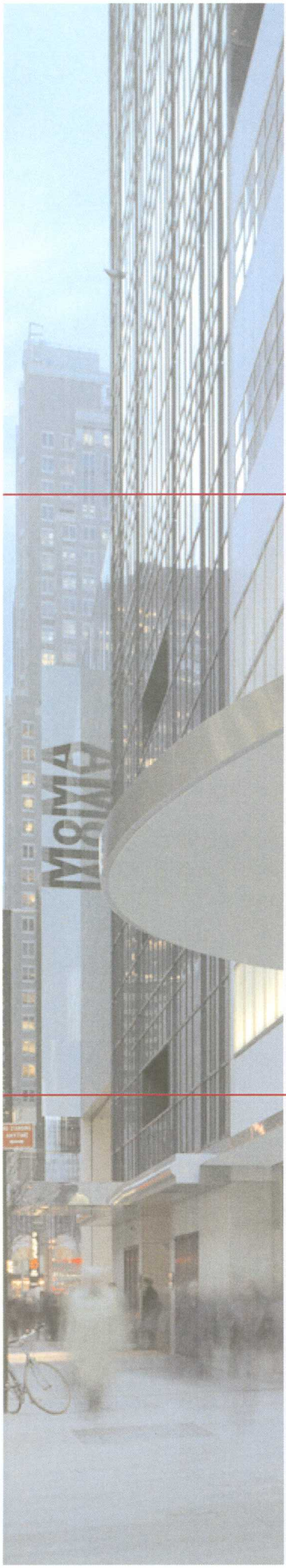

IRUG 7

The seventh biennial gathering of the Infrared and Raman Users Group

March 28–31, 2006

MoMA
The Museum of Modern Art
11 West 53 Street, New York

THE SEVENTH BIENNIAL GATHERING OF THE INFRARED AND RAMAN USER'S GROUP

IRUG 7

The Museum of Modern Art, New York, March 28-30th, 2006
New York University Institute of Fine Art, March 31st, 2006

ABSTRACTS AND EXECUTIVE SUMMARIES OF CONTRIBUTIONS

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Preface

Since the formal establishment of the Infrared and Raman User's Group (IRUG) in 1993, vibrational spectroscopy techniques have become more common in the museum laboratory. This, in addition to the advancements in micro-FTIR and Raman spectroscopy have made it easier to analyze a broad spectrum of unknowns found as artist's and archaeological materials. The ease with which this data can be collected is welcome; however were it not for IRUG our ability to interpret this information would be shallow and more difficult to share with colleagues at other institutions. We tip our hats to Jan Carlson and Raymond White who after years of voluntary service to the organization are now stepping aside to retire. Without their contributions the vision and expectations we have for IRUG today could not be as ambitious as it is at the time of this meeting.

There is much work that remains for IRUG and those who support the concept of a shared database. The number of reference spectra that have been contributed and carefully reviewed by editors in the last two years has been appreciable. The educational demands of IRUG are significant and will only grow. New users are accessing this information and it is imperative to make sure that IRUG fosters standards where these new users interpret their findings as rigorously as the editors have reviewed reference spectra. Biennial gatherings serve as a valuable opportunity to meet with colleagues to share their research and to have discussions that strive to achieve a consensus amongst the community of scientists working to serve conservation about the suitability of analytical techniques for the examination of artist's materials and where the future priorities of IRUG should be directed.

The biennial conference is also an opportunity to share new applications of vibrational spectroscopy applied to the examination of artist's and archaeological materials. For example, one area of recent work has focused on using Infrared and Raman to monitor the impact the environment has on certain materials. Whether this is to serve as a predictive tool to determine when a protective lacquer for silver should be replaced (Thickett, p. 38), measure the environmental factors most responsible for changes in wool (Odlyha, p. 10), leather (Ichihara, p. 84), or conservation materials (Cavicchioli, p. 34), these contributions illustrate the roles vibrational spectroscopy can play in preventative conservation in addition to its established niche of materials classification.

Furthermore, these contributions along with ones by Sutherland (p. 41), Gates (p. 40), van Oosten (p. 50), de Groot (p.61) and van loon (p. 39) prove that artist's materials take on a life of their own after they have been deemed finished by the artist. The formation of deterioration products may become the acceptable patina of an Old Master or they may be the result of a fabricator's foray into polymer science as a playful game gone sadly awry. In both cases information obtained by these analytical techniques provides a valuable means to obtain data to explain the present state of a particular material and may provide information that not only helps prevent or minimize further change but also illuminates the object's past condition. Although photo documentation is perhaps the single most important aspect of recording an object's state it is incapable of identifying certain aspects that may be key to an object's intent, function, or condition. Identification of degradation products, confirmation of polymer flexibility and sensitivity to solvents and environmental factors are aspects where vibrational spectroscopy has the capacity of providing another dimension of information that permits more enlightened discussion about the meaning of an object and how best to care for it.

Taken together, the contributions presented here prove that vibrational spectroscopy applied to the identification, examination and longevity of artist's materials is one of the most challenging of the applied sciences.

The use of FTIR to detect organic materials in wall paintings: a comparative study

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The OMWP project

To enhance the ways that science supports the conservation of wall paintings, the Getty Conservation Institute has partnered with several scientific laboratories to create the Organic Materials in Wall Paintings project (OMWP). Advanced investigation methods available today have demonstrated that organic materials were used in wall paintings far more frequently than it was thought in the past. Therefore their identification becomes an essential part of all conservation projects to attempt to minimize the risk of damage and to improve methods of intervention. The goal of the project is to develop a set of guidelines to facilitate the study of organic materials in wall paintings.

The OMWP project is divided in two phases: first, to evaluate various investigation techniques and to develop a series of guidelines for organic materials identification; and second, to apply these guidelines to wall paintings currently undergoing conservation to provide case studies of their application. For more information on this project visit the Getty website at www.getty.edu/conservation/science/omwp/index.html

In the OMWP project's recently completed first phase[1], project partners evaluated a number of analytical techniques by examining a group of wall painting analogue replicas; these were lime-based wall painting samples of known composition (in terms of binders and pigments), prepared by Leonetto Tintori in the 1990s to be used for scientific studies, and are archived at the Laboratorio per l'Affresco Elena e Leonetto Tintori in Prato, Italy, one of the OMWP project partners.

The techniques investigated by the partner laboratories can be grouped according to their impact on the work-of-art as follows:

- non-invasive techniques (not requiring sampling);
- invasive techniques (requiring sampling); these can be further divided by:
    - invasive non-destructive or para-destructive (that allow further testing on the sample taken);
    - invasive destructive (that completely consume the sample).

Over 170 types of paint composition were studied with non-invasive methods and of these 45 were also studied with invasive techniques. The binders used to make these paints are limited to rabbit skin glue, casein, whole egg, walnut oil, linseed oil, and gum arabic. Knowing the

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[1] The results of the first phase will be presented at a one-day Symposium at the new Restoration and Conservation Center La Venaria Reale, Turin, on May 12th 2006.

nature of the organic materials present in the replica samples tested allowed for an objective comparison of the results obtained with each method.

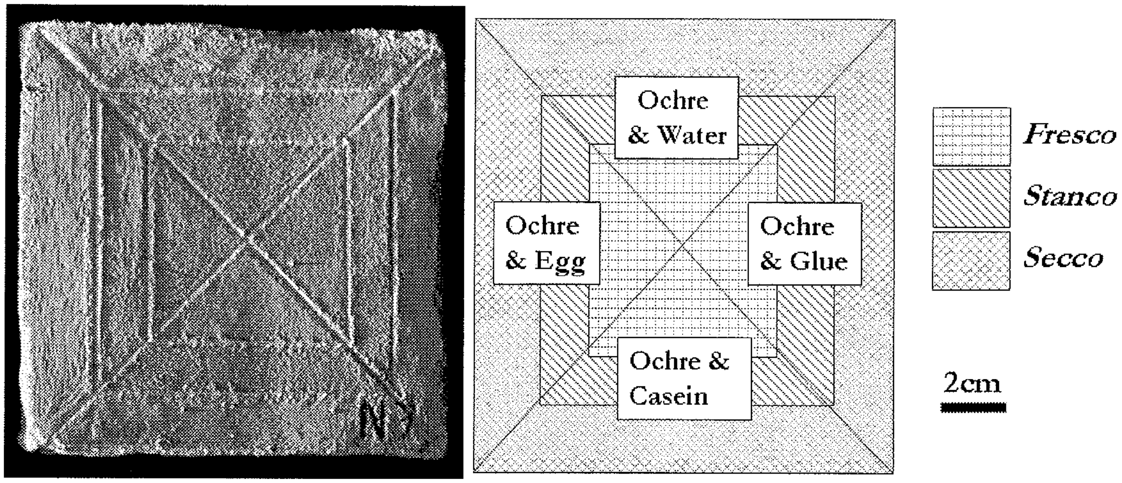

Image and diagram of a wall painting analogue replica used in the first phase of the OMWP project. This sample is divided in 12 sectors all painted with the pigment yellow ochre. The pigment was applied with 4 types of binders: water (i.e. only pigment no binder); whole egg; calcium caseinate; and rabbit skin glue. Each pigment/binder combination is applied in 3 phases: on fresh plaster (*fresco*); on semi-set plaster (*stanco*); and on set plaster (*secco*).

Description of the FTIR methods evaluated

As part of the OMWP project first phase, the following five types of FTIR methods were evaluated for the identification of organic materials:

- Fiber Optic mid-FTIR reflectance spectroscopy (non-invasive);
- FTIR reflectance micro-spectroscopy on cross-sections (invasive);
- FTIR Attenuated Total Reflection (ATR) micro-spectroscopy on cross-sections (invasive);
- FTIR transmittance diamond cell micro-spectroscopy (micro invasive);
- FTIR transmittance and reflection micro-spectroscopy on untreated sample and on solvent extracts (invasive);

Fiber optic mid-FTIR reflectance spectroscopy

Non-invasive infrared investigations were carried out with a compact portable FT-IR JASCO VIR 9500 spectrophotometer (50x50x50 cm^3; 35 kg weight), equipped with a fiber optic extension. The optical bench is made of a Midac Illuminator IR radiation source, a Michelson interferometer, and a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The Remspec mid-infrared fiber optic probe consists of a bifurcated cable containing 19 chalcogenide glass fibers, 7 of which carry the infrared radiation from the source to the sample, while the other 12 collect the radiation reflected off the surface. The chalcogenide glass fibers allow for the collection of spectra from 6500 to 900 cm^{-1}, having an excellent signal-to-noise ratio throughout the range with the exception of the 2200 - 2050 cm^{-1} interval, due to the glass fiber Se-H stretching absorption. All spectra were taken at 200, 400 and 1000 acquisitions, spectral resolution is 4 cm^{-1} and no corrections were applied. The fibre optic probe is kept perpendicular to the painting surface (0°/0° geometry) at a distance of about 2-4 mm. The investigated sample area, as determined by the probe diameter, is about 2 mm.

FTIR reflectance and ATR microspectroscopy on cross-sections(invasive)

Cross-sections were prepared in duplicate using two different embedding materials (polyester- and epoxy-based), and dry-polishing was carried out using Micromesh abrasives. Analyses were carried out on a variety of equipment, including a JASCO FTIR 470-plus spectrophotometer, equipped with a nitrogen cooled MCT detector and an IRT-30 optical microscope using the 16x

Cassegrain objective for observation of the sample and reflectance measurements and the ATR-objective for surface analysis. The instrument operates in the 4000-650 cm^{-1} spectral range. All spectra were taken with between 100 and 400 acquisitions, resolution of $4cm^{-1}$, and no corrections were applied. A variable area of the sample was selected for analysis based on the shape and width of the paint layers as found in cross-section. Analysis of cross-sections with ATR requires contact of the ATR-crystal with the surface of the cross-section, and is controlled using the automated xyz-stage and pressure-sensor. The ATR-crystal has a diameter of approximately 100µm.

FTIR transmittance diamond cell micro-spectroscopy

Analyses were carried out on a JASCO FTIR 470-plus spectrophotometer, equipped with a nitrogen cooled MCT detector and an IRT-30 optical microscope. Measurements were performed in transmittance geometry using a diamond cell (Cassegrain 16x objective). The instrument operates in the 4000-650 cm^{-1} spectral range. All spectra were taken with between 400 and 1000 acquisitions, resolution of 4 cm^{-1}, and no corrections were applied.

FTIR transmission and reflection micro-spectroscopy

*A*nalysis on untreated sample and on solvent extracts (invasive) were carried out with a Nicolet Magna 560 spectrometer coupled with a Spectra-Tech Continuum microscope. The instrument operates in the 4000-650 cm^{-1} spectral range with a MCT detector, cooled by liquid nitrogen. The spectra of the samples untreated were collected in transmission mode. Each sample was first observed under the optical microscope, flattened on a slide with a metal roller and then placed on a NaCl disc, and inserted into the sample holder. A particular micro area of the sample was subsequently isolated by a movable and adjustable aperture, and finally analyzed with transmitted radiation. The spectra of the solvent-extracted fraction (soluble and insoluble or precipitated fractions) of the samples were collected by the Reflection-Absorption (RA) methods for the identification of organic binders. The extractions of organic binders were carried out with dichloromethane (at 30-40°C for 1 h), hot distilled water (at 80 - 100°C from 1.5 to 4 hours) and ethanol (at 40-50°C for 1.5 h). Drops of the solution obtained were placed on a gold mirror sample holder. After solvent evaporation, reflectance spectra were recorded by focusing the infrared beam on a thick area of the remaining product.

Evaluation of the techniques

In order to evaluate the various techniques the OMWP team developed a series of criteria to assess the FTIR spectra in terms of the accuracy of information obtained. The criteria have been developed for the evaluation of this limited set of replica samples and are *by no means* for general application. Four levels of information on organic materials have been considered for the OMWP project and are defined as follows:

Level 1: Detection of the presence of organic materials
Level 2: Identification of the class of organic material present (e.g. proteins, lipids, gums)
Level 3: Identification of the type of organic material (e.g. whole egg, casein, animal glue, linseed oil)
Level 4: Detection and identification type of multiple organic materials (e.g. animal glue and linseed oil, etc.)

The various techniques were assessed for each of these levels in terms of the success rate. The success rate is calculated as the percentage of correct, possibly correct and incorrect results obtained for the sample tested.

It is important to note that the evaluation of the success rate and the conclusions obtained cannot be generalized but are limited to the set of replica samples studied. These samples are characterized by a number of factors limiting their resemblance to a 'real' situation that may be encountered when studying historic wall paintings: the range of binder and pigment combinations is limited; all the samples were painted with a single paint layer containing the organic material; and all samples painted with drying oil contained lead white as one of the pigments.

Preliminary summary of results

Fiber Optic mid-FTIR reflectance spectroscopy (non-invasive)

This technique provided a high success rate for the set of samples examined with all identification of presence of organic material correct (Level 1). As far as Level 2 is concerned, the identification of proteins was highly successful and almost all samples were correctly identified. Instead the identification of lipids was less conclusive and in several samples only a possible presence could be hypothesized. For assessment of Level 3 an innovative chemometric approach, Principal Component Analysis (PCA), was used to interpret the non-invasive reflectance spectra; promising preliminary results were obtained on the identification of the nature of the proteins present in the sample. More investigations and comparisons with transmitted FTIR are thought necessary in order to assess the reliability of the results. These results merit thorough investigation considering the non-invasive nature of FTIR reflectance spectroscopy. In fact, with this technique a vast number of surface readings can be undertaken and is of primary importance for determining a sampling strategy for further invasive organic materials analysis. Finally, further investigations on the influence of the surface morphology in the interpretation of the results are necessary.

FTIR methods on cross-sections

FTIR reflectance micro-spectroscopy on cross-sections (invasive) and FTIR Attenuated Total Reflection (ATR) micro-spectroscopy on cross-sections (invasive) were less successful.

FTIR measurements on wall paintings samples prepared in cross-sections were significantly limited by the interfering signals of the resin used to embed the samples and by the extremely thin and highly porous paint layers. In fact, all measurements showed the presence of organic material providing a positive result for Level 1 even when no binder was present.

Many of the FTIR spectra on the cross-sections, both in reflectance and with ATR, did not allow the identification of the class of organic material (Level 2) because of both the interference of the embedding resins and the spatial resolution limitations of the techniques. Therefore, the results from these two techniques were not considered in terms of success rate. In general, when the interference with the resin was limited, protein could be better identified with samples prepared in polyester resin while lipids could be better identified in epoxy resin.

FTIR transmittance diamond cell micro-spectroscopy (micro invasive)

Results for this technique have been extremely successful. The small percentage of failures seems to have been associated mostly with issues related to sampling. This technique requires extremely small samples and it is therefore essential for samples to be reliably representative. In fact, the wrong identification is found often at Level 1, i.e. a sample collected that does not contain organic material. For Level 2, the lipid identification is more successful than in non-invasive reflectance mode because the intensity of lead white combination band (v_1+v_4) at 1740 cm^{-1} is weaker and therefore the interference is less problematic.

FTIR transmission and reflection micro-spectroscopy on untreated sample and on solvent extracts (invasive)

In general this technique has provided extremely *good* results. Problems related mainly to having representative samples and to difficulties in sample preparation and extraction procedures (sample size). Also in this case, information at Level 1 and Level 2 can be obtained with a significantly positive rate of success.

Conclusions

Although the results provided interesting and important insights into the advantages and limitations of the FTIR methods investigated, it is important to note that the conclusions obtained—especially in terms of the success rate—should not be generalized, but are limited to the characteristics of the set of replica samples studied. In spite of these limitations, some interesting conclusions can be drawn:

- Non-invasive reflectance FTIR revealed a high potential for the identification of the presence of organic materials in wall paintings, even in the presence of interference factors such as carbonates or sulfates. The technique was particularly successful, especially when compared to other types of FTIR, for samples characterized by superficial applications of organic materials. Preliminary, but promising, results were obtained in the discrimination between different types of protein by means of a chemometric approach (PCA).

- The FTIR studies in cross-section were limited by sample type and preparation, in particular the type of embedding medium, its penetration and the polishing method. These are well-known problems. These issues appear particularly dramatic in wall painting samples which are generally highly porous with low organic material content. In fact, also the evaluation of other techniques on cross-sections, including examination of UV fluorescence and stain tests, generally provided low success rate in the OMWP project. The team has been working since on improving cross-section preparation procedures including both embedding and polishing methods.

- Solvent extraction FTIR revealed a high potential for the identification of organic materials, using relatively simple and low-cost sample preparation procedures.

Identification of previous conservation treatments used on the wall paintings from the Egyptian tomb of Nebamun *ca* 1400BC.

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The wall paintings attributed to the tomb of Nebamun are some of the most skilfully executed from ancient Egypt. They are keenly observed vignettes of the day to day life of Nebamun and his family, see Figure 1, hunting fowl in the marshes. The quality of the drawing, composition and use of colour as well as the information contained in the images make the 11 fragments some of the most important objects in the collection of the British Museum.

A conservation project was initiated to prepare the wall paintings for their redisplay in a dedicated gallery. The conservation involved cleaning, consolidation and stabilisation of the surfaces prior to removal of the modern cement backings and their replacement with a lightweight backing system more sympathetic to the wall painting construction. This conservation project was an opportunity for a full scientific examination of the materials and techniques used in the construction of the paintings.

As the work on the surface was conducted a history of conservation treatments on the wall paintings was revealed. Analysis of the previous treatments was needed to allow the selection of appropriate cleaning and consolidation regimes. An Avatar 360 Fourier transform infrared spectrometer with beam condenser and diamond cell attachment from Thermo Electron Corporation has been used to identify the past conservation treatments on the wall paintings. The materials identified included fatty acid waxes used to adhere sections of the surface, cellulose acetate and nitrate used as adhesives and consolidants, and acrylic-based adhesives also used as consolidants. Several layers of conservation treatments were identified and separated with solvent extraction. These suggested as many as three separate interventions have been made since the paintings were excavated. On some paintings large areas had been consolidated with cellulose acetate in one campaign to which a generalised coating of soluble nylon was applied during a later campaign, probably in the 1950s or 60's. The analysis was linked closely to the conservation with the fast identification of samples informing decisions on possible removal of conservation materials and the selection of the appropriate method for removal. Where removal was considered too dangerous to the painting surface the analysis informed the methods used in re-treatment.

This collaboration between scientists and conservators illustrates the importance of timely scientific support for the work of conservation and the versatility of the FTIR technique.

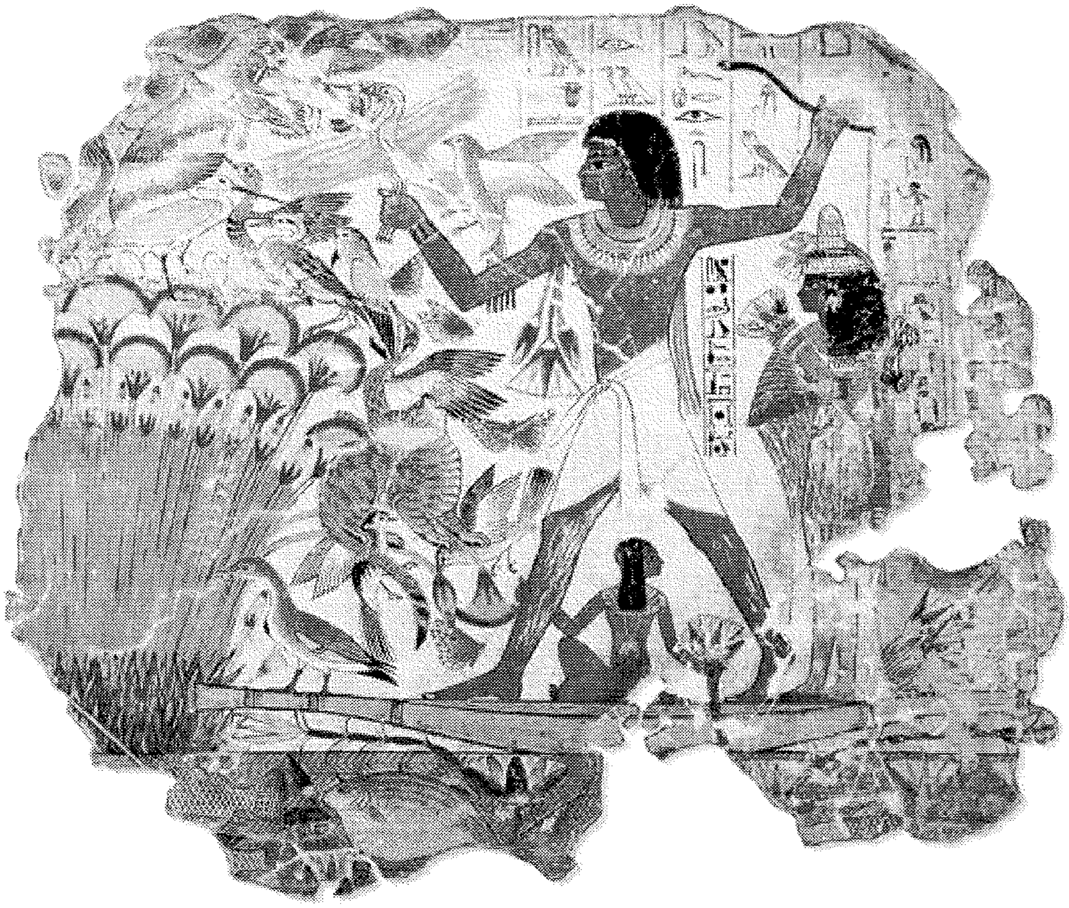

Figure 1: Nebamun hunting fowl in the marshes (prior to conservation)

Combined FTIR and Raman approaches to the investigation of 19th century pastel technology: Mary Cassatt's pastels

F. Casadio[1,*], T. L. Weis[2] and J.K. Weller[2]

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When compared to the knowledge base of painting materials, much less work has been dedicated to the scientific study of dry media. This paper presents the results of a comprehensive examination of the pastels used by American artist Mary Cassatt, including samples from pastel drawings and reference materials from one of the artists' pastels box, in the collection of the Art Institute of Chicago and the Boston Museum of Fine Arts respectively. As it is well known, pastel sticks are complex mixtures of organic and inorganic pigments with fillers, extenders and organic binders, requiring the use of a combination of different spectroscopic methods for complete characterization. Moreover, the extremely limited size of samples available from works of art on paper renders identification of the broad spectrum of their components extremely challenging.

This paper discusses a synergistic approach combining diamond cell FTIR microspectroscopy for overall characterization of the mixtures and Raman microscopy to thoroughly pinpoint all pigments present. An interesting use of filler materials has been brought to light: mainly calcite and kaolinite have been identified, but also gypsum, quartz, barium sulfate, hydromagnesite and aragonite were employed in a variety of combinations and proportions to craft the pastel sticks. In particular, the selective use of specific fillers in conjunction with organic dyestuffs appears of interest. Detection of red, pink and purple dyes and lake pigments in several pastel sticks points to the preference of the artist for an expanded palette, all inclusive of those fugitive colors that have been frequently observed to fade on Cassatt's pastel drawings by many conservators in Museums. Passages of vibrant pink protected by the rebate of a frame now often look a faded to almost white pink color in unprotected areas[1].

In the context of this project, the application of a portable fiber optics Raman microprobe to the non –destructive analysis of pastel drawings is discussed: as pastel drawings often contain very small amounts of binders and may not necessarily have superficial coatings of fixatives, the method has great potential. Advantages and limitations of the portable instrumentation are discussed, in comparison with the results obtained with a benchtop instrument on pigment samples from the artifacts.

As a result of the investigation of Mary Cassat's complete palette of colours an extensive database of the composition of the artist's pastel sticks has been put together. This acquired knowledge of pastels technology will constitute a valuable tool when critically evaluating, and possibly also authenticating the artist's works.

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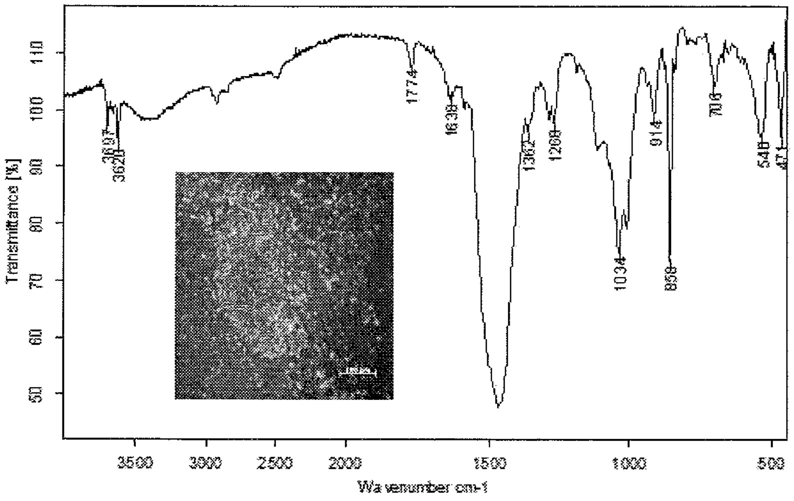

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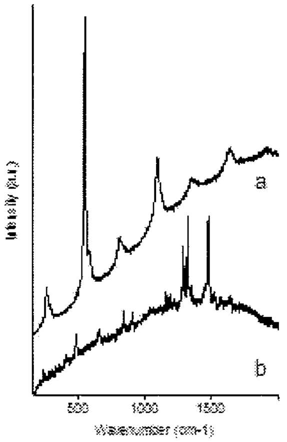

1) Diamond cell FTIR spectrum of a light purplish-pink pastel stick from Mary Cassatt's pastelbox (micrograph detail in the inset) showing dominant absorptions for aragonite and kaolinite and less intense bands for alizarin crimson. 2) Raman microprobe analysis of blue and red particles allowed to identify the pigments as ultramarine blue (a) and alizarine crimson (b) respectively.

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Acknowledgments:

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Damage Assessment in Model and Historical Tapestries by Fourier Transform Infra-red Spectroscopy (ATR-FTIR)

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Tapestries woven in renowned European centres during the 15th to the 18th centuries are among the most valuable testimonies of European cultural heritage. Their survival, however, is jeopardized by the degradation processes which occur in the wool, silk and metal threads. For this reason the European Commission recently funded the project "Monitoring of Damage in Historic Tapestries" MODHT (Contract no. EVK4-CT-2001-00048) where the aim was to develop methodology for improved damage assessment of tapestries. The three year project involved an interdisciplinary approach using a number of advanced and complementary analytical techniques. Selected tapestries from three collections were used; the UK Royal Collection, Hampton Court Palace, the Patrimonio Nacional, Palacio Real,Madrid and from sites in Tournai,Bruges and Brussels, Belgium. This paper reports on some of the results obtained in this project, in particular those using attenuated total reflection (ATR-FTIR) spectroscopy of woollen threads from model and historical tapestries. Reflectance IR spectroscopy is non-destructive and second-derivative FTIR spectroscopy is able to resolve overlapping bands and assist in quantifying observed changes. The approach was initially used in studying the effects of wool processing (Carr, C.M and Lewis, D.M 1993, Woodhead, A.L et al, 2005) and was adapted for this study.

In the MODHT project model tapestries were woven and dyed according to traditional procedures (http://www.hrp.org.uk). The dyes included madder and/or cochineal (red), weld and/or dyer's greenweed (yellow and green depending on the proportions) woad, and either iron sulphate FeIISO4 alone or both FeIISO4/ CuSO4 (black);the mordants included alum,oak gall, and alder bark. Accelerated light ageing was performed with dosage levels up to 360Mluxhrs. It was observed that on light ageing the cysteic acid signal increased with exposure time. It is known that amino acid residues are modified on light ageing, in particular the cystine residues which stabilise the structure of the wool fibre, and maintain its strength. Determination of wool degradation was carried out by the detection of cysteic acid (1040cm^{-1}) which increased for the model light aged and historical samples due to the oxidation of cystine residues. Another degradation product which was observed is the cysteine S-sulphonate (Bunte salt) which absorbs at 1022 cm^{-1}. This was also monitored. Some samples showed the presence of a sharp doublet of almost equal intensity due to cysteic acid and Bunte salt (Fig 1). Quantification of the two characteristic peaks in the 1040-1022cm^{-1} region was optimised using the 2nd derivative FTIR spectra. The rate of light-induced deterioration varied with the different dyes and the mordants. Black samples, in particular, were the most damaged. Levels of damage of the model light aged wool samples, in terms of the cysteic acid signal, correlated well with the loss of strength as measured by tensile testing of model wool threads ((http://www.hrp.org.uk). Tensile measurements on model silk samples have been further correlated with molecular weight of the silk samples (Hallett,K., and Howell,D., 2005). The infrared absorption of cysteic acid was also measured on a number of selected historical wool threads. Levels of damage of the historical samples, in terms of the cysteic acid signal, were compared with those of the accelerated light aged samples, and then with the data obtained from other analytical techniques. Records of previous conservation treatment of historical tapestries were also provided by the curators of the collections, and for the collection in Madrid from the Tapestries and Medieval Textiles curator (Carretero Herrero,C.,2004).

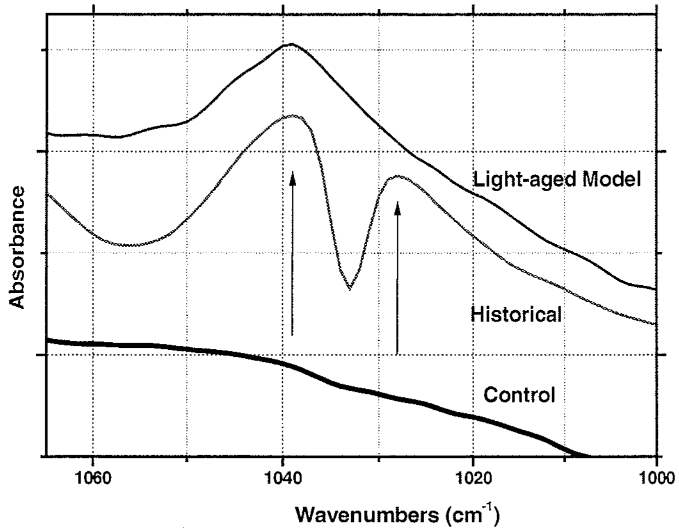

Fig 1. ATR-FTIR spectra show from top to bottom: the 1040cm^{-1} peak, due to cysteic acid formation (light aged model), the 1040cm^{-1} and 1020cm^{-1} peaks due to cysteic acid and cysteine S-sulphonate (Bunte salt) (in some historical samples), and the absence of these peaks in the undyed unaged woollen thread.

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The Analytical Toolbox: Using IR Spectroscopy and Microscopy (OM & ESEM/EDS) Techniques to Monitor Paint Surface/Near-Surface Chemistry and Associated Residues from Environmental Exposures

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Chemical surface/near-surface characterization and traditional microscopy measurement technologies are very powerful tools used to examine perfomance coatings and can also be applied to study changes in artwork. This presentation is intended as an overview of the *first stage analytical toolbox* used to obtain a more detailed understanding of the chemical composition of general paint/coating/metal systems as a function of the application environment, formulation, cure conditions, and exposure/storage history [1-11]. Optical microscopy (OM) and environmental scanning electron microscopy (ESEM) with elemental analysis capabilities are often employed with spectroscopy based investigations to more completely characterize chemical change and identify defect introduction. Application examples are taken from either problem solving or characterization of finishes in the automotive OEM and Refinish markets, as well as conservation efforts on *Minimalist* works of art [12].

Infrared (IR) Attenuated Total Reflectance (ATR) analyses:

IR/ATR analyses are performed top-down on a Nicolet Nexus 470 FT-IR ESP Spectrophotometer equipped with a Nicolet Smart Dura Sampl/R ATR module (Thunderdome). The zinc selenide (ZnSe) internal reflection element (IRE) with thin diamond surface wafer allows surface-specific chemical composition study of the uppermost ~1-5 microns [11]. General chemical composition and (sometimes) specific component analysis permits identification of degradation species, associated mechanism(s)/kinetics and contaminant materials. An IR spectral search capability using comprehensive commercial and in-house materials databases gives a principal investigator an efficient way to identify chemical species or to characterize sub-structure.

While established analytical methods are available for bulk analysis of traditional paints, the very thin residues (micron scale) of long chain aliphatic oils, waxes and fatty acids on industrial metal surfaces could be readily monitored by IR/ATR analysis. This technique, less common than the more traditional transmission- or DRIFT-mode experiments, was instrumental in proving the existence of randomly distributed greasy, organic substances on sculptures; all made of industrially produced metals and ranging from 1960's to date. Problems observed on the surfaces of these sculptures had been previously attributed to oxidation and corrosion only [12]. Although empirical observations had previously suggested the presence of these extremely thin organic residues on the surfaces of modern fabricated sculptures, the available analytical methods were not feasible or proved unsuccessful for full/effective characterization of these substances. An ATR accessory developed in recent years (IRE with ZnSe/Diamond) proved very effective at achieving intimate contact with a sample's surface. The diamond surface would not deform or degrade when in controlled pressure contact with the sample, permitting reproducible, high quality mid-IR range spectra.

Standard optical microscopy (OM) analyses:

OM analyses (using a Leica DMRXA optical microscope) are executed top-down, using cross-sections and on isolated particles, paint chips, fibers or residues. This measurement technology employs moderate levels of magnification providing a detailed review of surface morphology or particle shape, size and morphology. A variety of sampling techniques have been developed in our laboratories that permit detailed imaging of surfaces, interfaces and/or other loci of change/failure. The sampling techniques of particular utility in artwork material and surface characterization will be noted.

Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive X-Ray Spectroscopy (EDS) Analyses:
ESEM analyses (using a Philips XL 30 ESEM configured with EDS X-ray microanalysis capabilities) are also performed top-down, using cross-sections and on isolated particles, paint chips, fibers or residues. This measurement technology employs moderate to high levels of magnification providing a highly detailed look at surface, interface, object or cross-section distribution morphology. Careful sample preparation/isolation and the EDS capability allow isolation of a region or object in a magnified ESEM image and determination of the associated elemental composition.

The combination of IR/ATR, OM and ESEM/EDS analyses, together with specialized sampling techniques, have proven very powerful in characterizing organic and inorganic components at/near surfaces, associated with objects or domains, and in depth profiling studies. Art preservation efforts can take advantage of this type of first stage analytical toolbox to identify chemical composition changes in the paint/coating systems and substrate materials as a function of environmental exposure time and conditions. Analysis of a red Harley Davidson paint system on one of Donald Judd's earliest metal sculptures from 1964, provides a good example for the combined application of IR/ATR, OM and ESEM/EDS. Only the combined results of these techniques provided comprehensive information for the understanding of the severely flaking and delaminating paint. The Leica microscope with controlled multi-angle illumination was able to document deterioration in certain areas. Cracks in the top layer of the 3 layer paint system were characterized with IR/ATR and ESEM/EDS, explaining the extreme brittleness of the paint. The Phillips ESEM and OM analyses revealed a unique and uneven distribution of aluminum flakes in the middle layer. IR/ATR was instrumental in identifying the original paint and its condition, as well as for the re-production of a matching paint which was subsequently used for in-painting a significant portion of the consolidated original paint.

This IR/ATR, OM and ESEM/EDS *analytical toolbox* is termed as first stage in our materials characterization efforts. There are many other powerful tools that can offer additional or supportive information, including spectroscopy (IR/Trans, IR/PAS, MS, Raman, UV-VIS, and XRF), microscopy (Raman, TEM, and UV) and chromatography (GC, GC-MS, HPLC, LC-MS and SFC). Although less common, physical, mechanical and wet chemistry testing is done to further document composition or properties. However, when access to analytical resources and expertise is not unlimited, this aforementioned toolbox is often a good place to start an investigation.

Knowledge of chemical changes in the materials used offers a means of predicting how long the original appearance of an artwork's surface will last. For example, it would be possible to determine the appropriate UV-screener fortification package to provide expected paint/coating system durability for the artwork. Knowledge of the chemistry inherent in residues associated with certain environmental exposures (including various museum display and longer term storage conditions) that contaminate the many surfaces (paint/coatings, plastics or metals) would significantly help in cleaning and maintenance efforts.

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Mid-IR Fiber-Optic Reflectance spectroscopy versus traditional IR spectroscopic techniques: comparative tests on their application to the analysis of prints and mock-paintings.

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The development of non-invasive methodology for the material characterization of artworks is a priority in the cultural heritage field. However, the application of non-invasive techniques usually provides knowledge of the analyzed sample that is less profound than of the destructive ones.

UV, visible and near-IR remote spectroscopic techniques based on the use of optical fibers have already matured to the point that they are in routine use in laboratories. These spectroscopic techniques have important applications in industrial processes and, consequently, their presence in the study of artworks has increased, in particular in the visible range. In the mid-IR region, however, the development of suitable devices has been limited by the difficulty of making optical fibers transparent at these frequencies. Nevertheless, the first generation of high-performance Mid-infrared systems for reflectance spectroscopy (FORS) has become commercially available during the past decade. Recent studies have focused on the reliability and reproducibility of using mid-IR FORS for analyzing painted and powdered samples. These measurements can nonetheless present large distortions in the spectrum, both in band shape and absorption frequency, depending on the band strength, on the concentration of the sample, or on the optical layout of the measuring system. Due to the initial difficulties of comparing FORS spectra with spectra collected in the traditional modes (transmittance and ATR or micro-ATR), it was therefore interesting to explore the use of statistical-treatment approaches, such as Principal Component Analysis (PCA), for this purpose.

Two different types of mock-ups, paints and prints, were prepared. As far as pictorial layers are concerned, pigments and colorants were ground in linseed oil until they were absorbed and reached an adequate consistency. This made possible the application of a uniform single coat of paint layer having a smooth surface. These materials were subsequently spread over a classical preparation layer consisting of calcium carbonate and rabbit glue (Carmine and Lac Dye pigments), and over rectangular samples of canvas on cardboard support (3cm x 5cm) with a titanium dioxide (rutile) and kaolin preparation (Ultramarine Blue, Indigo, Prussian Blue, and Sevres Blue pigments). For the preparation of prints, a single layer of ink was applied over a substrate of Arches paper. The ink was spread over the linoleum matrix with a roller and then transferred to the paper by means of a printing press.

The results obtained in the measurement of oil-based mock-paintings made of Carmine (Kremer), Lac Dye (Kremer), Ultramarine Blue (Winsor&Newton), Indigo(Janssen), Prussian Blue (Janssen), and Sevres Blue (Zecchi) pigments using two different FORS systems (IFAC and UB) and micro-transmittance and micro-ATR techniques are presented. The spectra acquired on prints made of Phthalocyanine Blue, Prussian Blue, Ultramarine Blue, and Ivory Black inks on Arches paper using the above-mentioned techniques are also included.

Preliminary results indicated that the spectra acquired using FORS systems showed a poorer signal-to-noise ratio than that obtained using classical IR techniques. However, since the present research was mainly focused on checking whether useful sample chemical data could be obtained from the FORS spectra, statistical treatment analyses were performed on the complete spectral data sets.

Results obtained in the separate analysis of paints and prints, including all spectroscopic techniques, clearly showed the same type of behavior. In the score plots corresponding to the first two principal components, the different spectra were grouped according to the instrumental techniques used. In addition, the data acquired using the two different FORS systems were barely separated in these score plots.

When the sets of spectra acquired using FORS were processed separately, the points corresponding to the different spectra obtained from the same sample in the scores plot were grouped. This result, which was obtained in the analysis of both paints and prints, led us to conclude that the use of FORS makes it possible to recognize the composition of paints and prints.

Similar results were obtained using micro-transmission. Micro-ATR, on the other hand, did not provide with useful data in the analysis of the print samples. Indeed, the surface micro-ATR technique was greatly affected by the heterogeneity and irregularity of the print surfaces.

Conclusion

In comparing the use of FORS versus micro-Transmission, certain advantages and disadvantages were observed. First of all, both techniques showed similar capability for characterization of the chemical composition of the artworks materials. In addition, Micro-Transmission provided functional information about the compounds included in the sample, but its application usually required artwork sampling. On the contrary, functional information on these materials was more difficult to obtain when using FORS. However, FORS has the advantage of being a non-invasive technique and of providing information on surface macro areas of the samples. This latter aspect is particularly interesting for the study of heterogeneous systems, such as artworks.

The Near Infrared Analysis of Wood Objects

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Introduction

Many types of wood can be identified visually, without removal of material. However for those wood samples which are not easily identified, the typical analysis involves the microscopic examination of the wood structure. The preparation of wood samples for microscopy is destructive even though the samples are typically removed from a discreet location on the object. Near infrared spectroscopy offers certain advantages in the spectroscopic analysis of materials including the ability to test samples without any sample preparation or removal of material. Additionally near infrared spectroscopy deals well with samples that typically have very strong absorption bands in the mid infrared such as wood and fibers. Near infrared analysis also works easily with fiber optic probes.

Near infrared (NIR) spectroscopy offers some key advantages in the analysis of materials like wood and for sensitive samples where loss of material is undesirable. The near infrared region of the electromagnetic spectrum which we are using stretches from 4000 cm^{-1} up to 10,000 cm^{-1}. Unlike the bands in the mid infrared which are the primary stretches, the bands in the near infrared are combination bands and overtone bands of those bands observed in the mid infrared.

Experimental

A Thermo Electron Antaris MDS FT-NIR spectrometer was used in this project to collect the near infrared spectra of wood reference samples and panels. The Antaris MDS has several sampling modes that can be used for collection of NIR spectra including transmission, diffuse reflectance with integrating sphere, fiber optic probe, and two transmission detectors designed for larger clear or opaque samples such as pharmaceutical tablets. For the analysis of wood, the fiber optic probe offers the easiest way to collect data without any sample preparation.

Near infrared spectra of reference samples of wood were collected from several sources to build datasets for comparison. Samples of untreated woods which are part of a reference book on wood identification by Herbert Edlin were analyzed initially. These woods samples included the following references: Afromosia, Sycamore Maple, Aspen Poplar, Oak, Beech, Brown Oak, Birch, Ponderosa Pine, Cedar of Lebanon, Brazilian Rosewood, Western Red Cedar, Teak, Cherry, Australian Walnut, Douglas Fir, Black American Walnut, Ebony, Circassian Walnut, Elm, Eucalyptus, Birds Eye Maple, Honduran Mahogany, African Mahogany, Maple, and Zebrawood. Samples of wood blocks and veneers that were analyzed included American Linden, Clear Pine, Aspen veneer, Curly Olive Ash veneer, Beech veneer, Fir veneer, Larch veneer, Mahogany crotch veneer, Poplar veneer, Quartersawn Red Oak veneer, Rift Cut Red Oak veneer, Flat cut Red Oak veneer, Santos Rosewood veneer, and Flat Cut White Oak veneer.

Because of the natural variation in the structure and color of the wood samples and the intended data treatments, collection of multiple spectra from these samples were required to provide representative data for each sample. Six sites were sampled randomly on the veneer samples to collect representative spectral data.

Samples from the Art Institute of Chicago's reference collection that were also analyzed to generate reference spectra included Cherry (English), Common English Elm, Sycamore, European Birch, Horse Chestnut, Beech (English), English Oak, English Walnut, Cypress, White Oak, Southern Yellow Pine, White Pine, American Elm, American Walnut, Ash, Ash (English), White Ash, Butternut, Rift Cut Red Oak, Santos Rosewood, Sugar White Pine, and White Oak.

Additionally, samples of wood that had been treated in various ways with fillers, dyes, and finishes using products from the S.C. Johnson Wax Company were also analyzed to determine the impact of these treatments on the NIR spectral data. The coated samples are included samples of quartersawn white oak, red oak, maple and pine with a variety of dyes (light and dark) and glossy or flat wax finishes. The coated samples were only treated on one side so three spectra were collected from each of these samples.

The collected spectra were analyzed using TQ Analyst software. This software package offers a number of different processing techniques that allow the spectra to be applied to qualitative analysis of unknown samples. Initially a discriminant analysis method was built with the uncoated wood sample spectra. This method showed over 95% accuracy when the wood references were retested. A library was also assembled from the spectra. Several searching algorithms were tested and an absolute derivative algorithm gave the most accurate results, better than 90%. The coated samples could not be accurately identified using the library or discriminant analysis method for the bare wood samples. A second discriminant analysis method was developed with the spectra from the coated samples and it also showed very high accuracy for analysis of the coated samples.

Paintings on wood panels in the collection of the Art Institute of Chicago were analyzed to test the methods developed with the NIR standard spectra. Six panels were tested, in multiple sites on the back of each panel. The panels were painted in the 15th, 16th and 19th centuries. In each case the panels were dark in color, while a couple had exposed end grain that was available for testing. Spectra collected from the panels were compared with the spectral libraries and with the discriminant analysis method. Of the panels that had been previously analyzed in a traditional method for wood identification, the NIR methods agreed in most cases.

Conclusion

NIR analysis is a powerful tool for nondestructive analysis. NIR is a secondary method that requires a training set of samples to build a method or library to produce accurate results. For the panels analyzed the overall agreement was good between the NIR result and the reported identity of wood from traditional analysis methods. The wood samples used as standards were not dyed, and were all relatively new (less than 50 years old). Aging of the wood will likely have an impact on the spectral features in the NIR spectra. This work presents a good starting point for further work in nondestructive analysis using FT near infrared spectroscopy.

Examination study of Natural Dyes on Different substrates by means of SERS spectroscopy

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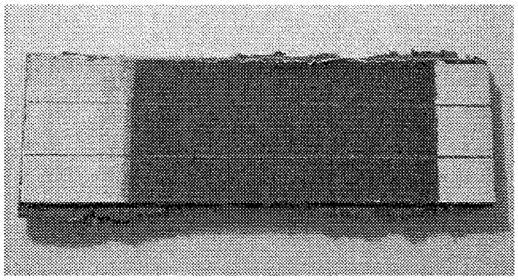
Natural dyes are highly fluorescent materials, photosensitives or do not give rise to Raman spectrum due to their high fluorescence emission. Moreover, in artistic objects, dyes are dispersed in binding media, thus decreasing their Raman effectiveness. The high fluorescence of these dyes and their low solubility in water seriously make difficult the employ of Raman spectroscopy for their identification. For these reasons Surface-Enhanced Raman Spectroscopy (SERS) is becoming an important technique in conservation science and archeometry [1]. The main advantages of SERS is the low concentrations of sample required, due to the high intensification of Raman emission produced, and the fluorescence quenching that occurs on the metal surface [2].

In this work we present the application of the SERS technique to the examination of natural dyes on different substrates of interest in Cultural Heritage, such as paper, egg-tempera (fig. 1), etc.

As SERS supports we have employed two different types of immobilized silver nanoparticles. One of them are made as usual by chemical reduction of silver nitrate by means of trisodium citrate [3] or hydroxylamine hydrochloride [4], followed by a concentration process of the nanoparticles by centrifugation [5] (3,600 r.p.m.) for 30 minutes. This process is necessary to obtain SERS spectra of the dyes, because no spectrum is obtained when using original colloids. The other kind of nanoparticles are prepared by a new method that consists of photoreduction of silver nitrate by means of the 514.5 nm line of an Ar^+ laser. A microscope is needed to focus the laser in a fixed place of the substrate. Thus, silver nanoparticles are formed and immobilized in the chosen place.

The advantage of immobilized nanoparticles made by chemical reduction is that they can be employed on every kind of substrates. Only a few microlitres of the colloids are needed to be deposited in the coloured substrates, so the damage to the object is minimum. On the other hand, nanoparticles made by photoreduction can be used only to detect dyes applied on hydrophilic surfaces. The utilization of these silver nanoparticles also origins minimum damage to the substrates, as in the other nanoparticles mentioned above.



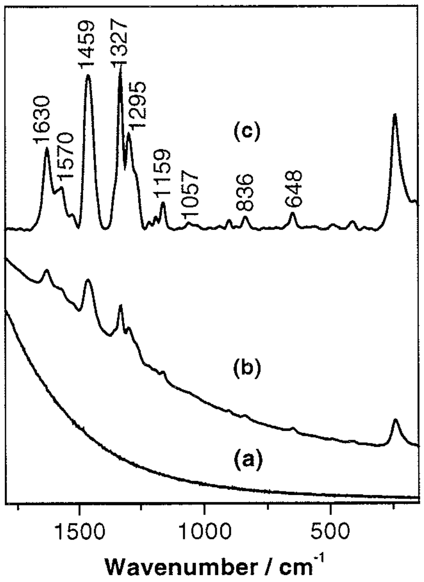


Figure 1 (right) Raman spectrum of alizarin in an egg-tempera sample (a); SERS spectrum of the same sample after depositing metal Ag nanoparticles (b); and spectrum (b) after correcting the fluorescence background (c).

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Use of Commercial Software to Create FTIR, EDXRF, and Raman Spectral Databases to Assist in Pigment Identifications

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Pigment identification in artifacts can be a real challenge. Modern commercial spectral libraries consist of a general collection of chemical compounds. Many times, they do not contain the chemical compounds that you are looking for. These commercial FTIR and Raman libraries lack both inorganic and organic pigments and are instrument and sample preparation specific. Fortunately, there are several commercial software programs "informatics" that are available for purchase. With these software packages, the user can construct their own in-house database of specialty compounds that fit with the objectives of the research agenda of the laboratory.

With this in mind, we purchased three informatics programs to construct our own in-house FTIR, Raman, and EDXRF pigment database libraries. The three programs were: KnowItAll (Bio-Rad), SpectralID (Thermo Galactic), and Curve Manager (Advanced Chemical Development). We also purchased the Colour Index International Pigments and Solvent Dyes database that contains over 5,000 pigment and solvent dye names and chemical structures along with the Colour Index name of the pigments and dyes.

The multi-spectroscopic techniques employed in our laboratory includes micro Raman, micro and macro ATR-FTIR, and micro EDXRF. We purchased numerous pigments from commercial chemical supply companies (Fisher, Sigma-Aldrich) and artist-pigment supply stores (Iconofile, Sinopia, Sennelier). The compounds were analyzed as received without any purification. In some cases, the pigment was not what was claimed on the label or in the supplier's catalog. All the samples were solids and were mounted onto plastic microscope slides for both Raman and micro ATR-FTIR analysis. For macro ATR-FTIR analyses, the samples were pressed onto the diamond crystal of the DuraScope ATR. For EDXRF analyses, the solids were sandwiched between two polypropylene films.

The Raman instrumentation used was a Renishaw system 1,000 micro Raman dispersive spectrometer equipped with a 785 nm diode laser. FTIR Instrumentation (macro): Bruker Equinox55 FTIR equipped with a DuraScope ATR. FTIR Instrumentation (micro): Smith Detection Illuminator micro ATR-FTIR attached to the Raman microscope. For multi-elemental analysis, we used an EDAX Eagle II micro EDXRF spectrometer equipped with an Rh X-ray tube.

Two types of databases were constructed. One for KnowItAll that is used for identification of pigments and dyes based on Raman and FTIR bands. In this database, we included the chemical structure, formulae, band assignments, and FWHM. KnowItAll is the only program available that allows the user to "double click" on a vibrational band in the spectrum and the program returns possible chemical compounds based on traditional correlation diagrams. Table I shows a typical entry into the KnowItAll FTIR database using Microsoft Access to reconstruct the IR or Raman spectra. We also used the molecular modeling program Gaussian 03W to predict the Raman and IR spectra of pigments in alternate binding environments with the artifacts. These alternate binding environments can cause shifts in the band positions of the pigments. Knowing these shifts can assist in understanding the Raman and IR spectra and how the pigments react or bind with different substrates in the artifacts.

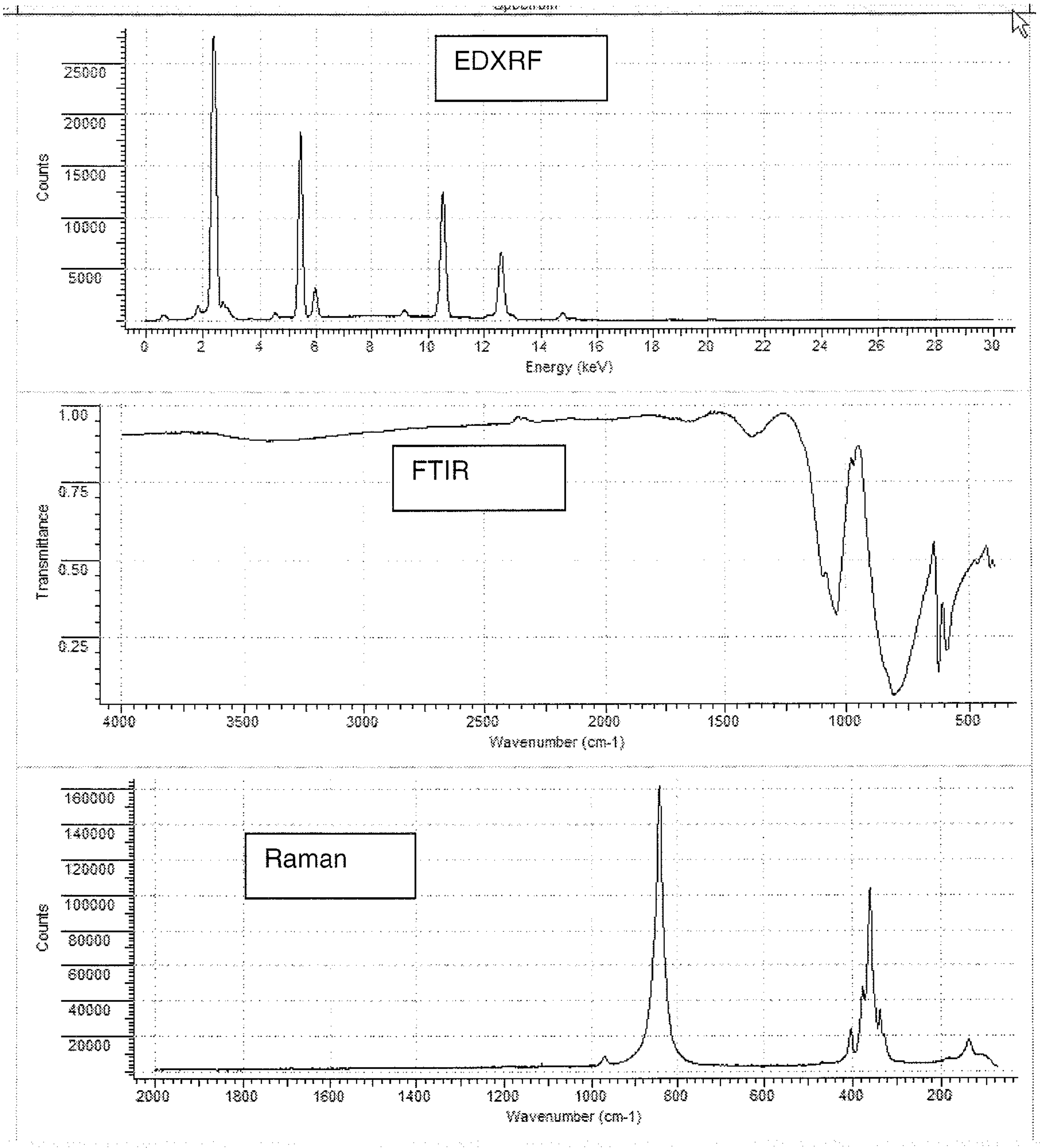
The second type of database is used for library searching. In this database, we compiled FTIR, Raman, and EDXRF databases comprising over 1,000 compounds and pigments. Each entry in the database included the spectrum, chemical structure, formulae, color, Color Index, and chemical properties. Figure I shows the user screen of one record of our ACD searchable pigment database for the pigment lemon chrome yellow. ACD is the only program that can database XRF, FTIR, and Raman spectra in one record. This was extremely useful because having all three spectra visible (Figure I) greatly increases the chances for correctly identifying the pigment. Having the EDXRF data was the key for successful pigment identification. ACD was also useful for spectrum manipulation in that the second derivative could be used in the spectral library searching that produced better "hits".

KnowItAll and ACD support was excellent and user feedback to make the products better was greatly appreciated. ThermoGalactic however, lacked support and did not appear to care about bugs in their programs. Detailed procedures for creating databases and libraries will be presented along with live demonstration of the three commercial software programs. Also presented will be information on how "user friendly" the programs are.

Table I. ATR FTIR KnowItAll Access Database Entries

Class Name	Functional Group	Bond	High	Low	Intensity	Mode	Notes	FWHM	rel intensity	prime sort field
Calcium carbonate	CO_3^{2-}	C=O	1550	1325	VS	ASTR	calcite	80	9	Carbonate
	CO_3^{2-}	C=O	900	830	S	OBEND		12	7	Carbonate
	CO_3^{2-}	C=O	730	680	W	IBEND		4	3	Carbonate

Figure I. EDXRF, FTIR, and Raman spectra of pigment lemon chrome yellow in ACD Database record.



Raman Spectroscopy in Art and Archaeology: some pitfalls

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The need of very specific information in the context of art and archaeology is promoting a closer interaction between the hard scientists and the conservation community, in a movement that has been fuelled by the accelerated developments in instrumentation in recent years. For conservation purposes, compound identification is a key point as such knowledge allows the choice of the best procedure and materials to be used in the case of restoration. It is also essential for conservators and conservation scientists, giving a chemical perception on how to prevent further or future degradation.

From the chemical characterization point of view, Raman spectroscopy is one of the most powerful techniques and is being largely used in Museums and Universities. What makes it such an attractive technique is its ability to determine molecular level information, electronic, vibrational and structural, in a non-destructive way and generally without need of sample manipulation.

Particularly in the case of Raman microscopy, the ability to obtain high quality data from very minute samples (few um^2) is extremely important in the analysis of heterogeneous materials and in stratigraphic or interface studies. The development of cheap and easy-to-operate equipment also boosted its application in the art and archaeological field as these improvements are making possible to the non-expert to obtain and to extract useful information from Raman data. This very welcome expansion has its side effects: there are several pitfalls that can lead to misinterpretations and some users might not be aware of them.

The present abstract aims to help in bridging the gap between the spectroscopy research lab and the applied spectroscopy user, through the highlight and discussion of some of the most common pitfalls.

The first point to be considered involves the use of a Raman microscope. The laser spot is small enough (ca. 1 μm^2) to permit single crystals to be probed in microcrystalline materials and in this case, a dramatic change in relative intensities is likely to occur and some bands may even disappear, depending on the crystal lattice symmetry. Good examples are found in the study of gems by Raman microscopy[1]. This is not generally a problem with conventional Raman equipments as the laser spot is much larger and an averaged spectrum is normally recorded. . For the same reason - and because the laser polarization is lost in the multiple reflections at the microcrystals interface - the measurement of depolarization ratio in microcrystalline solids is not straightforward and, eventually, misused[2].

It was already pointed out in a previous meeting, how important it is the dependence of band intensities with wavelength (resonance Raman effect)[3]. In some cases the spectrum obtained in resonance conditions is substantially different from the resonance one, what can interfere in the compound identification. Here, it has to be emphasized that only highly allowed electronic transitions give raise to such effect, thus d-d transitions, very common in inorganic pigments, are useless. Furthermore, no changes in band position are observed in a resonance Raman spectrum when compared to an ordinary one, except in the case of compounds with conjugated bonds, where different conjugation lengths are present[1]. The resonance Raman effect can promote such a high enhancement that some times poor light scatterers also present in the sample are not observed, leading to the wrong conclusion that they are not present. This one of the reasons why the impossibility in detecting a compound by Raman spectroscopy does not mean it is not present.

The energy density at the laser focus, particularly in a microscope, can be high enough to burn the sample, even when μW are used, because the spot laser area is too small (a few μm^2). Much more difficult to detect then burning, is thermally induced phase transitions as in the case of iron compounds for instance[5], and crystalline/disordered graphite[6]. In some cases such effect can be used in favor or art and art history investigations[6,7]. Laser wavelength induced phase transitions are also know to occur as in the case of realgar/pararealgar[8]

One obvious pitfall, less likely to occur, arise from the fact that generally only the 100 to 1800 cm^{-1} window is recorded. Some compounds such as prussian blue, have characteristic bands outside this range (in the case of prussian blue, the C≡N stretching vibration shows up at 2154 cm^{-1})[9].

Another point that deserves attention is the fact that depending on the sample absortivity and the laser wavelength, the penetration of the exciting radiation through the sample can be large enough to allow inner layers or substrate to be recorded. This is particularly important for lower energy radiation and for comparing FT-Raman (1064 nm) with visible excitation data.

Reference spectra are extremely important when analyzing real samples and standards have to be not only chemically pure but also with the correct crystalline phase as several compounds exist in more than one stable crystalline form.

In the context of museum conservators, the samples are generally a complex mixture of chemical substances eventually already exposed to aggressive environments and fluorescence arises as a very common problem. Some procedures have been developed to avoid it, which includes photobleaching. Such procedure is not recommended when fluorescence arises from the sample itself and not from impurities, as in this case photobleaching imply in sample photodegradation.

Some transition and rare earth metals, commonly found in minerals used as pigments, addictives or in catalysts manufacture exhibit very narrow and intense emission, which can be mistaken as Raman bands[10]. Changing the laser wavelength or, when possible, checking the anti-Stokes region allow the differentiation.

Fluorescence or luminescence can, however, be useful in research, as a Raman equipment can be employed as a very sensitive fluorimeter and a Raman microscopy is very helpful as microspectrofluorimeter. It also allows the best choice of areas to be analyzed in a painting, for instance, avoiding the risk of areas already were submitted to interventions. In this case, a previous sample inspection with a UV lamp is required.

Plasma and lamp lines are another source of spectrum misinterpretation or wrong compound identification[11] When a He-Ne laser is used, the plasma lines reflected by the environment can be collected by the objective and can be much more difficult to identify as their band width is larger than observed for plasma lines that has to be rejected from the optical path. Furthermore, Hg lines from fluorescent are likely to be detected.

Other point that deserves attention is the comparison of Raman spectra obtained from the solid state and from solution. Solid state spectrum depend on the group symmetry, whereas the solution spectrum depend on the molecular symmetry; this can eventually make necessary the use of correlation tables, furthermore, solvation effect has also to be considered. Solution and solid state data can be compared only when a complete sample solubilization occur, otherwise, the solution composition may not represent the bulk solid composition. In any case, the solid state spectrum contains information from the outer most parts of the sample, in spite of some laser penetration, whereas solution represents the bulk. Accordingly, when the interest lies in the study of sample processing or degradation, solid samples has to be used. For the same reason ATR techniques are the best option to obtain the complimentary IR spectrum, specially taking into consideration that other sampling techniques (KBr pellet for example) can lead to sample degradation[12]. Again, the same rational applies to other solution-based techniques, such as chromatography and mass spectrometry.

Considering all the above cited aspects, a reasonable knowledge of the most likely compounds to be present in a sample is desirable and the literature provide information on photochemical or thermal degradation, spectral window, wavelength selection etc. A careful reading of the published papers is also mandatory as contradictory data or conclusions indicate that the assignment may not be simple. Differences in the experimental setup may affect significantly the recorded spectrum even when no degradation occurs, as already discussed.

Finally, a special attention has to be paid when comparing Raman data with results from other techniques: XRD is a long range technique, whereas Raman is a short range one, thus XRD is useless for poor crystalline samples but this is not the case with Raman spectroscopy which still permits compounds identification. When XRF information is used, it has to be considered that the X-ray penetration in sample is much higher than visible or NIR radiation and underlying layers contribution can be mistaken as arising from the painting layer.

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Characterization of Painting Materials by micro-FTIR Measurements with Traditional and Synchrotron Source

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Micro samples coming from the frescoes of Filippo Lippi in the Cathedral of Prato, were analysed to characterize the painting materials and the contaminants or conservation products present on the examined surface. Gilding materials, polymeric treatments, natural organic materials such as wax and oil, were characterized together with traditional inorganic pigments and substrates.

FTIR spectroscopy coupled to the optical microscope is by far one of the most attractive equipment for the characterization both of the organic and inorganic compounds using very small (μm scale) fragments[1]. This kind of analysis enables one to collect a large number of results from the same micro-fragment, and to gain a rather good knowledge of the sample in a short investigation; some interesting examples are presented in the case of characterization of the famous painting cycle by Filippo Lippi "Hystory of S. Giovanni and S. Stefano". Nevertheless, as it is well known, FTIR spectra can't be exhaustive and sometimes don't allow the complete identification of the molecule, while the use of complementary analytical techniques permits to identify the different components.

Actually, what could definitely improve the analytical effectiveness of the FTIR analysis, in the case of a complex mixture, is the spatial resolution of the IR radiation and the optimal S/N ratio. This paper aims at presenting results obtained through the traditional lab instruments and the synchrotron radiation source FTIR technique, main features and advantages of the synchrotron source. The measurements were carried out at the Synchrotron Radiation Source at Daresbury Laboratory (UK). Synchrotron IR radiation source can provide unique information, thanks to its brilliance, high intensity and spatial resolution (5x5 μm), by far better than the resolution that can be obtained with traditional source[2,3]. The SR-FTIR incident light allows to focus select or mapping micrometric particles.

The problem of the degradation process of the gilded wax reliefs (Fig. 1), present as decoration on the "fresco" painted surface, has been studied with the aid of FTIR, XRF and XRD techniques coupled with the microscope[4-6]. The characterization of the dark layer that are often pointed out on the wax surface, the transformation of layer containing tin, the characterization of the organic compounds have been achieved. Micro-FTIR analyses confirm that the bulk of the wax fragment is composed of beeswax, while SR-micro-FTIR analysis allowed to characterize the surface black material as a mixture of beeswax and protein (Fig.2), the latter most likely being animal glue according to the literature and possibly used as adhesive for the application of the gold leaf.

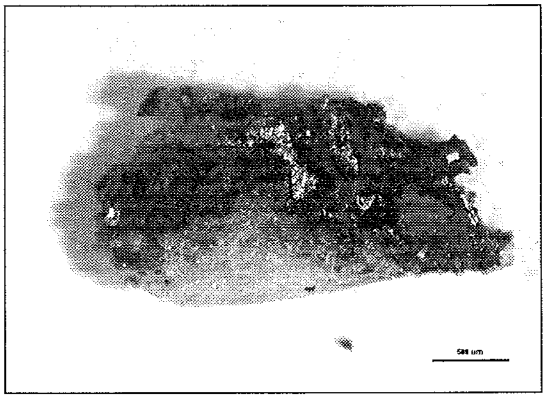

Fig. 1 Micro-sample of the gilded relief decoration (Bar 500 μm)

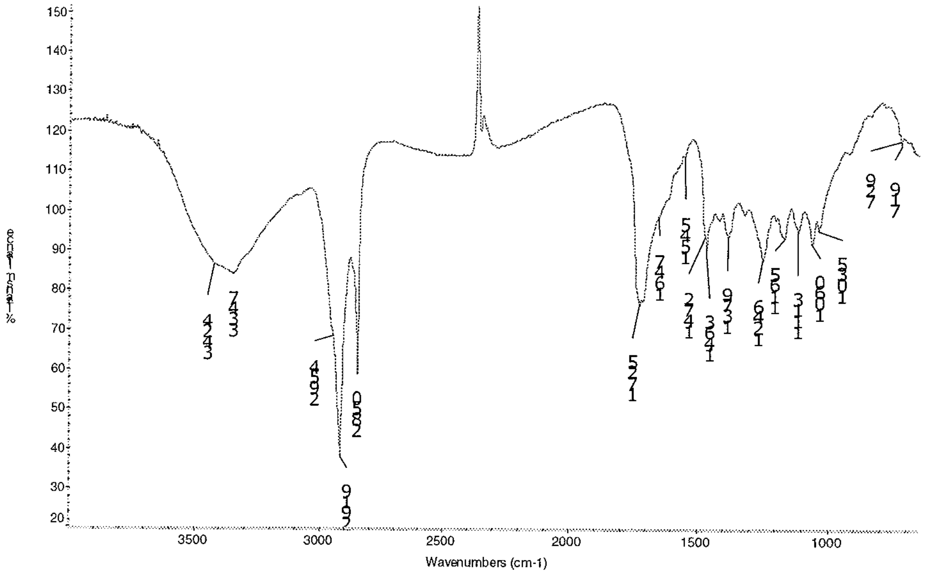

Fig. 2 SR-FTIR spectrum of the dark layer. IR absorption peaks: 3424, 3347 cm^{-1} (protein), 2954, 2919, 2850, 1725 cm^{-1} (beeswax), 1647, 1545 cm^{-1} (protein), 1472, 1463, 1414, 1379, 1165 cm^{-1} (both), 1316 (suspected CaOx), 1060, 1035. cm^{-1} (protein), 1113 cm^{-1} (gypsum), 729, 719 (beeswax).

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Using fiber optic infrared spectroscopy from mid to near infrared to assess non-invasively the polychromy composition of easel paintings

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The recent availability of mid and near-infrared fibre optics coupled with Fourier transform infrared benches has made it possible to perform completely non invasive reflectance measurements on unique objects such as easel paintings, without any sampling operation[1]. Moreover when the benches consist of portable FTIR spectrophotometers coupled with mid and near-IR fibre optics, it makes it possible to perform on site non-invasive analyses on object, which cannot be moved from museums.

There is, however, the drawback that reflectance spectra can present large distortions in the spectrum, both in band shape and position, which may depend on band intensity, sample concentration, and optical layout. For this reason it is difficult to compare reflectance spectra with those collected in transmission mode and, consequently, with the available databases. So, a careful laboratory study of the reflectance FTIR set-up performances, according to different compositions and morphologies of mock-up painting surfaces, has been the necessary preliminary step for carrying out meaningful *in situ* study.

Mid-infrared investigations have been carried out with a compact portable FT-IR JASCO VIR 9500 spectrophotometer (50x50x50 cm^3; 35 kg weight), equipped with a fiber optic extension. The optical bench is made of a Midac Illuminator IR radiation source, a Michelson interferometer, and a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector. The Remspec mid-infrared fiber optic probe consists of a bifurcated cable containing 19 chalcogenide glass fibers, 7 of which carry the infrared radiation from the source to the sample, while the other 12 collect the radiation reflected off the surface. The chalcogenide glass fibers allow for the collection of spectra from 4000 to 900 cm^{-1}, having an excellent signal-to-noise ratio throughout the range with the exception of the 2200-2050 cm^{-1} interval, due to the glass fiber Se-H stretching absorption[1]. The fibre optic probe is kept perpendicular to the painting surface (0°/0° geometry) at a distance of about 2-4 mm. The investigated sample area, as determined by the probe diameter, is about 2 mm^2.

Near-infrared investigations have been carried out with a compact portable FT-IR JASCO VIR 9600 spectrophotometer (50x50x50 cm^3; 35 kg weight), equipped with a fiber optic extension. The optical bench is made up of a halogen lamp as source, a Michelson interferometer equipped with a CaF_2 beam splitter, and room temperature InGaAs detector. The spectral range is 12500 cm^{-1} - 4000cm^{-1} with a energy resolution of 4 cm^{-1}. The spectrophotometer is equipped with a silica glass fiber optic Y sampling probe (2 meter long, 200/300 micron of core) which can remotely measure the reflection of painting surfaces with a spatial resolution of about 10mm^2.

Studying pure pigments and panel painting models it has been demonstrated that it is possible to identify the presence of azurite, malachite, lead white and sangiovanni white by the shape of the combination band (v_1+v_3) and (v_1+v_4) around 2500 and 1800 cm^{-1} respectively, which being forbidden are not subjected to reflectance distortions (see figure 1). Moreover, it has been proved that blue pigments such as smalt, Prussian blue, ultramarine blue and lapis lazuli are detectable by the presence of vibrational bands occurring in spectral regions quite free from both matrix distortion and varnish absorption.

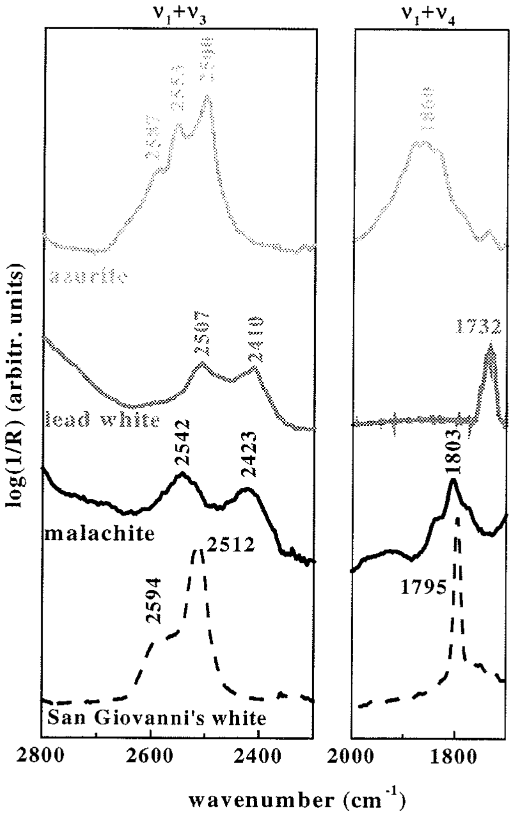

Figure 1: (ν_1+ν_3) and (ν_1+ν_4) combination bands of azurite, lead white, malachite and sangiovanni's white (Zecchi). The reflectance spectra were collected on mixtures of carbonate pigments and KBr (1/50 in volume).

Results of non invasive infrared measurements carried out using the portable equipments of the mobile laboratory MOLAB[3] on several easel paintings (by Perugino, Bronzino, Raffaello, Mantegna, Antonello da Messina, Cézanne, Renoir, Lampi etc.) highlighted the great potentialities of fiber optic infrared spectroscopy to study non-invasively both the painting technique and the conservation state. As an example, in figure 2 is reported mid&near-FTIR spectra recorded on blue areas of the painting *Pala Baglioni* by Raffaello (1507, Galleria Borghese, Roma)[4].

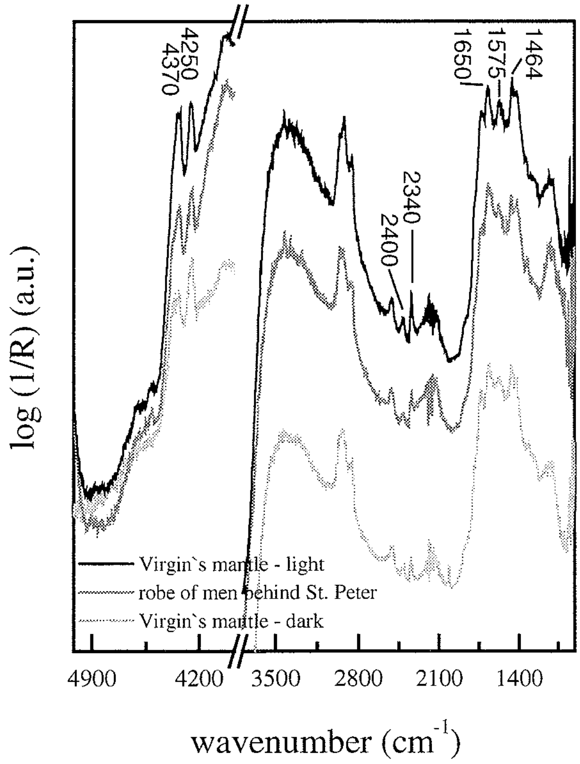

Figure 2: mid-FTIR and near-FTIR spectra collected on blue coloured areas. Main diagnostic features of azurite (4370, 4250 cm-1), ultramarine (2340 cm-1), lead white (2400 cm-1) and proteinaceous component (1650, 1575, 1464 cm-1) are marked.

All the blue areas of the painting showed azurite and lead white, as identified either in the mid-infrared, through the shape of combination band v_1+v_3 (at 2500-2400 cm^{-1}) of copper carbonate and lead carbonate, and in the near-infrared, through the presence of a double absorption of Cu-OH vibration (at 4250 and 4370 cm^{-1}) and the singlet absorption of Pb-OH vibration (at 4299 cm^{-1}). All the spectra collected in blue zones, unless the greyish Magdalene`s mantle, present besides azurite and lead white, other features with a characteristic sharp band at 2340 cm^{-1}. Following a previous study of the Getty Conservation Institute, this absorption band can be considered as a marker of ultramarine blue as used in several Italian paintings of the fifteenth and sixteenth centuries[5].

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The Flexible Opto-Mechanical Arm for FTIR Analysis of Samples Outside the Sample Compartment

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MeV Photonics and Harrick Scientific have developed an articulated opto-mechanical arm that allows analysis of large samples in-situ with greater sensitivity in the mid IR than fiber-optics can offer. The arm, named the DaVinci Arm, was designed to permit the analyses of samples by specular, diffuse and ATR reflection techniques and mounts into the sample compartment of most commercial FTIR spectrometers and uses the bench detector. The ability to use a DTGS detector provides the additional benefit of allowing spectra to be recorded below 650 cm^{-1}. Since the arm is articulated, it allows sample analysis within a range of distances in front, below, or above the sample compartment at a wide range of angles. The integral camera provides for magnified viewing and image capture of the sampled spot. The entire optical path of the IR beam is enclosed and integrated into the purge of the host spectrometer.

The flexibility of the arm comes from its ability to independently rotate around three axes: the IR beam axis, the axis of the first pair of knuckles and the axis of the second pair of knuckles (Fig. 1). The IR beam is picked up by the Arm in the sample compartment of the spectrometer, reflected via mirrors to the sampling spot some distance away from the sample compartment, and then brought onto the sample either by the non-contact reflection technique or by the diamond ATR (contact technique). The sampling spot can be over 20 inches (50 cm) away from the sample compartment beam.

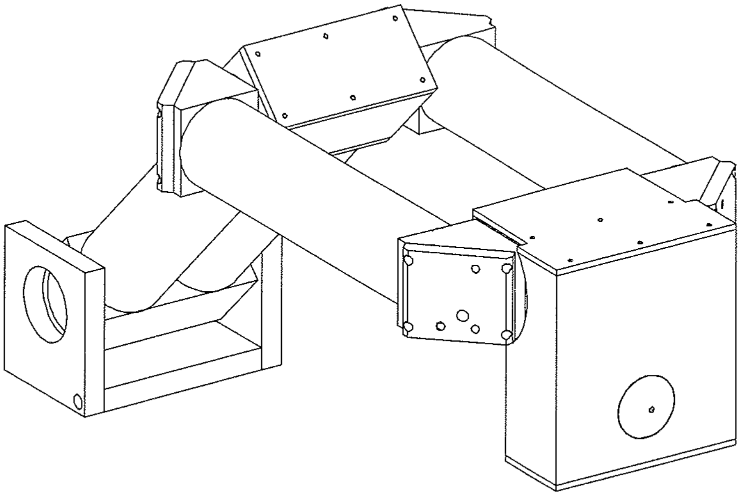

Figure 1: CAD drawing of the DaVinci Arm

In specular and diffuse reflection mode the sampled spot is about 1.25 mm in diameter. In ATR mode, the spot is 0.5 mm in diameter. Regardless of the technique, the integral digital camera provides a magnified image of the sampled area. The live image also guides in placing the sample into the focus of the IR beam. Since the IR beam is confocal with the visible light used for imaging, the sample is in the focus of the IR beam when the sample image is sharp. The visible light used for imaging is independent of the IR sampling optics so sample viewing can stay on while IR analysis is taking place.

Good contact between the ATR element and the sample is required to assure high quality ATR spectra. While the diamond ATR element is rugged enough for any application, it may indent the object that is analyzed. Although ATR is the preferred analytical technique that the DaVinci

Arm utilizes, it may not be appropriate for those objects that could become damaged by the analysis. For these objects the alternatives are the non-contact techniques of specular and diffuse reflection. The distinction between specular and diffuse reflection is brought about by the nature of the sample, not by the configuration of the DaVinci Arm, which is the same for both non-contact reflection techniques. A small opening (6 mm diameter) on the bottom of the shield enables IR light to reach the sample and the reflected radiation to return back. Small hole size combined with the slight positive pressure of the purge gas keeps the ambient air from entering the Arm. The DaVinci Arm can easily be converted into ATR mode by replacing the purge shroud with an ATR crystal holder. With the ATR crystal holder installed, the purge air inside the Arm is completely separated from the ambient air.

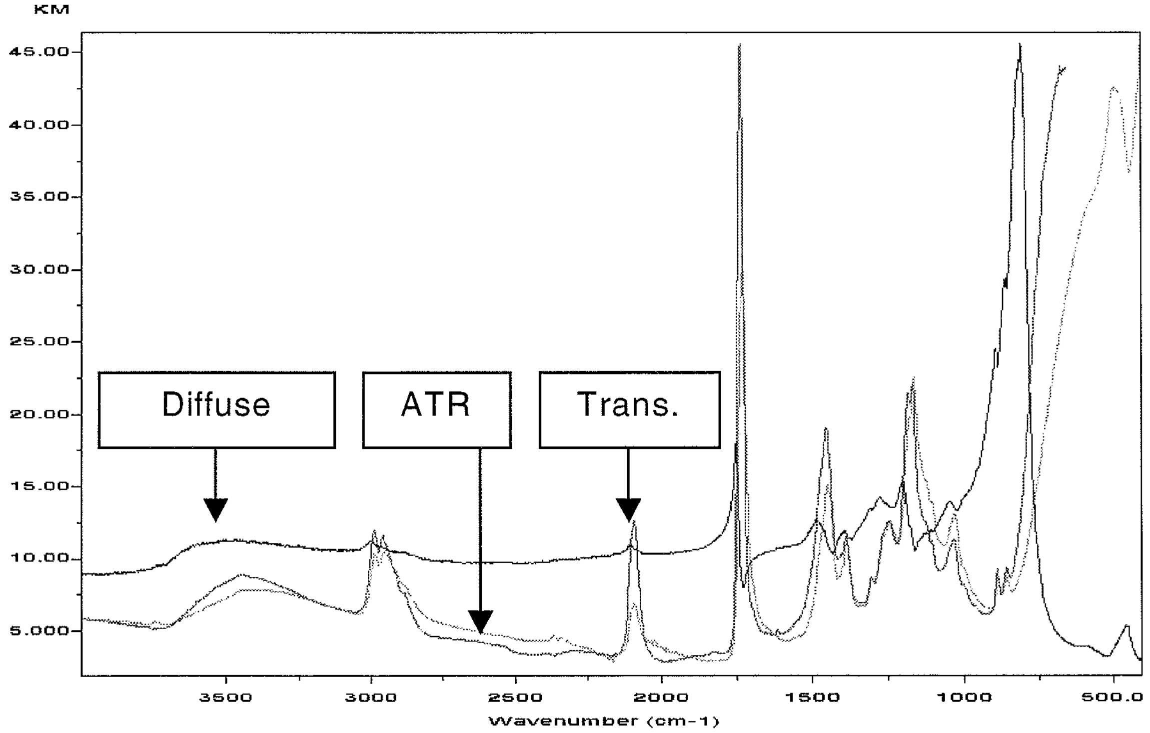

Figure 2: Transmission (via microscope), ATR and Diffuse Reflection Spectra of Prussian blue in Acrylic

To illustrate the influence of a spectroscopic technique on the shape of the spectra Fig. 1 shows the spectra of the same sample (approximately 1 part Prussian blue to 1000 parts titanium dioxide in acrylic) obtained using three different spectroscopic techniques. Prussian blue can be difficult to identify since it has a strong tint-strength and absorbs at 2154cm^{-1}, a region where diamond and chalcogenide fiber-optics absorb. The transmission and ATR spectra were transformed to absorbance and the diffuse reflection spectrum was transformed to Kubelka-Munk form. Transmission and ATR spectra appear closely correlated. This is quite impressive given that one method requires sample removal and the other does not. While the amount of information appears comparable in all three spectra, the nature of information is manifestly different.

Experimental:

The DaVinci arm was mounted in a Thermo-Nicolet Nexus 670 spectrometer with DTGS detector. Transmission data was collected using a Thermo-Nicolet Continuum microscope using a 15x objective and an MCT detector from 4000 – 650 cm^{-1}. All data was collected at resolution of 4cm^{-1}

Monitoring the Ageing of Synthetic Varnishes by FT-RAMAN, FTIR and Impedance analysis

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The interest for the environmental impact on the materials of the cultural heritage has always been a priority for conservation scientists. However, over more recent years the approach to the problem seems to have shifted from the mere monitoring of the individual environmental factors such as temperature, relative humidity, illumination type and intensity and, more occasionally, air pollutants, to the investigation of the actual structural (microscopic) changes caused by the complex interaction between material and its surroundings[1].

Our group has been developing a methodological strategy to assess the environmental impact on artistic varnishes based the combination of vibrational spectroscopy (FT-Raman and FTIR) and impedance analysis of piezoelectric resonators modified with such varnishes[2,3]. Piezoelectric quartz crystals are commonly used to make so-called Quartz Crystal Microbalances (QCMs), i.e. gravimetric devices for the measurement of small mass changes of materials deposited on its surface, where increases in mass give rise to a decrease in oscillation frequency of the piezoelectric crystal and vice-versa. Previous studies demonstrated that there is a clear correlation between the ageing of natural triterpenoid varnish film (dammar and mastic) and the negative shift in the oscillation frequency of these devices observed upon irradiation by visible light. This was attributed to autoxidation, a photochemical process which involves oxygen uptake and, therefore, mass increasing. Furthermore, by recording the impedance curves vs. frequency it is possible to observe consistent variations in the diagrams associated with changes in the films visco-elastic properties.

Sensors prepared in the described manner allow continuous and *in situ* monitoring of the target materials response to the stress caused by an specific microenvironment, which can either be a real conservation site or a climate chamber under controlled environmental conditions. However, such sensors do not give any indication of the actual molecular changes taking place in the materials and this information can be obtained from the materials deposited onto the crystals by FT-Raman and reflective FTIR. These techniques, being non-destructive, can be employed without affecting the functioning of the piezoelectric devices.

In the present work, this approach was tested and assessed by following the artificial ageing of dammar varnish and two other synthetic resins used in conservation science: Paraloid B76 (purchased from Casa do Restaurador, São Paulo) and Laropal K80 (purchased from CTS, Milan, Italy). The former is the trade name of a co-polymer of acrylic and methacrylic esters, namely methyl acrylate and ethyl methacrylate, which is widely used especially for consolidation and protection of works of arts[4,5]. The latter is a resin obtained from the product of condensation of the cyclohexanone and has been used since the 1950's mainly as a varnish or additive for paints and lacquers[6,8].

The main goal of the investigation was to confirm previous data on dammar varnish and to verify the validity of the approach for other types of varnishes. For this purpose, varnish-modified QCMs (10 MHz) were prepared and exposed, in an acclimatized chamber, to the action of visible (from a fluorescent lamp, 48 W) and UV light (monochromatic 365 and 254 nm lines). Although 254 nm UV radiation is realistically very unlikely to be found in the environment, it was chosen as a means for imposing a ageing condition different (and supposedly more severe) than the conventional visible light exposure and in order to verify the capability of the developed monitoring approach to discriminate different ageing situations. The ageing was carried out at $T=25\pm0{,}2$ °C and $45\% < RH < 35\%$, in a sealed chamber with constant renewal of air (hospital-grade without further purification).

Figure 1 shows the variation of the maximum impedance during the artificial ageing obtained from impedance vs. frequency curves (see example in the Figure's inset) of dammar, Laropal and Paraloid B72 modified QCMs. The outcome of the dammar sensor is the same observed in previous studies, that is, a distinct drop in oscillation frequency (increase in mass) during visible light exposure and an increase of the response under deep UV radiation. Already published infrared and FT-Raman spectra indicated that photooxidation takes place in both conditions, though at a greater rate under UV radiation, a fact that can explain the decrease in mass in terms of chain scissions and formation of volatile small molecular weight substances[3]. It must be

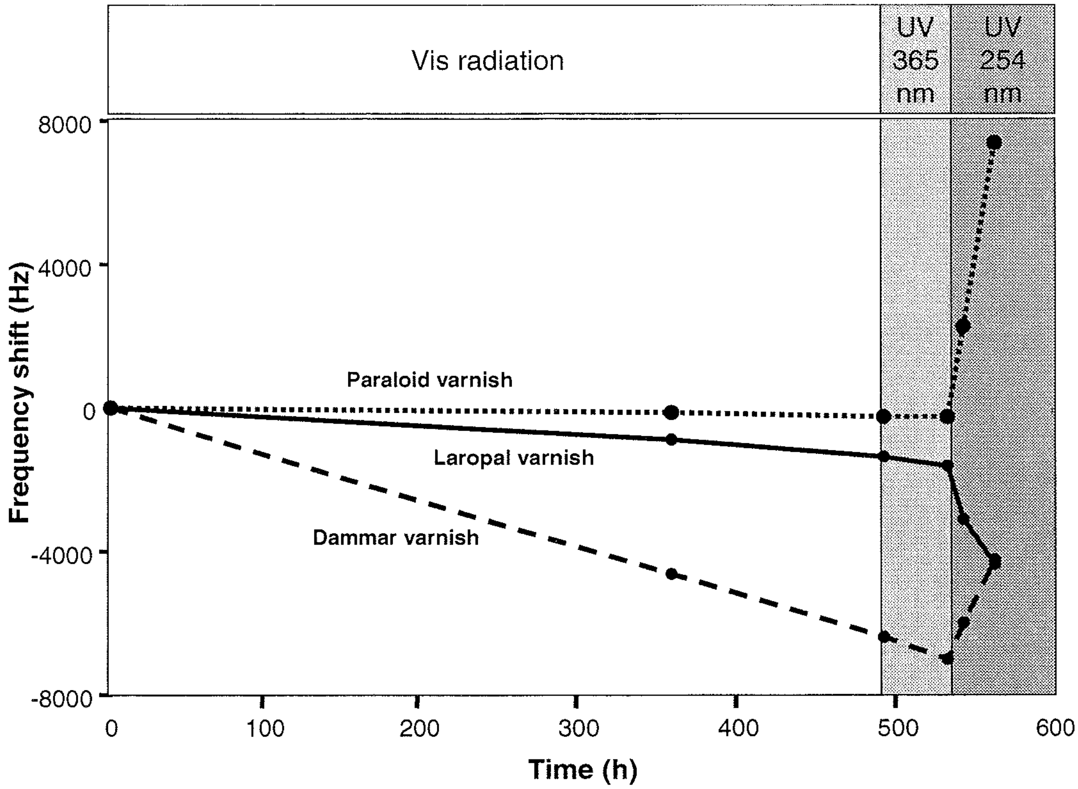

Figure 1: Frequency shifts of dammar, Laropal K80 and Paraloid B72-modified quartz microbalances (as variations of the maximum impedance value obtained from impedance vs. frequency curves) during the artificial ageing process

stressed that continuous frequency monitoring has highlighted the existence of steep decrease in the sensor signal in the very first hours upon of exposure to UV irradiation.

Laropal K80 follows a similar pattern under visible light, even though at a rather smaller rate, but does not clearly show a trend inversion under UV radiation, at least in the 30 h exposure period. Again, continuous monitoring indicates that there is in fact a change in the frequency signal, but much slower than observed for dammar and only after 40-50 h of exposure in the deep UV. FTIR spectra (transmission mode, obtained from resin-coated KRS-5 disks) and FT-Raman spectra (Figure 2) exhibit oxidation features, like dammar, hence the similar behavior. The vibrational data also show a increase in terminal C=C bonds (1600 cm^{-1} region) and a shift in the carbonyl and O-H stretching vibrations, what can be an indication of carboxylic acids formation. Once again 254 nm radiation leads to spectral changes similar to those observed under visible (and 365 nm) light, corroborating the idea that if polymer's chain shortening does take

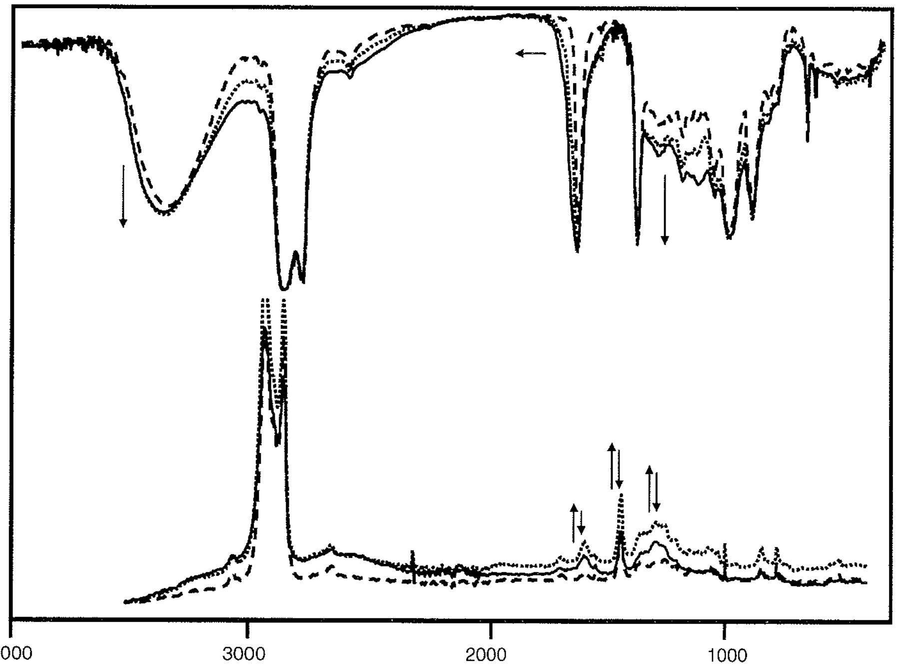

Figure 2: FTIR spectra (transmittance, above) and FT-Raman spectra (below) of thins films of Laropal K80 recorded before (long dash line) and after artificial ageing under visible light (360 h, dotted line) and after artificial ageing under 254 nm UV light (30 h, continuous line)

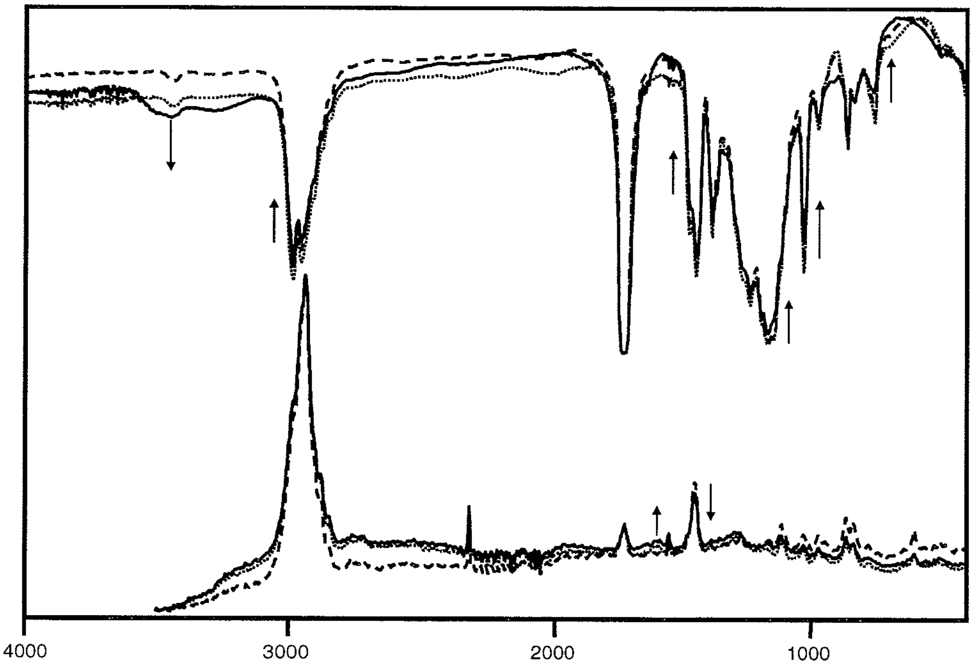

Figure 3: FTIR spectra (transmittance, above) and FT-Raman spectra (below) of thins films of Paraloid B72 recorded before (long dash line) and after artificial ageing under visible light (360 h, dotted line) and after artificial ageing under 254 nm UV light (30 h, continuous line)

place (as it seems) in these conditions, this is the result of extreme photochemical oxidation. In this sense, frequency increase can be regarded as the indication of an extreme decay process. Interestingly, a control sensor that was maintained protected during the visible light sessions and was exposed to 254 nm UV at the end of the trial, exhibited a reasonably similar overall shift in frequency, showing that the prior exposure to visible light did not have any particular protective role on the Laropal K80 resin (the same is valid for dammar and Paralloid B72).

Paralloid B72 displayed very stable impedance and spectroscopic responses under visible light ageing conditions, a fact already supported earlier literature data[6,7]. Only UV light affects the resin, causing a decrease in mass, likely ascribed to bond cleavage in the polymer structure. No strong indication of oxidative degradation can be depicted in the vibrational spectra (Figure 3), which means (as already observed[7]) that Paralloid B72 is not object of strong autoxidation and cross-linking, a fact that explains its chemical stability. On the other hand, under sufficiently aggressive conditions, e.g. deep UV (254 nm) irradiation, its main decay mechanism is direct bond breaking and formation of volatile fragments. Figure 3 (FTIR) indicates that some oxidation does take place (increase in 3443 and 3274 cm^{-1} O-H stretching band and the slight broadening of the 1736 cm^{-1} C=O band), together with a decrease in the intensity of the 1446 cm^{-1} $COO\text{-}CH_3$ bending, 1165 cm^{-1} C-O stretching (ester) and 2984 cm^{-1} $\text{-}CH_3$ stretching bands[6,7]. The band at 1597 cm^{-1} in the FT-Raman spectrum might be attributed (according to ref. 6) to the formation of terminal C=C bonds, resulting from bond scissions, thus reinforcing the fragmentation process suggested in the literature.

In conclusion, it is possible to establish interesting correlations between the impedance response of varnish-modified quartz microbalances and the spectroscopic spectra of the coatings obtained by FTIR and FT-Raman. The structural information obtained from such techniques confirms that mass increase is associated with moderate oxidative ageing, whereas mass decrease is likely to be due to extreme degradation leading to molecular cleavage, fragmentation and lost of small molecular weight species. In this sense, the present investigation validates the use of sensors based on quartz microbalance as a tool for the assessment of microenvironments impact on organic substrates, including synthetic resin varnishes.

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FTIR Analysis of Protective Coatings

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Cellulose nitrate lacquers are often used to slow the tarnish rate of silver objects in challenging situations such as open display in polluted atmospheres. Cellulose nitrate is subject to thermal, hydrolytic and light induced damage. Display causes de-nitration and formation of carbonyl groups in the lacquer which can readily be followed using FTIR spectroscopy. The lacquer loses its protective effect as it deteriorates. Correlation of the degree of protection, measured by electrical impedance spectroscopy and tarnishing rate of aged samples with the changes in FTIR spectra allows an estimate of the remaining effective lifetime of the lacquer.

Loss of solubility of a lacquer can limit its lifetime for conservation below its effective lifetime. Normal solubility measurements are difficult with thin layers. Reflection-absorption spectroscopy has been used to quantify the amount of lacquer remaining on a silver sheet after solvent removal, with extremely low detection limits.

The corrosion inhibiting oil Shield has been used to protect historic electronic equipment in the extremely corrosive environment of a series of maritime tunnels. Chemical changes to the oil film were assessed with reflection-absorption spectroscopy. Its long-term reversibility was assessed similarly.

The whitening of oil paint films containing bone black: a combined study of specular reflection FTIR imaging and SEM-EDX

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Using specular reflection FTIR imaging and SEM-EDX, we investigated the deterioration of dark oil paint films containing bone black. Whitish spots were observed in the dark paint of a number of oil paintings from the Oranjezaal, a unique mid-seventeenth century ensemble in the Royal Palace Huis ten Bosch in The Hague. As a result, the areas originally intended as black and dark brown–hair, eye pupils, shadows–have dramatically changed in appearance. Calcium phosphate was found as the white product. It is proposed that the carbonized organic matter in bone black has reacted away under these circumstances. Optically similar whitening phenomena of brown/black paints were found on a painted ceiling from the Johan de Witt House in The Hague, two paintings by Rembrandt and a painting by Wouwerman. Here, lead soap crystals, degraded yellow lakes in glazing surfaces layers, or deteriorated smalt caused the whitening. Specular reflection FTIR imaging turned out to be an effective technique to characterize the nature of the alteration products directly on the paint cross-section. It enables the distinction between the strong absorption bands of phosphates, sulphates, carbonates, oxalates and carboxylates that are characteristic of the different white products. SEM-EDX was used for morphology studies and elemental analysis.

Bibliographic information

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Copper carboxylates in oil-paintings-on-copper-supports at the Detroit Institute of Arts

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The Conservation Department at the Detroit Institute of Arts is conducting an examination of all fifteen oil paintings on copper supports in the DIA collection, with particular attention to the presence of copper carboxylates, or copper soaps. The paintings are Netherlandish, French, German or Italian, ranging in date from the late sixteenth century to the middle of the eighteenth century; two paintings possess a tin coating on the copper. Common to all of these paintings is the presence of a transparent "green layer" sandwiched between the metal support and the preparatory ground layers of the painting. Although similar green layers are described in the conservation literature, few analytical studies are described (Horovitz, I. *Copper as Canvas* Exhibition Catalog, p. 90, Oxford University Press, 1999). For this study, FT-IR is used to characterize this green layer, and it appears to be a copper carboxylate, as evidenced by the strong COO^- asymmetric stretch at $1592cm^{-1}$ (Robinet, L. and Corbeil, M. "The Characterization of Metal Soaps", *Studies in Conservation*, p.30, **48,** 2003). Additionally, these paintings exhibit the surface protrusions or eruptions that are characteristic of lead and zinc soaps. Using FT-IR, copper carboxylates are identified as one constituent in the protrusions; particles of copper metal are also identified in the protrusions using SEM-EDS. Finally, constituents of these protrusions are being examined and characterized using mass spectroscopy.

The characterization of degraded, oxalate-rich surface layers on paintings

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While oxalate salts have been the subject of extensive research as alteration products on calcareous substrates (such as stone and fresco), including numerous infrared studies, there has been relatively little discussion of their occurrence on other objects such as easel paintings. An understanding of these materials is important since they can be responsible for significant alterations in surface appearance of artworks and the solubility properties of the matrices in which the oxalates are formed. This paper will review the published literature discussing oxalates on non-calcareous substrates in artworks, before presenting examples studied at the Philadelphia Museum of Art.

Oxalate-containing deposits or encrustations have been reported on a variety of non-calcareous substrates including glass [1-2], bronze [3-8], human remains (mummy skin) [9], polychrome wood [10] and easel paintings [11-16]. The oxalate salts of calcium, whewellite (calcium oxalate monohydrate) and weddellite (calcium oxalate dihydrate), are those most commonly encountered, although copper oxalates have also been identified on bronze substrates [3-8] and on paint layers containing copper pigments [16]. In most cases these compounds are found in deteriorated surface layers or patinas.

Surface layers on a number of paintings in the collection of the Philadelphia Museum of Art, including three Italian paintings on panel dating from the fourteenth and sixteenth centuries, were characterised using Fourier transform infrared microspectroscopy (FTIR), in combination with x-ray diffraction (XRD), gas chromatography mass spectrometry (GCMS), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). The surface layers studied were remnants of what appeared to be coloured glazes, in the case of two paintings by Pontormo and Jacopino del Conte, and an early varnish on a painting by Ugolino de Nerio. Among the components detected in all three cases were significant levels of calcium oxalates. Figure 1 shows an infrared spectrum of a sample from a degraded brown glaze layer on Pontormo's *Portrait of Alessandro de' Medici* (1534-5), with characteristic peaks at 1645cm^{-1} (asymmetric C-O stretch), 1324cm^{-1} (symmetric C-O stretch) and 780cm^{-1} (O-C-O bending deformation) indicating the presence of weddellite [17]. Oxalate was also detected in GCMS analyses (as its tert-butyl-dimethylsilyl derivative), and its mineral form confirmed using XRD. The study of the materials of this painting is discussed in previous publications [14, 18].

The highly insoluble minerals may derive in the cases studied from degradation of organic materials in the surface layers, and their reaction with calcium-containing pigments and/or particulate dirt. The formation of calcium oxalates on the surface of paintings has implications for the analysis and characterisation of the materials of aged varnish and paint layers, and for the

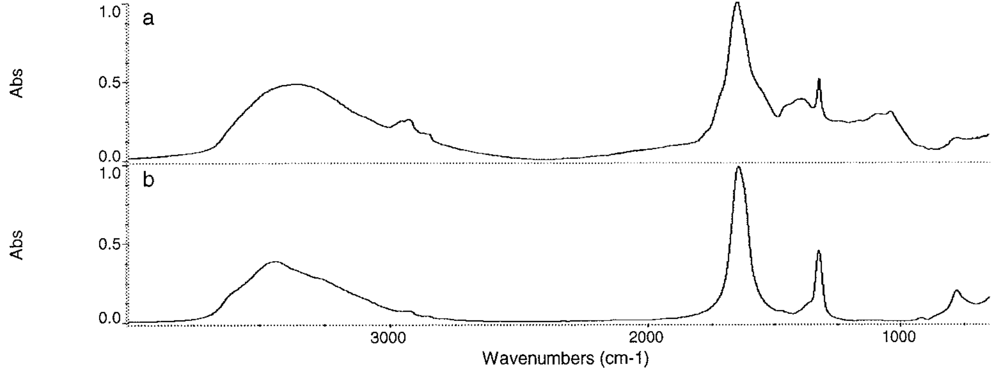

Figure 1. Infrared spectrum of a degraded brown glaze layer from Pontormo's *Portrait of Alessandro de' Medici* (a) with a reference spectrum for weddellite (calcium oxalate dihydrate) (b). Reference spectrum from NICODOM Kidney Stone FTIR Library (NICODOM, Prague).

interpretation and conservation of degraded paint surfaces; these and other issues will be discussed in the presentation.

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FTIR and UV-VIS emission microspectroscopy, in dialog with 12th century Portuguese manuscript illuminations

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Figure 1. Medieval manuscript Book of Birds, fl. 4 (1186)

Summary

Looking through the centuries, we can find out that illuminated manuscripts are one of the richest sources of medieval colours' information, as usually they did not suffer large interventions and also due to the fact that the illuminations were regularly protected inside the books.

In Portugal, during the Middle Ages, the Monastery of Lorvão was a prosperous *scriptorium* and a centre for the art of illuminated books. During the 12th century some of the most representative medieval Portuguese illuminated books were produced there, namely *Apocalypse of Lorvão* (1189) and *Book of Birds* (1186). (*figure 1*).

FTIR microspectroscopy is a powerful technique for the study of these treasures as it is possible to acquire information (from a 20-40 um sample), concerning the binding media and the eclectic palette used in illuminations: pigments, lakes and organic colorants.

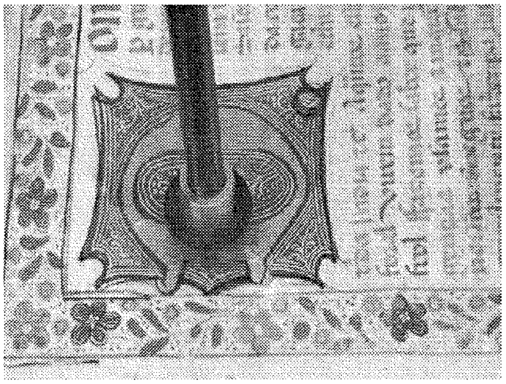


Figure 2. Main initial of the *Charter of Vila Flor* (1512), being analised by UV-Vis emission spectroscopy accoupled with fiber optic accessory.

Nevertheless, the identification of lakes and organic colorants in medieval manuscript illuminations is still a challenge, due mainly to the fact that these belong to multi-component systems; therefore, it is frequent to find the absorption signal of an organic compound masked by the binding medium and/or the extenders used.

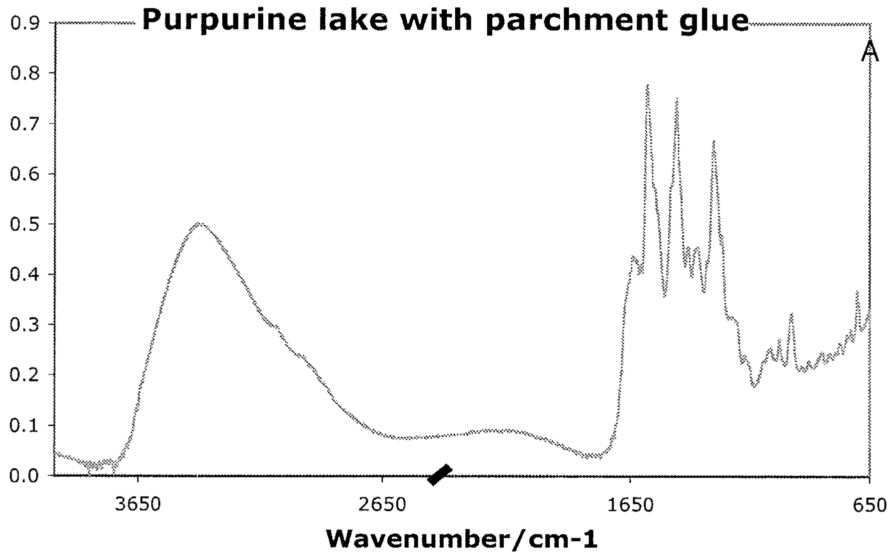
In this study we will discuss the possibility of extracting the FTIR fingerprint of an organic red lake from a complex signal. Moreover, we will also compare the results obtained to UV-Vis emission microscopy data. (*figure 2*)

Samples prepared in laboratory, following medieval recipes, such as purpurine lake, madder lake, lac dye in a proteinaceous matrix will be analysed.

Results and discussion

In Medieval Ages, to produce miniature illuminations, parchment glue or white egg were used as binders [1-5]. Their infrared absorption spectra overlap in great extent the fingerprint region of red lakes, making their identification, by FTIR, difficult. Latter these proteinaceous binders will be replaced by polysaccharide gums, such as arabic gum.

Historical reconstructions of these colours were made, preparing the lakes and parchment glue following historical recipes [1-5]. The FTIR spectra obtained (*figure 3*), are compared to what results for a simple computer simulation using the sum of the FTIR spectra of the single components. (*figure 4*)



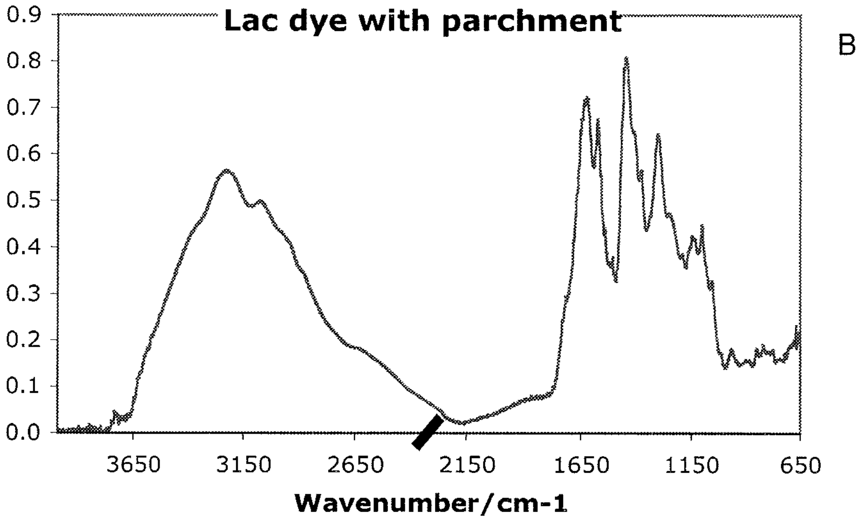


Figure 3. FTIR spectra of paints, made with different lakes (***A*** purpurine lake; ***B*** lac dye) and parchment glue. [The ratio of colorants/binders are: 0.18mg of purpurine lake to 0.7mg of binder; 0.5mg of madder lake to 0.7mg of binder; 0.5mg of lac dye to 0.7mg of binder]

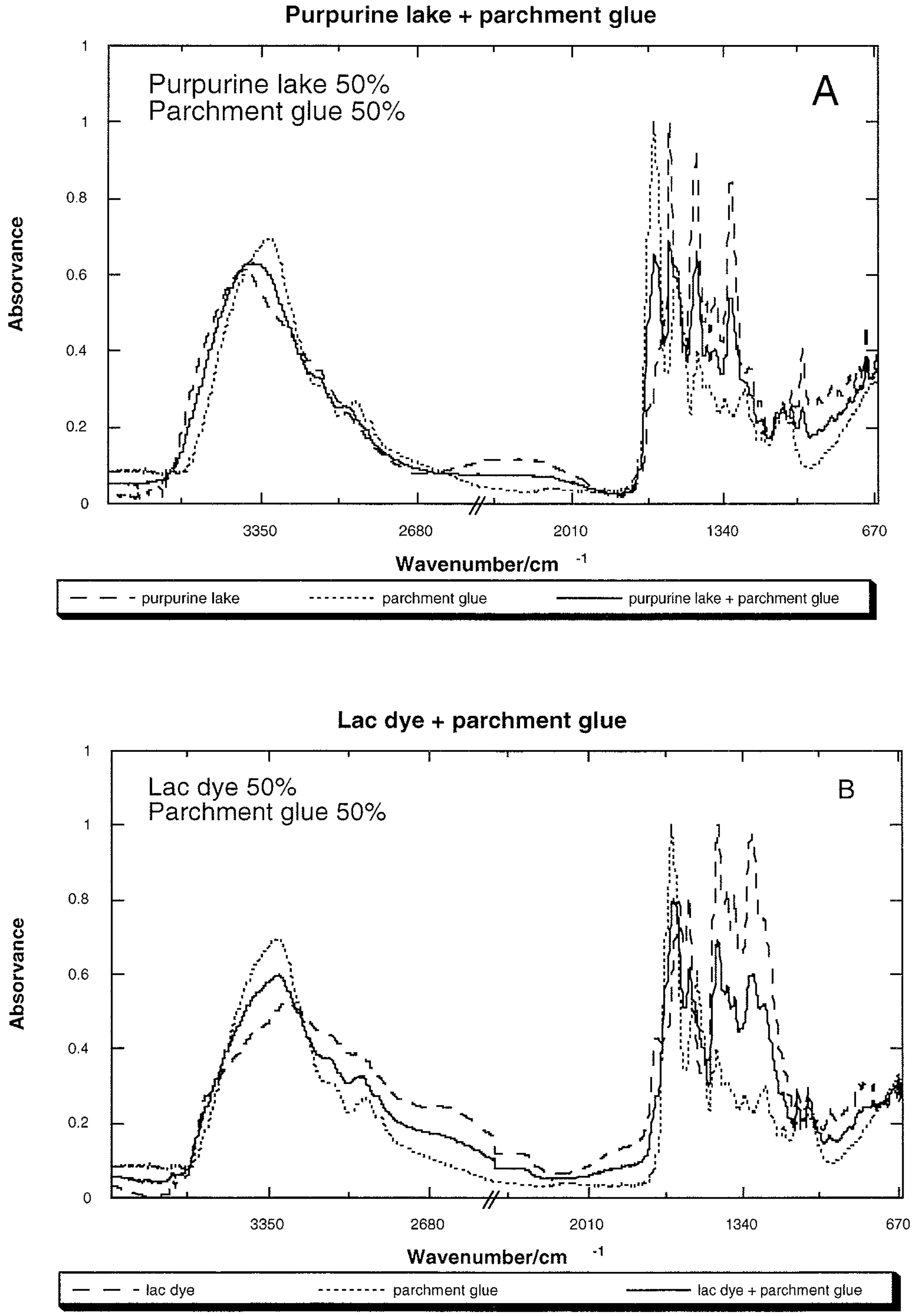


Figure 4. FTIR spectra resulting from the sum of the components of a paint, the colorants: ***A*** purpurine lake (norm at 1580 cm^{-1}) ; ***B*** lac dye (norm at14400cm^{-1}) with parchment glue (norm at1650cm^{-1})

With FTIR spectra, we found out that it is possible to extract information concerning the fingerprint of the organic chromophor. This information should be confirmed with other analytical techniques, such as UV-Vis emission spectra.

UV-Vis emission spectroscopy can be a powerful tool to the analyses of organic colorants, as it is a completely non-destructive and non-invasive technique, presenting a high spectral resolution when coupled to a microscope (from 2□m to □̃□m spot).

In this work it will be used, associated with a microspcope (*Book of Birds*) and with a fiber optic accessory (*Charter of Vila Flor*).

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The Determination of Artist's Palettes in the 17th C. Manuscript *Historia General del Perú* by Martín de Murúa

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The illustrated manuscript *Historia General del Perú* in the collection of the J. Paul Getty Museum (83.MP.159) is an artistic document of rare importance for its depictions and descriptions of Inca royalty and their history. The manuscript contains thirty-eight illustrated folios, the majority of which illustrate in detail the Inca nobility wearing their colorful royal garments (see for example the image of Capac Yupanqui, shown in Figure 1). The Getty manuscript is one of two existing manuscripts produced by Murúa, a friar of the Mercedarian order who worked in Peru and Bolivia in the late 16th and early 17th centuries. Several folios in the Getty Murúa (see, for example Figure 2) are believed to be from an earlier version of the manuscript currently in a private collection in Dublin, Ireland. The work presented here describes the initial phase of a larger project to study the illustrations of the two Murúa manuscripts. Investigation of the materials and techniques by which the illustrations were produced is used as a means to explore possible relationships between the garments as depicted in the manuscript and Inca textiles from the period, correlations between materials and artistic hands, as well as relationships between the illustrations in the two manuscripts. Both manuscripts will be featured in a 2008 exhibition at the Getty Research Institute entitled "The Marvel of Peru: Visual Histories 1560-1880".[1]

Figure 1: Martín de Murúa, *Historia General del Perú*, JPGM, Fol. 30v, Portrait of Capaq Yupanqui (28.4×19.7 cm).

Due to the importance and delicate nature of the manuscript, only the non-invasive techniques X-ray fluorescence spectroscopy (handheld Re target Keymaster Tracer III-V XRF spectrometer) and Raman microscopy (Renishaw InVia Raman Microscope, 785 nm excitation) were used. The initial analyses focused on the colors and colorants used to depict the garments. Although the rendering of the garments and their coloration is a remarkably accurate reflection of Inca textiles[2], no direct material correlation was observed between the colorants used in the illustrations in the Getty Murúa and those which would have been used in the production of textiles. The colorants identified in the manuscript were widely available to manuscript artists in the late 16th century and included mineral pigments and organic colorants of the Andean region.

Figure 2: Martín de Murúa, *Historia General del Perú*, JPGM, Fol. 89r, Inca queen in procession "Chuquillantu" (28.4×19.7 cm)

A number of pigments, including vermilion, lead white, indigo, and orpiment were found throughout the manuscript. However, unique marker pigments and/or pigment combinations were also identified from which five distinct palettes and up to six different execution campaigns or working sessions could be distinguished. One palette was identified by the use of yellow ochre, and was found to correspond to bound-in illustrations in the later part of the manuscript. By contrast, the bound-in illustrations in the first part of the manuscript correspond to a second palette characterized by the use of orpiment as the only yellow pigment. Two tipped-in folios near the beginning of the manuscript were each found to contain a uniquely occurring pigment (lead-tin yellow and an iron-based green), suggesting the possibility of a third and fourth palette. A fifth palette was characterized by the use of the arsenic sulfide pigments pararealgar and realgar and was found to be associated only with the tipped-in folios thought to have originally been in the Dublin manuscript[3]. The palette associated with these folios was further characterized by the use of indigo as the sole blue colorant; the majority of the other folios in the manuscript were found to contain both azurite and indigo. Finally, silver paint was identified in illustrations in the first part of the manuscript. The use of the silver paint is not classified as a separate palette but rather as part of a subsequent embellishment campaign, as it is seen on both the tipped-in and bound-in folios at the beginning of the manuscript, and, more significantly, corresponds precisely to the shading of the marble floors, which stops abruptly approximately halfway through the manuscript.

The identification of a number of distinguishable palettes might suggest that the illustrations were executed by a number of different hands, or at least different working sessions. Initial examination of the artistry and various drawing styles found within the manuscript suggests that several different artists may have been involved in the production of the Getty Murúa. As this work continues, the analysis of the colorants used to create the illustrations of both manuscripts will be used together with stylistic and codicological analyses to determine the processes by which the manuscripts were originally created and the subsequent changes and modifications that occurred to produce the manuscripts as they currently exist.

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Composition of Printing Inks on Stamps Using FTIR Spectroscopy

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Fourier Transform Infrared Spectroscopy (FTIR) was applied to the characterization of inks used to print stamps.

Different methodologies and accessories can be used depending on the amount of sample, destruction, and the information required. Because of the value of stamps, non-destructive or quasi non-destructive sampling should be applied.

This study has the purpose of using different types of sample preparation and infrared spectroscopy techniques for the characterisation of inks used for "one penny" stamps printed during the nineteenth century.

For this purpose a total of 71 stamps were analysed.

Three different accessories were used: specular reflection, diffuse reflection and microscope. The microscope can be used either in transmission mode with a diamond cell or with an attenuated total reflectance (ATR) objective.

The best spectra were obtained using a microscope with a diamond cell coupled to an infrared spectrometer. In this case, the extraction of a small particle of ink located between the fibres was enough to obtain a good spectrum. Calcium carbonate, calcium sulphate, lead chromate, cyano compounds, cellulose, and oil were identified. When bigger surfaces need to be analyzed, diffuse reflection or variable specular reflectance accessories can be used. Nevertheless, only cyano compounds and calcium carbonate can be characterized.

Results are in agreement with those obtained using scanning electron microscopy.

The chronological order of the 71 stamps studied showed that the chemical composition of the red ink changed during the period studied.

Polyurethane rubbers and Pratt chairs

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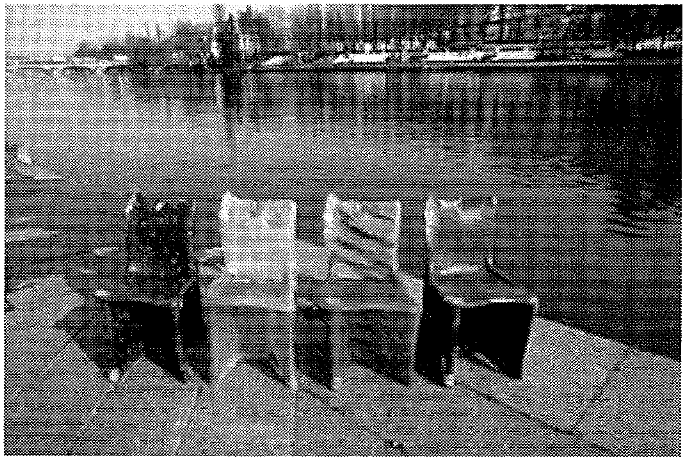


Introduction

An extensive collection of industrial design furniture from the 20th century belongs to the Vitra Design Museum in Weil am Rhein, Germany. The objects reflect a wide range of technologies and synthetic materials, which express the designer's concepts. Today the synthetic materials are in various states of preservation and accordingly, each shows unique signs of degradation. The AXA Art Conservation Project (2002-2005) in cooperation with the Vitra Design Museum was established to develop conservation treatment methods for amongst other chairs also the chairs made by Gaetano Pesce (above).

In 1984, Pesce designed four series of nine chairs at the Pratt Institute in New York. Each Pratt chair is made of a different hardness of polyurethane (PUR) rubber, from soft and unable to support its own weight until too rigid to be comfortable.

The Vitra Design Museum owns four different Pratt chairs: three stand upright, and one lies on the ground. It is not known whether those four chairs are parts of just one series or whether they belong to different series.

It is assumed that the chairs are made in a mould consisting of five parts. One of the chairs, a number 2, was standing upright, however after 20 years, it is sagging entirely. Because of the softness of the material and the enormous weight of 16 kg of the chair the proper right side is torn in two areas; there is a large tear in the proper right front leg visible (Figure 2).

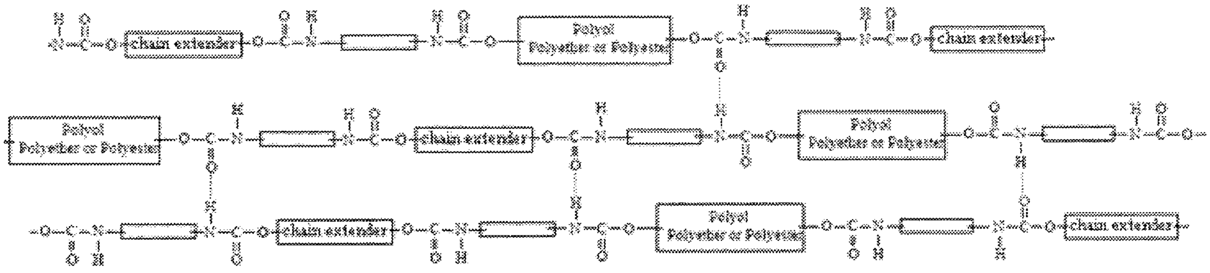
Figure2. Pratt chair no.2

Manufacturing of PUR rubber objects

Polyurethane (PUR) rubbers containing the same characteristic elastic property as natural or synthetic rubber were first developed under the trade name Vulkollan in Germany, in the 1940s (Bayer 1963). PUR rubbers are based on the polyaddition reaction products of diisocyanates and polyester or polyether polyols (long-chain diols) and short-chain diols (chain extenders).

The rubber-like property is a result of the composition of the segmented building blocks of the polymer; the rigid segment is composed of the diisocyanate and the chain extender, a diol or diamine, whereas the soft segment is composed of the long-chained polyol (See figure 2). This blend is reacted with a chain extender, usually a glycol to give a polymer with hard polyurethane segments. The reactions cause chain extension and by the formation of urea and urethane linkages they provide sites for cross-linking, since these groups can react with free isocyanate or terminal isocyante groups to form biuret or allophanate linkages respectively.

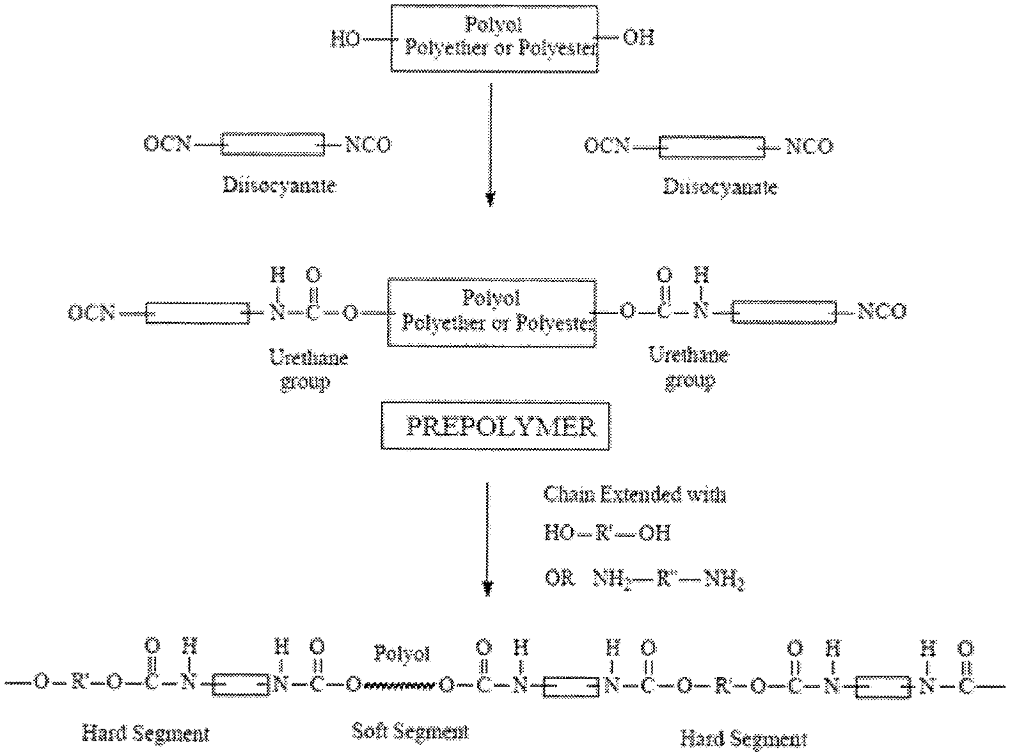
Figure 2. Building blocks of PUR rubber (editor's note: verticals read N-H··· O=C)



The most used di-isocyanates in PURrubber manufacture are 2,4- and 2,6 toluene di-isocyanates (TDI), 4,4-diphenylmethane di-isocyanate (MDI) and 1,5-naphthalene di-isocyanate (NDI). Most used polyols are polypropylene glycols for polyether urethane formation, and adipic acid and 1,4-butanediol for the manufacture of polyester urethane.

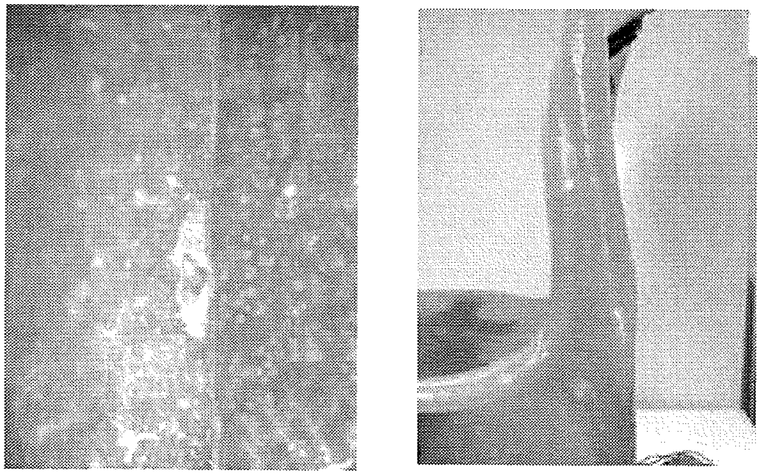
For cast systems, polyurethane rubbers are used in the form of stable prepolymer systems, which are first produced by reacting linear polyester with terminal hydroxyl groups of a similar polyether with molecular weights in the range of 800-2500, with an excess of di-isocyanate to give an isocyante-terminated polyol plus free unchanged isocyanate (Figure 3).

Figure3. Prepolymer of PUR rubber



Under normal storage conditions, between 0.3 and 0.7 per cent water is present and this amount plays an essential role in the curing process, resulting in a final polymer that contains both allophanate and biuret branching. However, in conditions of high humidity, this level can rise to a value of 2 per cent with an adverse effect on the properties of the cured material, the water competing with the hydroxyl-containing polyester of the di-isocyanates. Moreover, avoiding high moisture content in the environment is essential because otherwise carbon dioxide will be formed resulting in the formation of bubbles resulting in more or less foamed products (Figure 4).

Figure4. Air bubbles in yellow Pratt chair no. 8



In addition to the basic components, many PUR rubber formulations contain additives to facilitate production and processability. Further additives such as mould release agents, flame retardants, UV-stabilizers and plasticizers can also be included to modify specific properties.

Properties of PUR rubbers

The properties of the end product depend on the nature of components, reaction conditions, and amount of polyester, di-isocyanate and cross-linking agents. By varying these amounts, various PUR rubbers can be developed (Bayer 1963, Brydson 2000). PUR rubbers possess outstanding properties, such as high modulus, high tensile strength, excellent tear and abrasion resistance. With their resistance to oxygen and ozone and to aliphatic hydrocarbons they have properties that are lacking in natural rubbers. Moreover, having a high hardness and a low resilience they may regard as somewhat intermediate between conventional rubbers and flexible thermoplasts. The main disadvantage of PUR rubbers is their susceptibility to hydrolysis. The life expectancy of PUR rubbers will be influenced by several factors and is difficult to predict exactly, though Poly*ester*urethane rubbers are more sensitive to moisture than Poly*ether*urethane rubbers (Hepburn 1982, Brydson 2000).

Analysis

To determine the materials composition of the chairs, samples were taken and examined by Fourier transform infrared (FTIR) spectroscopy, thermal hydrolysis methylation pyrolysis gas chromatography–mass spectrometry (THM–Py–GCMS). To get insight in the polymer structure of the components of PUR rubber, test pieces were made with various shore hardness. Samples were taken from these test pieces, FTIR analysed and identified. This research is still in progress and the latest results will presented at the meeting.

FTIR analysis gives information about the polymer itself whereas THM–Py–GCMS can identify the various different components of the polymer. 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 600 cm^{-1}. The infrared spectra of the samples were compared with spectra of reference materials.

For the THM-Py-GCMS analysis, a Curie-Point Pyrolyser from Horizon Instruments was used. The pyrolysis temperature was 625°C (Dekker 1995). Using tetra methyl ammonium hydroxide (TMAH), polyurethanes are pyrolysed into MDA in TDA, amines of MDI and TDI. The GCMS used was a Thermo Finnigan GC8000 top-voyager combination. The separation was performed on a ZB5 (Zebron) column of length 15m, internal diameter 0.25 mm and film thickness 0.25 µm. The temperature program used was 40°C (1 min) – 20 C/min – 310 C (2 min). Mass spectral data were collected with a mass range of 40 -480 amu with a scan rate of 0.5 s. The results of the analysis of the unknown samples were compared with the analysis of reference PUR rubbers.

To gain insight into the mechanical properties of the PUR rubber used, Shore hardness of the PUR rubber of Pratt chair no 2 and the test pieces were measured using a HPS Durometer (shore A DIN 53505, Hans Schmidt & Co. GmbH, Control Instruments).

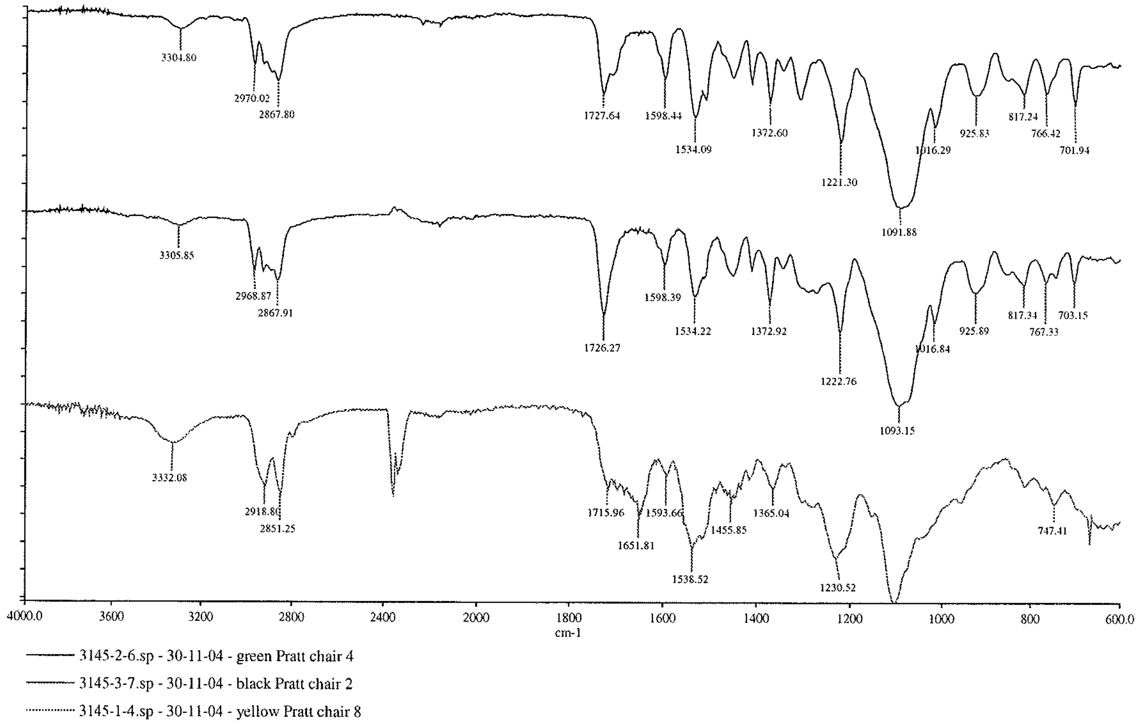
To evaluate the condition of the chairs, the temperature behaviour was measured and compared with the shore hardness of the PUR rubbers. The temperature behaviour of various PUR samples was determined with a Mettler Toledo differential scanning calorimeter; model DSC-12E, 30 -200°C at a heating rate of 10°$Cmin^{-1}$.

Results and discussion

FTIR showed that three out of the four chairs show weak absorption bands at wavelengths 3320 cm^{-1} (urethane N–H stretch), weak absorption at 1730–1680 cm^{-1}, (carbonyl C=O) and strong absorption at 1221, 1108 and 1018 cm^{-1} (C–O–C) which indicates a polyurethane ether type rubber. The carbonyl stretching region occurring at 1810–1670 cm^{-1} presents an excellent region from which identification of the particular species may be made. The amide I band of the urethanes (C=O) occurs at a different frequency from the C=O stretching vibrations of other compounds among such dimers and trimers. Results were confirmed by Py-GCMS (Table I).

It is not always possible to distinguish individual species in multi-component mixtures because these bands tend to coalesce. Though the building blocks of the polyurethane rubbers used for making the chairs are the same, due to the adding of different amounts of the starting components, cross-linking agents and circumstances during processing the chairs, different types of PUR rubbers are formed, which can be seen in the infrared spectrum at various absorption bands at 1730–1680 cm^{-1} of biuret and allophanate carbonyl stretching vibrations (Figure 5).

Figure5. FTIR spectra of PUR rubber Pratt chairs, No. 4 (top), No. 2 (middle) and No. 8 (bottom).



The infrared spectrum of the yellow transparent lying chair show absorption bands at 1721 cm^{-1} (C=O), 1275,1010, 1065 ,742 and 704 cm^{-1} indicating the plasticizer di-butoxy-ethyl phthalate (DBEP) (Figure 6). When manipulating the infrared spectrum by differentiation, weak absorption bands at wavelengths 3320 cm^{-1} (urethane N–H stretch), at 1730–1680 cm^{-1}, (carbonyl C=O) and strong absorption bands at 1221, 1108 and 1018 cm^{-1} (C–O–C) became visible, indicating a Poly*ether* urethane type rubber.

Figure6. FTIR spectra of Plasticizer DBEP (top) and Pratt chair No. 6 (bottom).

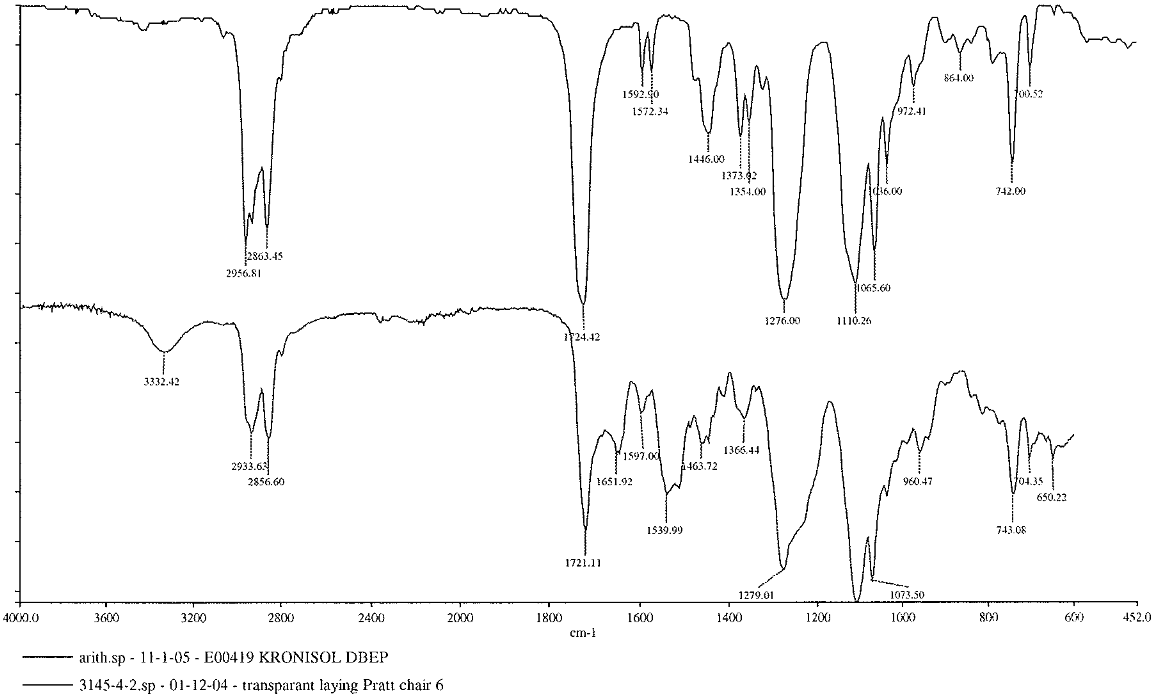


Table I. Results of FTIR, THM Py–GCMS analysis and hardness measurements

Type of chair	(number of samples)	FTIR	THM Py–GCMS	Shore hardness
Yellow Pratt nr. 8	(4)	All samples identified as the same polyurethane(ether)rubber network	4,4'-diphenylmethane di-isocyanate(MDI)	
Green Pratt nr.4	(6)	Four different polyurethane (ether) rubber network identified	4,4'-diphenylmethane di-isocyanate (MDI)	
Black Pratt nr.2	(6)	Two different polyurethane (ether) rubber network identified	4,4'-diphenylmethane di-isocyanate(MDI)	3, 16, 29, 46 measured in different areas
Transparent laying Pratt nr. 6	(6)	All samples identified as dibutoxyethylphthalate (DBEP), plasticizer) and polyurethane (ether) rubber	4,4'-diphenylmethane di-isocyanate (MDI) and DBEP	

Conclusions

The condition of a polyurethane rubber object depends on internal and external factors, such as the manufacture of the pre-polymer, the reaction of the cross-linking agents with the pre-polymer, the curing of the polyurethane rubber and the use of the object. The specific composition of the polyurethane rubber (the proportion of the pre-polymer and cross-linking agents) and also the moisture content, during curing, affect the curing process which can be seen as bubbles in the rubber material of the chairs.

It is not always possible to distinguish individual species in multi-component mixtures because these bands tend to coalesce. Though the building blocks of the polyurethane rubbers used for making the chairs are the same, due to the adding of different amounts of the starting components, cross-linking agents and circumstances during processing the chairs, different types of rubbers are formed, which can be seen in the infrared spectrum at various absorption bands at 1730–1680 cm^{-1} of biuret and allophanate carbonyl stretching vibrations. Research into the identification of the various components and their ratio using FTIR is still going on.

FTIR showed that all Pratt chairs contain Poly*ether*urethane rubber. The yellow Pratt chair no. 8, the most rigid one, contains only one type of polymerised network of rubber, whereas the green Pratt chair no. 4 and the black Pratt chair no. 2 consist of respectively four and two different polymer network PUR*ether* rubbers. The main component of the orange laying Pratt chair no. 6 is dibutoxy ethylphthalate (DBEP) a plasticizer, and a minor amount of PUR rubber. However, also styrene components were detected.

To create an effect of standing or lying chairs, Gaetano Pesce probably used various amounts of pre-polymer and cross-linking agents of the PUR rubber into the moulds. These differences in the materials applied, cause different conditions of the four Pratt chairs. Three of the four chairs examined are still in acceptable or good condition.

Concluding from the research performed on the black Pratt chair no. 2, consolidation and adhering will be performed. However, already an adjusted mounting system for the Pratt chair was developed.

Acknowledgements

We thank all those involved in the research and conservation, especially Henk van Keulen (ICN) and Dagmar Ulbrich, Ralf Günther, Franz-Jozef Bohne and Klaus-Peter Nierman (Bayer Leverkusen).

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Vinyl paints in Portuguese Modern Art (1960-90): a FTIR study

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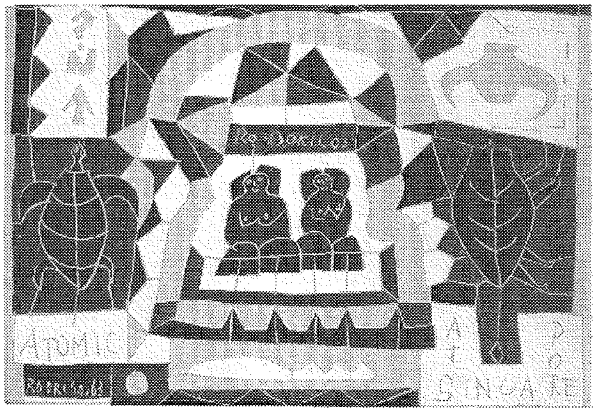


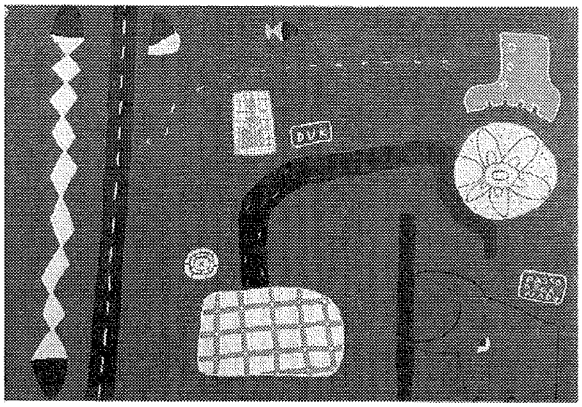
Mondo Cane
Joaquim Rodrigo 1963 *(MC-MNAC)*

Developed in the 1950s, after World War II, emulsion paints are, presently, the largest product worldwide in the paint industry. In the late fifties, vinyl paints were the first synthetic colours for fine arts produced in Portugal. Since than, these emulsions have been used by some of the most representative Portuguese artists, such as, Joaquim Rodrigo[1], Ângelo de Sousa[2] and Julião Sarmento. The binder in these vinyl media can be a polyvinyl acetate homopolymer (PVA), or it can be present as a copolymer or terpolymer (as example, vinyl acetate-ethylene-vinyl chloride)[3].

Most of these paintings, present in Portuguese Museums or private collections, are in a very good conservation state. Nevertheless, the knowledge about the long term ageing of these PVA polymers in paintings is scarce, and we do not know what will be required to preserve these paintings for centuries.

Furthermore, the PVA binding medium is part of a network containing a wide range of materials, organic and inorganic pigments, fillers and additives used in the stabilization of the emulsion, to name some.

The importance of FTIR microspectroscopy as a means of identifying and characterize the polymer and its degradation will be discussed. The main goal will be that of studying the photodegradation mechanism of PVA and vinyl formulations and to assert which are the factors relevant to the degradation. Finally, the evolution of the binding media in paintings from Joaquim Rodrigo, dated from the 60', 70', 80' and 90', will be considered as a first case study.



Lisboa-Oropeza
Joaquim Rodrigo 1969 *(MC-MNAC)*

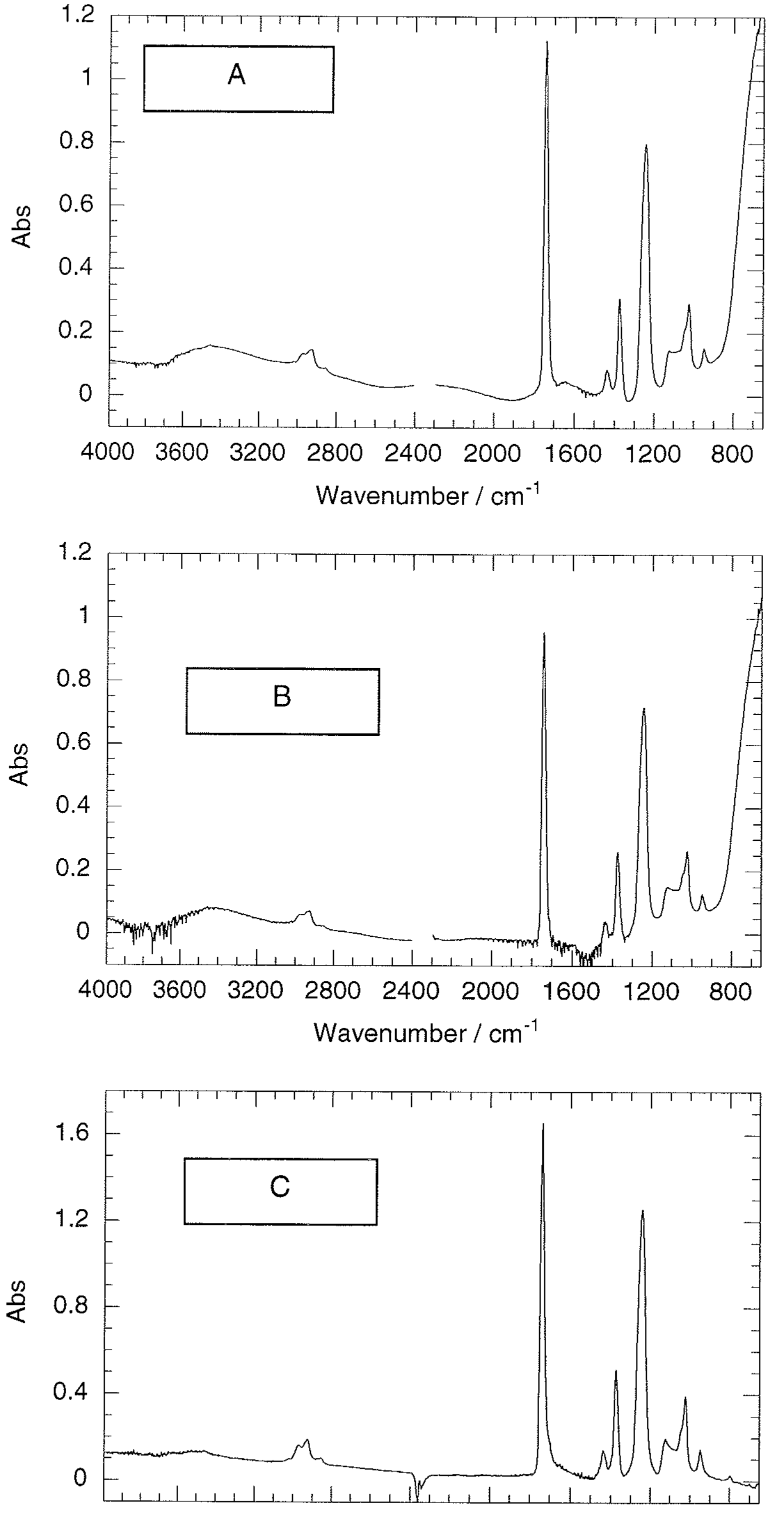


Figure 1: FTIR spectraof the white (A) and yellow (B) colours from Mondo Cane I (1963). Spectra C is an acetone extract of the last white colour found in the artist's studio (1995).

Results and Discussion

The works of Joaquim Rodrigo were painted in Lisbon and the materials he used were acquired in Portuguese Fine Artists shops, such as *Casa Varela*. In the sixties, he changed from the traditional oil media to PVA emulsions, and prepared is own colours by mixing, following a precise procedure, the PVA binder with the pigments. Even if acquired in Portugal, most of the pigments and the PVA emulsion were imported. For example, most of the iron yellows and reds were from the French company, *Lefranc&Bourgeois*. Joaquim Rodrigo believed that these were very durable materials.

A detailed study of the PVA photodegradation and the effect of pigments and other additives is in course through irradiation with a Xenon lamp as well as with monochromatic light, from a mercury medium pressure lamp.

In order to test the validity of our accelerated ageing experiments we performed a first micro-sampling of some works of Joaquim Rodrigo dated from: 1961 (*SM*), 1962 (*Kultur*), 1963 (*Mondo Cane, Liberté*), 1969 (*Lisboa-Oropeza*) 1971 (*Alassio-Nice*), 1983 (*Port-Ligat*). We also analyzed the final white colour left by the artist in his studio (≈1995), and the colours in some of his studies, figure 1C and figure 2.

In this first step, we wanted to confirm, by FTIR[4], the existence of a PVA binder, to characterize if we were in presence of a homo-polymer or co-polymer, and finally if some pattern of degradation could be already detected[5] and the influence of the pigment on it.

In order to assert the presence of the homo-polymer we used the intensity ratio as well as the area ratio between the absorption bands due to the carbonyl stretching (1738 cm^{-1}) and the asymmetric methylene stretching (≈2940 cm-1) or scissoring (1442 cm^{-1})[6] and compared it to the ratio obtained with the same carbonyl stretching and the asymmetric methyl bending (1373 cm^{-1}). The ratio between the (C=O) and the C-O (≈1242 cm^{-1}) stretching was also analyzed. The best results were obtained for the ratio between the areas of the absorption bands, and it was possible to confirm the presence of the PVA homo-polymer.

In figure 1 and 2 are shown some representative spectra obtained from micro samples, for yellow[7], black and white colours; in most of the white colours TiO_2 was the pigment used, sometimes also mixed with $CaCO_3$. Before extraction with acetone of the PVA polymer, the spectra of the "final white", figure 1C, was similar to the spectra of all the white colours, such as the one from *Mondo Cane I*, represented in figure 1A; that is, the absorptions present in the range 3400-3300 cm-1 are the result of an interference of the pigments or other additives. In which concerns the polymer degradation, in all the samples analyzed, we did not observe new absorptions due to the formation of -OH groups or hydroperoxides (3400-3500 cm^{-1}), nor the appearance of double bonds (≈1640 cm^{-1}) nor shoulders in the carbonyl absorption band due to the formation of intermediates such as lactones nor a broadening/weakening of the carbonyl absorption band[8]. Due to the photocatalytic activity of titanium dioxide we could expect to find, in the FTIR spectra, already some evidence for photodegradation, which was not the case.

In conclusion, in the samples analyzed, no relevant degradation could be observed through microFTIR spectroscopy[9]. These data are in agreement to what observed in the accelerated ageing experiments, but must be confirmed with the molecular weight distribution in selected samples, obtained by size exclusion chromatography. Currently under completion, is an exhaustive study aiming to compare the colours used in the artist sketches, that are conserved protected from light and that most probably were never retouched, with the colours of paints existing in Museums that are exposed to light and, more important, frequently prepared to be in exhibition.

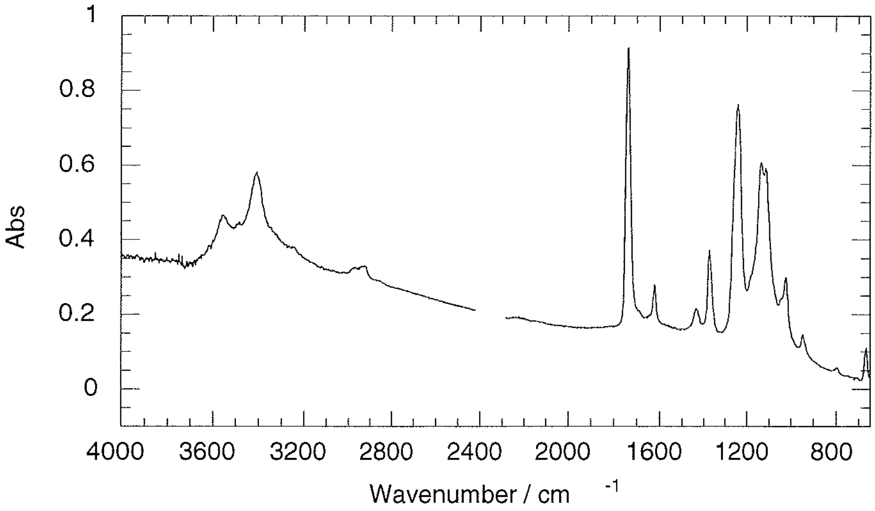


Figure 2: FTIR spectra a black colour.

Acknowledgements

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Man-made Fibres: Research into the degradation of Polypropylene fibres in modern wall tapestries

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INTRODUCTION

The book published in the 1962 entitled 'Welche Chemiefaser ist das?' (Which Synthetic Fibre is it?) describing the history, chemistry, microscopic examination, manufacturing processes, application of synthetic fibres and trade names has been the reason for this paper.
The book consists, besides the above-mentioned items also 126 reference materials of the described fibres varying from polyester, polyamide, polyethylene and polypropylene to polyurethanes. At this moment, the fibres are naturally aged for 43 years and some of them are discoloured and some already degraded totally.

The research is besides the investigation of the fibres present in the above mentioned book also focussed on the degradation phenomena observed on polypropylene (PP) fibres used in three works of art and polypropylene fabric used for cold relining of paintings in the 1970's.

The first of the researched works of art is the wall tapestry 'Fête I' made from polypropylene rope by Will Fruytier, a Dutch designer, in 1971. This work belongs to the collection of the Dutch ING bank and was in exhibition from 1971 until 2005. The tapestry shows severe degradation at the front, the fibres are very brittle and powdery (see figure 1). The reverse side shows hardly any degradation.

The second work of art is another wall tapestry by Will Fruytier 'Fête II' (1971) also made from polypropylene rope (see figure 2). This work was acquired by the University of Nijmegen the Netherlands, in 1971. The tapestry is in exhibition for more than 34 years in the hall of the University and especially the white fibres are degraded and brittle and make the work look messy.

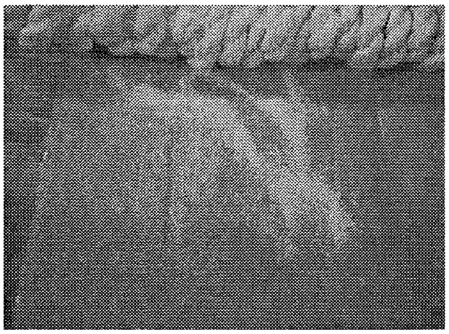


Figure 1: detail of Fête I

Figure 2: detail of Fête II

he third work of art examined is a carpet made from natural fibres and entitled 'the Knot' (see figure 3). It was made by the artist Herman Scholten in 1967 and acquired by the Rijksdienst Beeldende Kunst (RBK) after a merge; the Netherlands Institute for Cultural Heritage (ICN) in 1968. The history of this work is not known. In 2001, the tapestry (assumed made of natural fibres) was suspected to be infested with moths and was put in a freezer at –20 °C for three weeks for preventing infestation from beetles. Natural fibres withstand this treatment without damage, but in this work white coloured fibres, that were only present in a rather small area of the work, had become brittle (see figure 3). It was not known that in the tapestry a small part of the fibres were synthetic, nor was it described on the inventory card of the object.

The fourth researched object is the relining fabric, which was used for nap-bond cold lining on a painting in 1975 at the Central Research Laboratory (now part of ICN). According to the relining method, the linen of the painting was pre-treated with diaceton-alcohol and water, afterwards dried on a vacuum table followed by applying Plextol B 500, an acrylic methacrylate copolymer emulsion adhesive [Mehra, V., 1975]. The relining has become extremely brittle and is partly pulverised (see figure 4).

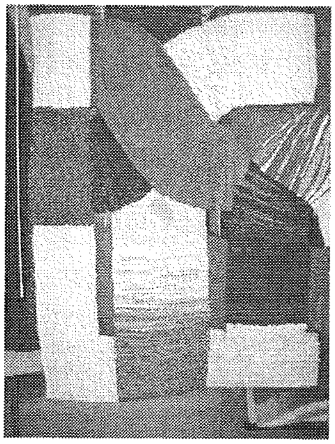


Figure 3: The Knot

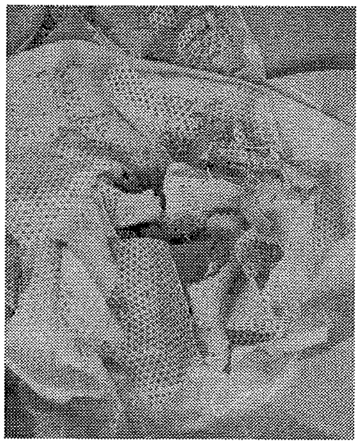


Figure 4: Relining fabric

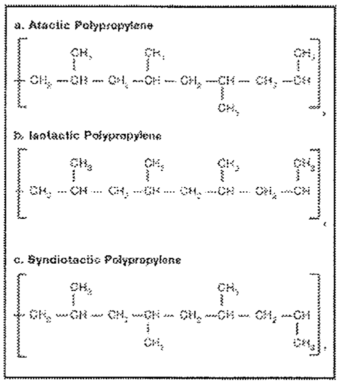
Fourier Transform (FTIR) infrared spectroscopy is used to relate the condition of the PP fibres from the book 'Welche Chemiefaser is das?' with the degraded fibres of the works of art and the relining fabric.

POLYPROPYLENE (PP)

Man made fibres started with the semi-synthetic fibres at the end of the 19th century and the beginning of the 20th century. It reached its boom with the development of fully synthetic fibres, all developed before the 1940th and some only applied from the 1960 – 1970 onwards, are nowadays common use. One of the most used fibres nowadays is polypropylene.

Polypropylene was developed in 1954 by the chemists Natta and Ziegler, by using special catalysts [Gordon Cook, 1993]. It is a long chain polymer made from propylene monomers. After exposing the propylene to both heat and pressure with an active metallic catalyst, the propylene monomers combine to form a long polymer chain, called "polypropylene". Several different polymerization methods are used to produce polypropylene.

Depending on the catalyst and the polymerization method used, the molecular configuration can be altered to produce three types of polypropylene: Atactic, Isotactic and Syndiotactic (see figure 5). Atactic polymers are characterized by their tacky, amorphous behaviour and low molecular weights. They provide the same effect as a plasticizer, by reducing the crystallinity of the polypropylene. From a commercial viewpoint, isotactic polypropylene is the most important. In comparison to atactic and syndiotactic, isotactic polypropylene is the most stereo-regular structure of polypropylene. From this, a higher degree of crystallinity is achieved. As a result, many of polypropylene's mechanical properties and processability are heavily determined by the level of isotacticity and thus crystallinity.



a. Atactic Polypropylene

b. Isotactic Polypropylene

c. Syndiotactic Polypropylene

Figure 5: atactic, isotactic and syndiotactic PP

Production process

Most of the world's synthetic carpets are made from polypropylene fibres, made by squeezing liquid material through many tiny holes, the spinning process and afterwards the material is stretched. However, the slit film method in which the polypropylene is extruded through a small slit was used from the beginning of polypropylene production. Biggest use for the slit film tape yarns was in carpet backing and industrial sackings. Fibrillated yarns were in the 1970's still under experimentation. Polypropylene can nowadays be found as monofilament, split or slit film in one form or another, multifilament and staple form. PP is usually pigmented before extrusion.

Degradation of polypropylene

The usefulness of polypropylene depends on the retention of their properties during a prolonged service life. Under mild conditions, not stabilised polypropylene will retain its properties for long periods of time. However in most applications, exposure to heat and light will occur which accelerate oxidative degradation, causing a decrease in elongation, loss in flexibility, development of surface cracks and discolouration.

Photo-oxidation

Polypropylene readily suffers photo-oxidation, resulting in embrittlement, yellowing and decrease in molecular weight. It is considered that the induction period represents the time necessary for the build-up of a sufficiently high concentration of peroxides which subsequently decompose by a free radical mode and cause rapid oxidation. The length of the induction period and the rate of subsequent oxidation depend upon availability of oxygen. Induction time is inversely proportional to the square root of the oxygen pressure, the maximum rate of absorption increasing directly with the pressure.

To retard oxidation and prolong service life, antioxidants and light stabilisers are normally added. These can be incorporated by any of the conventional thermoplastic compounding techniques. However, pigments are the most effective UV absorbers and a concentration of 5 percent of various organic and inorganic pigments has been found to restrict degradation of PP to surface oxidation, thus increasing the time to failure.

It is researched that channel black and furnace black are also mild antioxidants for PP. Their effectiveness increases with concentration and there is a correlation with the concentration of surface groups. However, they have a deleterious effect on mechanical properties at concentrations greater than 5% and at this level there are not efficient stabilisers at processing temperatures so additional antioxidants may be required [David, A., Sims, D., 1986].

The presence of metallic contaminants such as copper or copper compounds or Ziegler catalysts accelerate the thermal oxidation by catalysing the breakdown of hydro peroxides, producing a much higher concentration of radicals in polypropylene. It is known that the presence of the white pigment titanium dioxide (TiO_2) has a detrimental effect on the photo-oxidation of PP by absorbing large amounts of UV radiation [Shang J., 2003].

Thermal degradation
Polypropylene is rather stable to heat in the absence of oxygen and high temperatures are necessary to cause any significant decomposition. Activation energy calculated from decomposition rate is for PP close to the value of 66, 2 kcal/mole observed as the bond energy of a carbon-carbon single bond.

Chemicals
Polypropylene is highly resistant to chemical attack from solvents and chemicals in very harsh environments. Contact with some chemicals, such as liquid hydrocarbons, chlorinated chemicals, and strong oxidizing acids, can cause surface crazing and material swelling. In general, polypropylene is not susceptible to environmental stress cracking, and it can be exposed under load in the toughest environments.

ANALYTICAL RESEARCH

To verify the composition and study molecular changes, FTIR spectra of all 126 fibres of the book, and the fibres of the three works of art and relining material were recorded. Spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer combined with a Golden Gate single reflection diamond ATR unit (sample area 0.6 mm2). Spectra of the samples recorded from 4000 to 600 cm^{-1}, with 40 scans at a resolution of 4 cm^{-1} were compared with spectra of reference materials.

To study the orientation of the polypropylene polymer chains in the researched works, transmission spectra were measured with polarised radiation parallel and perpendicular to the sample surface. Spectra were recorded using a Perkin Elmer Spectrum 2000 FTIR spectrometer with a software controlled polarizer, combined with an Autoimage PerkinElmer FTIR-microscope. Spectra were recorded in the transmission mode (4000 to 700 cm^{-1}), 40 scans at a resolution of 1 cm^{-1}.

RESULTS AND CONCLUSION

The FTIR spectra of the three polypropylene samples of the book showed iso-tactic absorptions at 998 and 841 cm^{-1} due to the backbone of the PP structure, no carbonyl absorption was present. The spectra recorded with polarised radiation parallel and perpendicular to the sample surface, showed differences in the fingerprint region at 1168, 998, 973 and 841 cm^{-1} (see figure 6), this means that the PP chains are aligned in the fibre. It can be concluded that the PP fibres in the book are in perfect condition, due to the fact that they were never subjected to daylight. The book has been in the library, untouched, for more than 40 years.

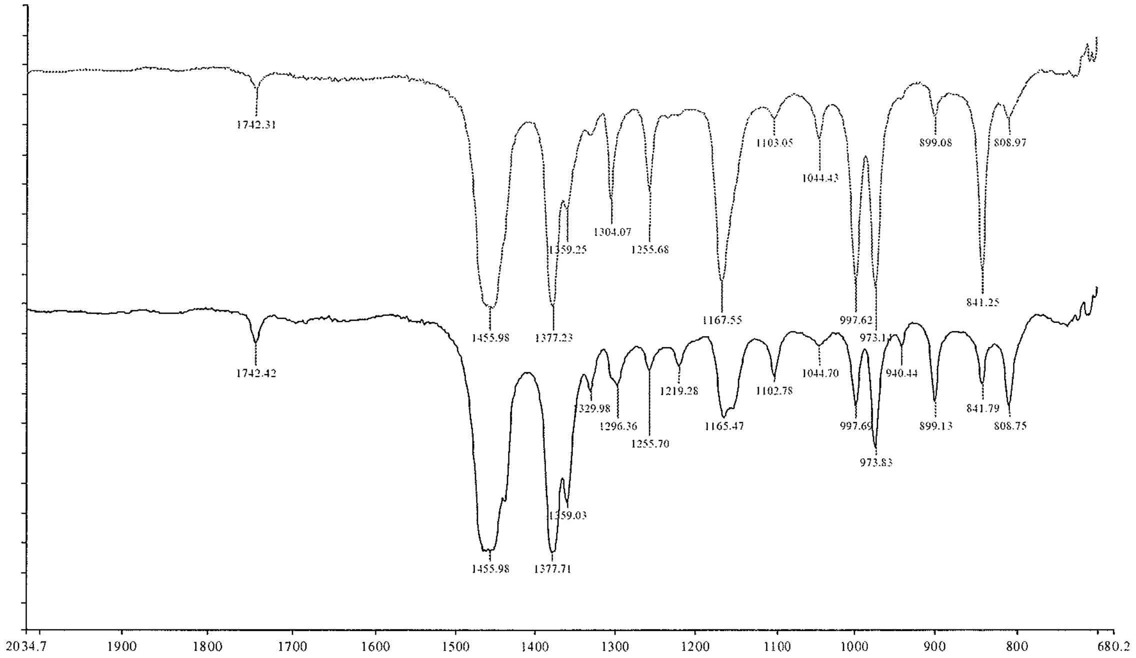


Figure 6:FTIR spectra of a PP fibre from the book: upper spectrum, ploarized radiation parallel to the sample surface and lower spectrum, polarized radiation perpendicular to the sample surface.

The FTIR spectra of the fibres of the white, blue, yellow, black and orange fibres of the tapestries 'Fête I' and 'Fête II' all showed absorption bands at 997 and 841 cm^{-1} indicating iso-tactic PP. Carbonyl (C=O) absorptions in the spectra indicate that degradation of the PP has occurred in a time span of 34 years. The infrared spectra of all fibres showed the presence of a polypropylene/polyethylene copolymer.

Polarized FTIR measurements of the black fibres of 'Fête I' showed differences in the fingerprint region of the spectra at 1168, 998, 973 and 841 cm^{-1}, indicating aligned PP chains in the fibre. The spectra of the yellow fibres (see figure 7) showed no differences in absorption, which means that the PP chains in the yellow fibres are randomly oriented. The other fibres from the two tapestries were not analysed using polarised radiation.

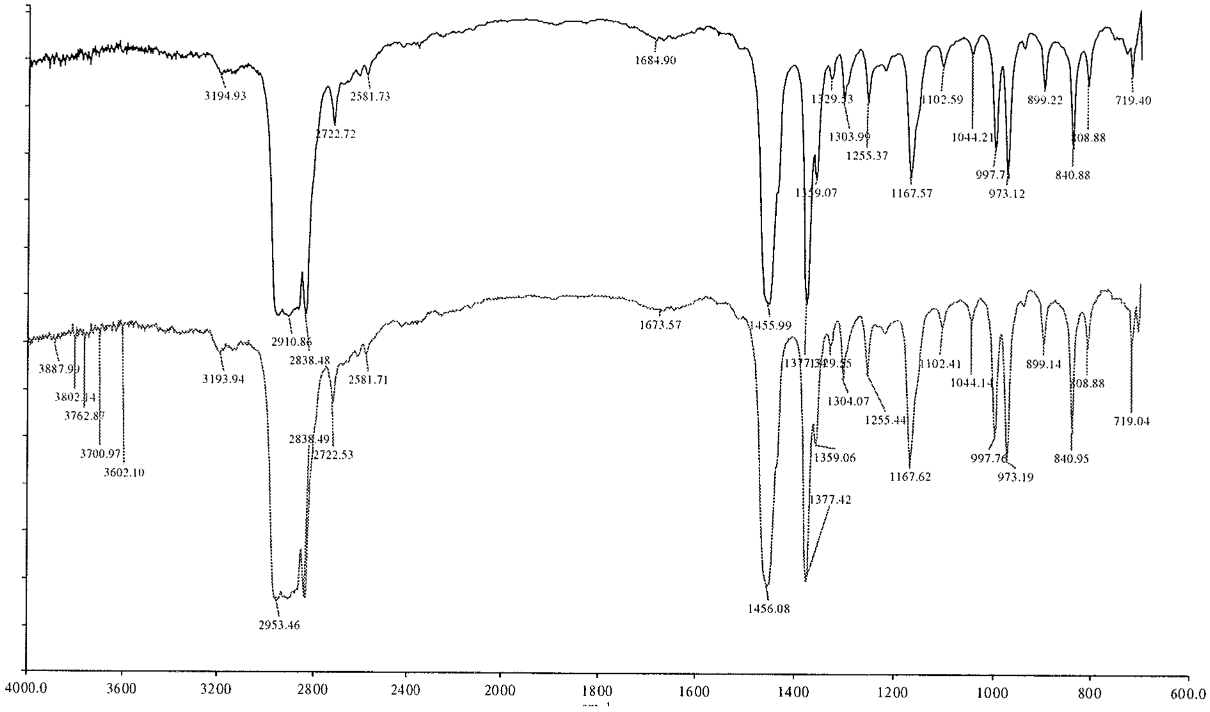


Figure7: FTIR spectra of a yellow fibre from 'Fête I': upper spectrum, polarized radiation parallel to the sample and lower spectrum, polarized radiation perpendicular to the sample surface.

Infrared spectra of the yellowed fibres of the art work 'the Knot' showed besides the carbon hydrogen absorption of iso-tactic polypropylene, also carbonyl (C=O) absorption and C-OH absorptions. Due to the oxidation of polypropylene, degradation products were formed, and moisture absorption had occurred. This tapestry has been put in a freezer at –20 ° C for three weeks for preventing infest from beetles, and therefore C-OH absorptions were noticed. The polarized radiation measurements showed no differences of absorption in the spectra, which means that the PP chains are randomly oriented in the fibre.

The infrared spectrum of the relining fabric showed absorption bands of iso-tactic polypropylene. Also carbonyl and water absorption bands are present, showing that the fibre is degraded and oxidation has taken place. Polarized radiation measurements showed aligned PP chains in the fibre. The results are summarized in table 1.

Table I. FTIR results and visual examination

Sample	**Poly propylene iso-tactic** (997 and 841 cm^{-1})	**Poly Ethylene** (717 cm^{-1})	**Carbonyl C=O** (1710 cm^{-1})	**C-OH absorptions** (3400 cm^{-1})	**orientation**	**Fibre or Film (SEM analyses)**	**Yellowed Brittle?**
PP (book) no. 95	+	-	-	-	aligned	Fibre	*
PP (book) no. 94	+	-	-	-	aligned	Fibre	*
PP (book)	+	-	-	-	#	Fibre	*
Fête II, white	+	+	+	-	#	Film	Brittle, not yellowed
Fête II, blue	+	+	+	-	#	Film	Brittle, not yellowed
Fête II, yellow	+	+/-	+/-	-	#	Film	brittle
Fête II, black	+	+/-	+/-	-	#	Film	brittle
Fête I, orange	+	+	+	+	#	Film	brittle
Fête I, white	+	+	+	-	#	Film	brittle
Fête I ,black	+	+/-	+/-	-	aligned	Film	brittle
Fête I, blue	+	+	+	+	#	Fibre	brittle
Fête I, yellow	+	+/-	+/-	-	randomly	Film	brittle
yellowed area "The Knot"	+	-	+	+	randomly	Film	Brittle, yellowed
Relining fabric	+	-	+	+	aligned	Fibre	Brittle/ not yellowed

+ present
± small amount present
- not present
* no changes
# not analysed

DISCUSSION

The three polypropylene fibres from the book are all in good condition. Neither degradation, nor yellowing was observed which was to be expected when PP is kept in the dark (as in the book).

UV-radiation/daylight and the freezer treatment have caused the serious degradation such as yellowing and embrittlement of the PP in the tapestries 'Fête I', 'Fête II' and 'the Knot'. It is known that normal extruded polypropylene (PP) can withstand a temperature of – 30° C, but iso-tactic polypropylene under stress becomes brittle at –20° C already.

The pulverised relining fabric is probably degraded by the solvent diaceton-alcohol that was not fully evaporated from the old linen from the painting before the PP relining fabric with the adhesive was applied.

Only 6 samples were measured with polarized radiation. The results show the possibility to differentiate between randomly oriented and aligned PP chains. In order to conclude if there is any relation of these results to the production method or degradation of the PP fibres, more research is needed.

Overall it can be stated that photo-oxidation has occurred in all cases where UV-radiation and or daylight is involved, which is not a new phenomenon, but not expected for works of art in a timescale of 40 years.

White fibres containing TiO_2 are more damaged due to the fact that TiO_2 absorbs large quantities of UV-radiation. The other degradation phenomenon due to freezing was not anticipated for PP was not supposed to be present in a natural fibres tapestry.

ACKNOWLEDGEMENTS

We would like to thank Judith van Beukering (Katholieke Universiteit Nijmegen) and Caroline Vos (Beheer Collectie of the ING bank) for giving us the opportunity to do research on the Wil Fruytier tapestries. We would also like to thank Kathrin Kirsch (Stichting Restauratie Atelier Amsterdam) and Martijn ter Horst (private conservator) for drawing our attention to the pulverized relining material. We thank Ineke Joosten (ICN) for performing SEM analyses on the different fibres. And thanks to Tom Visser and Fouad Soulimani from the University of Utrecht for allowing us to use their FTIR microscope in combination with the polarizer.

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Raman and SEM Study of Pigments from Frescoes of Roman Age in the Thamusida Site (Rabat, Marocco)

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The site of *Thamusida* is situated near the modern town of Kenitra, about 45 km north of Rabat (Morocco). The town was founded by the Romans in the 1st century A.D. to serve as a garrison, a large river port and a control centre along the boundary of the Empire.

Frescoes with geometric designs were mainly found in the bath complex. The decorations were made of red, yellow, green, blue, white and black pigments. Furthermore, several spheres of pure blue pigment were discovered and sampled for the present research.

MATERIALS AND METHODS

In this study, 12 fragments from the frescoes found in the Thamusida site were selected on the base of the following criteria: the context within the building, the colour of the pigments, the macroscopic characteristics of the plaster layers and the state of conservation of the fragments. Furthermore 2 spherical aggregates of blue pigment have been studied.

Micro-Raman spectroscopy was performed on the entire set of samples at the University of Siena. The instrument used is a Jobin-Ivon LTD confocal Labram multichannel spectrometer equipped with a Peltier-cooled charge-coupled device (CCD) detector and an Ar^+ Laser (λ = 514.5 nm). The scattered light was analysed using a Notch holographic filter with a spectral resolution of 1.5 cm^{-1} and a grating of 1800 lines x mm. Scanning electron microscope with energy dispersive spectrometer (SEM-EDS) were used to further characterise pigments. The instruments used were a SEM Philips XL 30 equipped with EDS EDAX-DX4 working at 20 kV.

RESULTS AND INTERPRETATION OF PIGMENTS INVESTIGATIONS

Raman analysis

- *Minium Cinnabaris* [Synonym: Vermilion. Constituent: Cinnabar. Chemical formula: HgS] (Fig. 1a). It appears as a pure red pigment.
- *Rubrica* [Synonym: Red Ochre. Constituent: Hematite. Chemical formula: Fe_2O_3] (Fig. 1b). Used as a pure red pigment.
- *Sil* [Synonym: Yellow ochre. Principal constituent: Goethite. Chemical formula: FeO(OH)] (Fig. 1c). Used for the yellow colour and mixed with *creta* to obtain the light yellow tonality.
- *Caeruleum* [Synonym: Egyptian Blue. Principal constituent: Cuprorivaite. Chemical formula: $CaCuSi_4O_{10}$] (Fig. 1d). It was widely applied, either as a pure blue pigment or as a component of the dark grey green (mixed with *Atramentum*).
- *Creta viridis* [Synonym: Terra Verde. Principal constituent: Celadonite. Chemical formula: $K(Mg, Fe^{2+})(Fe^{3+}, Al)[Si_4O_{10}](OH)_2$] (Fig. 1e). The Raman spectra obtained from this pigment show significant similarities with those of the celadonite from Monte Baldo (Verona-Italy) (Fig. 2f). Used for the green colour and mixed with *Atramentum* to obtain the grey green tonality.
- *Creta* [Synonym: Whitewash. Principal constituent: Calcite. Chemical formula: $CaCO_3$] (Fig. f) and *Atramentum* [Synonym: Coal black] (Fig. f). Used respectively for the white and the black colours but also to lighten or darken the other pigments.

The spherical aggregates of blue pigment contain crystals of cuprorivaite including quartz grains. The external surface of these lumps shows a light yellow layer of calcite.

The results of the pigments analysis allowed the reconstruction of the decorators' palette.

SEM analysis

SEM analysis were employed to determine the chemical composition of the minerals constituting the pigments and the textural features related to the painting technique. The chemical analysis confirmed the mineralogical identification obtained by micro-Raman spectroscopy and provided additional information on the blue pigment. The spherical aggregates of blue pigment resulted to be composed of cuprorivaite, quartz and calcite crystals with some Sn- and Cu-micro-nuggets (Fig. 2). The occurrence of these metals indicates a production technology that developed during roman times, employing rather cheap scrap metals instead of more expensive malachite.

As regards the painting technique, modest thickness variation of the painted layers has been observed, mainly depending on the kind of applied pigment.

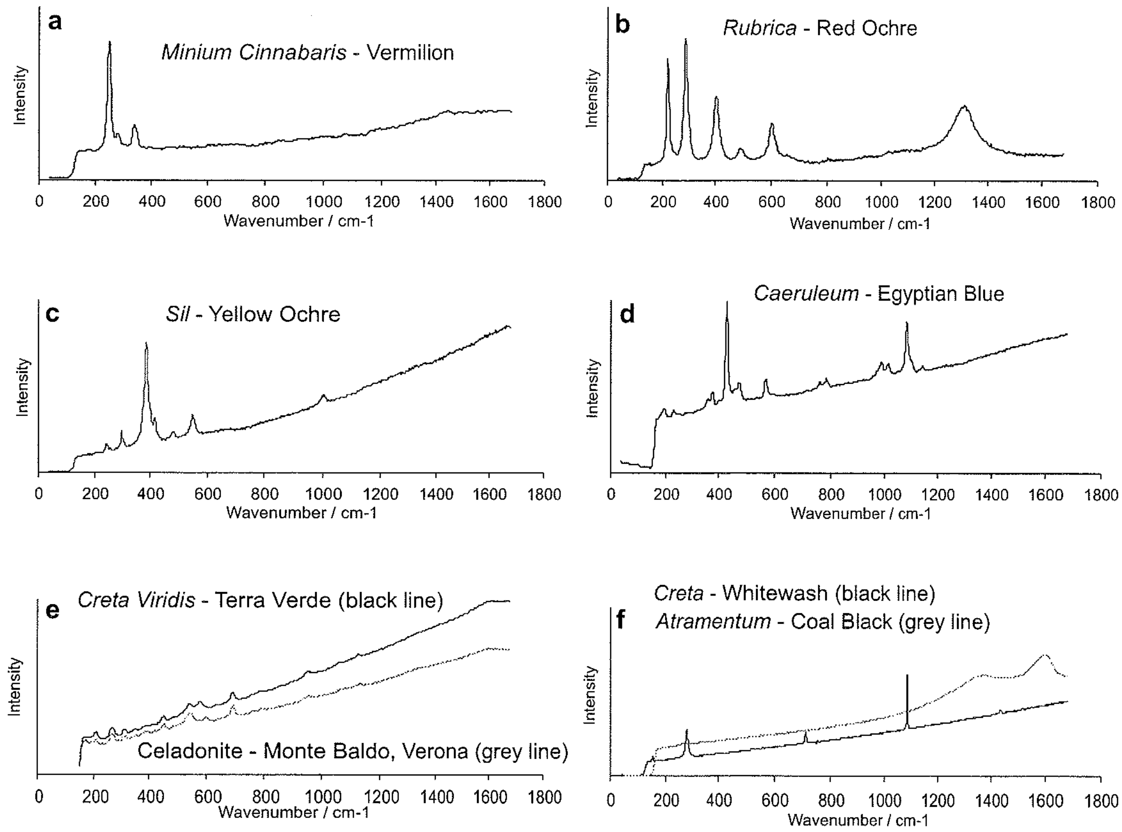

Figure 1 – Raman spectra of the sampled pigments.

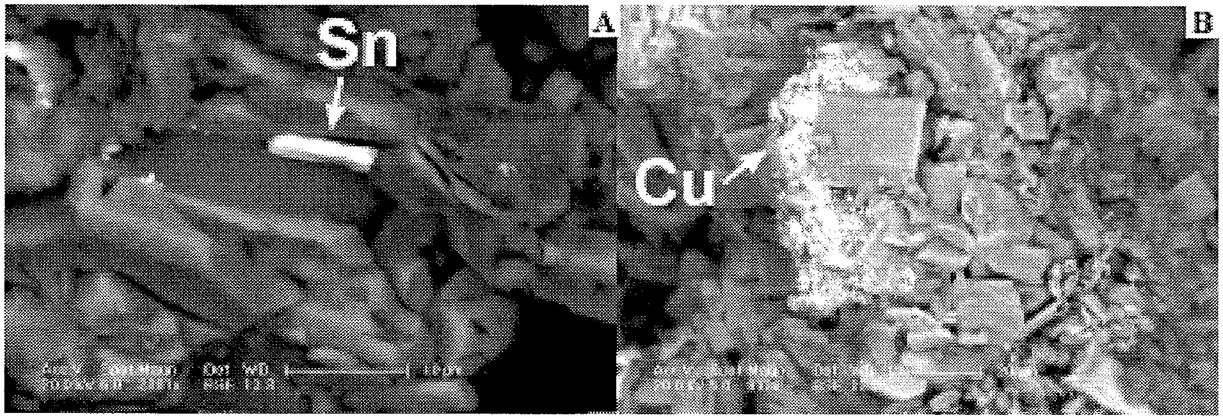

Figure 2 – SEM images of tin (A) and copper (B) micro- nuggets in the spherical aggregates of *Caeruleum.*

A combination of FT-IR, FT-Raman and GC-MS techniques for the identification of pastes from an archaeological site at Beagle Channel, Tierra del Fuego, Argentina

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Archaeological samples are very complex in composition, since their preparation generally involves a mixture of materials submitted to deterioration factors that are largely dependent on the environmental conditions. In the case of pastes, the presence of an inorganic and an organic phase, adds up to the system complexity. Therefore, the use of complementary analytical tools such as FT-IR, GC-MS and more recently non destructive FT-Raman spectroscopy can maximize the amount of information provided by a sample, allowing a better understanding of its degradation process.

In continuation of our studies on archaeological pastes [1-3] we have studied two samples of red painting residues that were in stratigraphic position in the archaeological site Shamakush I in Tierra del Fuego, Argentina. The two samples were found in strata dated by ^{14}C in 940 ± 100 B.P. and belong to hunter-gatherer-fisher societies that started their littoral adaptations in the Beagle Channel coast 6200 BP. Analysis by FT-IR of the pastes revealed the presence of strong bands at 543 and 470 cm^{-1} characteristic of hematite together with bands at 2931 and 2859 cm^{-1} due to C-H stretching vibrations in methyl and methylene groups and a carbonyl band at 1743 cm^{-1}. These bands are characteristic of lipids. The FT-Raman spectrum of one of the pastes confirmed the presence of hematite and showed an intense band due to double bond stretching at 1602 cm^{-1} characteristic of unsaturated lipids. Analysis by GC-MS of the mixtures of fatty acids obtained by transesterification of both pastes confirmed the presence of saturated (C_{15}, C_{16}, C_{17}, C_{18}) and unsaturated (C_{16}, C_{17}, C_{18}) fatty acids together with a mixture of hydrocarbons.

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A Study of the marble low-relief "Deposizione di Cristo" by Benedetto Antelami in the Parma Cathedral

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The famous marble low-relief "Deposizione di Cristo" is the first dated work (1178) of Benedetto Antelami (active 1170-1230) and is now located on the right wall of the right branch of the transept in Parma Cathedral (Italy). The Cathedral (or *Duomo*) is one of the main examples of 12th century Romanesque architecture in northern Italy.

Here we present an investigation by vibrational spectroscopic techniques (micro-Raman[1], micro-FTIR and fiber optic mid-FTIR reflectance spectroscopy[2]), X-ray fluorescence (XRF) and gas chromatography coupled to mass spectroscopy (GC/MS)[3] on the polychromatic inscriptions (red and green), black decorations and on the surface of the Antelami's artwork. The fiber optic mid-infrared reflectance and XRF measurements were performed *in-situ* then 21 sub-millimetric (20-40 mg) samples were taken for the study by micro-Raman and micro-FTIR spectroscopies and by GC/MS.

The red pigment was identified by micro-Raman spectra as cinnabar (HgS), in agreement with the XRF measurements, and no alteration products of cinnabar have been found. In the green inscriptions, a strong fluorescence masked any possible Raman signal from the copper-based pigment, detected by XRF The black material present as the background of the red and green letters and decorations, which appears of complex morphology, gives only the typical Raman spectrum of the carbon black. The XRF results indicate that this dark background contains iron, copper and lead.

In situ mid-infrared reflectance measurements show the diffuse presence of oxalates, silicates and sulphates on the marble surface, as well as an organic patina (lipids, amides and esters). GC/MS and FTIR measurements on the samples taken from the surface, indicate the presence of beeswax and protainaceous material due to the use of egg. Calcium oxalate and gypsum were also identified.

The study of such a complex artwork required the use of many techniques. Micro-Raman spectroscopy was useful to doubtless identify cinnabar, but failed to find other compounds due to the very strong fluorescence of the organics. The portable non–invasive techniques showed their ability to collect important information without damaging the artwork, in particular about the elements present in the pigments and on the dark background for the XRF, and about the organics and oxalates (which are non detected by XRF) for the fiber optic mid-infrared reflectance. The use of micro-destructive techniques (micro-FTIR and GC-MS) allowed to complete the characterization of the organic compounds, identifying the presence of beeswax and egg.

We may summarize the results as following:

- Marble surface: calcium oxalates, gypsum, silicates (probably from atmospheric dust), organic patina (beeswax, egg);
- Red inscriptions and red traces on decorations: cinnabar;
- Green inscriptions: copper based pigment;
- Black background of inscriptions, figures and vexillums: iron-copper-lead containing layer.
- Black background of the frame decoration (acanthus leaves): iron based material with titanium.
- Organic binders of the pigments and background: beeswax and egg.

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Raman and FT-IR identification of pigments in Roman wall painting fragments found in Parma (Italy)

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The study of pigments and compounds found in archaeological wall paintings gives important contribution in the chronological attribution of an artwork, in the painting technique understanding and to establish the provenance of the materials.

In this work we present some results of vibrational spectroscopy investigations on wall painting fragments from different archaeological sites, presumably of the Roman age, that have been discovered in the last thirty years in Parma (Italy). The present study was carried out in collaboration with the National Archaeological Museum of Parma, where the fragments are preserved.

The samples, analyzed by means of micro-Raman and FT-IR, are centimeter sized fragments of painted plasters, characterized by a thin layer of *intonachino*, decorated in plain color or with geometrical patterns. The aim of the study, performed also on cross sections of the samples, was to verify the compatibility of the pigments present in the decorations with the painting materials used in the Roman age.

The pigments found are hematite, goethite, calcite, cinnabar, carbon, magnetite, celadonite and Egyptian blue. The combined use of micro-Raman and FTIR allowed high spatial resolution together with a good sensitivity also for pigments with very weak Raman signal as the green earths.

A mural painting by Estrela Faria, a FTIR study of a vinyl synthetic medium

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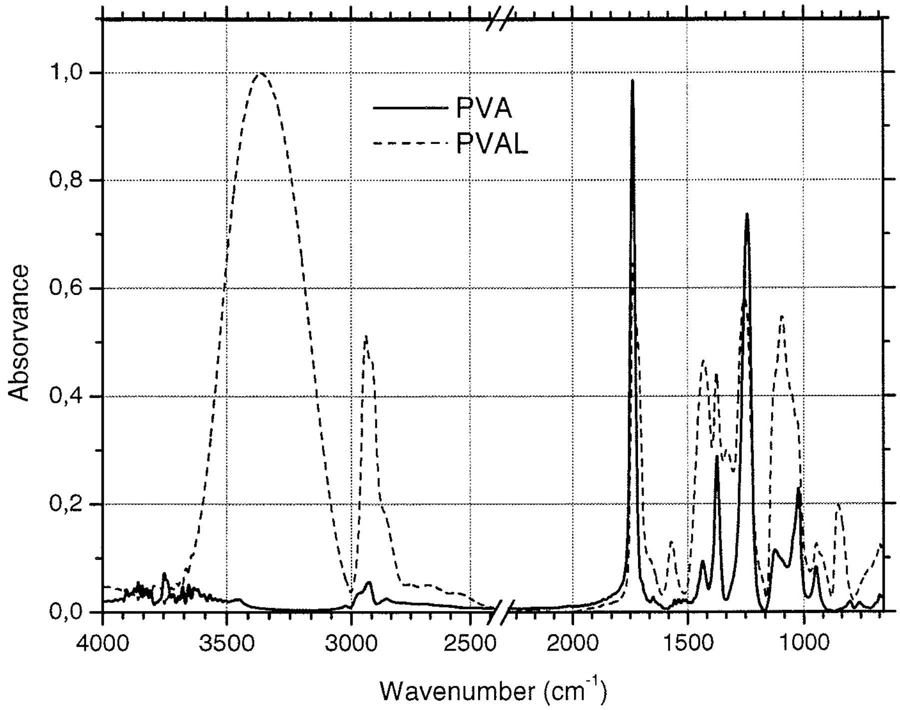
As it happened in other countries, Portuguese artists soon realized how much new synthetic paints had to offer. At least since the early sixties, Portuguese painters have been using vinyl emulsions as a binding medium; Joaquim Rodrigo (1912-1997) and Ângelo de Sousa (1938-) were certainly some of the foremost and their first vinyls date from exactly 1961.

Estrela Faria (1910-1976) was an eclectic artist and yet she typically used traditional painting techniques. For a while she was the responsible for a *fresco* class at a professional art school[1]. In the second half of the sixties, Estrela was nominated to paint a mural at the entrance of a new high school in Lisbon, *Escola Secundária Padre António Vieira*[2], where she exploited a synthetic binding medium, either for artistic or economical reasons. The aim of this study is to characterize, by FTIR microspectroscopy, the poly(vinyl acetate) paint employed by Estrela Faria on her mural, as well as to test the potential of the technique in the investigation of the vinyl binding media degradation.

For a complete characterization of the pictorial materials present, a FTIR database was built with the standard samples considered necessary to interpret the mural painting colors'. These standards were grouped as: binding media (PVA, PVAL, Mowilith DMC2, Vulcano V7 and V2), pigments, commercial white paints and paints reconstructions. Furthermore, we simulated the poly(vinyl alcohol), PVAL (figure 1), concentration increase on a poly(vinyl acetate), PVA (figure 1), spectrum; this was intended to test the detection limit for the PVAL on a PVA matrix (figure 2). The PVAL presence can be explained by its use as a copolymer, additive or as a degradation product.

Figure 1 – PVA and PVAL FTIR spectra



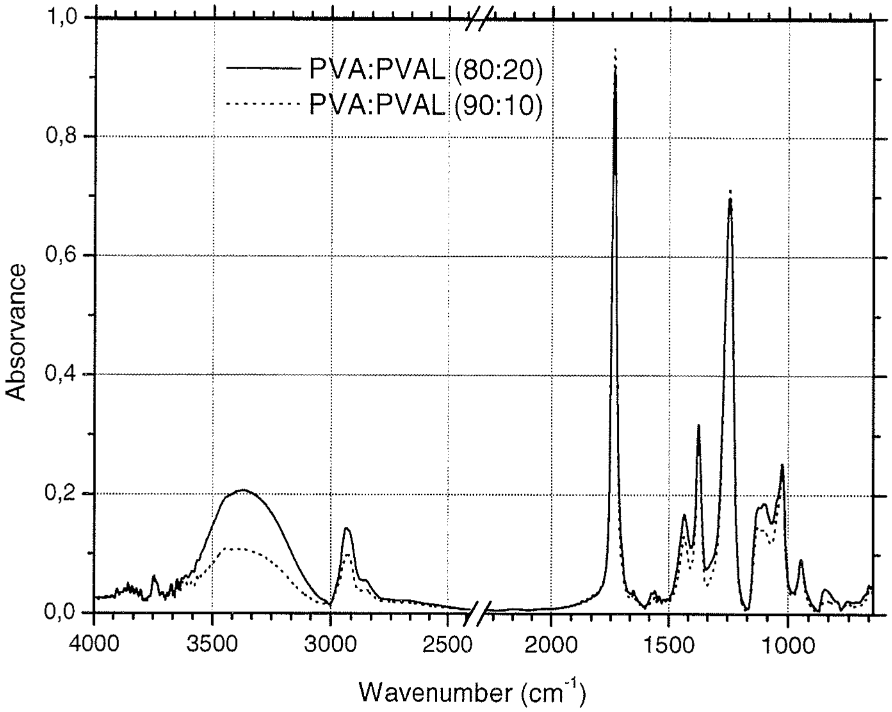


Figure 2 –FTIR spectra simulations of PVA and PVAL mixtures (PVA spectra norm. at 1740 cm^{-1} and PVAL norm. at 3367 cm^{-1})

The reliability of this computer simulation is further confirmed by comparison of the C=O/O-H ratio with literature spectra of copolymers[3] and standard samples obtained by mixture.

Based on these results, it was possible to predict that for concentrations below 5% it will be very difficult to ascertain the presence of PVAL in the PVA matrix. Only above 10% the PVAL presence is easily detectable. Therefore, if PVAL is used as an additive in amounts below 5% or is produced in the earlier steps of photodegradation it will be difficult to detect and quantify by microFTIR.

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4: Fundação Luso-Americana para o Desenvolvimento, FLAD
5: Fundação para a Ciência e Tecnologia – Ministério da Ciência, Inovação e Ensino Superior

Red lake pigments in Old Master paintings: What can FTIR spectroscopy tell us?

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The use of lake pigments in paintings

Natural organic dyestuffs obtained from various plant and insect sources can be used as artists' pigments if they are co-precipitated with an inert, semi-transparent inorganic substrate. The reaction between potash alum (potassium aluminium sulphate, $AlK(SO_4)_2.12H_2O$) and an alkali forms a type of hydrated alumina which precipitates from solution. Up to the 19th century, lakes were prepared by this means, the reaction taking place in a solution of dyestuff. Although lake pigments can be used in a range of binding media, artists often exploited the translucency of traditional lakes by using them as glazing pigments, applied in oil, or oil to which a little resin was added.

Use of FTIR spectroscopy in the examination of red lake pigments

The natural dyestuff components found in red lake pigments can readily be characterised in the pure state by IR spectroscopy but in traditional red lake pigments the dyestuff content is very low and the IR spectra tend to be dominated by bands deriving from the inorganic substrate. However a recent study undertaken at the National Gallery suggests that IR spectroscopy can, when used in combination with other analytical techniques, be a valuable tool in determining the method of lake pigment manufacture.

The recent National Gallery study focused on the technology of red lake pigment manufacture and investigated the influence of the dyestuff, the alkali and alum sources and the recipe on the composition of the resulting lake pigment. An analysis was made of the dyestuffs and other raw materials used to make the pigments, and of a range of lake pigments made in the laboratory following historical recipes, as well as of lake pigments in samples taken from paintings in the National Gallery Collection.

Influence of the recipe and method of substrate manufacture

The lake pigment substrate is normally loosely described as hydrated alumina. It is difficult to characterise, partly because it is amorphous and highly variable. The exact nature of the substrate produced depends on a number of factors including the order of addition of the potash alum and the alkali. EDX and FTIR examination of the substrates of the laboratory-prepared lakes and of the lake pigments in paintings revealed that essentially they fall into two groups, linked to the method of preparation.

Type 1: Amorphous hydrated alumina

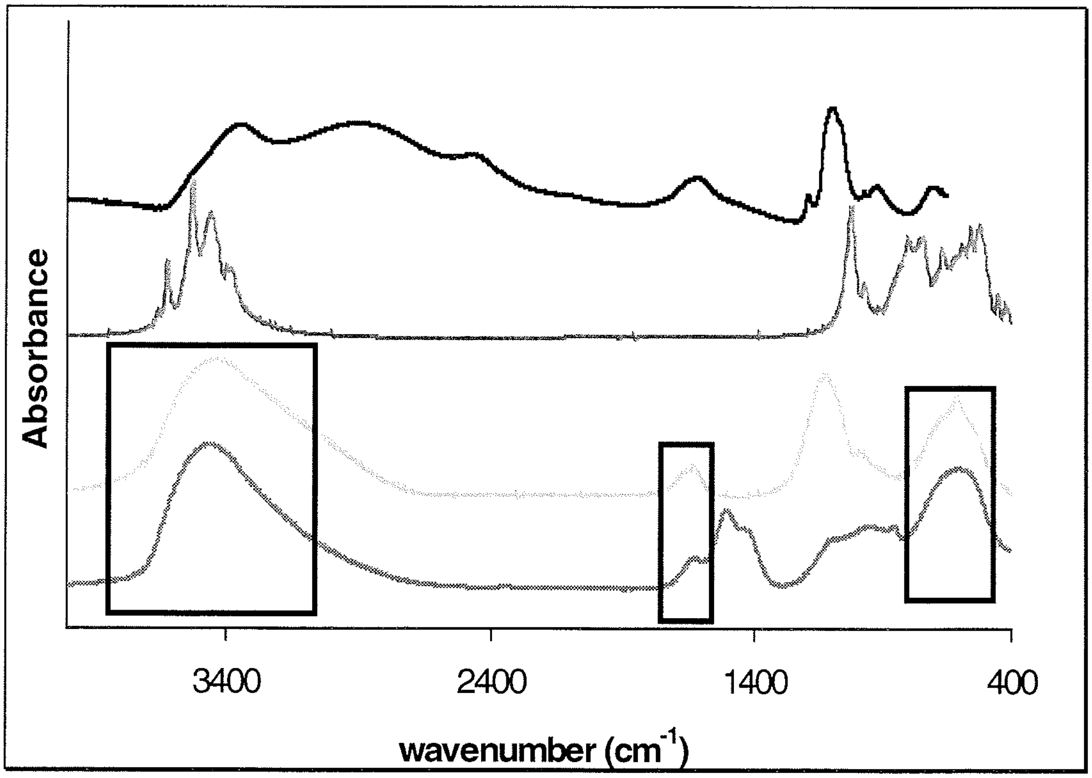
Most lakes, even into the eighteenth century, appear to have been made by extracting the dyestuff using alkali, followed by the addition of alum to precipitate the pigment, yielding a substrate containing Al and O which is best described as *amorphous hydrated alumina.* Examination by FTIR revealed the presence of Al–O bands. Hydrated alumina is gelatinous and highly absorbent when first precipitated; thus if precipitation is rapid, a certain amount of carbonate from the alkali may be brought down as well.

Type 2: Light alumina hydrate

The second type of substrate is more typical of 19^{th}-century lakes and is produced when alkali is added to a solution of alum. In this case sulphate anions become incorporated into the substrate as it precipitates. It has been described as *light alumina hydrate.*

FTIR spectra show sulphate S-O bands (S–O vibrations at 1125 and 985 cm^{-1}) of similar size to the Al-O bands, and sulphur is detected in addition to Al and O by EDX.

In addition to sulphate and carbonate anions, other anions may become incorporated into the amorphous hydrated alumina substrate. For example phosphate anions have often been found in lake pigments from paintings and in pigments prepared in the laboratory. If they are present in significant quantities then the sulphate band can be shifted to c. 1080 cm^{-1}. Phosphate anions are most common in lakes where the dyestuff comes from an insect source, especially where the dyestuff is obtained directly from the insect.

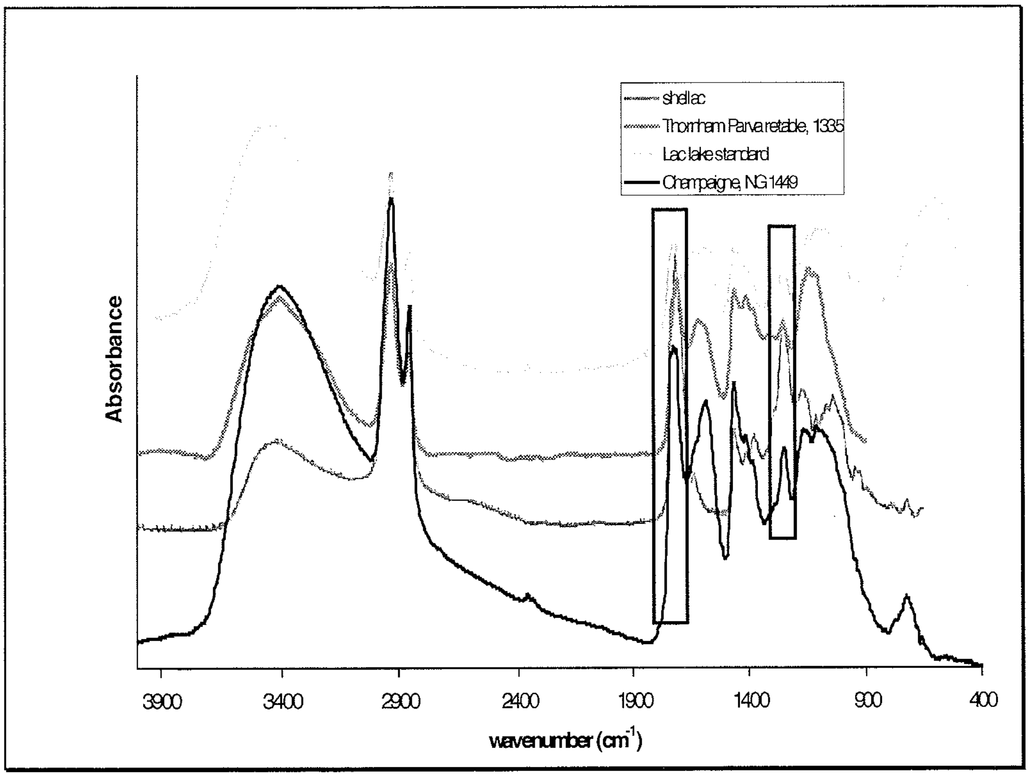


Broad bands linked to vibrations of the Al–O crystal lattice may be observed below 950 cm^{-1} and vibrations due to coordinated water occur as broad bands at c.1650 and 3400 cm^{-1}.

Influence of method of dyestuff extraction and problems of binding medium identification

The evidence from documentary sources suggests that from the 14th to the 17th century for lakes prepared from kermes, cochineals and probably madder, the source of the dyestuff was shearings of textile dyed with these colorants. However lac (in the form of sticklac) and brazilwood were probably used directly as sources of dyestuff.

In most recipes for lac lake pigments the entire raw material, sticklac – which is also the source of shellac resin – was ground and extracted with alkali; alum was then added to precipitate the lake. Alkaline extraction of sticklac brings into solution not only the water-soluble dyestuff components, the laccaic acids, but also the alkali-soluble dyestuffs and the shellac resin itself.



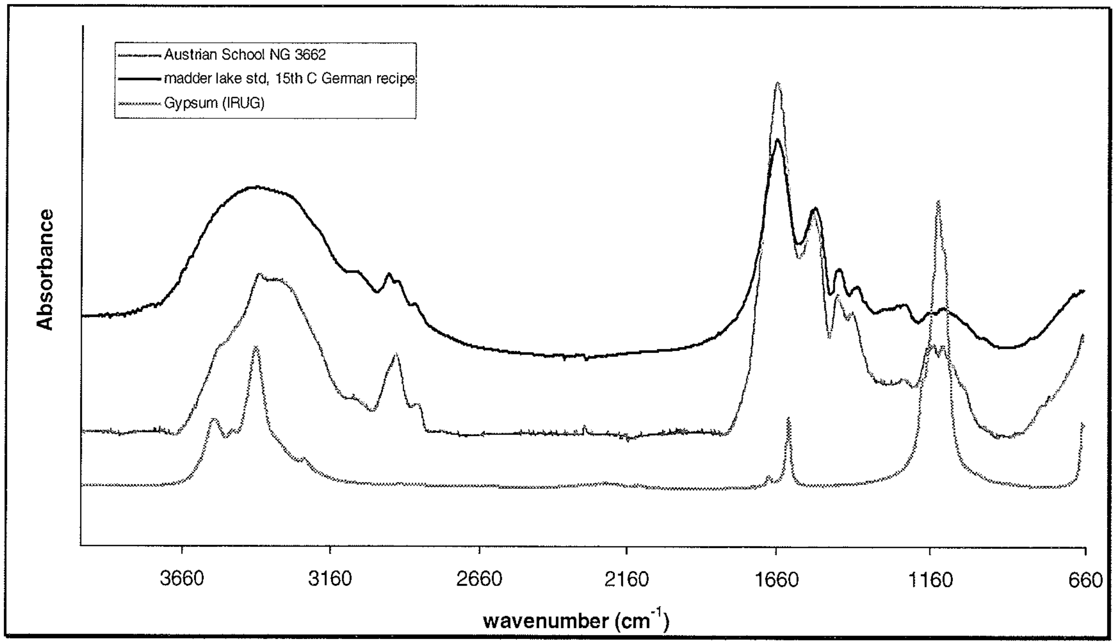
Shellac constituents have been detected by FTIR spectroscopy in red lake samples from paintings dating from the 13th to 17th century including Philippe de Champaigne Cardinal de Richelieu (NG 1449) 1633-40 and English School, Thornham Parva retable, 1335

Shellac resin can readily be identified by IR spectroscopy (bands at 1735 and 1715 cm^{-1} [ester and acid C=O bands] and 1240 cm^{-1} [ester C–O band]) and its presence in lac lake pigments prepared in the laboratory by alkaline extraction, and in samples from paintings, has been confirmed by FTIR microscopy and GC–MS analysis. Because a small amount of resin was often added to red lake-containing glaze paints (to increase transparency), it is important to appreciate that the lake pigment itself can sometimes be the source of resin absorbance bands.

Extraction from dyed textiles

In some lake pigment recipes which describe the extraction of the dyestuff from dyed textile material, the alkali used is described as strong enough to dissolve a feather; it would therefore be capable of dissolving a proteinaceous textile fibre such as wool. The madder lake pigment used in the Angel's wings and God's robe in the Austrian School, *The Trinity with Christ Crucified* (NG 3662), c. 1410 seems to have been prepared in this way from madder-dyed wool, since the IR spectra of the pigment are dominated by amide bands (c.1650 and 1550 cm^{-1}). The pigment particles have distinctive ragged edges in the back-scattered image in the SEM and the substrate was surprisingly rich in sulphur (shown to be present as organic sulphur derived from wool rather than sulphate) with relatively little aluminium.

The protein content of the paint from the Austrian school work as seen by IR spectroscopy was initially taken to suggest the use of a proteinaceous paint medium, but was contradicted by the GC-MS analytical results which detected linseed oil, as elsewhere in the painting. The apparently contradictory analytical results obtained for the Austrian School painting were resolved once it was appreciated that red lake pigments prepared by the alkaline extraction of dyed wool and silk could contain significant proportions of protein.



Note: The Austrian School sample contains a little hydrated calcium sulphate as a component of the red lake. The madder lake standard was produced following a 15th-century German recipe (Nuremburg Kunstbuch), using a strong alkali solution to extract the dyestuff from wool dyed with madder.

Experimental

The methods used for investigation of the inorganic constituents of the lake pigments were SEM–EDX and FTIR microscopy and spectroscopy. HPLC was used to analyse the dyestuffs; the medium and other organic constituents of the paint samples were identified by GC–MS and FTIR. In certain cases microchemical tests were used. Equipment details: Nicolet 710 Series FTIR bench with DTGS detector (spectral range 4000–400 cm^{-1}) connected to a Nic-Plan IR microscope with MCT-A detector (spectral range 4000–650 cm^{-1}). Samples examined in diamond micro compression cell under microscope or as 13 mm KBr pellet in bench (with paper inserts and beam condenser for paint samples)

Acknowledgements and references

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Analytical Investigations of wall paintings from Mogao Grottoes

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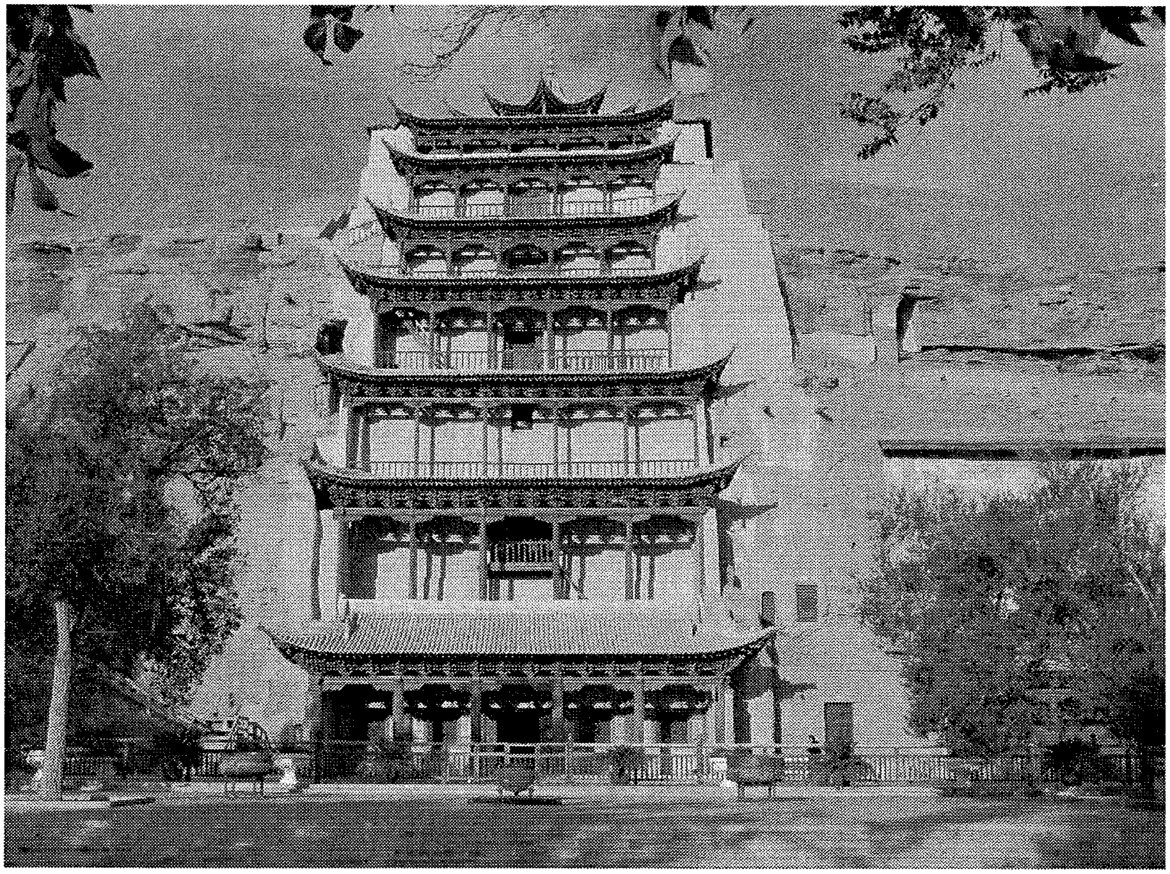
In efforts to advance the understanding of materials and techniques associated with wall paintings from the Mogao Grottoes in Dunhuang, China several analytical techniques, including Raman and FTIR spectroscopy, were utilized in the study. Located on the Silk Road and designated as a World Heritage Site, the area was an important historical stop for traveling caravans as well as religious pilgrimages by Buddhist monks to India. The grottoes dating from the 4th to the 14th centuries contain 700 caves that were excavated into a 1.6 km of cliff face, and of which, 492 are decorated with beautiful wall paintings and polychrome sculptures. The wall paintings were executed as line drawings in red and black ink on plaster, and filled in with bright pigments and organic colorants.



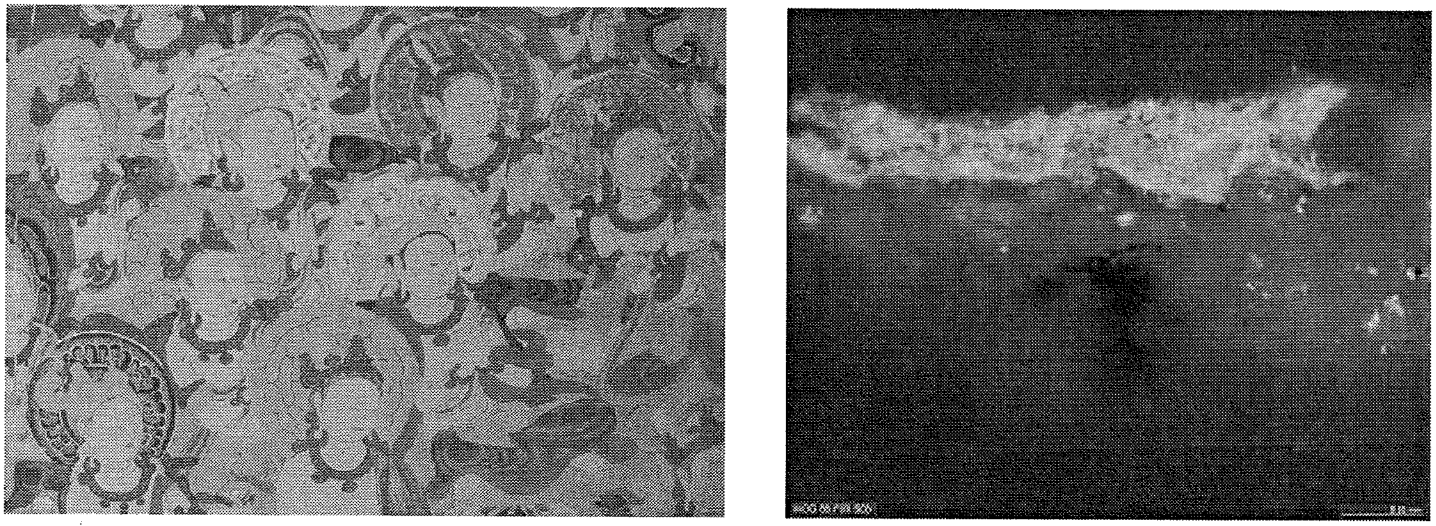
The distinct nine-story pagoda located on the facade of Mogao Grottos

An important component of the analysis was understanding the detailed composition of the paint samples and determine whether the top layers contained any organic pigments or dyes that might be sensitive to light exposure. The findings were intended to help Chinese cultural heritage officials design proper lighting systems to minimize exposure of wall paintings and enhance visitor viewing experience.

FTIR was utilized in the identification of top fluorescing layer from paint flake samples originating from caves 98 and 323. The presence of proteinaceous coating material as well as oxalates, iron oxides and talc were confirmed. In addition to the FTIR, the Raman technique was utilized in the identification of material in paint samples origination from the same and other caves. The purpose of the analysis was to understand the composition of paint layers, including organic pigments or dyes, that might be sensitive to light exposure. Most of the samples were found to contain hematite and vermilion.

The GC/MS technique was employed to better understand the composition of organic materials, including the top fluorescing layer and binding media. Fruit gums such as peach and tragacanth as well as glue were found in various layers of paint. Other monosaccharides present in dyestuff were found in select areas of wall paintings.

Both the x-ray fluorescence (XRF) and scanning electron microscope (SEM) techniques were used to further investigate the composition of outer layers. The presence of lead, mercury and sulfur were confirmed with SEM while the XRF showed high concentrations of iron, lead and calcium.



Sample 8 originating from cave 85 shows the presence of cinnabar

NIR-FT Raman and SEM analyses of cross sections from wall paintings at Lumby Church, Denmark from 15th century

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Near-infrared Fourier transform Raman investigations were employed to investigate cross-sections, taken from wall paintings at Lumby Church. The church is one of the well-preserved churches from the 15th Century in Denmark. The wall paintings, which were performed in limewash painting, were first revealed in 1959, when the church was undergone restoration. The cross sections represent four different pigments, taken from different motives, being one yellow, two red and one green. The results from NIR-FT Raman have shown that the yellow pigment is litharge. SEM/EDX analysis was also employed, and the results from Raman were confirmed. Here, we report on this novel study and the results will be discussed.

Examination of Degradation Behavior of Book Binding Leather Using FT-IR spectroscopy

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FT-IR micro-spectroscopy was applied to examine specific absorptions of degraded book binding leather. Powdery samples (red-rot) of book binding leather and fresh samples were compared. Leather is composed of collagen, a kind of structural protein or scleroprotein, having polypeptide structure of many different amino acids. Leather usually shows strong absorptions of Amide1 (1650cm^{-1}), Amide2 (1550cm^{-1}) and Amide3 (1243cm^{-1}). Remarkable spectral differences were observed commonly between the powdery and the fresh samples. Degraded samples show strong absorption at both 1717cm^{-1} and 1400cm^{-1} and weak absorption at 1030cm^{-1} compared with the fresh samples. The absorptions of 1717cm^{-1}, 1400cm^{-1}, 1030cm^{-1} were attributed to C=O stretching vibration, symmetric bending of CH_3 and symmetric bending of CO in hydroxymethyl group, respectively. These chemical changes of collagen are associated with natural aging. It has already reported that leather collagen break down by hydrolytic, oxidative and photochemical degradation. However, the spectral features we observed cannot determine which of these environmental factors is responsible for the change. Therefore, we are examining behavior of spectral changes of fresh vegetable tanned leathers in the process of degradation by three conditions of artificial accelerated aging: exposing to high moisture (40°C 90%R.H.), sunlight and acidic air by SO_2 gas. Changes of specific absorptions to the accelerated aging conditions are investigating to discuss aging mechanisms of book binding leather.

Application of a self-built cell for in-situ IRRAS investigation of non-transparent materials

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A new experimental set-up for studying reactions occurring on the surfaces of materials in controlled atmospheres by InfraRed Reflection Absorption Spectroscopy (IRRAS) is presented. It consists, as shown in Fig.1, of the reaction cell, where the sample is mounted and the in-situ investigations are carried out, a gas mixing unit, where the moist air is generated with or without corrosive gases (Fig. 2), and an optical system coupled to the Fourier Transform InfraRed (FTIR) spectrometer (Perkin Elmer FTIR Spectrometer, Spectrum 2000). It was applied in combination with in-situ Tapping Mode Atomic Force Microscopy (TM-AFM) and Phase Detection Imaging (PDI) to study the early stages of weathering of pure copper and pure zinc as well as to determine the influence of increasing zinc contents in brass. Additionally, ex-situ Secondary Ion Mass Spectrometry (SIMS) was carried out on the specimen after exposure. The investigations were accomplished in synthetic air with 80 % Relative Humidity (RH) and synthetic air with 80 % RH and 250 ppb SO_2 and showed that an increase of the zinc content in the brass alloy yields to an increase of the corrosion formed on the metal surfaces during weathering. Additionally, investigations on pure iron as well as silver and silver-copper alloys have been carried out. The setup proofs to be a useful tool also for studying the degradation processes of glass and polymers.

(Illustrations on following page.)

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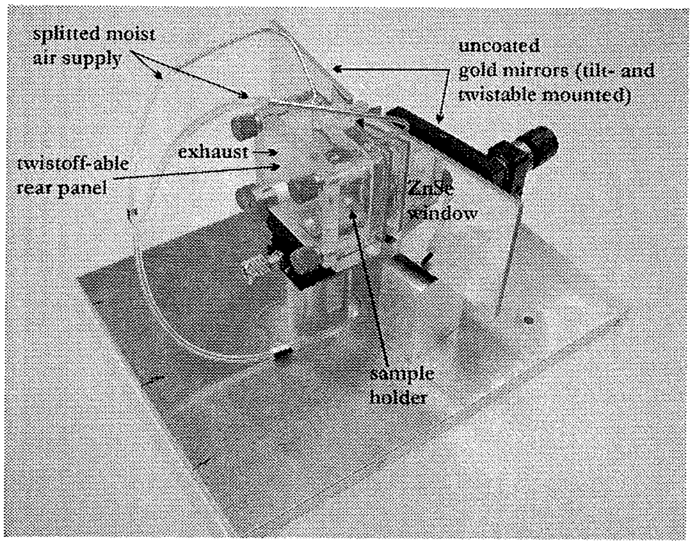

Fig. 1a

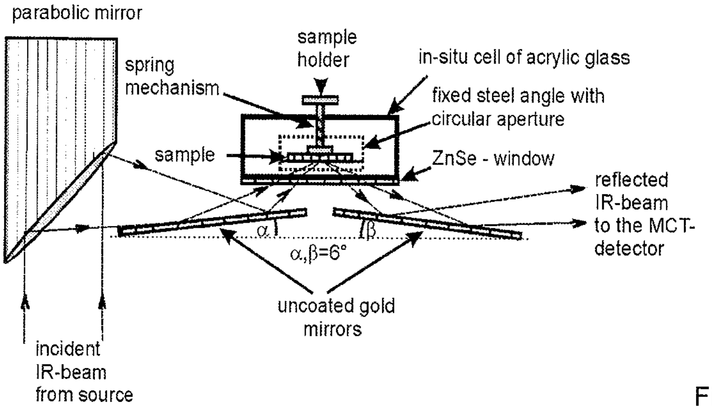

Fig. 1b

Fig 1: Image (a) and scheme (b) of the self-constructed and self-built cell for in-situ investigations of degradation (corrosion) processes on surfaces of non-transparent materials in controlled atmospheres. The incident angle on the sample surface is 14°.

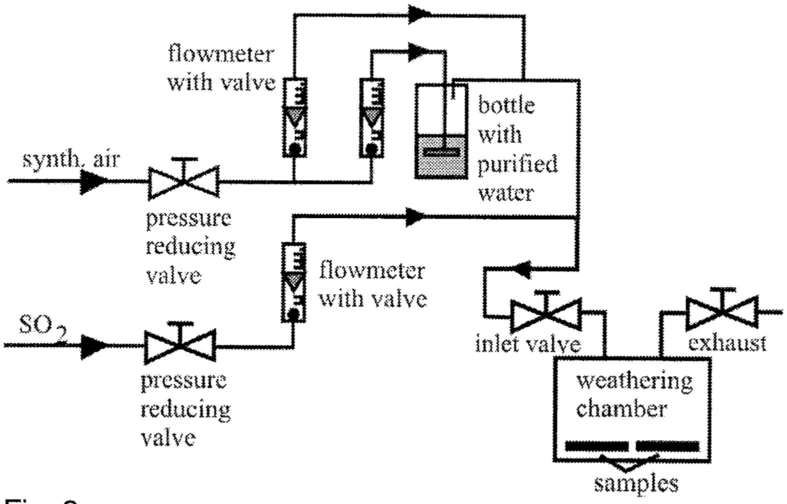

Fig. 2

Fig. 2: Set-up for the corrosion of samples in a weathering chamber. Dry synthetic air is humidified with 2-step-distilled and de-ionized water up to 80% RH. For the second series of weathering experiments 250 ppb SO_2 were added to the moist air stream.

Combining Raman Spectroscopy with Multivariate Calibration: A Quantitative Approach to Natural Organic Binding Media

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Spectroscopic examinations of organic binding media mostly are restricted to qualitative analysis. Recent work has shown the potential of Raman Spectroscopy to characterize mixtures consisting of linseed oil and dammar resin solved in chloroform. Establishing mulitivariate calibration concentration ratios of these binding media could be determined in solution. The application to dried paint is strived.

Combined Raman and FTIR study on thecotrichite and related efflorescence

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Intense deposits of fine white needles were observed on various calcium containing objects (for an example see Figure 1). They were identified as thecotrichite, a crystalline compound with a complex chemical composition: $Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}7H_2O$. Thecotrichite as well as related calcium acetate compounds were noted on objects stored in oak wooden cabinets for a long period of time. It is supposed that the acetic acid evaporates from the wood reacting with calcium contained in the object. Nitrate and chloride may be contained in the object itself, they may be originated by former cleaning procedures or deposited during burial. Moreover, adhesives, restoration materials (*e.g.* cellulose nitrate), and sealing materials in show-cases are possible sources of acetic acid and nitrate.

Calcium acetate $(Ca(CH_3COO)_2){\cdot}H_2O$ has been firstly described as an efflorescence on a mollusca [Byne, 1899]. Later calclacite $(CaCl(CH_3COO){\cdot}5H_2O)$ and thecotrichite have been identified as efflorescence on shells, mollusca, and other calcium containing objects in museums of natural history and on limestone and ceramics in various art and archaeological collections. $Ca_2(CH_3COO)_3(NO_3){\cdot}2H_2O$ was found on a coral brooch. Further compounds belonging to the system $Ca\text{-}CH_3COOH\text{-}Cl\text{-}NO_3$ may be found on museum objects in future.

The aim of this study is the investigation of thecotrichite and similar compounds of efflorescence by Raman spectroscopy in combination with FTIR analysis. In this investigation thecotrichite and other calcium acetate compounds were examined. For this purpose the following reference materials were synthesized: thecotrichite, two modifications of calclacite, and calcium acetate nitrate compounds without chloride content. The results were applied to the identification of the efflorescence materials found on art objects. Furthermore the Raman data were used to get information on chemical bonds in the thecotrichite crystal in combination to FTIR analysis. The Raman spectrum provides sharp and separated bands which allows an accurate determination of the position of the maxima. In the FTIR spectrum broad absorptions occur which are partly overlapped. The FTIR spectrum was taken to complete the analytical data and to check the information available by FTIR analysis. The structure of thecotrichite was not completely elucidated. Thecotrichite crystallizes in bundles of very thin needles which are not suitable for single-crystal structure determination. Spectroscopic studies may help to get further information on the structure of thecotrichite. In addition powder-X-ray-diffraction was carried out.

Raman spectroscopy complements former studies concerning the characterisation of these compounds using powder-X-ray diffraction (XRD), ion chromatography (IC) and atomic emission spectroscopy, and FTIR spectroscopy [van Tassel, 1958; Gibson *et al.*, 1997; Voncken, 2001]. The phenomenon of the occurrence of thecotrichite on art objects was examined by Halsberghe et al. [2005] from the conservation point of view. Gibson et al. [2005] investigated the formation of this deposit based on the evaluation of the phase diagram.

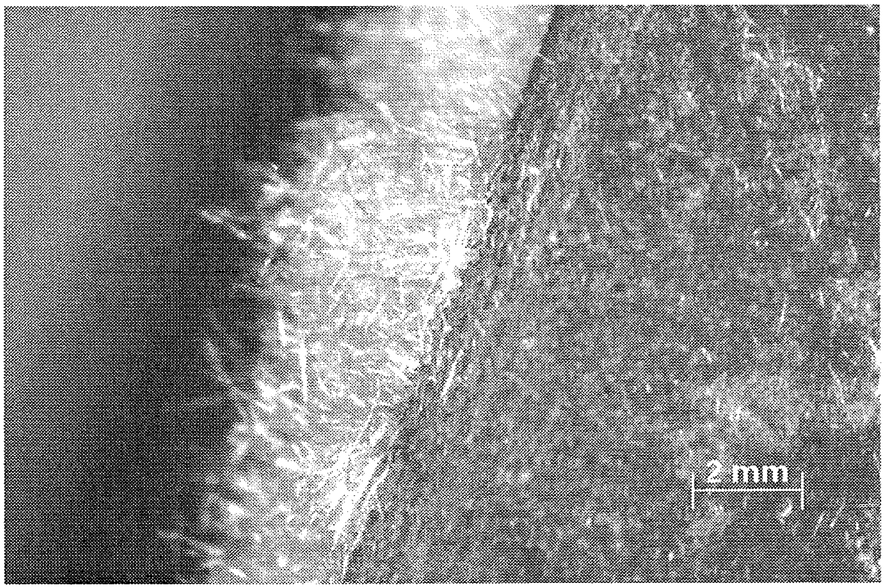

Figure 1: Thecotrichite efflorescence on the surface of an oven tile

Analysis of thecotrichite by Raman spectroscopy

The most intense signals in the thecotrichite spectrum were observed at 1061 and 1049 cm^{-1}. In this range the most intense band of calcium nitrate was registered at 1053 cm^{-1} appearing as single band. They are assigned to vibrations of the nitrate ion in the compound. A further vibration was found at 716 cm^{-1} which belongs also to the nitrate ion. Furthermore four bands occur in the range around 3000 cm^{-1} at 2929, 2955, 2987, and 3016 cm^{-1}. Analyzing calcium acetate as reference three signals were found in this range deriving from the acetate group in this salt. Therefore it is assumed that these bands in the Raman spectrum of thecotrichite are related to the acetate group. The vibrations under 3000 cm^{-1} are assigned to the carbon-hydrogen bonds only present in the acetate anion of the compound. The signals observed in the range under 400 cm^{-1} represent vibrations of bonds between the calcium ion and the different anions. The positions in the spectra of thecotrichite and the reference salts are given in the table in detail.

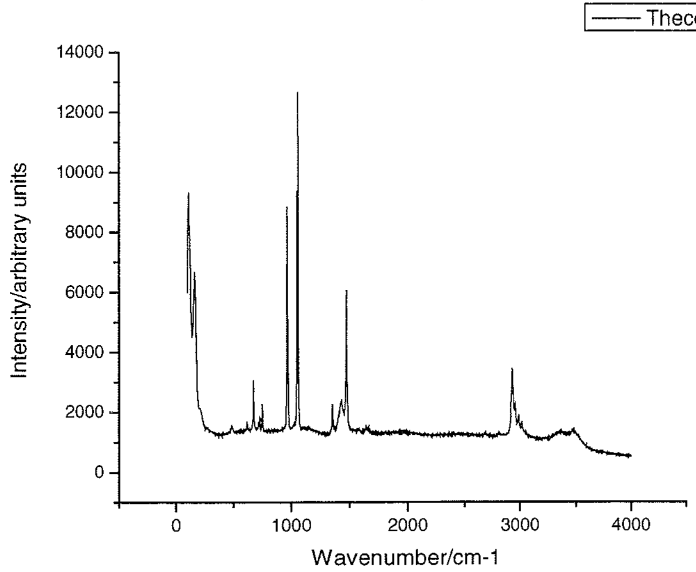

Figure 2: Raman spectrum of thecotrichite (in the crystalline state)

Table 1 Characteristic frequencies of thecotrichite and reference materials on art objects in the crystalline state (cm^{-1}) key: sh band occurs as shoulder

Thecotrichite	**Calcium acetate**	**Cacium chloride**	**Calcium nitrate**
–	–	3493	3600-3200 broad
3479	–	3454	overlapped
3357	–	–	overlapped
3016	3011	–	–
2987	2980	–	–
2955	–	–	–
2929	2929	–	–
1642	–	–	1643
1473	1479	–	1472
1429	1426	–	1426
1406	–	–	–
1359	1352	–	1360
–	1341	–	–
1061	–	–	–
1049	–	–	1053
971	–	–	–
964	965, 957, 950	–	–
–	928	–	–
751	–	–	748
746	–	–	744
726	–	–	721
715	–	–	716
669	669, 674 sh	–	–
–	646	–	–
615	621	–	–
483	478	–	–
		171	–
160	–	165	160
–	138	–	–
no evidence	125	125	123
–	–	118	–
109	107	–	–

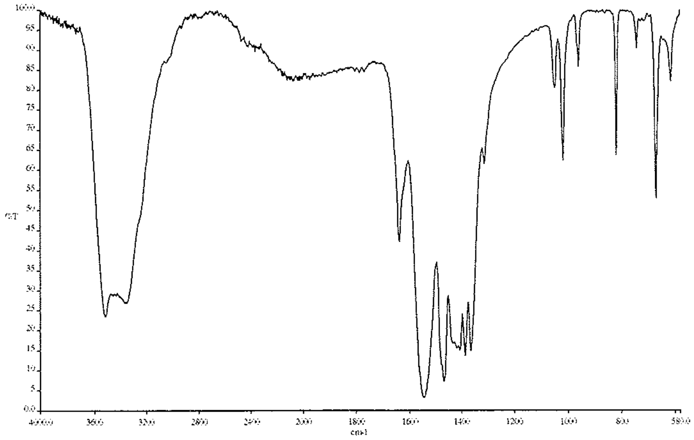

Figure 3: FTIR spectrum of thecotrichite (in the crystalline state)

Analysis of the efflorescence materials on art objects by Raman spectroscopy

On several art objects thecotrichite was identified as efflorescence on the surface using Raman and FTIR-spectroscopy. The efflorescence of an oven tile is to be seen in Figure 1. The Raman and FTIR spectra of the efflorescence of this object are given in Figure 4 and 5, respectively. In addition powder-XRD was performed. The oven tile belongs to collections of the Württemberg State Museum in Stuttgart. The ceramic tile is dated in the late 16 th century and is attributed to a region of Southwest Germany. It has a green lead-containing glaze with a relief ornamentation showing a couple in splendid habit.

In the Victoria & Albert Museum another object was found showing a characteristic deposit. It was also identified as thecotrichite applying Raman and FTIR spectroscopy and powder-X-ray-diffraction. It is the Figure of St. John the Baptist as a child, a glazed terracotta sculpture and is dated in the second half of 15 th century.

A kylix (a shallow drinking bowl with stem and foot) from the Goethe Nationalmuseum in Weimar (AK Nr. 2593) also carried a considerable amount of thecotrichite needles, identified by XRD and FTIR [Kutzke and Eggert 2001].

Needle crystals from fragments of a cuneiform tablet (Museum für Angewandte Kunst Frankfurt /Main, sample taken by Andrea Schwarz) could also be identified as thecotrichite by Raman microscopy.

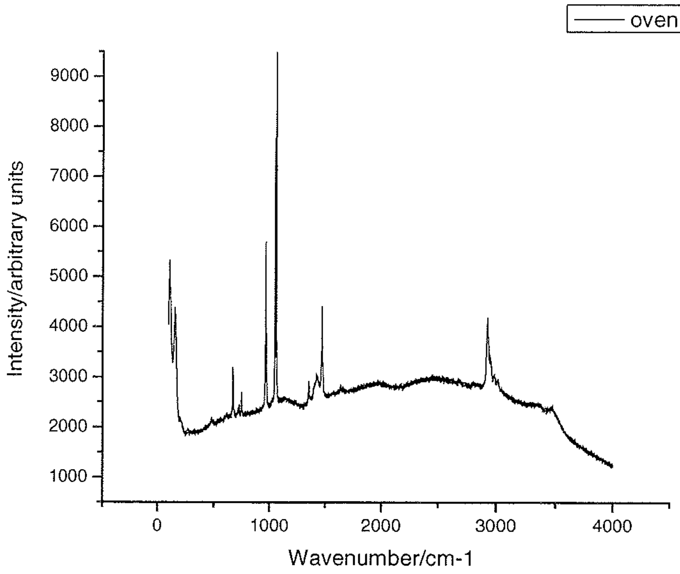

Figure 4: Raman spectrum of an efflorescence sample of the ceramic oven tile (in the crystalline state)

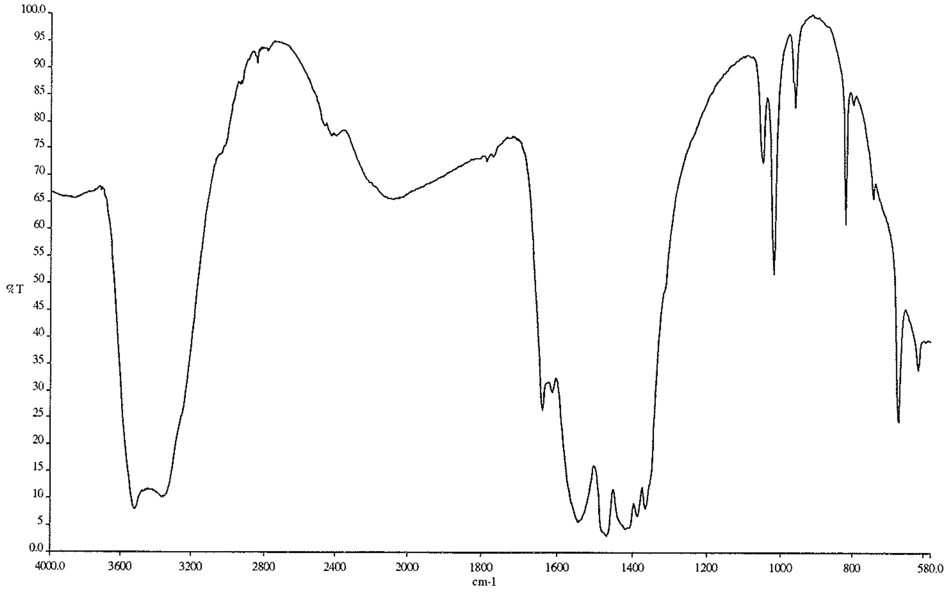

Figure 5: FTIR spectrum of an efflorescence sample of the ceramic oven tile (in the crystalline state)

Conclusions

Raman spectroscopy is a useful method for the examination of efflorescence on calcium-containing objects. Raman spectroscopy represents an alternative method for the identification of thecotrichite to X-ray diffraction. It is the aim of the study to include further compounds of similar chemical composition to figure out if both methods are necessary for their identification. Characteristic signals are given in the spectra above derived from vibrations of the acetate,

nitrate, and chloride group. Other calcium acetate compounds can be identified easily by Raman spectroscopy. The spectra of the different compounds differ in characteristic scattering bands which are shifted or missing in comparison to the thecotrichite spectrum. The results of the reference materials synthesized in the lab were applied successfully to the identification of unknown efflorescence. In addition to the Raman analysis powder-X-ray diffraction and FTIR-spectroscopy was performed to get the complete analytical information of the efflorescence.
An advantage using Raman spectroscopy is the opportunity to carry out the analysis directly on the objects under the microscope or in case of bigger objects using the fibre probe.

Instrumentation

The Raman analysis was carried out using a Horiba Jobin Yvon instrument Labram HR equipped with an Olympus microscope, two lasers with excitation wavelength of 633 and 785 nm and a Peltier-cooled CCD detector. The measurements were performed using the helium neon laser with 633 nm excitation wavelength, whereas the semiconductor laser of 785 was applied for measurements in comparison. Spectra were taken in the range of Raman shifts from 4000 to 150 cm^{-1}. The FTIR spectra were taken using a Perkin Elmer I series microscope combined with a instrument spectrum 2000. The microscope was equipped with a mercury-telluride (MCT) detector. The samples were prepared in a diamond anvil cell and measured in transmission mode. Spectra were collected in the range of 4000 to 580 cm^{-1} with 60 scans, a resolution of 4.0 cm^{-1} and a strong apodization.

Preparation of reference materials

Calclacite was synthezied by evaporating an equimolar solution of calcium chloride and calcium acetate. Under these conditions the stable form of calclacite was formed. The instable modification of calclacite was obtained by the preparation of a medivial copper pigment. It was formed as minor product in the mixture of acetic acid, calcium oxide, and ammonium chloride.

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Micro-Raman Spectroscopy Characterization of Della Robbia Glazes

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Micro-Raman spectroscopy and laser-induced transformation technique were used for systematic study of five coloured glazes on *Saint John the Baptist* (29" tondo), a majolica terracotta relief attributed to Luca Della Robbia on permanent exhibit in The John and Mable Ringling Museum of Art. We suggest that S_3^- ions in a lead silicate matrix, named lead ultramarine, contribute substantially to the famous Della Robbia blue colour in addition to the effect of Co atoms as suggested previously. The original yellow glaze contains lead (II) antimonite. The green is a mixture of yellow and blue, the brown contains hematite and the white glaze contains tin oxide as an opacifier. The use of lead oxide as a main fluxing agent is confirmed by laser-induced micro-crystallization.

Spanish (CSIC) Thematic Network of Cultural Heritage: The IR and Raman group

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The Spanish National Research Council (**C**onsejo **S**uperior de **I**nvestigaciones **C**ientíficas, **CSIC**)[1] is the largest public research Institution in Spain with a multidisciplinary character covering all fields of knowledge, from basic research to advanced technological developments. CSIC has over 120 Institutes across Spain, some of them including activities related to Cultural Heritage (CH) from humanistic to technical aspects. In order to achieve a better coordination of such activities, a "Thematic Network of Cultural Heritage" (TNCH)[2] was created in 2001, grouping thirty research teams from 17 Institutes with total/partial dedication to CH studies. The Network is a reference for diagnosis and studies on the conservation of Spanish Cultural Heritage. The Spanish Ministry of Culture, as well as the Culture departments from most regional governments, has signed agreements for the study and control of outstanding monuments such as the Altamira Cave, the cathedrals of Avila, León, Salamanca, Sevilla, Toledo, archaeological areas, Roman cities and necropolis, medieval castles, baroque palaces, museums, archives and cinematheques, paintings, archeological objects, etc.

The CSIC-TNCH shows activity in the following five research areas, with some lines specified:

- ***Archaeology and Architectural Heritage*** (knowledge of CH as basis for adequate conservation; photogrammetry and historical analysis of buildings)
- ***Biology*** **(**molecular biology methods and microbiology for the diagnosis of organisms involved in biodeterioration in CH objects)
- ***Chemistry and Material Sciences*** (conservation and protection of mortars and concretes, historic glass, etc; new materials for surface treatments; archeometry)
- ***Geology*** (petrographical and petrophysic characterization of materials; geochronology)
- ***Physics*** (non destructive and micro destructive techniques for analysis of artwork materials and their conservation state: IR and Raman spectroscopies, LIBS, PIXE)

In 2004, the CSIC-TNCH obtained an *EU Marie Curie Contract* for "Advanced Research Training on the Conservation of Cultural Heritage". Nine EU graduates (non spanish) are doing their PhD on different groups belonging to the Network, supported by the mentioned Contract.

The IR and Raman group belonging to the CSIC-TNCH is located at the Institute of Structure of Matter in Madrid. Its members are vibrational spectroscopists mainly involved in the development and application of new metallic nanostructures for Surface Enhanced Raman (SERS) and IR (SEIRA) Spectroscopies. In this field, and related to CH materials, the group has pioneered the application of SERS to organic pigments of interest in artwork, beginning with the anthraquinone dye alizarin[3]. At the same time, we have also investigated other methods which allow the Raman identification of alizarin in a mixture of organic red dyes[4].

Since the creation of the TNCH, the group is collaborating with other groups of the Network associated to the different research areas mentioned above. Thus, in collaboration with the Laser Induced Breakdown Spectroscopy Group (LIBS) we have analyzed the effect of laser wavelength in the laser cleaning of wood[5,6] and terracotta[7] polychromes, and of stone facades[8] of Spanish Monuments. Related to the conservation of historical glass heritage, Raman spectroscopy has been applied to the characterization of patination of lead cames of monuments located in different parts of Europe[9], while special Raman techniques - mapping and Confocal – have allowed the diagnosis of crust in weathered stained glass windows of the Avila Cathedral[10]. The IR and Raman group is also collaborating with another Materials Science group involved in the conservation of mortars and concrete[11,12] and with geologists interested in the proper use of protective surface treatments (consolidants and water-repellents) of historical buildings[13]. Some results will be presented at the Meeting

Additional IR and/or Raman reports of historical objects have been prepared for other conservation groups as, for instance, the Institute of History of CSIC (dating of decorated wooden boxes) and the Culture Department of the Castilla-La Mancha Regional Government, at Toledo (dating of a collection of Cusco paintings). Near future projects include collaboration with the Institute of Archaeology (CSIC, Madrid) and the Institute of Natural Resources (CSIC, Sevilla) for the integral documentation of the prehistoric rock art in Spain.

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Expanding the Infrared and Raman Users Group Spectral Database through Online Submissions

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Abstract

The Infrared and Raman Users Group (IRUG), a non-profit organization, was established in 1993 as a resource for scientists and others working in the field of art conservation and historic preservation. IRUG maintains a website, www.irug.org, that contains a spectral database of over 1250 reference materials, bibliography, and discussion forum and is being developed for the goal of providing open access to publicly funded scientific research. IRUG has recently expanded its capabilities by providing online software for submitting spectra and a mechanism for peer review. We describe here the basic steps for submitting spectra into IRUG and briefly describe how spectra are approved for inclusion into the IRUG Spectral Database.

The overall process for contributing a spectrum involves a submission sequence, a review process and incorporation of approved spectra into the database. The process for submitting spectra is outlined in Figure 1. The submission steps are as follows: 1) convert native spectrum to raw JCAMP-DX file using spectrometer software, 2) login to IRUG website, 3) attach JCAMP-DX file and fill out submission form, 4) submit form 5) confirm submission details and send to review committee.

The JCAMP file type is non-proprietary and can be used by any computer platform, and thus facilitates global sharing of spectral information. After contributors submit their spectra, they are automatically sent via the web software to the Review Committee, consisting of twenty-two conservation scientists who evaluate submissions for quality and completeness. IRUG protocol requires that a minimum of two reviewers evaluate each submission.

The online spectral submission capabilities described ensure that IRUG will be a continually expanding resource for individuals within the art conservation and historic preservation fields, while the peer review mechanism ensures spectra included in the IRUG Spectral Database are of the highest quality.

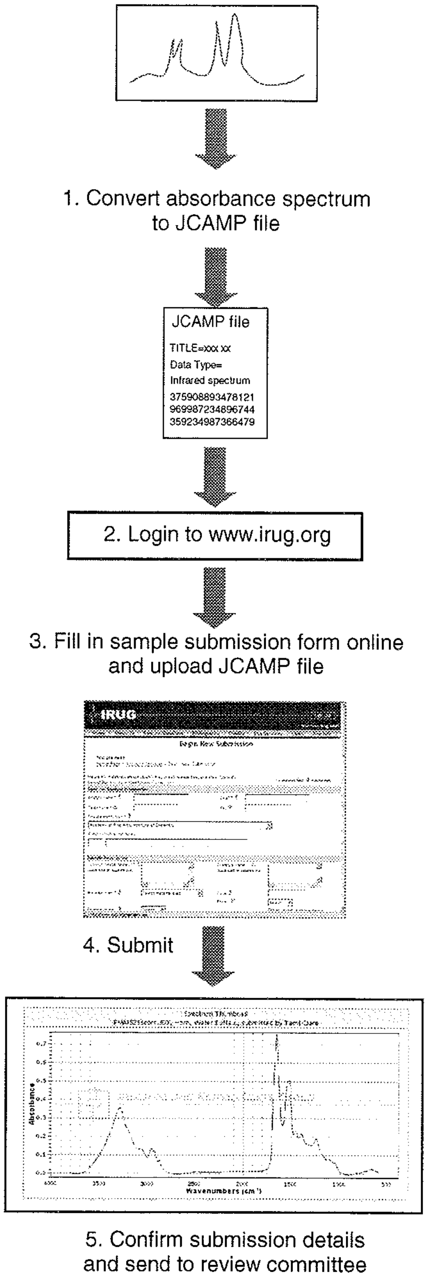

Figure 1: Flow chart illustrates process to submit reference spectra to irug.org