris in gum arabic or glair readily alters to the relatively stable, green basic verdigris with humidity; 3) brown-black tenorite (CuO) forms rapidly from neutral verdigris > 70 °C and slowly > 50 °C in the presence of humidity, although it does not appear to develop naturally; 4) tenorite can also be formed by exposure to a 785 nm laser during Raman analysis if the power and/or beam density are too high; and 5) the substrate and/or medium can influence the course of neutral verdigris alteration. In contrast, results show that basic verdigris is relatively stable in gum arabic under the same conditions up to 287 hours. By tracing the paths that verdigris may take in both natural and artificial aging, this study ultimately aims to facilitate the interpretation of evidence that is typically gathered from suspected verdigris pigments on historical artifacts.

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Poster Presentation

Synthetic materials in art objects

Irina Burtseva

The study of modern polymer restoration materials in art objects was provided by µ-FTIR spectroscopy. PVA, Paraloid and acryolnitrile/butadiene copolymer were found.

Preconservation studies are important for contemporary conservation techniques. Usage of new materials should be delicate not to make harm to art objects. One of the demands of conservation science is reversibility, but the introduction of polymers does not always satisfy it. Sometimes aggressive solvents have to be used to extract them from the objects.

Analyze of art samples is the difficult problem as they are multicomponent systems of pigments, binders and early used conservation substances. So the received IR-spectra differ greatly from basic ones. For right identification the additional methods such as microchemistry and XRD analyses are applied. This is especially important when polymers were used in oil painting, graphics and tempera. Sometimes solvents were used to extract polymers from the objects. When analyzing wood, bone, ceramics or porcelain, it is possible to see polymers under optical microscope and take tiny sample of it with the help of needle-spatula.

In this work the tiny sample was put on metallic reflection platform under optical microscope, then pressed to be flat and analyzed by µ FTIR spectroscopy (spectrophotometer “Cary -600 FTIR” with microscope “Cary-610 FTIR” Agilent) with resolution 4 cm^{-1}, 64 scans in reflection mode. IRUG 2000 Spectral Database and own database were used for identification IR-spectra.

PVA was often used in 70-80 years of 20th century for consolidation basic materials of icons and painting layers. PVA were found in the coating film of the wood basic in icon “Saint Nicolai” (18th century), in “St John the Baptist” (14th century) and in places of early restoration and upper coating layers of “Tsar’s gates” and “Paraskeva Friday” “ Trumpeting Angel”. To identify PVA one should pay attention to almost equal intensity of two peaks: 1227 cm^{-1} and 1740 cm^{-1} and the presence of peak 1024 cm^{-1}. In all our experiments we were able to get spectrum almost equal to database one.

Synthetic polymer materials are also used in oil painting too. The upper coating layer of S. Ivanov’s picture “Artist’s model” was covered by acrylic polymer. Its spectrum was close to Paraloid B-48 (IRUG-2000). The film penetrated deeply into painting layers so at first it was difficult to understand its nature. The following washing and separating from pigments and other binders allowed to interpret its original.

Acrylonitrile/butadiene copolymer was found as a glue on the surface of the 19th bone fan. The further research showed that the glue with this copolymer under the trade mark “Mars” is produced for sticking different materials.

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Poster Presentation

Identification of pyroxene minerals used as black pigments in painted human bones excavated in Northern Patagonia, Argentina

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The skeletal remains of seven individuals were uncovered by archaeologists in a secondary burial context in the site of Cima de los Huesos, in the coast of Northern Patagonia, Argentina. Two samples, a skull fragment and a tooth, corresponding to different individuals from the site were dated by AMS to 1173±45 and 1225±47 years BP. Among these remains, the bones of an adult male carefully painted with alternating red and black lines were found.

The SEM-EDS analysis of microscopic sample scrapings removed from the painted areas showed that iron is the main component of the red paint and that the black paint contains manganese and iron. The FTIR-ATR spectra recorded *in-situ* in painted bone areas and in areas with no visible paint gave features characteristic of feldspars, hydroxyapatite, and collagen. No other organic compounds were detected.

Raman spectra acquired in scrapings of the red paint showed peaks due to hematite (α-Fe_2O_3), while the main features observed in the spectra of the black paint are consistent with the presence of members of the pyroxenes series ferrosilite ($FeSiO_3$) and enstatite ($MgSiO_3$). Minerals of the pyroxene group ($MSiO_3$) are one of the most abundant rock-forming minerals on Earth. Ferrosilite forms a solid solution with enstatite and the position of the Raman bands for this solution depends on the content of Mg, which partially replaces the sites occupied by the Fe atoms. The Raman spectra recorded in the black paint revealed the presence of another pyroxene, kanoite ($MnMgSi_2O_6$) for which scant spectroscopic information has been published. The identification of these compounds was confirmed by XRD measurements. Raman spectra recorded from white particles present in the red paint allowed to identify calcite and hydroxyapatite, while in the white particles found in the black paint samples, microcline feldspar ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$) were observed.

This is, to our knowledge, the first report on the use of pyroxene-containing black pigments in South American painted bones, possibly because in most studies only elemental analyses were performed. The results will be discussed in the context of burial practices in the region for that period.

Poster Presentation

A Painted Etruscan Sarcophagus – Original or Forgery?

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An Etruscan sarcophagus of the Antikensammlung (Collection of Classical Antiquities) Berlin was purchased by the Royal Museum Berlin in 1898. It shows a polychrome decoration, which is unusual in some of its details. Furthermore conservation treatments seem to have been carried out without any documentation. Therefore it was the aim of a Diploma thesis at the University of Applied Sciences Potsdam to identify, distinguish and date treatments, including those to the paint layer, more accurately [1].

A variety of non-invasive and invasive techniques were used in the technical examination of the sarcophagus. Part of the examination was to determine layer sequence and to identify material compositions and conservation treatments. A limited number of small samples were analyzed by Vis- and UV-microscopy, microchemistry, staining techniques, ATR-FTIR, ATR-FTIR-Imaging and Transmission-FTIR as well as Py-GC/MS (F. Mucha, University of Applied Sciences Erfurt), XRD and ESEM (Rathgen-Forschungslabor, Berlin).

This work focused on different methods of IR measurement used for the characterization of the painting materials. Analyses were performed with a Perkin Elmer Spectrum 100 and Spotlight 400 Transmission and Imaging System. The Spectrum 100 instrument is equipped with an MCT detector and a diamond crystal. The Imaging system containing a single element MCT detector combined with a linear array MCT imaging detector, a germanium crystal for ATR mode and a diamond cell for transmission mode. Spectra were recorded between 4000 and 650 cm^{-1} in transmission and 4000 and 750 cm^{-1} in imaging mode.

Binding materials were analyzed using Transmission-FTIR with the diamond cell and ATR-FTIR using chloroform extraction. Vis- and UV-Microscopy in combination with staining techniques, microchemical analysis and Py-GC/MS provided additional results.

Pigments were analyzed using microscopy, microchemistry, Transmission-FTIR, ATR-FTIR- and ESEM-Imaging. ATR-FTIR-Imaging of cross sections was used to generate supplemental information to ESEM-Mapping although the spatial resolution is quite different. Similar to ESEM-Imaging, the ATR-FTIR-Imaging is able to distinguish compositions and layers even if a microscopic differentiation is impossible. It can illustrate variances between areas without identifying a complete composition. Thus, it can be useful in distinguishing unexpected details, small variations in the composition as well as certain components of mixtures.

Due to the spatial resolution, without further data processing only inorganic materials were indicated by the IR-spectra of the cross sections. The distribution confirmed our interpretation of pigment use in the paint layers and of some aging processes.

Through interdisciplinary research and scientific examinations it was possible to conclude that the Etruscan sarcophagus was decorated in Italy before being sold to Berlin in the nineteenth century. The object subsequently underwent conservation treatments in Berlin or during a transfer to the Soviet Union after the Second World War.

References:

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Poster Presentation

The Cut-Outs of Henri Matisse: a study of his gouache palette

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In the last 18 years of his life, Matisse produced some his most admired and influential work, the Paper Cut-Outs. During this period the artist turned away from painting and developed a practice involving his studio assistants and then finally professional mounters. His assistants would brush large sheets of paper with Linel gouache. Matisse would spontaneously cut shapes from these sheets of colored paper and arrange them in compositions, pinning them to a board or on the walls of his studios with the aid of his assistants. These compositions were later mounted, either in the studio or by a firm in Paris.

In October 2014, The Museum of Modern Art will host an exhibition entitled Henri Matisse: The Cut-Outs. In preparation for this exhibition, the Conservation Department received a generous donation of seventy nine small sections of painted papers that had been preserved in the artist's estate. This set has been assembled under the premise that it represents the majority of colors and tones that Matisse selected from the larger Linel gouache line, manufactured by Lefranc Bourgeois. These painted paper samples, which have never been exposed to light, represents a phenomenal opportunity to study not only the palette of colors used by Matisse and the materials that were used in the preparation of the painted papers, but also allows us to determine to some extent the alterations to his oeuvre of cut-outs which has occurred over time and therefore how to best preserve his works.

We have just embarked on a comprehensive analytical characterization of the cut-out papers samples to identify the materials both in the gouache and in the papers. We are particularly interested in selecting non invasive and portable techniques suitable for both the reference papers and works in the museum collection or other collections. Techniques such X-ray fluorescence (XRF) and in-situ reflection infrared (FTIR) spectroscopy will not only provide meaningful information on the organic and inorganic composition of the reference papers, but the spectra obtained can also be compiled into libraries of "fingerprints" to be used in the characterization and comparison of different artworks. Considering, however, that the composition of commercially available artist materials is usually complex, complementary invasive methods will be necessary to thoroughly characterize the papers. The data acquired is expected also to validate the information obtained with the non invasive techniques, increasing the confidence in the comparison methods based on the libraries of spectra.

In this presentation, we will report on the progress of this project, namely the elucidation of the gouache compositions based on the examination and analysis with non invasive as well as destructive techniques. The validity of the paper cut out fingerprint approach will be demonstrated also with case studies.

Poster Presentation

Identification of pigments used in traditional bark paintings in the Northern Territory of Australia

Georgina Rayner, Narayan Khandekar and Katherine Eremin, Straus Center for Conservation and Technical Studies, Harvard Art Museums; Rita Giannini, and Andrew J. Shortland, Cranfield Forensic Institute, Cranfield University

Harvard Art Museums are undertaking a major investigation into traditional bark paintings from Arnhem Land, Groote Eylandt and the Tiwi Islands; locations in the Northern Territory of Australia. This study is focusing on the pigments used by Aboriginal artists and is the first major analytical survey of bark paintings from the late 19th to 20th century.

These naturally occurring pigments contain a wide range of elements in varying amounts, characteristic of pigment types such as ochres, clays and mineral blacks. An earlier study conducted at the University of Western Australia demonstrated that laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can be used to group pigments from various regions around the Australian continent according to the distribution of trace elements. Our study focuses on the trace element differences in a more closely defined region of Australia, namely the Northern Territory. To identify the pigments we are using LA-ICP-MS alongside complimentary techniques, including scanning electron microscopy, Raman and FTIR spectroscopy.

The samples in this study include natural deposits of pigments, obtained from recorded historical expeditions and collected directly by the authors in consultation with local artists, as well as approximately 200 samples from 50 bark paintings collected from galleries and museums from Canberra, Sydney and Melbourne. The paintings were all chosen because they used traditional methods and materials and spanned over 100 years, with the location and date of painting being known for some examples. For instance, Melbourne University's sampled paintings all come from the same community on Groote Eylandt and date to 1941-1945. A sample of each paint color present was collected to provide a statistically valid database of the range of natural pigments available from the 1870s to 1980s. The opportunity to compare samples from paintings with samples of natural raw materials from sites around Arnhem Land, Groote Eylandt and the Tiwi Islands provides us with a unique opportunity to trace the geographical origin of the pigments. It is anticipated that this will shed new light on the movements of raw materials through trade.

The study is ongoing and will be included in the catalogue for an upcoming exhibition at Harvard Art Museums opening in January 2016.

Poster Presentation

Seeing the unseen: applicability of hyperspectral VNIR and SWIR imaging to cultural heritage artifacts

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As evidenced by the existence of a large number of museums across the globe, the importance of preserving cultural heritage artifacts is immense. Cultural heritage artifacts are important not only for the peoples they represent, but are also valuable indicators of the state of technology and historical events of their respective time periods. One of the dilemmas in the study and preservation of cultural heritage items is how to gain the information we need about the artifact without damaging it, which is difficult considering that up until recently, chemical information could only be obtained by taking small samples of the artifact for destructive analysis. Fortunately, hyperspectral imaging is emerging as a cost-effective, non-destructive technology that can be used to study the many issues pertaining to artifact conservation.

Some of the questions faced by conservators include, but are not limited to:

1. What materials and techniques were used to make the original? Are they appropriate to the purported date and place of manufacture of the object?
2. How has the artifact deteriorated over time?
3. Has the artifact been altered by previous treatment, and to what extent?
4. What is the best physical set of conditions in which to store an artifact and minimize future degradation?

In this study, we aim to answer some of the aforementioned questions pertaining to two particular cultural heritage artifacts by performing hyperspectral scans in the visible near infrared (VNIR) and shortwave infrared (SWIR) wavelength regions, spanning 400-1000 nm and 950-2500 nm, respectively.

The first is a Mayan vase from the Museum of Fine Arts, Boston (1988.1175) depicting the Hero Twin Yax B'ahlam holding a large plate containing the jadeite jewelry of the Maize god. Although the vase appeared intact under visible light, examination under x-radiography and ultraviolet light revealed details of the methods used in its fabrication, as well as indication of previous restoration of the bottom. Anomalous results of neutron activation analysis of samples from the bottom of the vase suggest that the base is a replacement. Hyperspectral imaging has revealed additional details of features associated with both the original condition and restoration, and could additionally provide information about fabrication materials and their sources.

The second subject is a set of etchings by French artist Jacques Callot, titled “The Miseries of War,” held by the Johnson Museum at Cornell University; six prints from the series (numbers 69.36, 69.37, 69.40, 69.41, 69.45, and 69.46) were imaged at Cornell's Kroch Library. Some of these prints bear handwritten inscriptions from a previous owner but little visible evidence of them now remains. Preliminary results show that the faded ink is only visible in the VNIR range. The aim for these works is to determine the language and content of the inscriptions, which may provide information about the early geographical location, use, and understanding of the prints.

Poster Presentation

Does size matter? Comparing the Alpha-P and the Hyperion for FTIR paint analysis

Brooke W. Young

"Mere colour, unspoiled by meaning, and unallied by definite form, can speak to the soul in a thousand different ways."

Oscar Wilde

Infrared spectroscopy is often used in art and architectural conservation to analyze historic pigments and their media. Infrared is capable of detecting both organic and inorganic compounds, thus serving as a perfect tool for analyzing the composition of paint and other finishes. Fourier Transform Infrared (FTIR) was introduced in the 1980s, followed quickly by the development of the Infrared Microscope. Because the configuration of instruments costs over $100,000 with testing samples priced at hundreds of dollars, it is often cost prohibitive for many conservators, consultants and scientists. Recently, a less expensive and smaller FTIR instrument was introduced. At $15,000, the Brucker Alpha-P presents a much more approachable cost.

This study, which was part of a Masters Degree thesis, compares the results of the pigment and media analysis made with the Alpha-P to those made on the much larger and more expensive Hyperion FTIR microscope. The Alpha-P, introduced by Bruker Optics in 2007, is the world's first portable entry level Fourier Transform Infrared spectrometer. It is no large than a sheet of paper, measuring 8.5" by 11", and with the addition of accessories, is touted by Bruker to be as effective as its larger scale competitors. The Hyperion is Bruker's most popular FTIR microscope, and when paired with a Tensor series spectrometer, almost any sample is capable of accurate IR analysis.

In addition to investigating the accuracy of the Alpha-P's results, I would also like to discern what the smallest sample size an operator may use before significantly altering the results. There is currently no published information available as to whether this machine performs to the same standards and levels as the larger FTIR microscopy with regard to pigment and media analysis. Because the Alpha-P is generally used to analyze large samples due to the sample window of the ATR attachment, it may be better applied to architectural pigment testing because of the availability of a more invasive paint sampling than permitted in the world of art conservation.

Should this test perform and produce comparable, if not better, results, then conservators may find pigment testing less expensive and easier to execute. Currently, the Hyperion is available only to those who have the resources of a large institution to perform the analysis. Realistically, these resources are not available to all clients. If the Alpha-P permits the same tests to be executed at a lower cost and with greater ease, paint research could become more of a standard in historic structure documentation and conservation by its increased availability.