IRUG5

The Fifth International
Infrared and Raman Users Group Conference (IRUG5)

Conference Program and Abstracts

March 4-8, 2002

The Getty Center
Los Angeles, California

The Getty Conservation Institute

THE GETTY
CONSERVATION
INSTITUTE

March, 2002

Dear IRUG Conference Participants,

On behalf of the Getty Conservation Institute and the J. Paul Getty Trust, I am delighted to welcome you to the Getty Center for the fifth international conference of the Infrared and Raman Users Group.

The Getty Trust is firmly committed to providing opportunities for professionals in the conservation science community and related disciplines to come together to exchange ideas and to benefit from collective research.

As IRUG continues to grow, it furthers the significant contribution that infrared and Raman spectroscopy makes in the analysis of art materials. We are honored to have been chosen as the location where so many dedicated individuals have gathered to share the increasingly groundbreaking results of their research.

We recognize the importance of sharing these findings with others in conservation. For that reason, we look forward to exploring opportunities for the dissemination of this valuable body of information that we are creating together.

While you are here, I hope that you will take time to visit the Getty Museum's galleries and labs, and that you will come away with a better understanding of the Getty's commitment to conservation as a whole.

Timothy P. Whalen
Director
The Getty Conservation Institute

PROGRAM

MONDAY, MARCH 4, 2002

8:00 a.m. Registration: Harold Williams Auditorium Lobby, Getty Center
Continental Breakfast

9:00 **WELCOME**
Timothy Whalen
Director, Getty Conservation Institute

9:05 **WELCOME**
Boris Pretzel
Victoria & Albert Museum; European Chair, IRUG

SESSION I MODERATOR: HERANT KHANJIAN, GETTY CONSERVATION INSTITUTE

9:15 FTIR Imaging of Embedded Paint Cross-Sections of Modern Art Paintings
Suzan de Groot, Erik van Hensbergen and Thea B. van Oosten
Netherlands Institute of Cultural Heritage

9:45 The Application of FTIR and Associated Spectroscopy Techniques for the Identification of Composition Materials and Techniques of the Amfissa Cathedral Wall Paintings
Ioannis Liritzis[1] and Elisa Polychroniadou[2]
[1] University of the Aegean; [2] E. Polychroniadou & Associates

10:15 BREAK

10:30 Organic and Inorganic Pigments Using Raman Microscopy
Kenneth Smith
McCrone Associates

11:00 The Use of Raman Microscopy for the Study of Corrosion Products on Metal Artifacts
Karen Trentelman[1] and Lowell I. McCann[2]
[1] The Detroit Institute of the Arts
[2] Department of Physics, University of Wisconsin—River Falls

11:30 Non-Destructive Analysis by Micro-Raman Spectroscopy and Ion Beam Techniques: Application to the Study of Two Glaze Palettes from a French Ceramist of the 19th Century

Sylvie Colinart[1], Anne Bouquillon[1] and Christel Pouthas[2]

[1]Centre de Recherche et de Restauration des musées de France

[2]Institut de Formation des Restaurateurs d'Oeuvres d'Art

12:00 p.m. Lunch

Session II Moderator: Marco Leona, Los Angeles County Museum of Art

1:30 Quantitative FTIR Spectroscopy: A Powerful Tool in the Work of Art Conservation

Barbara Salvadori, Elizabeth Melnik, Valentina Errico, Marcello Mauro and Luigi Dei

Department of Chemistry & Consortium, CSGI, University of Florence

2:00 Infrared Spectroscopy in The Art Conservation Program at Queen's University: Some Applications of a Diamond ATR Accessory

H. F. (Gus) Shurvell and Alison Murray

Art Conservation Program, Queen's University, Canada

2:30 In Situ Vibrational Spectroscopy

David Thickett and Laurianne Robinet

The British Museum

3:00 Break

3:30 IRUG Database Presentation

Jan Carlson[1], Beth Price[2], Boris Pretzel[3], Ken Ehrman[4] and Andrew Lins[1]

[1]Winterthur Museum; [2]Philadelphia Museum of Art; [3]Victoria & Albert Museum

[4]Digital Bridgeway Inc.

5:00 End of Session

5:30 Cocktail Reception, The Getty Restaurant

6:00 Dinner, The Getty Restaurant

8:00 Dinner concludes

TUESDAY, MARCH 5, 2002

SESSION III MODERATOR: BETH PRICE, PHILADELPHIA MUSEUM OF ART

9:00 a.m.

IR-Spectra of the Grounds from Paintings by Some Well-Known Russian Artists of the 18th and 19th Centuries

B.V. (Boris) Zhadanov[1], G.N. Gorokhova[1], M. G. Cononovich[1]and L. A. Pirogova[2]

[1]Grabar Art Conservation Centre; [2]PerkinElmerInstruments

9:30

Changes in Adhesive Resins as a Result of Laser Irradiation: Study of Laser Wavelength Effects

Marco Leona, Meg Abraham and Stefanie Scheerer

Los Angeles County Museum of Art

10:00

Identification of Blue Pigments in Yoruba Wood Sculptures

Margaret Merritt[1] and Kate Duffy[2]

[1]Wellesley College; [2]Williamstown Art Conservation Center

10:30 BREAK

10:45

Organic Materials Used in the 'Paints' on Peruvian Qero Cups

Richard Newman and Michele Derrick

Scientific Research Lab, Museum of Fine Arts, Boston

11:15

Infrared Spectroscopy Applied to the Analysis of Papers and Inks in Manuscripts and Engravings from Cultural Heritage

Núria Ferrer[1], M. Carme Sistach[2], Anna Vila[3] and José F. García[3]

[1]Scientific Technical Services, University of Barcelona; [2]Arxiu de la Corona d'Aragó
[3]Paintings Department, University of Barcelona

11:45 LUNCH

SESSION IV MODERATOR: TBA

1:30 p.m. Examination of Fresh and Accelerated Aged Tung Oil Using FTIR-Microscopy and ATR-Technique
Anna Schönemann
Stifftung Preußische Schlöser und Gärten Berlin-Brandenburg, Germany

2:00 A Combination of FTIR and PY-GCMS as Tools for the Legal Authentication of Paintings: A Case Study in Brazil
Luiz Antonio Cruz Souza[1], Patricia Schlosser[1], Edson Motta Jr. [2], João Cura D'Ars de Figueiredo J. [3], Isabel Fortes[3] and Fernando Carazza[3]
[1]Center for Conservation and Restoration of Cultural Movable Properties (CECOR)
[2]School of Fine Arts, Federal University of Rio de Janeiro, Brazil
[3]Department of Chemistry, Federal University of Minas Gerais, Brazil

2:30 Micro-ATR Study of the Depth of Penetration and Distribution Profile of Water-Repellent Polymers into Porous Stone Materials
Francesca Casadio[1] and Lucia Toniolo[2]
[1]Getty Conservation Institute; [2]Centro C.N.R., Italy

3:00 BREAK

3:15 FTIR Reflectance Spectrometry Analysis on Ancient Yellowed Papers
Rodorico Giorgi[1], Massimo Ceccato[2], Luigi Dei[1] and Pierro Baglioni[1]
[1]Department of Chemistry & Consortium, CSGI, University of Florence, Italy
[2]Rifinizione Santo Stefano, Florence, Italy

3:45 Infrared Spectroscopic Studies of Photographic and Modern Painting Materials
Herant Khanjian[1]; Tom Learner[2] and Alberto de Tagle[3]
[1]Getty Conservation Institute; [2]Tate Gallery
[3] Netherlands Institute of Cultural Heritage

4:15 END OF SESSION

WEDNESDAY, MARCH 6, 2002

SESSION V MODERATOR: LUIZ SOUZA, CECOR

9:00 a.m. Characterization and Aging of Commercial Acrylic Resins
Oscar Chiantore
University of Torino, Italy

9:45 The Conservation of Acrylic Paintings: A Review
Elizabeth Jablonski[1] and Mark Golden[2]
[1]Menil Collection; [2]GoldenPaints, Inc.

10:30 BREAK

10:45 Basic Paint Research and Development
Mark Golden
Golden Paints, Inc.

11:30 Characterization of Acrylics at Rohm and Haas
Peter Eastman
Rohm and Haas

12:15 LUNCH

SESSION VI MODERATOR: LUIZ SOUZA, CECOR

1:30 p.m. Spectroscopic Identification of Acrylic Polymers
Gerald Lillquist
3M

2:15 Recent Investigations in Contemporary Artist Paints
James Druzik[1], Tom Learner[2] and Michael Schilling[1]
[1]Getty Conservation Institute; [2]Tate Gallery

3:00 BREAK

3:15 Roundtable Discussion
Oscar Chiantore, Elizabeth Jablonski, Mark Golden, Peter Eastman, Gerald Lillquist and James Druzik

5:00 END OF SESSION

THURSDAY, MARCH 7, 2002

SESSION VII MODERATOR: HERANT KHANJIAN, GETTY CONSERVATION INSTITUTE

9:00 a.m.	Reflectance Accessory for Spectroscopic Analysis of Scrolls and Paintings **Milan Milosevic and Denis Yang** *Harrick Scientific Corporation*
9:30	A New Approach to Infrared Microspectroscopy Instrumentation: An FT-IR for Your Light Microscope **John Reffner** *SensIR Technologies*
10:00	Use of the Raman Microprobe for Art Conservation **Fran Adar[1], Andrew Whitley[1], Meg Abraham[2] and Stefanie Scheerer[2]** *[1]Jobin Yvon – Horiba; [2]Los Angeles County Museum of Art*
10:30	BREAK
10:45	Advancement of Infrared and Raman Microspectroscopy **Bonnie Leimer and Jesse Gallop** *Thermo Nicolet*
11:15	Infrared Imaging: Applications in Conservation Science **Norman Wright** *Digilab*
11:45	Rapid Scanning Infrared Imaging and Micro-Internal Reflectance of Historical Works **Samuel White and Richard Spragg** *PerkinElmer Instruments*
12:15 p.m.	LUNCH

1:30 p.m. **INSTRUMENT DEMONSTRATIONS**

Harold Williams Auditorium lobby

REVIEW OF POSTERS

Lower Level

1:30 p.m. From Classic Antiquity to Contemporary Art: Some Applications of Reflection FTIR Microspectroscopy Disclosing the Composition of Multilayered Artifacts

Francesca Casadio[1], Franco Cariati[2], Chiara Colombo[3] and Lucia Toniolo[3]

[1]Getty Conservation Institute [2]University of Milan; [3]Centro C.N.R., Italy

Polychromy on Wooden Furnishings in the Scrovegni Chapel in Padova (Italy): The Use of FTIR Spectroscopy

Umberto Casellato and Rossana Arbizzani

C.N.R.-ICTIMA [Italian National Research Council, Chemistry, Inorganic Technologies and Advanced Materials Institute]

Applications of FTIR Spectroscopy to the Study of Ancient Chinese Jades

Janet Douglas

Freer Gallery of Art/Arthur M. Sackler Gallery, Smithsonian Institution

Raman Spectroscopy of Brazilian Museum Objects

Dalva L. A. de Faria[1], Marisa C. Afonso[2] and Howell G.M. Edwards[3]

[1]Instituto de Quimica, City University of Sao Paolo, Brazil

[2]Museu de Arqueologia e Etmologia de Universidade de Sao Paolo, Brazil

[3]Department of Chemical and Forensic Sciences, University of Bradford, United Kingdom

Gelatin Content of Historic Papers Using FTIR Techniques

Mark Ormsby

National Archives and Records Administration, USA

4:00 Tour of the GCI Labs

6:00 END OF SESSION

FRIDAY, MARCH 8, 2002

SESSION VII

9:00 a.m.	IRUG Business Meeting
11:00	End of Meeting
1:00 p.m.	Shuttles depart for Los Angeles County Museum of Art (LACMA)
1:30	LACMA tour
3:30	End of Tour; shuttles return guests to respective venues

MONDAY MARCH 4, 2002

ORAL PRESENTATIONS

FTIR IMAGING OF EMBEDDED PAINT CROSS-SECTIONS OF MODERN ART PAINTINGS

Suzan de Groot, Erik van Hensbergen and Thea B. van Oosten

Netherlands Institute for Cultural Heritage (ICN) Gabriël Metsustraat 8, 1071 EA Amsterdam, The Netherlands email: suzan.de.groot@icn.nl; erik.van.hensbergen@icn.nl; thea.van.oosten@icn.nl

INTRODUCTION

Identification of the binding media and pigments of the various different paint layers of modern art paintings is important, not only for conservation but also for art historical documentation. Infrared mapping microspectroscopy is a valuable technique that can characterize the binding media in multi-layered cross-sections. Earlier, FTIR reflectance spectra of embedded cross-sections had given no satisfactory results. Infrared analysis of cross-sections in transmitted light can only be done by thin sectioning of the embedded cross-sections.

The use of various embedding media and thin sectioning of embedded cross-sections has already been researched [Stringari, 1991; Derrick 1994] and good FTIR results have been achieved. A big problem with this technique, however, is infiltration of the embedding material into the sample. This causes interference of the analysis of the sample due to overlapping of characteristic absorption bands of the binding media and the embedding material. This problem may be avoided by combining two complementary embedding materials for the same paint sample. Each material has its own absorption-free regions in the infrared spectrum. By combining the results of the absorption-free regions of both materials, the infrared spectrum of the sample can be obtained. With this composed spectrum, the components of each specific layer in a paint sample can be analyzed without wondering what is hidden beneath the peaks of the embedding material.

EXPERIMENTAL

FTIR: FTIR analyses were performed using a PerkinElmer Spectrum 1000 FTIR spectrometer combined with a PerkinElmer AutoImage System FTIR Microscope, fitted with an MCT detector cooled by liquid nitrogen. The cross-sections were run as thin sections on a KBr window with 40 scans and a resolution of 4 wavenumbers.

Microtoming: Cross-sections were cut using a Leica RM 2165 steel knife microtome with a 10° knife; the cutting thickness was set to 10 μm.

EMBEDDING MATERIALS

A good embedding material should meet the following requirements:

- Will cure at low temperatures, high temperatures may affect the samples.
- Be inert; it should not react with the sample or with other materials.
- Be easy to microtome.
- Be transparent.
- Should not expand nor shrink during curing; this will cause unnecessary forces on the sample which makes it more difficult to microtome.
- Be free of water.
- Alow minimal penetration into the sample; otherwise the embedding material will strongly interfere with the IR-spectrum of the sample.

Several types of embedding material (listed in table I) were tested, all available in the Netherlands.

- Polypol (Poly-service): a one-component polyester based on a phtalic ester. It is the most commonly used embedding material by conservators in the Netherlands, due to its transparency and easy polishing. The embedding material takes about 24-36 hours to cure at room temperature.
- Epoplast (VEM metallurgy company): a two-component epoxy, easy to use and has a good transparency. It takes about 24-36 hours to cure at room temperature.
- Paraffin (Lamers & Indemans): a soft paraffin with a melting point of 54-56°C.
- Paraplast (Aurion): a harder paraffin with a melting point of 99°C.
  Both paraffins must be melted before they can be poured into the mold, meaning that the sample is exposed to the temperatures of the melted paraffin, which can cause problems when trying to identify binding media with a lower melting point than the used paraffin. Both of the paraffins have the advantage that the curing time is exactly the time the paraffin needs to coagulate, which happens within a few hours.
- Durcupan (Fluka; Aurion): a four-component acrylate with the disadvantage of a long curing time (3-4 days) and the use of toxic chemicals.

RESULTS

The embedding materials were tested to compare their working properties during use and preparation, microtoming and FTIR spectroscopy.

Use and microtoming: Polypol was easy in use. The thin sections produced, when microtomed within a week after curing, were of good quality. Yet, after a week the material became too brittle to obtain good thin sections. The main problem encountered with paraffin was the softness of the material, which caused the spreading of the embedding material over the sample while microtoming. Better results were achieved with Paraplast, a paraffin with a higher melting point, which spread less. The acrylic embedding material gave good quality thin sections. The disadvantages of this material are its toxic components and the long curing time. The epoxy gave good results too, provided it was microtomed within a week after curing. After the first week the material became too brittle to cut.

FTIR: The infrared spectra of the embedded paint samples all showed infiltration of the embedding material. Polypol, being a polyester, has infrared absorption bands in the same regions where nearly all binding media contain absorption bands as well. The tested paraffins proved to be good embedding materials due to their "clean" spectra (only a few sharply defined absorption peaks). The epoxy embedding material is suitable for identifying components in the 1800-1600 cm^{-1} region of the infrared spectrum, while the acrylic embedding material allows identification of components containing absorption bands in the lower region (< 1000 cm^{-1}). The absorption free regions of the tested embedding materials are given in Figure 1.

Figure 1: Absorption free regions of embedding materials

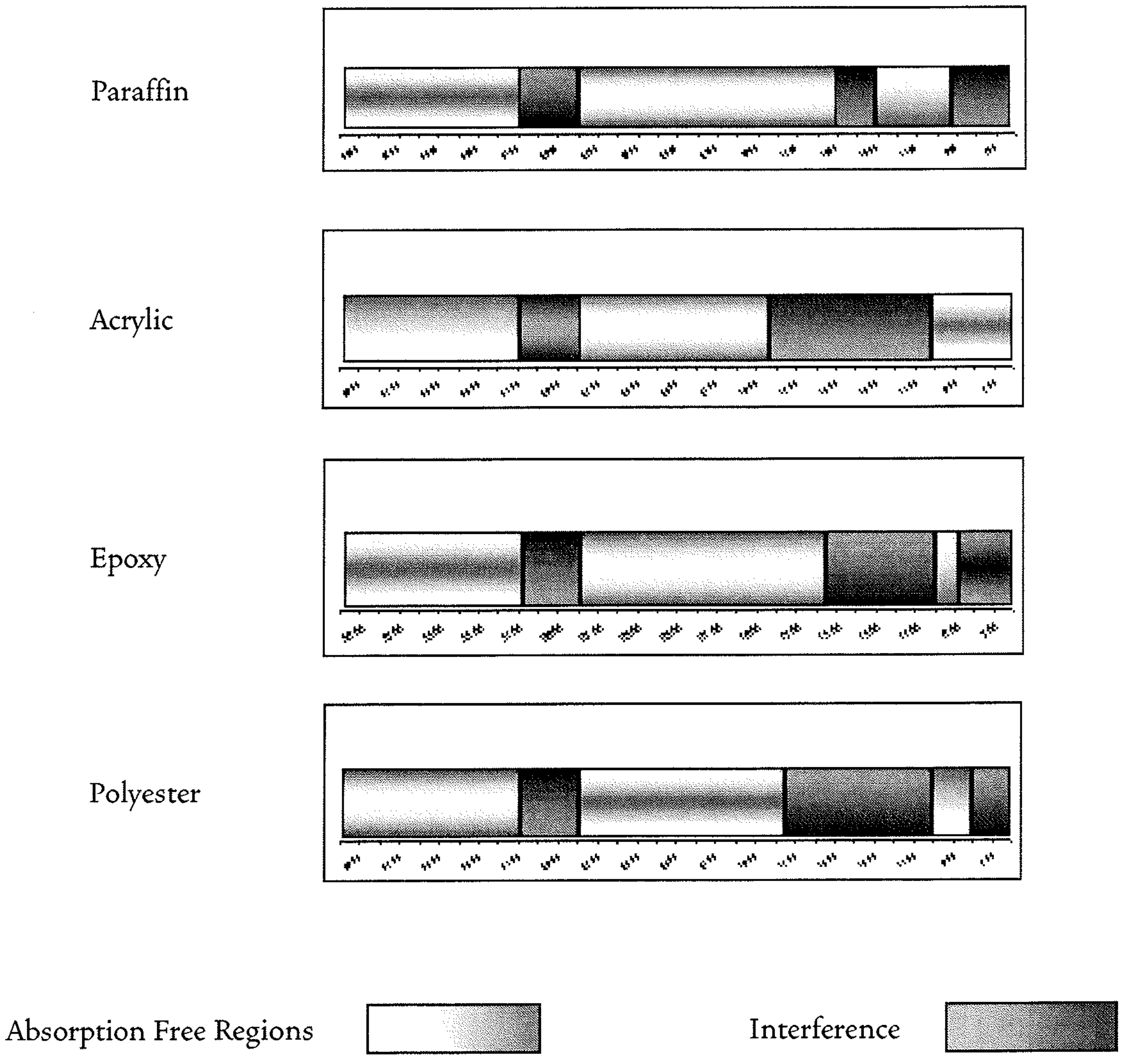


Table I: Embedding materials

Name	Type	Distributor	Use	Remarks	Microtome	FTIR
Polypol	Polyester	Polyservice	++	toxic	++ <1week	-
Paraplast	Paraffin (mp 99 oC)	Aurion	++	melting pointquite high	++ ++	++ ++
Paraffin	Paraffin (mp 54-560C)	Lamers & Indemans	-	too Soft	-	++
Durcupan	Acrylic	Fluka	+	Toxic Long curing	++	+
Epoplast	Epoxy	VEM	+		++ <1 week	+/-

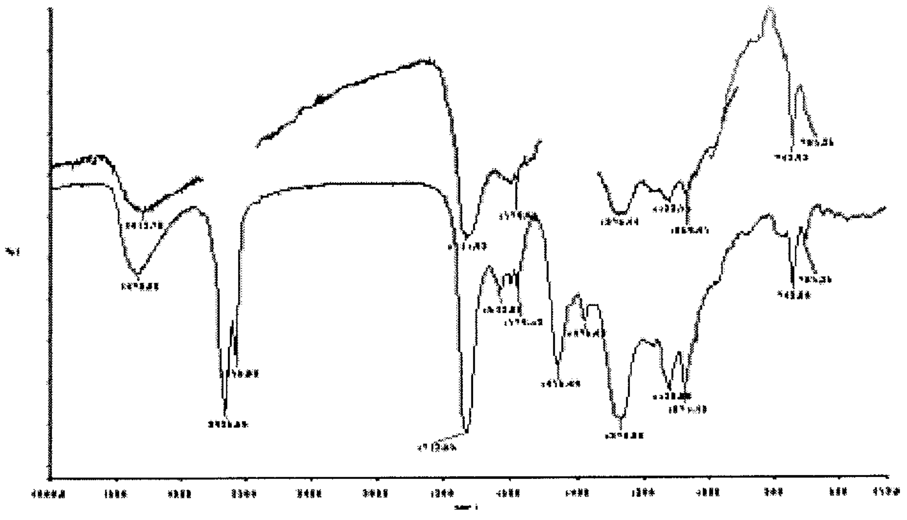
Table 1 lists the working properties of the various embedding materials. Judging microtomability and the absorption free regions, the combination of Paraplast and Durcupan provides the best pair for the complementary combination technique.

APPLICATION

The above-mentioned method was applied on paint samples of a painting by Pablo Picasso. For the restoration of 'Femme nue devant le jardin' (1956, Stedelijk Museum Amsterdam), it was important to know which materials the artist had used. For identification of the black and the ground layer, a sample containing both paint layers was taken from the black area of the painting. One half was embedded in the paraffin and the other in the acrylic embedding material. Using the microtome, 10 µm thin sections were cut from both embedded samples. The thin sections were placed on a KBr window and from the different layers the infrared spectra were collected.

The spectra of the black layer in the embedded samples in the two different embedding materials both showed absorption bands of the embedding material. However, in the absorption peaks free regions, absorption bands from the binding medium were present. As expected, no absorption bands of a black pigment were present.

Figure 2: composed infrared spectrum of the black layer



Black spectrum:	black layer: absorption free regions in Paraplast
Red spectrum:	black layer: absorption free regions in acrylic embedding media
Blue spectrum:	reference spectrum of an alkyd resin

By combining the results from both embedding materials, a composed infrared spectrum of the black layer was obtained (see figure 2), showing specific absorption bands of an alkyd resin. Specific absorption bands in the reference spectrum of an alkyd resin are: 1733 - 1632 - 1579 - 1456 - 1270 - 1120 - 1071 - 742 - 705 cm^{-1}. The white ground layer was analyzed in the same way, revealing an oil as a binding medium and lead white as a pigment.

Conclusion

When analyzing the various layers in a paint sample, one has to take into account infiltration of the embedding material. This causes interference with the analysis of the paint sample due to overlapping of characteristic absorption bands of the binding media and the embedding material. By using two embedding materials for the same paint sample, various absorption free regions in the infrared spectra can be obtained. By combining the results of the absorption free regions, a composed infrared spectrum can be obtained. With this composed spectrum, the components of each specific layer in a paint sample can be analyzed.

Combining the infrared spectra composed from the free absorption regions of a paraffin and an acrylic embedding material, a composed infrared spectrum can be made. In this way, all commonly used binding media used in modern art paintings can be identified. The advantage of the identification of binding media in separate paint layers amply compensates the disadvantage of double preparation.

ACKNOWLEDGEMENTS

The authors would like to thank Elisabeth Bracht (Stedelijk Museum Amsterdam), Irene Glanzer (Stedelijk Museum Amsterdam), Klaas Hulshof (Stichting Kollectief Restauratoren Atelier) and Kathrin Kirsch (Stichting Kollectief Restauratoren Atelier) for providing the samples and Agnes Brokerhof (Instituut Collectie Nederland) for her useful comments.

ADDRESSES

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Allison Langley, Aviva Burnstock, 1999. *"The analysis of layered paint samples from modern paintings using FTIR microscopy"*, In: Bridgland, J.ed. Preprints of the 12th Triennial Meeting ICOM-committee for Conservation. London: James and James (Science publishers) Inc. 234-241.

Suzan de Groot studied analytical chemistry at the Hogeschool Amsterdam and graduated in 1996. She started work at the Netherlands Institute for Cultural Heritage (ICN), Conservation Research Department in 1996. She is currently engaged in Fourier Transform Infrared Spectroscopy (FTIR) analyses of organic materials used in objects of cultural heritage, testing physical and mechanical properties of paper and carrying out artificial aging experiments. She is also responsible for the ICN quality standards for archival materials.

Erik van Hensbergen is studying analytical chemistry at the Hogeschool Alkmaar and will graduate this year. He is currently working as an intern at the Netherlands Institute for Cultural Heritage (ICN), Conservation Research Department. His graduate project is FTIR imaging of embedded paint cross-sections of modern art paintings. He is also working on a database containing FTIR spectra and DSC results of various modern materials used for restoration.

Dr. Thea B. van Oosten is a conservation scientist working at the Netherlands Institute for Cultural Heritage (ICN), Conservation Research Department since 1989. She studied analytical chemistry at Amsterdam University. She is currently engaged in Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC) analyses of organic materials, especially plastics in objects of cultural heritage and modern materials in modern and contemporary art objects. She also is coordinator of the Working Group Modern materials of ICOM-CC.

NOTES

THE APPLICATION OF FTIR, RAMAN AND ASSOCIATED SPECTROSCOPY TECHNIQUES FOR THE IDENTIFICATION OF COMPOSITION MATERIALS AND TECHNIQUES OF THE AMFISSA CATHEDRAL WALL PAINTINGS

Ioannis Liritzis[1] **and** **Elisa Polychroniadou**[2]

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Amfissa, an ancient city, is the capital of the municipality of Fockida, situated in a valley surrounded by the mountains of Parnassos and Giona, overlooking the ancient port of Kirra and the archaeological site of Delphi. The Cathedral, 27m height and 30m breadth, is constructed on the ruins of an early Christian basilica in the historical center of town. The wall paintings, a significant monumental work of post-Byzantine art, were carried out by the Greek painter Spyros Papaloukas (1892-1952) between 1926-1932.

In these works, Papaloukas attempts a new approach to the aesthetic merits of Byzantine iconography by depicting startlingly geometrical figures and introducing elements inspired by the Impressionists, the Fauves and the Nabis, mainly observed in ornamental compositions. Color was not applied with a view of ascribing the object's natural hues, but rather by composing "phrases" which, in combination with a theme stated by the line work, carried through the artist's own vision of the subject matter.

Light was a subject of major concern for the artist as the most potent means of expression and the dominant backbone of the composition. Papaloukas plays with light, experimenting with the warmth and darker hues by applying various bindings and pigments. This divergence from the Byzantine tradition of set rules and forms dissatisfied the Orthodox clergy, and as a consequence they refused to pay the artist for his work. However, the innovative techniques and painting materials applied by the artist in conjunction with moisture, seismic activity of the region, inappropriate construction materials, and previous defective conservation treatments all have acted as agents of serious alteration and damage to the mural paintings.

In May 2000, a conference on Papaloukas was held in Amfissa, where local authorities decided to proceed with a conservation project of the wall paintings. The spectroscopy techniques of FTIR, Raman , XRF and optical microscopy (in the visible and UV regions) and GC-MS were combined as an integral part of the technical examination. The steps undertaken were:

a) In situ XRF measurements (using a portable XRF Spectrace 9000 TN with three isotope excitation sources) as well as some laboratory measurements for the first approximation recognition of pigments from a major element presence, from the wall, and from the anthivola (the initial compositions drawn by pencil or charcoal, then transferred to the wall);

b) Application of FTIR to locate any organics, e.g. the presence of lacquers (binders, varnishes), and for identification of inorganic pigments;

c) GS-MS for identification of any organics present (amino acids, etc);

d) Raman spectroscopy (1000 μ Raman, Renishaw, with a He-Ne laser light source, and use of x50 and x100 objective Olympus lenses) for the recognition of particular colors attributable to certain pigments and chemical compounds. The focusing of around 1 mW power laser beam was made on single spots of a cross-sectioned sample; and on the surface with a spectral resolution of 4 cm^{-1};

e) A photographic recording of surfaces and sides using an optical microscope stimulated by white polarized light and UV (Hg source), with objective lenses of x20 and x50. This way, any painted layers as well as other carriers were identified for further detailed microanalysis; and

f) X-ray diffraction for the mineral identification of plaster.

Here we present the first results [2] of analysis of materials derived from the wall paintings of the Amfissa Cathedral, painted by Spyros Papaloukas. The results obtained so far are summarized below:

1) The painter used a wide 'palette' during the testing stage. Among the various pigments, ultramarine, coal, hematite, yellow ochre, Prussian blue, white lead, yellow of chromium, and lapis lazuli were detected.
2) Several painted layers were recognized – in one case, five layers—consisting of yellow ochre (kaolin), calcite for white, red ochre (anhydrous iron oxide), carbon black and ultramarine.
3) Animal glue was found, caseine and egg, as a binding substance in the preparation of grounds and in painted layers.
4) Gas chromatography was employed to identify tempera (egg binder) and animal glue.

REFERENCES:

[1] Raman, FTIR, and GC were executed at the Ormylia Diagnostic Centre of Art Objects, Athos, Greece.

[2] A detailed report entitled, "Physical methods of chemical analysis applied on the Amfissa Cathedral wall paintings (hagiography) by Spyros Papaloukas (1920-30)", is under publication by the authors in the Mediterranean Archaeology & Archaeometry (Dec. 2002, in press).

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[10] Michailidou, M. The Poet of the Colour, Kathemerii newspaper, vol 2, Greek painters p 158-163.

Ioannis Liritzis is Professor of Archaeometry at the University of the Aegean. He is the founder and director of the Laboratory of Archaeometry at the Dept. of Mediterranean Studies, Rhodes, Greece. He has published more than one hundred papers in international scientific journals on nuclear physics, nuclear geophysics, geology, palaeoclimatology, solar-terrestrial phenomena, planetology, physical methods in archaeology (dating, analysis, prospection); written another hundred papers in Greek journals; and is the author of five books on dating in archaeology, radioactivity, archaeomagnetic dating, geomagnetic field and the Greek pyramids. He is on the editorial board of two international journals on Coastal Research (USA) and Radioanalytical & Nuclear Chemistry (Kluwer, Hungary). His present research interests include archaeoastronomy, nuclear dating in archaeology, obsidian dating, wall painting analysis, and geoarchaeology.

Elisa Polychroniadou graduated from the Technical Institute Department of Conservation in Athens. She holds degrees in conservation and art history; and an M.A. in Museum Studies from Leicester University. She is in charge of several conservation/preventive projects in Greece and abroad, including the collection of wooden objects of the Peloponnesian Ethnoghraphic Museum; the Pieridis archaeological collection and the Pieridis Gallery; the 4th Ephorate of Dodecanisa; the Temple of Athena Nikae in the Acropolis of Athens; The Panagia Ammou; Artemona Sifnos, Cyclades Greece; the Monastery of Saint Ioannis Chrysostomos at Fikia, Sifnos; the Historical Archive of the National bank of Greece; the Cultural Foundation of the National Bank of Greece; and the wall paintings of the Amfissa Cathedral . She has published several articles in related fields. She is a member of IIC, ICOMOS, and other museum associations.

NOTES

ORGANIC AND INORGANIC PIGMENTS ANALYSIS USING RAMAN MICROSCOPY

Kenneth Smith

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McCrone Associates has been involved in analysis of works of art including oil and watercolor paintings, sculpture, metalwork and textiles for many years. The primary tool for examination of pigments and substrates has been the polarized light microscope. The polarized light microscope can quickly reveal unique optical properties of pigments such as color, size, morphology, crystalline habit, opacity and birefringence. As techniques and instrumentation have developed, additional techniques have come to be used to develop a fuller characterization of samples from works of art. Currently, analyses employ optical microscopy; Raman microscopy and FTIR microscopy; scanning electron microscopy with energy dispersive x-ray spectrometry (SEM/EDS); transmission electron microscopy; and GC/MS.

Raman microscopy is a technique used in conjunction with polarized light microscopy (PLM), FTIR microscopy and electron microprobe analysis (SEM/EDS) to identify pigments as completely as possible. We use a Renishaw Raman microscope system that incorporates a polarized light microscope, providing molecular information along with the optical characteristics of a pigment. Because Raman spectral features tend to be sharp and the Raman spectrum can include the region from 100 to 1000 cm^{-1}, the technique can often provide more definitive results for inorganic compounds, such as metal oxides (titanium dioxides, iron oxides, lead oxide) than infrared analysis. This molecular data is often combined with elemental data from the electron microprobe for a definitive identification of a pigment.

Raman microscopy is also a powerful tool for analysis of organic pigments. Pigment samples collected from paintings and dispersed on a glass slide for light microscopy analysis can also be analyzed directly with Raman. This capability is an advantage over infrared analysis, which requires isolation of organics from other sample materials and the PLM mounting medium. If necessary, the spectrum of the mounting medium can be easily subtracted.

The small spot size typically used in Raman microscopy has definite advantages in pigment analysis. The small sampling area provides high spatial resolution, allowing analysis of individual pigment particles, or analysis of small domains of pure pigment in areas where more than one pigment has been used. Raman microscopy can be utilized with little or no sample preparation, leading to in situ analysis.

Work in the "in situ" analysis of watercolor pigments has been performed using a known artist's palette and a watercolor painted from that palette. The analysis demonstrated the capability of a Raman microscope to analyze pigments without removal from a watercolor painting. The fiber background and watercolor media of the test sample did not interfere with the spectra of the pigments. Analysis of additional watercolor paintings also demonstrated the ability of the Raman microscope to collect spectra of pigments in situ. These additional paintings were older (30-80 years old), and the fiber substrate did show some background fluorescence apparently due to oxidation of the paper fibers. However, careful selection of the areas for analysis can reduce this observed fluorescence if the pigment is at least a few micrometers thick.

The Renishaw Raman system used for this work was limited with regard to the size of painting that could be analyzed. Due to the constraints of the microscope stage and proximity to the spectrometer bench, we could not collect spectra of pigments that were more than 4.5" from the painting edge. The fiber optic system available from this manufacturer does not necessarily provide a solution to this size constraint. The fine focusing of the fiber optic lead is not as accurate as the focusing of the optical microscope; therefore, the advantage of small laser spot size is lost when going to the fiber optic accessory.

We have also used the Raman microscope to study variations in samples of red chalk from drawings attributed to Watteau and some unattributed works from the Art Institute of Chicago. We found correlation among the Raman spectra of the chalks with regard to the iron oxide components.

Overall, Raman microscopy has proven to be a powerful technique for the analysis of organic and inorganic pigments in watercolor paints, oil-based paints, chalks and pastels. The Raman data is often crucial in reconciling data from light microscopy analysis and SEM analysis. The technique is fast and specific, and is has become and integral part of our analysis scheme for pigments.

Kenneth J. Smith, Ph.D. holds a Bachelor of Science degree in Chemistry from Bradley University, Peoria, Illinois in 1987 and a Doctorate in Analytical Chemistry from Miami University, Oxford, Ohio, in 1992. Since 1993, he has worked as a Senior Research Chemist with McCrone Associates (Westmont, IL) in the Chemistry Group, providing chemical analyses and method development for analysis of particles, contaminants, trace level compounds and primary ingredients in a wide variety of materials. The work involves extensive hands-on particle isolation, manipulation and identification work with pharmaceuticals, polymers, pigments, coatings, electronics, forensic and manufacturing samples. Analyses utilize light microscopy techniques, FTIR microscopy, Raman microscopy and UV/VIS spectroscopy, HPLC, GC/MS, ion chromatography, gel permeation chromatography, and wet chemical methods. He is a co-instructor for the Advanced FTIR Microscopy course offered through McCrone Research Institute; and is a member of the Society of Applied Spectroscopy, American Chemical Society, Coblentz Society, and Chicago Area Conservators Group.

NOTES

THE USE OF RAMAN MICROSCOPY FOR THE STUDY OF CORROSION PRODUCTS ON METAL ARTIFACTS

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Raman microscopy is rapidly becoming recognized as an important tool for the study of artistic and historic works, as evidenced by the ever-increasing number of publications in the literature reporting its use. Raman microscopy has been used to perform non-destructive analyses of pigments on illuminated manuscripts, wall paintings, frescos, ceramics, and textiles. In this paper, the application of Raman microscopy to the study of corrosion products on museum objects will be discussed, and illustrated using examples from studies of copper alloy artifacts.

Raman microscopy can be used to perform non-destructive in situ analyses of the surfaces of objects. In a study of the bronze branches of Han Dynasty Money Trees, Raman microscopy was used to characterize the corrosion products and other materials found on the surface of the branches, including modern pigments that had been applied to disguise repairs or to simulate a corroded surface [1]. The high spatial resolution of the Raman microscope enabled the examination of individual grains of pigment or corrosion product, facilitating the identification of the various materials present.

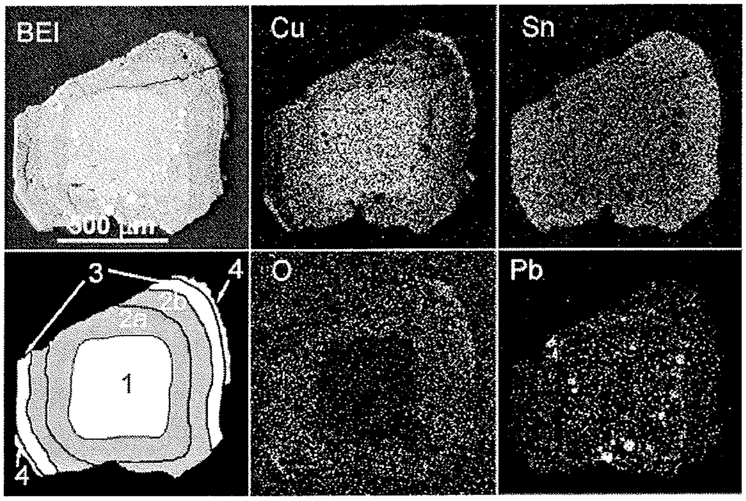

Figure 1: Backscatter electron image (BEI) element distribution maps of Cu, Sn, O and Pb from cross-section of branch from DIA's money tree. Region 1 is uncorroded core, region 2 is inner region of corrosion, region 3 is corrosion layer just below surface and region 4 is corrosion layer external to original surface. Figure taken from Trentelman et al (reference 2).

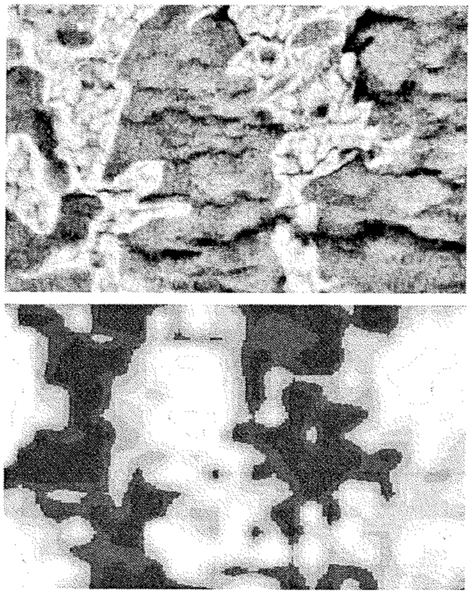

Figure 2: Top: backscattered electron SEM image (lighter regions are Sn-rich a+B eutectoid phase and the darker regions are the corroded a phase). Bottom: Raman map of Cu_2O. Figure taken from McCann *et al* (reference 1).

In order to more thoroughly understand the nature of the corrosion mechanisms that have occurred throughout the lifetime of an object, it is usually necessary to remove small samples and prepare cross-sections to reveal the layers of metal and corrosion products. In the study of the branches from several Money Trees, Raman microscopy was used in conjunction with scanning electron microscopy with energy dispersive x-ray spectroscopic (SEM-EDS) analysis to examine the layers of corrosion products [2]. The pairing of these two techniques proved particularly fruitful, as the elemental information provided by the SEM-EDS, such as that illustrated in Figure 1, served to help select areas to be studied by Raman microscopy and, furthermore, helped narrow the search in identifying the molecular compounds.

A technique known as Raman mapping was used to study the spatial distribution of corrosion products within a cross-section. The high spatial resolution of Raman microscopy enables these maps to be generated on the same scale as the metallographic grain structure, thus revealing any correlation between corrosion products and individual metallographic phases. As illustrated in Figure 2, in the study of a bronze branch from a Money Tree having the typical grain structure of a low-tin copper-tin alloy (a phase dendrites surrounded by a+d eutectoid), Raman mapping was used to identify cuprite, Cu_2O, as the nascent corrosion product, as well as the fact that the a phase was undergoing preferential corrosion. Such knowledge can provide insight into the corrosion mechanisms that have occurred, and the environments to which an object may have been exposed over time.

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[2] Trentelman, K., Stodulski, L. Lints, R. and C. Kim. A comparative study of the compositin and corrosion of branches from Eastern Han Dynasty money trees. *Studies in Conservation* 44, 170 (1999).

Dr. Karen Trentelman is a conservation research scientist at the Detroit Institute of Arts. She received a Ph.D. in physical chemistry from Cornell University in 1989, and did post-doctoral work at Northwestern University and the University of Illinois at Chicago. She joined the DIA in 1995 following an appointment as Assistant Professor of Conservation Science in the Art Conservation Department at the State University College at Buffalo. Her research interests include the application of spectroscopic techniques to the study of metal corrosion processes.

Dr. Lowell McCann is a member of the Physics Department at the University of Wisconsin-River Falls. He received a Ph.D. in Condensed Matter Physics from Michigan State University in 1998, where he also did post-doctoral research prior to joining the faculty at University Wisconsin-River Falls in 1999.

NOTES

NON-DESTRUCTIVE ANALYSIS BY MICRO-RAMAN SPECTROMETRY AND ION BEAM TECHNIQUES: APPLICATION TO THE STUDY OF TWO GLAZE PALETTES FROM A FRENCH CERAMIST OF THE 19TH CENTURY

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Among the set of techniques currently available at C2RMF (ion-beam techniques, X-ray diffraction, X-ray fluorescence, and gonio-spectrophotometry), the introduction of micro-Raman spectrometry is a great opportunity to study the structural composition of works of art and archaeological artifacts by direct analysis without sampling.

This communication presents the first results of a research program dedicated to Charles Avisseau's glazing ceramic techniques and motivated by an exhibition planned in France in 2002. The complementarity of micro-Raman spectrometry and ion-beam techniques (PIXE and PIGE) will be shown: PIXE and PIGE leads to the global elemental chemical composition of the first ten micrometers in depth, while micro-Raman spectrometry provides structural information on the different components of the glaze, from the surface to the body.

Charles-Jean Avisseau was a French ceramist from the 19th century. He is considered by art historians to be a "neopalyssist", i.e., his production is characterized by many dishes ornamented with naturalistic representations, as Bernard Palissy had introduced the theme in Renaissance times. From the technical point of view, Avisseau worked at a time when chemistry and ceramic industry drastically changed: new colorants, new processes, the beginning of industrialization. Nevertheless, the legend is reported that Avisseau was looking for retrieving the exact knowledge of his idol, Palissy. One of the aims of our research was to show if indeed the techniques were those of the Renaissance, or if Avisseau had used the newly available materials.

Two of his palettes were studied. One, rectangular-shaped, is an association of small rectangles and squares of glaze terra cotta embedded in plaster and presenting a large range of colors and aspects (Fig. 1). The second palette, circular-shaped, shows triangular shards embedded in terra cotta but with a fewer number of colors: dark blue, pale yellow, orange and green.

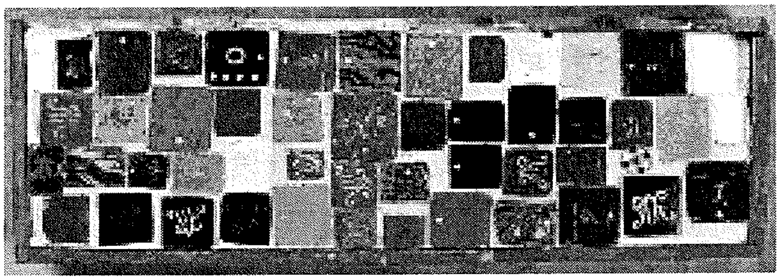

Figure 1

Taking some micrometric flakes was out of the question on such an artifact, so non-destructive analysis without sampling was carried out instead. The Raman tests were performed with a Labram Infinity from Jobin Yvon supplied with Notch filters, two lasers (532 nm YAG laser and a 632 nm He/Ne laser). The Labram Infinity system comes with a microscope and a horizontal exit on which an objective from the microscope can be fixed. Such a configuration was used to study the glaze palettes. Ion-beam analysis was carried out with a micro-beam extracted in air and produced by AGLAE [1]. Twenty-three elements were looked for by PIXE mode (Na, Mg, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Sr, Sn, Ba and Pb); and detected by two Si(Li) detectors optimized for the detection of low (1-10 keV) and high energy (6-25 keV) X-rays. Boron was quantified using the PIGE technique.

All the glazes are characterized by a lead siliceous matrix, sometimes containing boron. The results obtained by PIXE clearly indicate the present of transition metal ions dissolved inside of the glassy network for some blue and green colors (Co: marine blue, Cu: green). But some brown squares and some green ones did not reveal any coloring agent by superficial chemical analysis.

To solve this problem, micro-Raman spectrometry was applied. The results are complex because of the heterogeneity of the glazes: presence of crystals dispersed within a vitreous phase, non or incompletely fused quartz grains; and neoformed crystals, especially at the interface between the body and glaze. Nevertheless, we succeeded in identifying the use of hematite for the brown and maroon materials. For some green, we proved the presence of garnet structures (uvarovite), and for reddish hues the use of a chrome-tink pink with a tin sphene structure (fig 2).

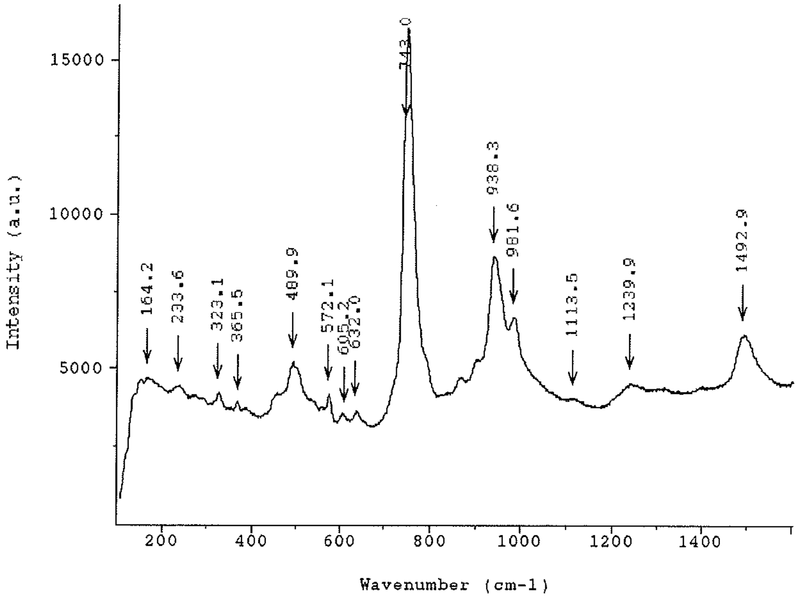

Figure 2

All these results show unambiguously that the techniques used by Avisseau are very different from those employed by Palissy. The association of micro-Raman spectrometry and ion-beam techniques allows us to reveal the use of new components that the ceramist had at his disposal to recreate the subtle colors of nature at the end of the 19th century. This research on Charles Avisseau's technique shows the changes due to the evolution of chemistry during this period. The complementarity of these non-invasive analytical techniques is primordial to study such artifacts. Thanks to them, the different glazing processes employed by the ceramist are now well established: glaze colored with metallic oxides; glaze colored with crystalline phases spread over the whole depth; and under-glaze paintings.

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Sylvie Colinart has a Master's degree in organic chemistry. At C2RMF, she is in charge of the polychrome artifacts department. As of now, her time is mainly spent working on Egyptian works of art.

Dr. Anne Bouquillon has a Doctorate in geology, and is currently in charge of pyrotechnology, stone and datation department of the C2RMF. At the moment, she is working on Palyssi's process and lead glazes.

Christel Pouthas has a Master's degree in analytical techniques. She is now working in the laboratory of the IFROA, which is a school for students learning conservation and restoration techniques.

NOTES

QUANTITATIVE FTIR SPECTROSCOPY: A POWERFUL TOOL IN WORKS OF ART CONSERVATION

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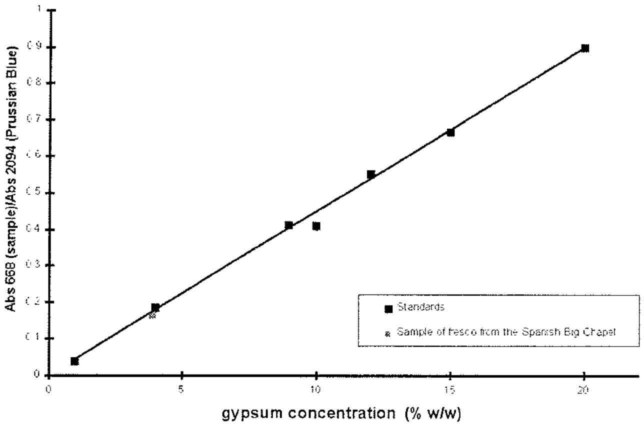
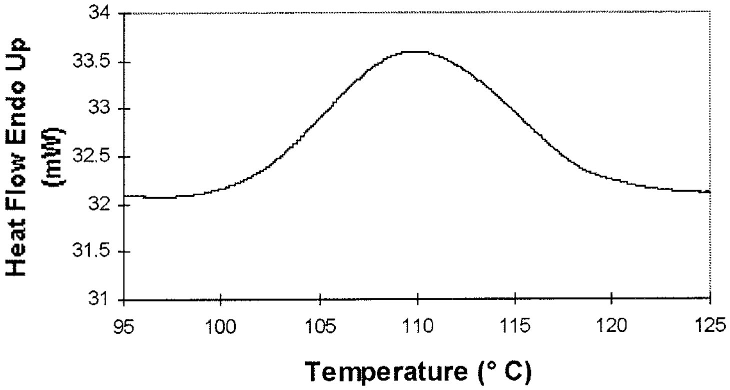
The present contribution reports the results of an investigation that has allowed us to develop a procedure based on quantitative FTIR spectroscopy to evaluate the amount of some contaminant agents in wall painting, mortar, and stone micro-samples. Calibration straight lines of absorbance versus analyte concentration were determined by adopting both the internal and external standard methods. As an external standard, we used Prussian blue, $Fe_3[Fe(CN)_6]_4$, that presents an unique infrared peak at 2094 cm^{-1}. The samples which were prepared to obtain the calibration curves were constituted of a mixture of $CaCO_3$/quartz (35% $CaCO_3$ and 65% quartz by weight) and contaminant agents in various concentrations between 1-20% by weight with respect to the above-mentioned mixture. These samples were diluted in KBr to obtain the usual pellets. As a contaminant agent we choose gypsum, one of the most common polluting substances present in the architectural porous materials. Many of the infrared peaks typical of gypsum were tested, but the best results were found for the peaks at 604, 668, and 3545 cm^{-1}; the internal standard method was shown to be more accurate giving better calibration straight lines. Figure 1 shows the calibration straight lines obtained with the internal standard method. In the same figure, we also report also a point obtained on a real sample.

Figure 1



In order to verify the finding achieved for the real sample, we compared it with the results that can be obtained by DSC calorimetry [1,2]. Figure 2 shows the DSC curve of this sample, coming from a fresco in the Spanish Big Chapel (Church of Santa Maria Novella, Florence), with the typical endothermic peak of gypsum dehydration. The calculated amount of gypsum is 3.9 ±0.5 % by DSC, in perfect agreement with the FTIR datum that gives 3.8 ±0.3 % (see Figure 1).

Figure 2



Another check of reliability of the method was performed on a sample coming from a 17th-18th century fresco in the Palazzo Frescobaldi at Florence. DSC calorimetry had given 15.0 ± 0.5 % by weight of gypsum, and FTIR analysis gave 15.1 ± 0.3 %. Taking into account these positive results, the method is going to be extended to other contaminants such as nitrates, oxalates, and organic compounds.

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2. L. Dei, M. Mauro and G. Bitossi, Characterisation of Salt Efflorescences in Cultural Heritage Conservation by Thermal Analysis, *Thermochimica Acta,* 317 (1998) 133.

Barbara Salvadori graduated in Chemistry (February 2000), University of Florence. At present, she is a Ph.D. student in Science for Cultural Heritage Conservation, working on a project of Inorganic Nanomaterials for porous materials conservation.

Elizabeth Melnik graduated in Biochemistry (August 2001) at the University of Arizona. In summer 2001, she visited the Department of Chemistry at the University of Florence, conducting research on the quantitative use of FTIR in cultural heritage conservation.

Valentina Errico graduated in Chemical Engineering (July 1999) from the University of L'Aquila. At present, she is working on physicochemical characterization of polymeric materials in cultural heritage conservation in the frame of a fellowship by Campec Consortium, Naples.

Marcello Mauro, graduated in Chemistry (April 1996), University of Florence. He is the author of many publications on physical chemistry applied to works of art conservation. At present he is a research assistant at the Consortium CSGI, Department of Chemistry at the University of Florence, working on diagnostics and new materials for frescoes conservation.

Dr.Luigi Dei graduated in Chemistry in 1980 and earned his Ph.D. in physical chemistry in 1987; he is now associate professor of physical chemistry at the Faculty of Sciences of the University of Florence. He is the author of more than ninety publications in the field of colloid and interfaces and physical chemistry applied to the works of art conservation. He is also currently lecturer of biological physical chemistry and chemistry of restoration at the Faculty of Sciences of the University of Florence. He has for years been a scientific consultant for many national and international conservation projects.

NOTES

INFRARED SPECTROSCOPY IN THE ART CONSERVATION PROGRAM AT QUEEN'S UNIVERSITY: SOME APPLICATIONS OF A DIAMOND ATR ACCESSORY

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The recent acquisition of a Nicolet Avatar 320 FT-IR spectrometer, with "Golden Gate" single pass diamond attenuated total reflectance (ATR) and diffuse reflectance (DRIFTS) accessories has enhanced the Master of Art Conservation program at Queen's University. Lectures on the theory and applications of vibrational spectroscopy (both IR and Raman) are now reinforced with practical "hands-on" instruction in the use of the IR spectrometer, sampling techniques and accessories. Many students now make use of the diamond ATR accessory in their research projects. The Golden Gate accessory is shown below, mounted in the sample compartment of the Nicolet spectrometer. This accessory will be described; and the advantages and limitations of the ATR technique will be discussed.

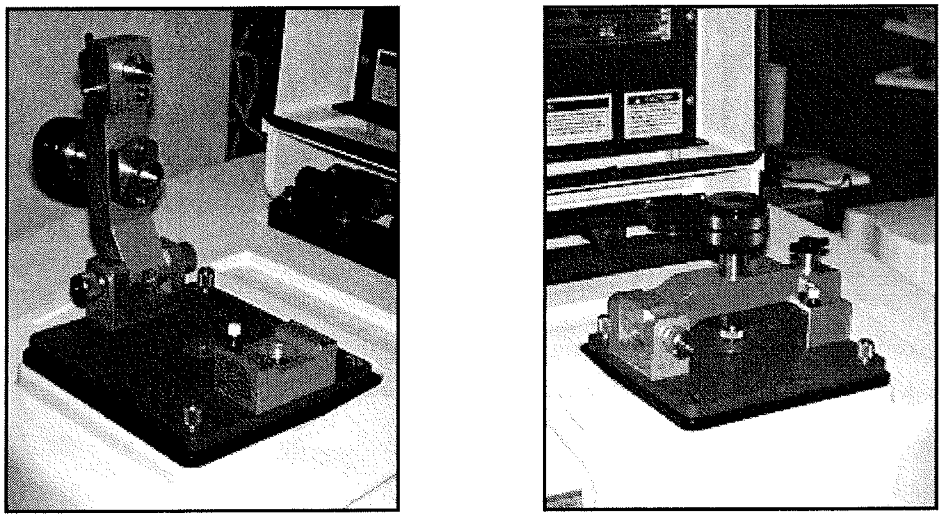

Figure 1. The Golden Gate diamond ATR accessory

The talk will be illustrated by some recent contributions of infrared spectroscopy to student research projects. These include: attempted identification of the binding medium in a painting attributed to the Rubens' School (student Agata Sochon); attempted identification of the binding medium in an ex-voto painting (student Sophie Roberge); and examination of a dark patina found on some Egyptian bronzes at the Royal Ontario Museum (student Alison Whyte). These studies were all carried out using the

diamond ATR accessory. A study of residues left on metal surfaces after treatment with commercial metal polishes was carried out using the DRIFTS accessory (student Michael Belman).
The Golden Gate accessory has been used to study the effects of aqueous detergents used in the cleaning of acrylic paintings. The results of swabbing paint surfaces with aqueous detergents and immersing different samples in cleaning solutions have been examined using infrared spectroscopy. The detergent solutions were also examined before and after use to look for any materials that might have been removed from the acrylic paint surface. The dilute detergent solutions were concentrated by freeze-drying. Preliminary results indicate that any effects of the detergents on the paint surface are not detectable by infrared spectroscopy, and the amounts of material removed by swabbing or leached from the paint during immersion is below the level of detection. However, Tom Learner and Herant Khanjian have reported detecting differences in standard acrylic films before and after water immersion using a micro-ATR accessory.

Before the acquisition of the Nicolet spectrometer and the ATR accessory, infrared transmission spectra were obtained using a PerkinElmer Model 983G dispersive (grating) spectrometer interfaced to a personal computer. This instrument, located in the laboratory of the author (H.F.S.) in the Department of Chemistry, was used by several students for their research projects. Several examples of this earlier work will be presented. A study of pigments on coated papers was carried out (student Sharon Wightman), the effect of an odor-remover on acrylic paint was studied (student Elizabeth Jablonski) and the pigments present in several blue watercolor paints were identified (student Jan Cavanaugh). Both infrared spectroscopy and Raman microscopy were used to study the Maya Blue pigment and other materials found in wall paintings in the recently excavated Great Temple of Tenochtitlan in Mexico City (student Dulce Maria Grimaldi).

Dr. H.F. (Gus) Shurvell is an Emeritus Professor of Chemistry and Adjunct Professor in the Art Conservation Program at Queen's University, Kingston, Ontario, Canada. He holds B.Sc. and D.Sc. degrees in chemistry from Exeter University, U.K.; and M.Sc. and Ph.D. degrees from the University of British Columbia. He was an Attaché de Recherche at the Faculté des Sciences de Marseille, France and has spent sabbatical leaves at the Queensland University of Technology and the University of Queensland in Brisbane, Australia and at The University of York, U.K. He was a Visiting Research Fellow at the Thornton Research Centre, Shell Research Ltd. Chester, U.K. He was a Visiting Professor at the University of Cape Town and at the Universidade Federal Rural do Rio de Janeiro. His area of research is the application of Raman and infrared spectroscopy to the study of the structure and properties of materials. He has over 160 scientific publications to his credit, including co-authorship of four books.

Dr. Alison Murray is an Associate Professor in the Art Conservation Program at Queen's University. She received her Bachelor of Science degree in chemistry from McGill University and her Master of Science and Ph. D. degrees in materials science and engineering with a specialization in conservation science from a joint program between Johns Hopkins University and the Smithsonian Institution. She has held fellowships at the Canadian Conservation Institute and the National Gallery, London. Her areas of research include degradation in art objects and identification of artist's materials and techniques. She is conducting research into the cleaning of paintings using mechanical testing and other techniques.

NOTES

IN SITU VIBRATIONAL SPECTROSCOPY

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INTRODUCTION

The identification of materials, and particularly deterioration products is fundamental to conservation research. The sample size required for vibrational spectroscopies (infrared and Raman) has shrunk dramatically over the past twenty years, and analysis of sub-microgram samples is now routinely undertaken in conservation work. However, situations are often encountered when removing a sample is undesirable or indeed impossible. Obtaining an unadulterated sample can be very difficult with extremely small, mixed phenomena such as salts on glass surfaces and corrosion products. Even microsampling can be disfiguring to high gloss, intact surfaces such as amber. Sampling can also be hazardous with hard, brittle materials such as glass, ceramics and some minerals. The British Museum has recently purchased two systems that allow in situ, non-interventive analysis of object surfaces.

INFRARED MICROSCOPY

The Nicolet Inspect IR is a fixed focus reflectance infrared (IR) microscope. Thin layers over reflective surfaces can be readily analyzed with the reflection-absorption technique. This has been instrumental in a recent study of unusual silver tarnish effects on display. The technique has identified several instances of tarnish concentrated at breaks in cellulose nitrate lacquer layers. The fixed geometry and focal length of the infrared beam allowed a calibration of absorbance values against lacquer layer thickness (measured with a permascope) for standard thickness lacquer films. In three instances, differential tarnishing was associated with different thicknesses of lacquer. The degree of degradation of the lacquers was determined from the carbonyl and nitrate absorption bands at 1740 and 1650 cm^{-1}, allowing a comparison of lacquer stability under different display environments. Analyses from the porous areas of the silver surfaces also produced reasonable quality spectra from residues of previous conservation treatments. These residues were identified by comparison with a library of aged conservation materials prepared on silver.

In some situations identifiable spectra can be collected from a surface by direct reflectance. This technique has been successfully applied to amber, glass, mineral surfaces and corrosion products. Infrared microscopy has been used to rapidly survey an artifact surface to control interventive sampling of complex multiphase surfaces such as archaeological iron. A collection of glass intaglios by James Tassie was examined to identify any deterioration occurring during storage. Analysis of surface deposits identified silicone rubber casting materials (which could be distinguished under magnification), potassium salts, calcite (again a residue from casting) and some dust. These final three materials could not be distinguished visually, and FTIR microscopy allowed identification. The potassium salts are a sign of ongoing deterioration of the glass, with potassium being leached out of the glass structure and reacting with gases in the environment. The state of deterioration of glass surfaces can also be determined by the relative absorptions due to bonding and non-bonding silicate vibrations. One intaglio was very badly cracked, but infrared microscopy showed minimal deterioration of the glass surface. The intaglio had been incorporated into a ring, and XRF analysis of the hoop identified a significant silver content in the metal alloy. Silver has a high coefficient of thermal expansion, and the fracture pattern shown by the intaglio corresponded with that expected from the alignment of the hoop.

The small area from which a spectrum is collected (0.1mm diameter) allowed the intaglio deterioration mechanisms to be further elucidated. Several intaglios had undeteriorated engraved and recessed surfaces, while the flat glass surfaces were deteriorated. Two of these intaglios had small areas of Paraloid B72 coating over their registration numbers on the reverse sides. Those (flat) surfaces were generally deteriorated, except for approximately 2mm bands running around the paraloid coated areas. These observations indicated a material holding moisture and pollutants in contact with the flat surfaces of the intaglios, as opposed to reaction with airborne gases. Examination of photographic records of the collection revealed a likely culprit in the paper tissue packaging material.

RAMAN MICRO-ANALYSIS

The Dilor Infinity confocal microraman system allows analysis of smaller areas, down to 4.5 μm diameter, and a much more flexible geometry towards the sample. Microraman spectroscopy has elucidated the very complex and intimate mix of materials present on the corroded surfaces of archaeological iron artifacts. It identified sub-micron lepidocrite crystals strongly adhered onto quartz grains incorporated in the corrosion layer of iron artifacts from Sutton Hoo. Other techniques such as FTIR and XRD could not identify the iron compounds due to the large excess of quartz. The iron compounds were well adhered, precluding physical removal and chemical removal could alter their nature. Raman has advantages over infrared microscopy for the detection of soluble salt species on a surface. Infrared microscopes require sensitive MCT detectors which cut off at 650cm^{-1}, losing much valuable information for these species. The minimum wavenumber of Raman microanalysis systems is determined by the notch filter and homogeneity of the laser, and 100 is generally achieved.

The versatility of the analytical geometry of the Raman technique was illustrated with an analysis of corrosion products at the bottom of a narrow crack (less than 1mm wide) through a corrosion layer. A group of Egyptian figurines was covered with a very thick layer of a pale blue corrosion product. Although this material had been encountered and analyzed previously, its massive appearance on these objects was unusual, and conversion of an existing corrosion product was suspected. The composition of the corrosion product was shown to be identical throughout the thickness of the corrosion layer, arguing against its formation by conversion of an existing corrosion product.

THERMAL INFRARED SPECTROSCOPY

Thermal infrared spectroscopy holds the promise of non-interventive analysis for a much wider range of materials than what are suitable for reflectance IR microscopy. While good quality spectra can be produced if one of the absorption mechanisms predominates, mixed spectra do occur, making interpretation difficult if not impossible, and thus providing a major limitation to reflectance IR microscopy.

Thermal IR involves heating the sample surface by a few degrees with laser pulses. The emitted IR radiation is passed into an interferometer and converted from the time domain to the energy (frequency) domain by Fourier transform, producing a conventional spectrum. Appropriate choice of illuminating laser wavelength and signal processing in the time domain can also yield some control over the information depth, producing a form of depth profiling. Such information would be beneficial to deterioration studies, and to overcome surface contamination problems without the need for cleaning. The British Museum is presently involved in a collaboration with South Bank University to develop a spectrometer based on this technique.

CONCLUSIONS

Both infrared and Raman microscopies have made a valuable contribution to conservation research at the British Museum, allowing previously impossible in situ analysis to become routine. The value of both techniques increases greatly when combined with other analytical techniques such as SEM, XRD and ion chromatography. The combination of this holistic approach with the ability to analyze very small areas has helped to understand some of the complex deterioration mechanisms encountered in conservation research. Such in situ analysis also shows great potential for the monitoring and evaluation of conservation treatments.

David Thickett obtained an honors degree in natural sciences from Cambridge University and worked for two years in ceramics research before joining the British Museum in 1990. His research interests include the deterioration and conservation of stone, metal and glass artifacts. His previous work has included preventive conservation measures and particularly those associated with emissions from storage and display materials.

Laurianne Robinet obtained a degree in chemistry from the Institut Universitaire de Technologie in Orsay, France, in 1997. She then specialized in organic and analytical chemistry and completed her Master's degree in 1999. She joined the Conservation Research Department of the British Museum in 2000 as a Conservation Scientist, where she is responsible for preventive conservation in the museum and performing analysis on museum objects.

NOTES

THE NEW IRUG INITIATIVE: A WEB-BASED SPECTRAL DATABASE

Beth Price[1], Janice Carlson[2], Boris Pretzel[3], Ken Ehrman[4] and Andrew Lins[1]

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The Infrared and Raman Users Group (IRUG) promotes the sharing of technical expertise and spectral data among professionals using infrared (IR) and Raman spectroscopic techniques for the study of the world's cultural heritage. The Group has made significant strides in the last several years: reformatting, annotating, compiling and distributing a peer-reviewed database of over 1,250 IR and Raman spectra; instituting quality standards for spectral submissions; and organizing technical meetings. A milestone event of IRUG occurred last spring when the compilation of the *IRUG Edition 2000 Spectral Database* in digitized and hardcopy forms was widely distributed. This achievement was the result of a collaboration spanning several years of work by more than 70 individuals representing over 50 institutions.

With *Edition 2000 Spectral Database* in hand, IRUG has now embarked on a new web-based initiative that will greatly facilitate the further development of the *Database* and expand its audience and benefits. This new international initiative will allow for the first time large-scale web-based exchange of data by scientists in the fields of conservation and historic preservation.

The primary goal of the IRUG web initiative is to encode the *Edition 2000 Spectral Database* into a secure, searchable database accessible via IRUG's worldwide web site at www.irug.org. The password-protected, online *Database* will be accessible as a research tool for searching and viewing IR and Raman spectra. Through this site, contributors will be able to supplement the *Edition 2000 Database* by submitting new spectra online. The contributors may upload their spectral files and employ a user-friendly program to annotate and modify the files to a consistent format. Spectral submissions will then be evaluated according to standardized criteria by a group of editors. A contributor may check the status of his or her submissions online; until they are accepted, however, submissions will not be viewable.

Another objective of the web initiative is to expand communication between scientists via the IRUG site, enhancing IRUG's sense of community. The new website will feature an online forum where colleagues may discuss data and share information. A searchable bibliography of spectroscopic literature, news of upcoming events, pictures of members' activities, and hyperlinks to contributors' websites and other web-based resources will also be made available via a new, easy-to-use graphic design.

The web project's estimated completion date is early 2003. The project will progress through the following phases: database infrastructure and offline prototype construction; website graphic design, construction, and certification; site functionality testing; and launch of the system to the IRUG website. Construction of the new site and procedures is currently underway by Digital Bridgeway, Inc., a web development consultancy. During this project, IRUG will continue to accept spectral contributions under its current submission guidelines.

The success of IRUG and its *Database* thus far has been due in large part to the support of a community that represents conservation and historic preservation endeavors on an international scale, beyond the interests of any single institution or organization. Its growth and accomplishments are the product of the collaborative efforts of the larger scientific community in conservation, which it is intended to serve. After reviewing the history of the IRUG and its *Database,* this paper will present the plans and progress made to date on IRUG's new web initiative. IRUG welcomes spectroscopist volunteers to test the online system and provide comment. Interested individuals may contact IRUG through one of the chairpersons listed on the IRUG website at www.irug.org.

Beth A. Price is senior scientist in the Conservation Department at the Philadelphia Museum of Art, where she has worked for more than twelve years. Prior to joining the PMA staff, she spent six years in corporate research and development as an organic chemist. She holds degrees in Art History and Chemistry from the State University of New York at New Paltz. She has been an invited lecturer at the Winterthur/University of Delaware Program in Art Conservation and the University of Pennsylvania Historic Preservation Program. She has published numerous papers on the application of analytical techniques to the understanding of cultural artifacts. Of particular note is her work in compiling several infrared spectral databases for use in the conservation science profession.

Janice H. Carlson is senior scientist in the Conservation Division of the Winterthur Museum and adjunct associate professor in the Winterthur/University of Delaware Program in Art Conservation (WUDPAC). She received a B.A. in chemistry from the College of Wooster and an M.S. in analytical chemistry from the University of Michigan. After working as an analytical chemist in industry for several years, she joined the staff of Winterthur Museum in 1974 as Museum Chemist. In the past 28 years, Jan has done research on the X-ray fluorescence analysis of silver, brass, pewter and glass objects as well as on the use of infrared spectroscopy in the examination of artistic and historic objects. She has presented her work at a number of national and international conference, and has authored or co-authored more than 25 papers in the field of conservation science.

Boris Pretzel was born in West Berlin, and was educated chiefly in Europe. He graduated from Bristol University with a B.Sc. in Chemical Physics, followed by postgraduate qualifications and a term as researcher in Bristol. Subsequently, he worked as a Patent Examiner in the European Patent Office in The Hague and Berlin, where his main field of responsibility was in solid-state physics devices, manufacturing and materials. Since 1989, he has been the Materials Scientist in the Victoria & Albert Museum Conservation Department's Science Section. His responsibilities cover a broad range of preventive conservation issues relating to the storage and display of artifacts. Research interests include the interaction of artifacts with environments, lighting, color, and materials analysis. He is a member of the editorial board for the Journal of Cultural Heritage; European Chair of IRUG; and a chartered physicist.

Ken Ehrman is a software developer and consultant; and is currently President of Digital Bridgeway, a software development consultancy which he founded. Ken has worked as an Internet specialist for well over a decade in many different capacities in the graphic arts and software development technology fields. In 2001, Ken decided it was time to move out on his own and launched Digital Bridgeway, which so far has met with great success. When not working, Ken is either in front of his computer producing his own artwork for fun, enjoying dining out, or traveling.

Andrew Lins is Chair of the Conservation Department at the Philadelphia Museum of Art. Andrew's academic background includes an M.A. from New York University in Art History and an M.S. in corrosion science and engineering from Sir John Cass College, London. He joined the conservation department of the Philadelphia Museum of Art in 1979. His research interests include the history of modern technology and the study of corrosion mechanisms.

NOTES

TUESDAY MARCH 5, 2002

ORAL PRESENTATIONS

IR-SPECTRA OF THE GROUNDS FROM PAINTINGS BY SOME WELL-KNOWN RUSSIAN ARTISTS OF THE 18TH AND 19TH CENTURIES

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In the course of the present work, IR-spectra of microscopic amounts of the grounds (91 specimens) from a number of well-known Russian artists of the 18th (F.S. Rokotov, I.P. Argunov, M.L. Kolokolnikov, P.S. Drozhdin) and 19th centuries (O.A. Kiprensky, N.M. Podkluchnikov, M.D. Milnikov, I.K. Aivazovsky, V.G. Perov) were examined. Earlier, in works [1-6], it was shown, by use of microchemical analysis and microscopy, that the basic components of the grounds, which are being analyzed in the present work, are oil, animal glue, lead white, chalk, and ochres, as well as quartz and alumosilicates; the last two are the parts of their chemical compositions. The present IR spectroscopic examination was undertaken to get additional information on the grounds' compositions.

The microtablets with KBr were being prepared from the specimens to take their IR spectra by use of spectrophotometer 983G of PerkinElmer in the range 4000-180cm^{-1}. IR spectra of some specimens of grounds were taken by use of spectrometer "Spectrum one" of PerkinElmer in the range 4000-600 cm^{-1}, when it was impossible to take a satisfactory spectrum of the ground by use of spectrometer 983G. After taking the IR spectrum, some tablets had been dissolved in hydrochloric acid and the solutions were analyzed by use of emission spectrometer PS-2 of the "Baird" firm to find out if they contain Ca, Mg, Ba, Pb, Al, Fe, Si, Zn, Ti and Cr for more precise definition of element composition of the grounds.

To identify the components of the grounds' compositions, the spectra characteristics of oil (2925, 2855, 1740-1700 cm^{-1}), animal glue (1680-1650, 1550-1510 cm^{-1}), chalk (1430, 875, 714, 320 cm^{-1}), dolomite (1430, 880, 726, 361 cm^{-1}) and quartz (1165, 1080, 797, 778, 694 cm^{-1}) were used, as well as data of element analysis. IR spectroscopic analysis allowed us to identify oil, animal glue, lead white, chalk, quartz and alumsilicates (i.e., confirmed the results of microscopic and microchemical analyses). Whereas dolomite ($CaCO_3 \bullet MgCO_3$) was identified in all the grounds of F.S.Rokotov's paintings and in some other grounds of the artists who worked in the 18th century, along with a small amount of barium sulphate which was identified in the number of grounds of the artists who worked in the 19th century. The presence of dolomite in the grounds can be explained by the fact that artists used ochre, which contained dolomite. The presence of barium sulphate can be explained by its wide use in the production of the materials for painting since the early 19th century.

It should be noted that the spectra of dolomite and chalk are rather close to each other, and dolomite can be identified reliably in the far wave zone of spectrum by the 361 cm^{-1} band, while the analogical band of chalk is 320 cm^{-1}. Comparison of the intensities of the absorption bands of the components in IR spectra of the grounds allowed us to obtain information on approximate quantitative correlation of oil, lead white, chalk, dolomite, quartz, alumsilicates and barium sulphate in the grounds' compositions.

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Born in 1979, **Dr. Boris Zhadanov** graduated with a chemisty degree in 1962, and earned his Ph.D. in 1969. He was a staff member Research Institute of Chemical Reagents (IREA) from 1962-1995, and since then has been a conservation chemist at the Grabar Art Conservation Centre in Moscow.

NOTES

CHANGES IN ADHESIVE RESINS AS A RESULT OF LASER IRRADIATION: AN FTIR STUDY OF LASER WAVELENGTH EFFECTS

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Epoxy resins are widely used to consolidate glass and stone objects because of their durability, good adhesion and excellent mechanical strength. A major drawback of epoxy resins is their poor reversibility. The use of solvents for removing epoxies is not effective; and very often, mechanical treatment is the only option available to the conservator.

In order to evaluate the possibility of using lasers for the removal of epoxy from works of art, a preliminary study was conducted on two epoxy formulations: HXTAL NYL-1 and ARALDITE AY103/HY991. The study focused on the behavior of the resins under irradiation at four different wavelengths: 1064 nm, 532 nm, 355 nm, and 2940 nm. FTIR spectroscopy was used to investigate changes in the polymer films after laser treatment.

EXPERIMENTAL

A - Resin systems - ARALDITE AY103/HY991 is based on Bisphenol A Diglycidyl Ether (DGEBA) as the epoxy pre-polymer, with dibutyl phthalate added as a diluent. The hardener is a combination of triethylenetetramine (TETA), polyamide resin and tris(dimethylaminomethyl)phenol. HXTAL NYL-1 is based on the diglycidyl ether of 4,4-isopropylidenedicyclohexanol. The hardener contains polyoxypropylene diamine, trimethylolpropane (TMP), and an unspecified substituted imidazole.

B - Laser equipment The Infinity Q-switched Nd:YAG laser was used at 1064 nm (NIR), 532 nm (VIS) and 355 nm (UV), pulse duration 3ns, energies between 50 and 100 mJ, repetition rate 3 Hz, and spot size 5 mm. The "Conservator" Er:YAG laser was used at 2940 nm (MIR), pulse duration 200 µs, energies between 50 and 100 mJ, repetition rate 15 Hz, and spot size 3mm.

SPECTROSCOPIC PROPERTIES OF THE RESIN FILMS

UV-Vis spectrophotometric analysis of the two resin films was performed between 190 nm and 1100 nm, with a Cary 50 UV-Visible Spectrophotometer. Araldite AY103/HY991 absorbs considerably in the UV at 355 nm, while it is relatively transparent in the visible and NIR. HXTAL NYL-1 does not absorb in the examined range, at wavelengths longer than 255 nm.

IRRADIATION RESULTS

Nd:YAG Laser - The effect of the Nd:YAG laser at all three wavelengths was more noticeable on Araldite AY103/HY991 than on HXTAL NYL-1. Irradiation in the NIR, VIS and UV produced yellowing, darkening and partial ablation of the Araldite film, with the more pronounced transformations occurring at VIS and UV wavelengths. HXTAL NYL-1 showed only slight damage after exposure to 1064 nm and 532 nm radiation at the same fluences used for Araldite. Laser UV treatment of HXTAL NYL-1 resulted in slight yellowing and fragmentation of the resin film.

Er:YAG Laser - Treatment with the Er:YAG laser at 2940 nm damaged considerably both resin films. Araldite resulted more sensitive than Hxtal. Absorption of the MIR radiation developed considerable heat in both polymer films, and material flow occurred in both resins. The darkened resins were partially soluble in a range of organic solvents.

DISCUSSION

Microscopic Examination of Laser Irradiated Resin Films - For both resins, irradiation with the 2940 nm Er:YAG laser resulted predominantly in thermal processes, and eventually in a partial breakdown of the film. The use of UV, VIS and NIR radiation led to a more gradual transformation sequence. Localized absorption of laser radiation (probably by oxidized impurities) gave way to overheating and formation of bubbles throughout the matrix. HXTAL NYL-1 was found to be considerably more resistant to damage than Araldite AY103/HY991, at all wavelengths employed.

FTIR Spectroscopy Araldite AY103/HY991 exposed to MIR radiation showed a complex IR spectrum. The splitting of the carbonyl absorption into various peaks between 1739 cm^{-1} and 1712 cm^{-1} and a similar splitting of the amide I band indicate the oxidation of several chain positions. Irradiation at 355, 532 and 1064 produced a marked increase of the carbonyl peak at 1725 cm^{-1}, the appearance of a small peak at 1699 cm^{-1}, the increase of the n-CH_3 bands at 2870 and 2961 cm^{-1}, and a marked decrease of the amide I and II bands. This is probably due to partial depolymerization of the polyamide hardener, and the appearance of ester functions conjugated with a C=C bond on the resin chain. The changes were more evident in the spectrum of the UV treated sample. Treatment of HXTAL NYL-1 with MIR radiation results in the appearance in the spectrum of peaks at 1720 cm^{-1} and 1734 cm^{-1}, together with a broad band at 1650 cm^{-1}. This is consistent with oxidation at several positions on the chain. UV treatment resulted in a net increase of the amide I band, pointing to the oxidation of the carbon atom in a to the amine group.

CONCLUSIONS

The use of FTIR spectroscopy, together with microscopic examination can assist in the identification of the transformations occurring during laser treatment of cured epoxy resins. Some differences in deterioration mechanisms dependent on the nature of the resin and on the wavelengths used have been identified. The importance of secondary components in defining the behavior of the resin system cannot be neglected, and further studies on model systems are under way to better define the dynamics of epoxy resin systems under laser exposure.

Dr. Marco Leona recevived an M.S .in chemistry and a Ph.D. in crystallography from the University of Pavia, Italy. His main area of interest is the development of non-invasive techniques for the study of works of art and artists' materials. He is currently Senior Conservation Scientist at LACMA.

Meg Abraham holds a B.Sc. in physics and a M.S. in archaeology. She is currently a doctoral candidate in materials science at Oxford University. She has been conducting studies on the application of lasers to the conservation of works of art for over ten years. In July 1996, she became the Principal Investigator for the LACMA/NCPTT Laser Conservation Program.

Stefanie Scheerer, Diplom-Restaurator (Fh), has been a Mellon Fellow in the Laser Conservation Research Facility of LACMA for the period November 2000 - November 2001. She graduated in 1999 from the objects conservation course at the University of Applied Sciences in Berlin (FHTW Berlin) and spent one year as a graduate intern at the GCI Museum Research Laboratory. Her principal interests are the conservation and technology of ethnographic materials.

NOTES

IDENTIFICATION OF BLUE PIGMENTS IN YORUBA WOOD SCULPTURES

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A variety of infrared techniques, in conjunction with light microscopy and SEM-EDS, have been used to identify the blue pigments in several Yoruba *Gelede* helmet masks. These results indicate the feasibility of a larger study to relate pigment usage to the development and adaptation of European colorants into West African art. European laundry bluing has been used widely as a colorant in ethnographic objects in cultures around the globe including Yorubaland in present day Nigeria. It is not clear if indigo, the dye for the famed Adire cloth of the Yoruba, was gradually replaced as the blue pigment for painting wood sculptures as European traders brought their laundry products with their vibrant blues into this area.

The particular pigment contained in these products, for correcting yellowness in white fabric by adding blue, changed with the overall development of the chemical industry. Early products contained indigo; these products were first replaced by ones containing Prussian blue. A well-known liquid form of this laundry blue solution, Mrs. Stewart's, became available in 1883 and continues to be distributed in the US and Canada. The name associated with ultramarine laundry bluing is the English manufacturer Reckitt's, which began to market products containing this pigment in 1873, and began direct distribution to Africa in 1890 with a starch-ultramarine dry product called Robin Blue. The vibrant blue of the ultramarine from this source appears widely in 20th century Yoruba painted sculpture.

Consistent with ethnographic studies, diffuse reflectance spectroscopy using fiber optic probes shows the characteristic spectrum of ultramarine as the blue pigment in the surface paint on two 20th ceremonial *Gelede* masks in this study. These masks, as well as other Yoruba sculptures, are repainted annually so that, if not subject to repainting as a "conservation" measure, the surface paint provides a snapshot of the materials used by the African artist at the time of collection. Polarizing light and infrared microscopy along with SEM-EDS analysis revealed that Prussian blue was the surface pigment of one *Gelede* mask, collected in the 1920's; a second mask, thought to originate from this period, was colored with ultramarine. Although the extensive late 19th century collecting expeditions introduced the patrons of western museums to African art, a relatively small portion of these museum collections have well-documented provenance.

The results of fiber optics reflectance spectroscopy for preliminary pigment identification of such late 19th and early 20th century Yoruba sculpture in several museum collections will be presented along with more detailed infrared spectral analysis of selected pieces. Despite the limited studies of pigments in Yoruba sculpture from this period, even less is known about the binding media in these objects. Characterization of the binders is particularly important for conservation of the unstable matte paints, characteristic of these objects. Detailed studies of samples taken from a *Gelede* mask, purchased in 1911 by Sir Henry S. Wellcome from the UCLA Fowler Museum of Cultural History, identified the blue pigment as ultramarine, the white as calcium carbonate, and the binder as starch with gypsum and clay as extenders.

Dr.Margaret V. Merrritt is Professor of Chemistry at Wellesley College where she teaches courses in analytical and introductory chemistry as well as a course for non-science majors, Chemistry and Art. She received her B.A. in Chemistry from The College of Wooster and a Ph.D. in analytical chemistry from Cornell University in the 1960's, followed by postdoctoral appointments at UC Riverside and Carnegie-Mellon University. She taught for two years at Franklin & Marshall College prior to joining The Upjohn Company (now Pharmacia) where she spent ten years as a research scientist in physical and analytical chemistry research. She joined the Wellesley College faculty in 1982. Professor Merritt's recent studies of West African sculptures developed from her use of art objects in teaching analytical chemistry at Wellesley.

Kate Duffy graduated from Hood College with a B.A. in Chemistry and received her M.S. in Chemistry from Tufts University. She served as Advanced-Level Science Intern at the Museum of Fine Arts, Boston, followed by two years as a Science Research fellow at the Los Angeles County Museum of Art. Prior to joining the Williamstown Center in 2000, she was the Associate Museum Scientist at the Winterthur Museum and Gardens, Winterthur, Delaware.

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ORGANIC MATERIALS USED IN THE 'PAINTS' ON PERUVIAN QERO CUPS

Richard Newman and Michele Derrick

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Qeros are wooden drinking vessels that have been used for millenia in the Andean region for ritual consumption of maize beer. In the Inka period, most were decorated with carved geometric motifs. From the cusp of the Inka-Colonial period, painted decoration became more common. Most of this painted decoration actually consists of thin layers of a pigmented rubbery material that was cut out and inlaid into shallow carved cavities.

Nearly 350 samples of 'paint' from about fifty qeros have been analyzed in conjunction with a larger study of the technology of over 150 qeros in the collections of the Brooklyn Museum of Art, National Museum of the American Indian, Metropolitan Museum of Art, and American Museum of Natural History. IR microspectroscopy has been a very important tool in the research on the 'paint' samples. The results of the research will be discussed in this presentation.

Richard Newman has a B.A. in Art History, an M.A. in Geology and a certificate for completion of a three-year apprenticeship in conservation science at the Harvard University Art Museums. He has been Research Scientist at the Museum of Fine Arts, Boston for the past 15 years. Following administrative reorganization three years ago, he now also serves as Head of Scientific Research, one of the divisions in the Conservation and Collections Management Department. Among his projects are research on the materials used by stone sculptors in ancient India and a collaborative project with art historian Gridley McKim-Smith on the painting materials and techniques of Diego Velazquez, research based on examination and analysis of about two dozen of the artist's works in the Prado Museum in Madrid. He teaches in the Museum Studies program at the Harvard University Extension School; serves as coordinator and is a lecturer in a Museum of Fine Arts seminar course, 'Preservation and Scientific Examination of Works of Art,' offered to students at six Boston-area universities and colleges; and is also a lecturer in the undergraduate 'Archaeological Science' course offered by the Center for Materials Research in Archaeology and Ethnology at MIT.

Michele Derrick has an M.S. in analytical chemistry. She worked at the Getty Conservation Institute for 12 years before moving to Boston, where for the past four years she has worked as a conservation science consultant at the Museum of Fine Arts. Her book, Scientific Tools for Conservation: Infrared Spectroscopy, was published by the Getty Conservation Institute in 1998. She is the principal developer of the 'Conservation and Art Materials Dictionary,' which was created with the aid of a grant from the National Center for Preservation Technology and Training. This database, which now includes basic information on over 10,000 materials used by artists and conservators, was made available on the Museum of Fine Arts, Boston website in mid-2000. She is currently working on various enhancements to the database, and works with Richard Newman in carrying out examinations and analyses in the scientific research lab at the MFA.

NOTES

INFRARED SPECTROSCOPY APPLIED TO THE ANALYSIS OF PAPERS AND INKS IN MANUSCRIPTS AND ENGRAVINGS FROM CULTURAL HERITAGE.

Núria Ferrer[1], M. Carme Sistach[2], Anna Vila[3] and José F. García[3]

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Infrared spectroscopy has been successfully applied to many fields related to cultural heritage. In our laboratories, different samples concerning problems of conservation and fraud have been analyzed in the last decade. Artworks are, in many cases, unique and valuable. These characteristics imply important restrictions to removing even small amounts of matter, and necessitate coupling some accessories to the spectrophotometer in order to minimize the samples required. Comparisons among different methodologies applied to the same sample have to be checked carefully in order to choose the best one for each problem.

This study compares different ways of sample preparation and infrared accessories applied to characterization of papers and inks, both in ancient and modern samples: diffuse reflectance; KBr pellets in transmission; diamond cell with microscope or beam condenser; microscope with attenuated total reflectance objective; and remote analysis.

The two main restrictions in infrared spectroscopy analysis are the size and difficulties of handling. Three kinds of sample compartments are available, depending on the size of the sample to be placed in the spectrometer:

- macro compartment: employs a beam between 2-10 mm and any type of accessory might be fitted.
- semimicro compartment: requires the use of a beam condenser and the spot of the beam in the sample is about 1 or 2 mm.
- micro compartment: the size of the beam is less than 1 mm and a microscope needs to be used.

Obviously, large samples can also be located on the microscope, but in such cases the measurement area is reduced to less than 100 microns. Therefore, if an analysis of the predominant material in the sample is required, its homogeneity must be assured and defects or pollutants must be avoided. This methodology has been applied to the study of ancient manuscripts and contemporary engravings.

In manuscripts from historical archives, a knowledge of the state of the artwork before proceeding any further is necessary in order to know the paper aging, and therefore applying the best conservation and restoration treatment. Ancient manuscripts of cellulose and parchment degraded by acidic conditions have been analyzed, and a good correlation between pH and infrared bands belonging to calcium carbonate, hydroxyl groups and carbonyl groups could be established. Attenuated total reflectance objective (ZnSe) was the best methodology when analyzing inks on ancient degraded papers (Figure 1), whereas fibers gave good results using the diamond cell. Diffuse reflection accessory (DRIFT) also gave comparable results when big samples (about 1 cm diameter) could be analyzed. Figure 2 shows pH differences in papers using the DRIFT accessory.

Figure 1.

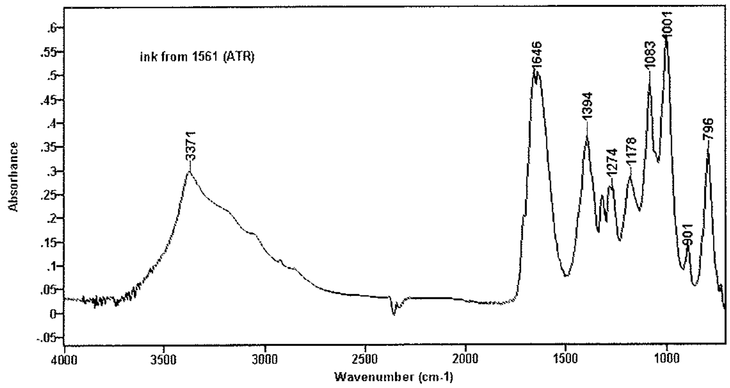
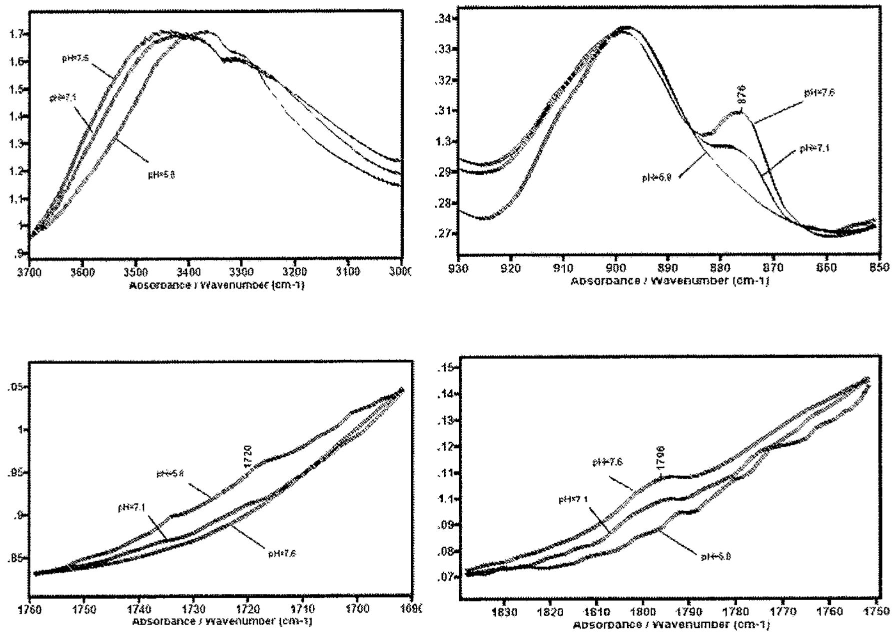


Figure 2.

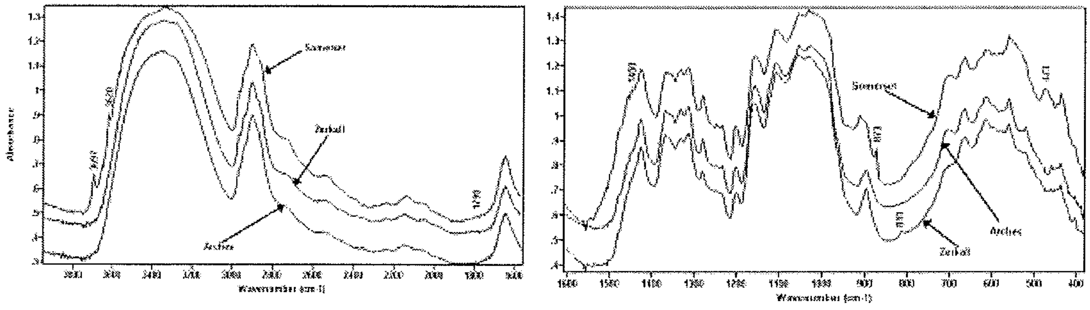


Cellulose oxidation and dehydration can be tested in acidic samples from manuscripts degraded by microbiological agents or by corrosive irongall ink. Characteristic C-O band increases in acidic samples and hydration capacity of cellulose decreases. Both results certify degradation in cellulose.

Engraving is one of the most popular forms of art because it combines originality with multiple production. The enormous amount of engravings produced by contemporary artists obliges us to restrict our studies to one artist and period in order to achieve conclusions about the capability of the different infrared techniques compared in this study. The possibility of analyzing and identifying microscopic particles, the accurate comparison of samples from different origins, and the fact that the sample is not destroyed have converted infrared techniques into valuable tools for engraving characterization and discrimination. Forensic analysis requires fast analytical instruments and the possibility of attaching an objective proof to a sample.

Modern samples of papers and inks from different brands and origins were compared using all described methodologies. Different brands of papers could be identified according to their infrared spectrum. Diffuse reflectance, a diamond cell in the beam condenser and remote infrared gave good results for papers. Figure 3 shows spectra of different papers using a diamond cell in the beam condenser. Different brands of inks were also analyzed. Bands corresponding to carbonate could be associated to wine black ink and bands corresponding to phosphate were identified in inks coming from burned bones.

Figure 3.



To sum up, chemical characterization of these papers and inks allows us to produce a database for comparison of materials used by artists and consequently the ability to characterize original works of art.

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NOTES

EXAMINATION OF FRESH AND ACCELERATED AGED TUNG OIL USING FTIR-MICROSCOPY AND ATR-TECHNIQUE

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Tung oil is a drying oil that was more rarely used as a binding medium for works of art. It is obtained from the fruits of the tung tree originating in Asia; it contains triglycerides with a high content of conjugated polyunsaturated fatty acids [1]. Due to the composition, characteristic changes were expected during aging at the molecular level. For the study of the aging behavior of tung oil, IR examinations were carried out using fresh reference materials in comparison to accelerated and naturally aged samples.

Tung was already known in China before Christ and had been applied to fortify ships against water [2]. At the end of the 19th century, there were attempts to introduce tung oil as a binding medium for paints and varnishes. Due to its strong drying properties, it was used as a substitute for linseed oil. In tung oil, the property to form solid films is based primarily on the presence of a conjugated-unsaturated fatty acid, which is a-eleostearic acid. Due to the high drying capacity and the rapid drying process, frosted films occur, which is typical for conjugated oils. Therefore tung oil has a limited use as a binding medium, and it was mixed e.g. with linseed oil.

In a fresh state, tung oil shows typical absorption bands of triglycerides (see figure 1). Intensive absorptions were observed in the range 2960 – 2850 cm^{-1} deriving from C-H stretching vibrations in methyl and methylene groups. Furthermore, a strong band at 1744 cm^{-1} was observed, a characteristic group frequency of esters, which occurs due to the carbonyl group as stretching of the C=O double bond in esters. Further indications of triglycerides are the absorptions in the fingerprint region at 1238, 1163 and 1099 cm^{-1} caused by stretching of C-O bond in the C-O-C fragment of triglycerides and by skeletal vibration of C-CO-O. This absorption occurs often as a multiplet with broad bands due to different coupling effects and rotational isomerism [3]. For tung oil, two absorptions are characteristic at 992 and 964 cm^{-1} which are caused by C-H out-of-plane deformation vibrations of conjugated double bonds.

Due to light aging, changes were observed considering the carbonyl band and the absorptions caused by the double bond system. Furthermore, an additional band occurs deriving from hydroxyl absorptions. The absorption at 3012 cm^{-1} is decreased so strongly that it cannot be detected. It is assumed that the C-H stretching vibration in tung oil was caused by both trans- and cis-configured double bonds. A strong decrease was observed of the C-H out-of-plane deformation vibration of the conjugated trans,trans- and cis,trans-configured double bonds at 992 and 965 cm^{-1}, respectively. A slight additional band at 971 cm^{-1} showed that isolated trans double bonds occurred due to light aging. The corresponding C-H out-of-plane deformation vibration of cis-configured double bond at 728 cm^{-1} is also decreased. That suggests that a decrease of double bonds took place.

The degree of conjugation is strongly reduced, but isolated trans-configured double bonds can be detected. Because fresh tung oil does not contain fatty acid groups with isolated trans double bonds, this is a result of the accelerated aging. A broad hydroxyl stretching vibration occurs additionally in the region 3700 to 3100 cm^{-1}. Oxidation products are expected with hydroxyl and hydroperoxy groups as a result of the radical chain reaction with oxygen uptake which was determined in linseed oil [2].

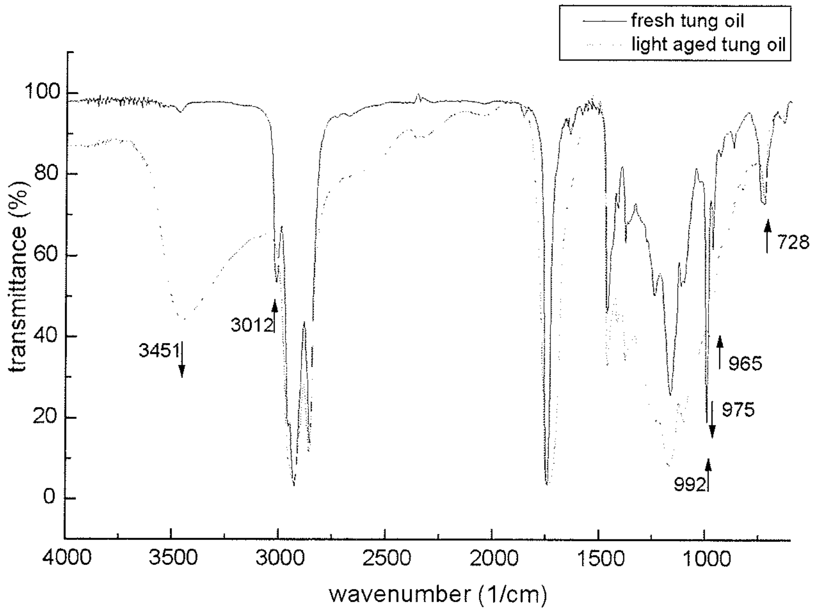

Figure 1 Detail of the IR spectra of tung oil in fresh and light aged state showing the decrease of conjugated trans,trans-configured and the occurrence of isolated trans-configured double bonds.

In the spectrum of accelerated aged tung oil, a significant loss occurs of both absorbances which were caused by conjugated trans-configured double bonds. It can be concluded that a degradation of double bonds took place. The spectrum provides indications that a rearrangement in the double bond system took place. The formation of isolated trans-configured double bonds was found in accelerated aged oil.

EXPERIMENTAL

The spectra were obtained using a FTIR-microscope which is combined with a FTIR- spectrometer (PE 1000i, PerkinElmer Instruments, GB). The microscope was equipped with a narrow band mercury-cadmium-telluride (MCT) detector. Spectra were measured in transmission mode from 4400 cm^{-1} to 500 cm^{-1} with

60 scans, a resolution of 4.0 cm^{-1} and a strong apodization. Tung oil (Propolis, Germany) was used as a reference material. For the procedure of accelerated aging, the experimental conditions were adopted from literature [4]. To this end, films of the reference oils were prepared on glass slides with a film thickness in a range of 0,2-0,3 mm. The thin films were aged artificially by exposure to light of 366 nm using a UV-cabinet (model 29200, CAMAG, Switzerland). The UV-lamp was equipped with a low-pressure mercury arc lamp (8 W) and a special filter reducing the visible light [5]. The aging experiments were performed with a distance of light source to sample of about 22 cm. The radiant intensity at this distance amounted 195 $\mu W/cm^2$, whereas the portion of visible light was kept at approximately 0.18 $\mu W/cm^2$. The study was performed over a time range from 0 – 72 h.

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Dr. Anna Schönemann studied chemistry at the University of Halle-Wittenberg, and in 1990 received her master's degree of "Diplom-Chemikerin" with her thesis, "Investigation of UV-spectroscopic methods for the determination of acidity of a - CH-acidic compounds with a structure of dithiocarbonic acid." Since that time she has been a conservation scientist at the Analytical Laboratory of Foundation for Prussian Palaces and Gardens in Berlin-Brandenburg. In 1995, she assumed responsibility for the Analytical Laboratory. In November 2001, Anna received her Ph.D. from the University of Vienna, with her thesis, "Spectroscopic and chromatographic investigation of binding media of art objects." Since 1999, she has been a trainer and supervisor of student conservators at the University of Applied Sciences in Potsdam.

NOTES

A COMBINATION OF FTIR, PLM AND PY-CG/MS AS TOOLS FOR THE LEGAL AUTHENTICATION OF PAINTINGS: A CASE STUDY IN BRAZIL

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Acrylic and vinylic polymers are synthetic resins widely used as binders in paints. They were first synthesized at the end of the 19th Century and became pictorial materials in the 1920's. After the First World War, they were produced in industrial scale. Nowadays, the use of these materials is spread widely among artists, conservators, and also in the decoration of architectural works. The chemical and/or physico-chemical characterization of the binding media present in a work of art is very important for conservation-restoration activity; but in the field of art and authentication of paintings, the proper identification of the material can also be used as legal evidence.

In this work, the analytical evidence is described in a legal case in Rio de Janeiro, Brazil, involving works attributed to very important Brazilian and European artists such as Portinari, Di Cavalcanti, Matisse, Picasso, Jawlensky and Signac, among others, where the above-mentioned techniques have been used to characterize acrylic and vinilic polymers present in the paintings. The methodology included a combination of a first phase with the use of Diamond Window Cell Fourier Transform Infrared Spectroscopy (FTIR) and Polarized Light Microscopy (PLM), in which we were able to identify paint chips composed of a mixture of kaolin, calcium carbonate, titanium dioxide and PVA; followed by a second phase of TG and Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-CG/MS) to confirm the organic binders. The results were good enough to be used as proof that the paintings were fakes, since some of the artists, such as Boccione, had died even before some of the materials found in the paints were available on the market. These results contributed as well to the consolidation of the necessary interdisciplinary work between the scientist, the art historian and the conservator.

Dr.Luiz A. C. Souza holds a Ph.D. in Chemistry, with experimental work performed at the Getty Conservation Institute, where he stayed for two years (1992-93) as a Research Fellow at the Scientific Department, working on the technology of polychromed sculptures from the Baroque period in Minas Gerais, Brazil. Mr. Souza is also a teacher of Scientific Principles of Conservation at the Graduate Program in Visual Arts of the School of Fine Arts - Federal University of Minas Gerais, Brazil. Mr. Souza is a Researcher at the same University, at CECOR - The Center for Conservation and Restoration of Cultural Movable Properties. Mr. Souza is currently a member of the Directory Board of the ICOM-CC, Committee for Conservation of the International Council of Museums, and is the coordinator of the organizing committee for the forthcoming ICOM-CC meeting in Rio de Janeiro, Brazil, in September 2002.

Patricia Schossler is a recent graduate (Master's program) from the Department of Chemistry at the Federal University of Minas Gerais, where she performed research on the development of analytical methods of analysis of paintings by combination of PI/GC/MS, under the co-orientation of Prof. Souza.

Edson Motta is a historian and conservator from the Federal University of Rio de Janeiro, where he teaches conservation of paintings at the School of Fine Arts. Mr. Motta is currently engaged in his doctoral thesis at the Universidad de Valencia, Spain.

João Cura D'Ars Figueiredo Jr. is an undergraduate student of chemistry at the Department of Chemistry of the Federal University of Minas Gerais, and also a grantee of the Ministry of Education in Brazil, performing his grant work at CECOR - Center for Conservation and Restoration of Cultural Movable Properties, under the tutorship of Prof. Souza.

Dr. Isabel Fortes holds a Ph.D. in Chemistry. Her current research is focused on development of analytical techniques in PI/GC/MS. Mrs. Fortes is a researcher and teacher at the Department of Chemistry of the Federal University of Minas Gerais, Brazil.

Dr. Fernando Carazza holds a Ph.D. in Chemistry and his current work is related to wood chemistry, more specifically separation methods and fine chemistry of tar products. Mr. Carazza is the head of the Department of Chemistry of the Federal University of Minas Gerais.

NOTES

MICRO-ATR STUDY OF THE DEPTH OF PENETRATION AND DISTRIBUTION PROFILE OF WATER-REPELLENT POLYMERS INTO POROUS STONE MATERIALS

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Prevention of physical and chemical weathering of stone materials of historic buildings, stonework and sculptures due to external deterioration factors (primarily water, either as rain or surface-condensation water) has been of concern to mankind since antiquity. In order to inhibit decay induced by water penetration into the porosity of stone, protective treatments consisting of various natural and synthetic products have been applied throughout the ages to the surfaces of artifacts exposed to outdoor conditions [1]. In the last few decades, conservation of monuments and stone masonry has witnessed an increasing use of polymeric materials during restoration interventions, aimed at conferring some hydrophobicity to the treated surfaces.

Nowadays, a good knowledge of the performances of different polymers has been achieved with regard to their water-repellency properties and long-term protection effectiveness. Besides, the macroscopic, physical properties of the treated stones have also been thoroughly evaluated (by means of colorimetric measurements, porosimetric data, static and dynamic contact angles measurements, water-vapor permeability, capillary water absorption and water microdrop absorption time) and the results of such testing are widely published [2]. Nevertheless, the ability of the different polymers to penetrate deeply inside the porous matrix of the stone is also considered a key parameter when evaluating the efficacy of treatments (besides, of course, the chemical-mineralogical nature of the stone and chemical-physical characteristics of the various polymers). Indeed, as far as highly porous lithotypes are concerned, it is found that the most penetrating products achieve the most durable performances.

The present work reports on the study of penetration depths and spatial distribution of different protective polymers (selected among acrylic, partially fluorinated acrylic and siloxane resins) within the microstructure of a highly porous, calcareous stone.

The aim of the research work was to study the polymer applied to stone substrates by direct analytical techniques, coupled with appropriate sampling methods. Actually, the major problem affecting such measurements is the sensitivity of the instrumentation, considering the masking effect of the dominant signals of the stone matrix. Various analytical approaches to the problem have been tested, using vibrational spectroscopic techniques such as FTIR, micro-FTIR, micro-Raman, micro-FT-Raman, NIR, DRIFT and micro-ATR, besides thermogravimetric and microscopic techniques. As a matter of fact, micro-ATR spectroscopy proved to be the most effective method and was applied to the investigation of cross-sections of the treated samples.

The technique is very promising because it allows direct, locally non-destructive probing of the examined surfaces, coupling microscopic visible-light observation to direct infrared unambiguous fingerprinting of the compounds present, with a spatial resolution of 50-100 mm, without further manipulation or preparation of the samples. A major drawback of the method is the need of a perfect contact between the Ge crystal ATR probe and the investigated micro-area (100 mm in diameter) in order to obtain a reasonable signal and an acceptable spectrum: a condition not always met when testing stone/polymer systems. However, by following a characteristic absorption band, chosen as compound tracer for each polymer, the presence/absence of treatment could be ascertained at definite points on the cross-section's surface as a function of Cartesian coordinates. In Figure 1, an example of spectra obtainable is reported; in Figure 2, the decrease in intensity of the chosen marker band at increasing depths inside the treated sample is evidenced.

Overall, penetration depths measured are significant (up to the whole thickness of the treated specimens) and reach increasing values passing from the acrylic to the siloxane polymer (the trend observed is: acrylic copolymers < partially fluorinated acrylic copolymers < polysiloxane). Moreover, by means of semi-quantitative spectroscopic data treatment (including normalization of obtained spectra and calculation of ratios of areas of marker bands at different depths), it was possible to assess the actual dose of polymer present at different depths (i.e. its distribution profile), thus mapping the spatial distribution of the protective products within the treated samples. The obtained results highlighted different impregnation behaviors of the various treatments, with Paraloid B72 mostly confined in superficial layers of the specimens, its fluorinated homologue (TFEMA/MA) still present in quantities equals to 66% of the superficial dose down to 2.5 mm from the treated surface, and Wacker 280 evenly impregnating the whole bulk of the stone (with gradually decreasing quantities, still equals to 20% of the superficial value even at the bottom of the specimen).

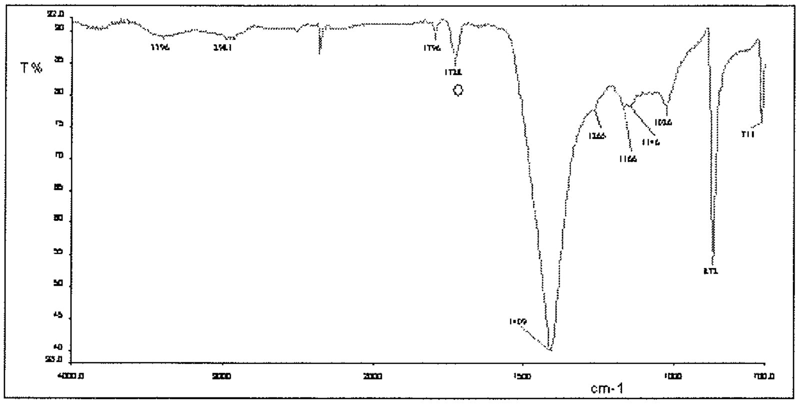

Figure 1 – Micro-ATR spectrum recorded on the surface of a cross section of organogenic Noto limestone treated with Paraloid B72 (the yellow dot indicates the selected marker band for the polymer).

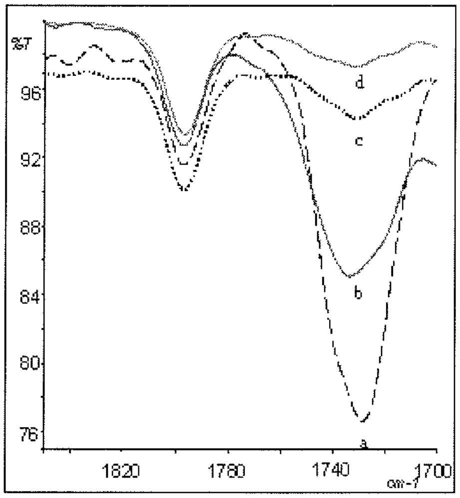

Figure 2 – Micro-ATR spectra recorded at different depths inside the Paraloid B72 treated stone cross section (expanded view): a) 0.5 mm; b) 1 mm; c) 1.5 mm; d) 2.5mm below upper surface. The decrease in intensity of the polymer's marker band centered at 1728 cm^{-1} is immediately evident.

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NOTES

FT-IR REFLECTANCE SPECTROMETRY ON ANCIENT YELLOWED PAPERS

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This study was carried out in the framework of research addressed to setting up an innovative methodology for antique paper deacidification. The methodology was based on application of kinetically stable calcium hydroxide dispersions in nonaqueous solvents. The deacidification effect was primarily achieved by a neutralization reaction of $Ca(OH)_2$ with acidic groups of degraded paper. Secondly, a $CaCO_3$ reservoir, which worked as alkaline buffer preventing further degradation, was formed from the reaction of the calcium hydroxide, in excess, with CO_2 in the air.

pH measurements, before and after the treatment, showed that the method worked with efficacy, inducing a 3-4 pH unit variation. Scanning electron microscopy allowed us to detect the applied $Ca(OH)_2$ particles linked to cellulose fibres; and EDX microanalysis provided information about the increased calcium content. A complete overview about the involved mechanisms required a deeper knowledge of the carbonatation process, since efficacy of the method depended on it. This goal was experimentally achieved by Fourier Transform-Infrared spectrometer (FT-IR) combined with a probe for Attenuated Total Reflectivity (ATR) analysis.

Infrared reflectance spectrometry is a powerful tool for the characterization of paper. The technique is not invasive and this is particularly useful for studying the effects of the longtime evolution processes. This contribution shows that FT-IR provided a complete picture of the whole process.

Some acidic yellowed paper samples, coming from rags (14th, 17th and 19th centuries) and wood-pulp paste (20th century), suffering for yellowing phenomena and missing of the mechanical strength features, were selected for the experimentation. A commonly used chemical spot-test provided information about the sizing used in the papermaking. A low amount of starch had been applied on the 14th century paper. The paper sheets from the 17th and 19th century had been sized with gelatine. Rosin resin and kaolinite had been used in the 20th century paper sheet.

Although the FT-IR spectra of paper were quite complex, two frequency ranges were suitable for the detection of the calcium hydroxide/carbonate bands. The first was at 3642 cm^{-1}, corresponding to the O-H stretching of the calcium hydroxide and close to the broad signal of hydroxyl groups of the cellulose. The second was around 870 cm^{-1} and was attributed to the out-of-plane bending of CO_3^{2-} in $CaCO_3$.

Spectra were collected one hour after the application of the $Ca(OH)_2$ particles dispersed in 2-propanol and, successively, once a day for two weeks. We observed a rapid decrease of the calcium hydroxide signal and, subsequently, an increase of the calcium carbonate peak. Our investigation showed that after one week a complete carbonatation reaction occurred. This was a remarkable point; actually, a rapid transformation into calcium carbonate is to be desired, since excess $Ca(OH)_2$ solubilized in the residual moisture adsorbed by cellulose fibres is sufficient to lead to an aggressive high pH environment dangerous for the paper.

Successively, the side effects induced by the treatment by $Ca(OH)_2$ dispersions on molecular structure of paper components were evaluated. Infrared spectra were carried out on treated and untreated paper samples and then compared. This allowed us checking the chemical effects induced by the $Ca(OH)_2$ treatment, including possible effects of the dispersing media. Spectra performed on untreated 14th and 20th century samples showed that some peaks, after deacidification process, disappear.

Finally, some deacidified paper samples were subjected to artificial aging, and the resulting chemical transformations were checked. The examined samples were aged storing at 85% RH and 90°C, for 15 days. Induced yellowing was relevant on untreated materials; particularly the 17th and 19th century samples, became deep brown colored, while the degradation of the treated paper was significantly slowed. FTIR investigations provided a chemical characterization of the degradation products. Comparing the treated and untreated samples' spectra, the chemical structure modifications induced by the treatment were evidenced in the 17th and 19th century samples, both of them sized with gelatine. Treated samples, after aging, showed two shoulders at 3528 and 3400 cm^{-1} and a peak at 779 cm^{-1} that were not evidenced in untreated and aged paper spectra. A similar behavior was also shown by a paper sample dating from the 17thcentury. An in-depth study on such features is in progress.

This contribution collects some starting-point investigations based on FTIR technique concerning the application of this new methodology. These preliminary results provide original information about deacidification treatment side effects. Presently, new experiments are going to be carried out to elucidate the physicochemical mechanisms driving the deacidification process.

Dr. Rodorico Giorgi is a graduate in Chemistry and holds a Ph.D. degree in Science for Cultural Heritage Conservation Sciences at University of Florence. Currently, he is a research fellow in the chemistry department and Consortium CSGI, University of Florence. His research interests include: application of nano- and micro-technologies for paper deacidification; conservation of wall paintings; and NMR tomography for studying porous stone decay processes. He is the author of 15 publications in the field of colloid and interfaces and physical chemistry applied to the works of art conservation. He is a scientific consultant for many national and international restoration projects.

Massimo Ceccato is a textile chemist, earning a degree in chemistry at the University of Florence. Currently, he is a manager in R.&D. Dept. of a textile finishing and research company. His research activity includes the development of innovative experimental techniques for textiles quality control.

Dr. Luigi Dei is a graduate in chemistry, earning a Ph.D. in physical chemistry at the University of Florence. He is now associate professor in physical chemistry in the chemistry department and Consortium, CSGI. He has authored more than 90 publications in the field of colloid and interfaces and physical chemistry applied to the works of art conservation. He is also a scientific consultant for many national and international restoration projects.

Piero Baglioni is full professor of physical chemistry in the chemistry department at the University of Florence; and is director of the *Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase,* CSGI. He is the author of over 150 publications in the field of colloid and interfaces and physical chemistry applied to the works of art conservation. Additionally, he has been a scientific consultant responsible for many national and international research projects. He is a member of the Academy of the Arts of the Drawing in Florence.

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INFRARED SPECTROSCOPIC STUDIES OF PHOTOGRAPHIC AND MODERN PAINTING MATERIAL

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In efforts to advance the understanding of early photographic processes and techniques, Fourier transform infrared spectroscopic studies of photographs was conducted at the GCI Scientific laboratories. The technique has been successfully utilized in the past for the study of composition and degradation of photographic materials. The infrared technique offers several advantages including rapid analysis, reduced sample size requirement, and sensitivity to both organic and inorganic components. The study primarily focused on the use of non-destructive, reflectance and ATR type techniques to better understand the coating composition of historical photographs. A side port reflectance accessory attached to a Nicolet "Nic-Plan" infrared microscope was also utilized. The analyses enabled the identification of several natural coatings such as resins, waxes, gelatin, and albumin. Artificially aged test samples of natural material, both pure and mixed, were also analyzed to enhance the understanding and interpretation of infrared spectral changes. Additional studies using cross-sectional analysis were conducted on photographs from the same period. These destructive type analyses helped characterize the composition and layering of these early photographs.

The use of infrared spectroscopic technique has been extended to the study of acrylic paint emulsions, primarily the make-up, behavior and aging of modern paint. The GCI, in collaboration with Dr. Thomas Learner of Tate Gallery, conducted preliminary analysis on samples from modern artists' tube colors. Paint samples applied uniformly to glass slides were exposed to light aging for various exposure times to simulate artificial aging. In addition, some of the dried paints were also washed with water to simulate cleaning effects during conservation work. The infrared spectroscopic studies using ATR technique revealed changes in the chemical composition of the paints during the aging and washing processes. The light aging process, conducted over a period of 32 weeks, primarily reduced the concentration of surfactants while inducing slight spectral peak broadenings with the acrylic resin component (Figure 1).

Infrared spectral analysis, after washing with water, indicated the surfactants were completely removed from aged and unaged films. However, changes related to the acrylic resin were more difficult to evaluate.

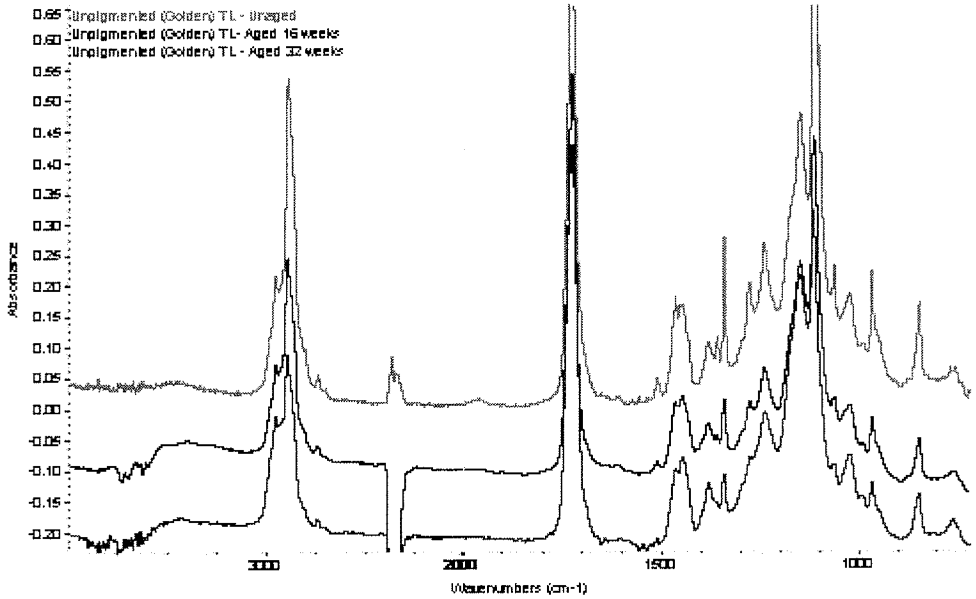

Figure 1

Herant Khanjian received his chemistry degree from California State University, Northridge. His research interests involve the detection and identification of organic media found in objects of art and development of quantitative methodologies for the examination of gel residues on cleaned paint surfaces. He is currently an Assistant Scientist in the Science Department of the Getty Conservation Institute.

Dr. Tom Learner received an M.A. in chemistry from Oxford University in 1988 and a Diploma in the conservation of easel paintings from the Courtauld Institute of Art, University of London in 1991. He spent a year as a Getty Intern in the painting conservation and scientific research departments at the National Gallery of Art, Washington DC. Since 1992, he has been a conservation scientist at Tate Gallery, principally researching analytical techniques for the characterization of twentieth century painting materials. He received his Ph.D. in chemistry from Birkbeck College, University of London in 1997. Since then, he has combined his research as a conservation scientist with practical conservation work on Tate's newly acquired modern paintings.

Dr. Alberto de Tagle is Director of Scientific Research at the Netherlands Institute of Cultural Heritage. Formerly, he was head of the Science Department of the Getty Conservation Institute. His specialties include Conservation Science, Architecture and Artistic Materials Conservation, and Analytical Chemistry. From 1992-1995, he served as Head Scientist at the Winterthur Museum in Delaware. He holds a Ph.D. in Atomic Spectroscopy received in 1980 in Germany. He also holds an M.S. in Analytical Chemistry and a B.S. in Chemistry. He is a professional member of AIC, ICOM, ICOMOS and ACS.

NOTES

WEDNESDAY MARCH 6, 2002

GUEST SPEAKERS

CHARACTERIZATION AND AGING OF COMMERCIAL ACRYLIC RESINS

Oscar Chiantore

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The success of acrylic resins as base materials for the formulation of paints, surface coatings and adhesives derives from their good film-forming characteristics, as well as excellent optical clarity and weathering stability. As their mechanical properties can be modulated from soft to rigid and hard materials, depending on the different monomer structures involved, acrylic polymers are also positively used for structural applications. Acrylic resins have been employed in the field of artists' materials and cultural heritage conservation since the beginning of their commercial development, and their presence continues to be important in our time, particularly in the form of the emulsion paints used by many artists.

In this presentation, a summary of the results obtained during a systematic investigation program regarding acrylic-based polymers will be illustrated, with particular reference to the characterization and aging behavior of commercial acrylic products used in conservation and as artist materials.

Acrylic paints and resins are, in most cases, complex polymer molecules formed by more than one monomer. The characterization of such materials may be performed at increasing levels of depth, with corresponding increasing instrumental and labor difficulties. The problems to be afforded range from relatively simple qualitative chemical analysis to more demanding quantitative approaches. In most cases, only average composition values are obtained, whereas complete characterizations call for determination of the composite chemical composition and molar mass distributions. It must be also considered that industrial production of resins may occur with changes in formulations over the time, either for occasional reasons or for product development. The differences of monomer content or monomer compositions, which in several cases have been detected in some commercial acrylic products, may be attributed to such types of manufacturing procedures.

Modulation of final properties in polymer paints is generally done by tuning the copolymer monomer compositions through control of the polymerization process; similar results may be sometime more easily obtained—in the case of acrylics, by blending copolymers with different chemical compositions or with different monomers. To detect if a resin sample is made from one copolymer type only, or from a mixture of different copolymers, it is a case requiring the application of particular separation techniques.

Difficult situations may arise with emulsion paint formulations where a number of additives are present, even in low amounts, and where chemical composition and molar mass distributions are often not obtainable because of the incomplete solubilities of the resins. Detailed knowledge of acrylic resins compositions and formulations is a fundamental prerequisite for the approach we have followed in the investigation of their long-term stability characteristics. The natural aging of polymer materials is a process mainly influenced by sunlight-promoted degradation; photooxidation reactions are involved, eventually exacerbated by temperature, moisture, and the presence of pollutants. The aging studies have been performed in the laboratory through properly selected artificial conditions for simulation of outdoor or indoor degradation processes with short-term experiments.

The behavior of the most important commercial acrylic resins used in conservation, and of acrylic artist paints, has been thoroughly investigated, principally by means of accelerated photooxidative treatments. Stability characteristics under thermooxidative conditions have been also determined. For comparison reasons, and in order to help in the analysis of the results, parallel aging experiments have been run on reference acrylic/methacrylic homopolymer samples. The structural and molecular changes taking place in the polymer samples during the degradation have been systematically monitored with different spectroscopic and chromatographic techniques, and by following the formation of insoluble network structures and sample weight losses resulting from evaporation of low molar mass decomposition products.

The results have shown that in the resins, the first degradation events to be detected are the molar mass distribution changes due to chain scissions and/or the coupling between polymer radicals. Overall stability of the polymers is strongly influenced by the nature of the alkyl side groups. Polymers containing long ester groups undergo fast and extensive crosslinking reactions, together with the accumulation of oxidated groups. Ethyl- and methyl-methacrylate units, on the other hand, proved to be very stable against oxidation and scission reactions. The acrylate units in the copolymers were found to be more reactive sites, due to easier formation of macroradicals by abstraction of tertiary hydrogen atoms.

The acrylic emulsion paints we have examined after aging were all ethyl acrylate – methyl methacrylate copolymers, and the samples were treated with light irradiation suitable for correlating with museum conditions. A set of samples with approximately five years of natural aging was also available. In all cases, independently from the pigments and at any level of aging, no sign of oxidation products was detected in the polymer structures. Film changes due to surface segregation and degradation of surfactants were followed with different techniques, and the only effects of aging found on the acrylic polymers were solubility changes (in most cases a solubility decrease, suggesting that crosslinking reactions took place preferentially under irradiation). This behavior is opposite to that shown by the resins with similar monomeric components, irradiated with light reproducing outdoor conditions and without pigments. It is possible that some pigments have a promoting effect towards formation of polymer networks, similarly to what happens in the drying of oil paints, but the interaction of pigments with the acrylic polymer chains clearly needs to be investigated further.

It may finally be stated that overall stability characteristics of acrylic polymers are well established. However, deeper mechanistic details giving further experimental supports to the proposed reaction schemes should be obtained by careful analysis of chain fragments and low molar mass compounds formed during aging treatments. Other improvements may be conceived for better characterization of the complex paint formulations and for tracking the changes during aging, namely the application of high-sensitivity techniques capable of detecting additives or degradation products in traces and impurities. The combination of liquid chromatography separations with laser desorption mass spectrometry is now becoming applicable to macromolecular compounds, with great potential for the characterization of soluble materials. For monitoring the behavior of insoluble samples and of films containing gel fractions, on the other hand, a useful way seems to be the measurement of viscoelastic parameters by means of dynamic mechanical, and dielectric, analysis.

In combination with the structural informations from infrared spectroscopy, and with details on the sol fractions eventually present in the samples, it should be possible to build adequate models for correlating the mechanical properties with the aging characteristics of the resins. It is also worth mentioning that atomic force microscopies are more and more being applied for the investigation of polymer surfaces; and the examples of application to acrylic films and to their morphological changes deriving from some kind of treatment look very promising.

Oscar Chiantore is full professor of Chemistry and Technology of Polymers at the Faculty of Sciences, University of Torino, Italy. He is chairman of the University Program in Science and Technology for Cultural Heritage; a member of the governing board of the International Symposium of Polymer Analysis and Characterization (ISPAC); and also a member of the editorial board of *International Journal of Polymer Analysis and Characterization.* His main research interests and areas of specialization are the structural and molecular characterization of complex polymer systems, the mechanisms of polymer degradation, and the development of polymers for cultural heritage conservation. He is currently involved in a project on the behavior of synthetic polymers used in contemporary art. Other investigative areas are the characterization and molecular aspects of aging in triglycerides; and natural resins and proteic substances used as binding agents or varnishes in artworks and museum objects. Chiantore is author of more than one hundred papers in refereed scientific journals and many conference communications. He has been a lecturer at national and international polymer courses, and has given seminars and invited lectures at scientific institutions around the world.

NOTES

B72

old – MA-EMA (68-32)

1978 new – MA-EMA (70-30)

1996 MA-EMA-BMA (32-65.8-2.2)

Acrylic Paints

EA-MMA → BA-MMA 2000 Tom Learner

Photoxidation of acrylic homopolymers

PMA → chain scission → PMA

PEA → oxidation → PEA

PEMA → + very low oxidation

PBMA → crosslinking → chain fragments
side chain
oxidation
loss of ester groups

change in MWD 1st. indicator of change

Co Polymers

crosslinking
loss of ester groups
oxidative scission

Acrylic latexes – migrating surfactant

Whitmore SiC 41, 250–255, 1996

75yrs surfactant disappear
crosslinking cause polymer to become insoluble

What's role of pigments

THE CONSERVATION OF ACRYLIC PAINTINGS: A REVIEW

Elizabeth Jablonski[1] and Mark Golden[2]

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Acrylic paintings present great challenges to conservators, yet very few studies of this medium exist. As early as the 1920's, some artists were using modern synthetic paints, based on resins such as cellulose nitrate, ethyl silicates, vinyl acetate and vinyl chlorides, as a means of expression that was distinct from oil painting and its associated history and traditions. A group of artists known as the Mexican Muralists (including David Alfaro Siqueiros and Jose Gutierrez) believed that modern synthetic paints, developed primarily as housepaints and automobile coatings, better suited their needs than traditional oils, fresco, tempera and casein paints. Synthetic paints were perceived to be more durable and easier to use; artists were encouraged to educate themselves about these products and exploit the possibilities that recent advances in technology had to offer (Gutierrez 1956).

Other artists in New York City (including Roy Lichtenstein, Morris Louis, Barnett Newman and Jules Olitzki) took advantage of the new acrylic artists paint, Magna®, developed in 1947-49 by Leonard Bocour and Samuel Golden. The resin was the Rohm and Haas Company product called Paraloid® F-10, a poly (n-butyl methacrylate), soluble in mineral spirits, like oil paints.

Beginning in 1963, several brands of waterborne acrylic paints were available to artists, many based on the Rhoplex® series of polymers by Rohm and Haas, two of which were Henry Levison's Permanent Pigments, Liquitex® brand, quickly followed by Bocour's Aquatec®. These waterborne acrylics were used by Helen Frankenthaler, Agnes Martin, Kenneth Noland, Larry Poons and Andy Warhol, among others. Concerns with the construction of modern paintings and their materials have been addressed in conservation literature as early as 1962, and increasing in frequency since the 1980's (Feller et al 1985; Krueger 1992; Lamb 1982; Lodge 1988; Murray et al 2002; Pomerantz 1962; Stringari and Pratt 1993; Watherston 1974). The introduction of these materials to artists will be discussed, followed by the conservation concerns, including the identification of acrylic medium, its sensitivity to solvents and to temperature and relative humidity, observed yellowing and haziness and other inherent vices.

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Elizabeth Jablonski is a recent graduate of the Queen's University Program in Art Conservation in Kingston, Ontario. Some of her past internship sites include the Fine Arts Museums of San Francisco, the Denver Art Museum, the Frans Halsmuseum, Golden Artist Colors, Inc. where she was able to conduct much of the research for this paper; and the National Gallery of Art, Washington, DC, assisting with the Artists' Materials Collection. She is currently an Andrew Mellon Fellow in Paintings Conservation at the Menil Collection in Houston, Texas.

Mark Golden is CEO and cofounder of Golden Artist Colors, Inc. in 1980. His company began by making custom products for artists, many whom were customers of Mark's father, Sam Golden, during his 50-year career as paint maker and partner with his uncle Leonard Bocour. Golden continues to produce Custom Products for artists, conservators and museums, as well as several lines of acrylic artist's paints and mediums sold around the world. He has been a guest lecturer at Smithsonian Institute, Tate Gallery, College Arts Association and numerous colleges and universities. Golden is co-author of several research and review articles on acrylic artist paint. He was selected as Small Business Person for New York State in 1996.

NOTES

Pyroxyline → N/C c/N
Barnett Newman - mixed oil w/acrylic
Waterborne acrylic paint → water dispersions
Liquitex
Aquatec
AC 22, 33, 234 → Rhoplex
MMA - EA blends
formulations → poly n-butyl →
have changed
since late 1980's T. Learner

Pin holing = foam craters
Yellowing / discoloration
Haziness → turbidity
treatment concerns
Sensitivity to ~~[illegible]~~ solvents
Dirt (imbibed)
Loss of uniform surface gloss
~~temp~~ thermoplastic in nature

BASIC PAINT RESEARCH AND DEVELOPMENT

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This presentation will attempt to demystify the 'art of paint-making' of acrylic artist colors. The following topics will be detailed: manufacturing process; the balance required for a stable, workable and permanent paint system; and finally, the components and their implication to the success in making an artist acrylic emulsion paint.

Acrylic paint-making is a combination of blending and shearing operations intended to develop the optimum color and complete mixing of all the ingredients. The process is divided into two distinct formulating procedures: pigment dispersion and binder formulation. Pigment dispersions are first created or bought, which are mixtures of pigment, water, surfactant and wetting agents and often glycols. To this mixture may be added coalescents, thickeners, rheology modifiers, preservatives and defoamers.

The two most important machines in our small industry are the high-speed disperser and the three roll mill. Together they shear and blend these dispersion mixtures, reducing pigment agglomeration. Several other machines might be used by other manufacturers in this dispersion process, depending on the viscosities and specific requirements of a paint.

The most significant order of ingredients is determined by the need to fully develop color, especially before the acrylic emulsion is added. It is difficult to reduce agglomerate size even with extreme shearing once the emulsion is added. The binder is blended separately from the dispersion, including defoamers, preservative, thickeners or rheology modifiers, and glycol until smooth. The completed dispersion is then added to the acrylic mixture, which is then milled again. There are some exceptions to these processes.

The 'Art of Paint-making' is the balancing of all of the competing needs while keeping upfront the artist's desire for any potential working style or property. The properties that are balanced for performance are: shelf life considerations, application properties, dry film properties, health and safety properties and commercial issues. Shelf life considerations of the finished paints include: varying temperatures, length of storage and changes in the paint over time. Application properties are those conditions required by the artist while working with the paint including: consistent color, consistent 'feel', good 'yield' in paste paints and good flow in thinner-bodied paints, ease of mixing with colors and assorted mediums, ease of dilution, foam control, drying rate and compatibility with other materials.

Dry film properties include those characteristics of the paint when immediately dry and following those characteristics that may change over the lifetime of the painting. These include: resistance to photodegradation, flexibility, durability, thermal stability, adhesive quality, block resistance, chemical sensitivity, surface clarity, time to ultimate clarity, surface gloss, color development, bleeding or staining, film formation and any change in these properties over time. Health and safety considerations for artist paints include regulatory compliance issues, domestically and foreign, environmental impact of product, custom and professional use products, safe use within the studio and safety of staff working with product and formulation ingredients. Commercial considerations for artist paints include market size for all of these products, the costs of ingredients and finished products, and traditional expectations of the fine arts marketplace.

For professional artist paints manufactured by companies dedicated to making fine art materials, the quality of the finished product is paramount, followed by the remaining consideration of those items presented above, in some ranking order as determined by the primary focus of each individual company. The components of the artists acrylic emulsion paint will provide the best opportunity to review the issues that may result from their inclusion or exclusion from an acrylic paint formula. For the last 5 to 7 years, acrylic emulsions in artist paints are mostly made from Butyl Acrylate and Methyl Methacrylate monomers. Emulsion acrylics are selected first for their durability, then for wet and dry clarity and for lack of surface anomalies. From these are selected products that are capable of supporting stable color development. Once stability checks are confirmed, the polymers are then subject to accelerated aging studies and for their ability to contribute to support induced discoloration. Multiple polymer emulsions will be selected to allow a wider degree of formulation controls, including adjusting film formation temperature and hardness of the resulting paint.

Pigment selection is a continual process. Manufacturers replace pigments, go out of business, change formulas or are unable to maintain controls on materials. To be able to provide the artist with a palette that does not change requires constant sourcing of pigments from multiple companies. The first consideration is the level of permanency and lightfastness of the pigment within a basic water environment. ASTM D4303 provides a list and procedures for testing pigments for their degree of lightfastness. Additional tests require system stability checks at elevated temperatures, interactions with other colors and inter coat adhesion. Dried films are tested for sensitivity to water and ammonia and their degree of bleeding.

Surfactants, already contained in the emulsion system, are a major part of paint-making. Each pigment has, because of its size, shape, surface topography or chemistry, a required balance of surfactants. These surfactants aid in several ways: by assuring complete wetting of pigment surfaces, and by providing a bridge between incompatible materials. Most typically these nonionic surfactants in artist acrylic paints have been ethylene oxides. Surfactants need to be added at the minimum amount that allows for an effective dispersion. They dramatically increase foaming of the wet paint and water sensitivity of the dried paint. It is well known in the commercial field and has been shown through others and our own research that surfactants will exude to the surface of an acrylic film during drying.

Thickeners or stabilizers include cellulosics, urethane modified thickeners, and acrylic acid thickeners. Each of these allow for adjusting the viscosity and rheology of the resulting paint so that each product may be consistent across a wide range of colors. Each of these thickeners again can create significant stability issues in the resulting paint. Defoamers can be of the mineral oil or silicone type. They are essential because of the degree of blending and mixing of these surfactant and water-filled paint systems. Coalescents are required for softening the acrylic so that it is able to form a film at the desired temperature. They also aid in film forming over time and can assist color development as well as help preserve the system. Their selection can also dramatically shift drying time and time to reduced tack. Other additives and the effects on the drying properties of the film will also be discussed.

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Mark Golden is CEO and cofounder of Golden Artist Colors, Inc. in 1980. His company began by making custom products for artists, many whom were customers of Mark's father, Sam Golden, during his 50-year career as paintmaker and partner with his uncle Leonard Bocour. Golden continues to produce Custom Products for artists, conservators and museums, as well as several lines of acrylic artist's paints and mediums sold around the world. He has been a guest lecturer at Smithsonian Institute, The Tate Gallery, College Arts Association and numerous colleges and universities. Golden is co-author of several research and review articles on acrylic artist paint. He was selected as Small Business Person for New York State in 1996.

NOTES

Shelf life - viscosity stability
separation
freeze / thaw
settling of solids
flocculation
pH
loss of H_2O / volatiles
spoilage

Durability

Formulation

New BA / MMA

TiO_2, C

phthalo green

Old EA / MMA

South Florida
UVA351 fluorescent bulb) lightfastness

Thickeners
Hydroxy Ethyl Cellulose
Poly(acrylic acid)
Fumed Silica
Urethane modified.

Defoamers
Pet. Distillates (waxes ([illegible])
Organosiloxane polymers

Other
Talc
Calc
Silicas
etc

CHARACTERIZATION OF ACRYLICS AT ROHM AND HAAS

Peter Eastman

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INTRODUCTION

This paper will give an overview of the role of Rohm and Haas Company in the development of acrylic polymer chemistry; discuss the various polymerization technologies employed by Rohm and Haas with a focus on formulation issues of interest to the conservation community; and cover the characterization of acrylics within Rohm and Haas, with a particular focus on infrared spectroscopy.

Rohm and Haas and Acrylics

Rohm and Haas is a major specialty chemical company with $6 billion a year in revenue and more than 17,000 employees worldwide. It operates nearly 140 research and manufacturing locations in 27 countries. Acrylics became a core business for the company during WWII, notably with the usage of Plexiglas by the military. Acrylic chemistry continues to form the backbone of the company's largest business unit, Performance Polymers. P2 (as it's known internally) makes products ranging from monomers to materials such as coatings binders, rheology modifiers, adhesives, sealants, and plastics additives.

Acrylic Polymer Chemistry

This paper will explore the basics of acrylic polymer chemistry, briefly discussing solution polymerization, but concentrating on emulsion polymerization. Factors influencing the selection of monomer, initiator, surfactants and other components as well as process variables, will be discussed. Physical properties of important acrylic polymers will be detailed with emphasis on molecular weight, glass transition temperature, particle size and distribution and dry film properties.

The film formation process will be discussed in general terms, with specifics of paint properties and weatherability. Typical paint formulas and additives and their effect on product properties will be covered. Non-paint acrylic chemistries and products such as solid acrylics, impact modifiers, caulks and sealants, will be mentioned briefly.

CHARACTERIZATION OF ACRYLICS AT ROHM AND HAAS

The characterization of its materials and products are critical tasks for analytical scientists at Rohm and Haas. A wide variety of instrumental techniques are used to characterize these materials. Infrared spectroscopy is one of the most common and widespread techniques. This paper will give examples of common uses of IR

spectroscopy such as monomer composition analysis, identification of unknowns, identification of defects or inclusions, and quality control of raw materials and product conformance in production facilities.
Various forms of IR instrumentation are in use at Rohm and Haas. Conventional FTIR bench and microscope instruments are used throughout the company. ATR-IR is being used increasingly for varied applications in both research and plant settings. More recent techniques such as focal plane array IR, photoacoustic-IR and Raman-IR are used only in research settings.

The limitations of IR analysis and the use of complementary techniques are addressed. Examples of analyses posing difficulties for IR, such as distinguishing materials that are similar compositionally but differ in morphology, distinguishing polymer blends from copolymers or distinguishing multiphase from single-phase systems, will be presented. Despite the challenges, various forms of vibrational spectroscopy will nevertheless remain powerful tools due to their widespread applicability, ease of use, efficiency and relatively low cost.

Peter Y. Eastman is a scientist in the Microscopy group in the Analytical and Computational Technology Center at Rohm and Haas Company. Prior to joining Rohm and Haas, he worked as a furniture conservator, both privately and for the Philadelphia Museum of Art. While at the PMA, he also developed a database of conservation treatment records and worked in the Conservation Department's Analytical Laboratory. The author received a B.A. in Political Science from Swarthmore College and an M.S. in Wood Science and Technology from the University of California at Berkeley.

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SPECTROSCOPIC IDENTIFICATION OF ACRYLIC POLYMERS

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Acrylic polymers have been used for years as plastic parts and as coatings. There are numerous types of acrylics that include acrylates, methacrylates, acrylamides, copolymers with non-acrylates, and blends. Infrared spectroscopy is the best method to obtain basic information concerning the structures of these polymers on very small samples. This talk will show some of the spectral regions that are most useful for the identification of these polymers. Numerous examples will be given.

Jerry Lillquist is a Senior Research Specialist at 3M Co. in St. Paul, MN. While receiving an M.S. at the University of Minnesota in Organic Chemistry, he found that he liked determining what he had synthesized rather than doing the synthesis—a lot safer, too. He started at 3M in 1965 in the Analytical Laboratory of the then Central Research Laboratory using IR; and then NMR [H, C, and F] spectral analysis for CRL personnel and a broad range of divisions. Later, a Raman spectrometer was added to his direct analytical tools. With that group, he co-authored a chapter in "Practical Guide to Infrared Microspectroscopy." In 1995, he transferred to the SMMD division of 3M and specialized in the interpretation of Fluorine NMR spectra though still using the other methods of analysis.

NOTES

ACRYLIC PAINTINGS: A NEW CHALLENGE FOR CONSERVATION RESEARCH

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Painting in the twentieth century, particularly in the second half, is defined by the emergence of many new paint systems that have ridden the wave of consumer products like no other century before. Nitrocellulose was introduced in the 1920's. Alkyds were introduced in the 1930's and PVA emulsions in 1940's; both had become widely used by the late 1950's. Other emulsions based on vinyl and styrene acrylics and styrene-butadiene blends also became popular, and 20th century artists' synthetic binders rode these consumer trends as well. Thus, a walkthrough of any major art museum with a contemporary art collection provides, in one sense, a retrospective exhibition of 20th century polymer chemistry. Not only is the list of artists who use these materials huge, but so also are the square hectares of painted surfaces.

Unfortunately, our knowledge of how these systems will age and how we will treat them when they inevitably enter the conservation studio have not kept pace with all of this creation. This state is, indeed, troubling to many, and it is not surprising to find a number of conservators and conservation scientists struggling with it. One of the authors (Learner) prepared a short list of immediate analytical research "needs" to help address these issues. They include:

[1] Quantitative analysis of synthetic paints (including mixed media) and ratios of pigment to medium
[2] Identification of organic pigments and additives
[3] Molecular weight determinations of emulsions
[4] Characterization of mechanical properties
[5] Measurements of change during aging
[6] Measurements of change during conservation treatments

The last "need" has taken on new urgency. Before the 1990's, soiling in museums was considered primarily a housekeeping nuisance. But in the last 12 years, through the works of Brimblecombe in the U.K. and Cass and Nazaroff in the U.S., it has become clearer that, while some forms of soiling were theoretically reversible, others were not. It was demonstrated that soiling on the largely unprotected surfaces of Color Field paintings could accumulate to 0.2% coverage as quickly as 5-15 years for coarse particles, and 1-20 years for finely divided soot particles. Moreover, taking five different ventilation and HVAC systems into consideration, the average time for soot to become visible to the average observer is 56 years, although size and background color do affect what is "just perceptible" soiling. Going backwards in time, this puts us at the start of the careers of artists like Morris Louis, Ellsworth Kelly, Jackson Pollock, Kenneth Noland, Mark Rothko, Helen Frankenthaller, Clifford Still, Franz Kline, Willem de Kooning, Barnett Newman, and many others. A soiling problem is growing, and many of these artists painted in materials that we have no idea of how to clean.

During the guest scholarship of one of the authors (Learner) at the GCI, some of the issues surrounding acrylic emulsion paint systems were investigated with Fourier-Transform Infrared Spectroscopy (FTIR, reflective ATR), Thermomechanical Analysis (TMA), Differential Scanning Calorimetry (DSC), Environmental Scanning Electron Microscopy (ESEM), Gas Chromatography (GC-MS), and Elemental Analysis (CHNOS) with aged and unaged paint samples. The studies were performed in order to clarify the following questions:

[1] Are paint components leached out by water exposure treatments?
[2] Do aging and aqueous treatments cause chemical and/or physical changes in paints?

The answer to both of these two questions is "yes", and recently we have sought to explore more fully the implications of photochemical and natural aging on changes in mechanical properties. After measuring the leaching of freeze-thaw and/or surfactant additives by tracking the change in carbon in the wash water using EA, several important thermomechanical properties of six-year-old paint films were determined (such as the linear coefficient of thermal expansion, glass transition temperatures, softening points, and valuable insights into stiffness).

Light aging was carried out in a specially prepared exposure apparatus for 16 and 32 weeks at 18,000 lux, giving an approximate museum exposure equivalent of 90 and 180 years respectively. Using TMA, the glass transition temperature (T_g) for Rowney acrylic crimson emulsion was measured as 12° C regardless of light exposure. However, after immersion in water for 24 hours and subsequent drying, the T_g was reduced to 3° C. Marion Mecklenburg was one of the first to point out the risks of acrylic paintings to mechanical damage during shipment in freezing weather. After "washing", these paint samples measured in compression under a load on 0.1N revealed that the paint samples were significantly stiffer (i.e., more brittle) at temperatures where the original films were well within their rubbery state. Under the same load in elongation, dark-aged Rowney Mars Black paint became stiffer before and after washing than did light exposed Mars Black paint. This suggests that more leachable material was lost before light exposure than after. Clearly, water extraction has changed some important physical properties in acrylic emulsion paint films regarding their flexibility. This study is ongoing and it is risky to make generalizations before a great deal of more work is done. Yet the implications are many.

From the FTIR findings, surfactants become concentrated on film surfaces. PEG-type (non-ionic) surfactants lower the T_g of acrylic films, thereby increasing the surface tack and thus also increasing the likelihood of dirt pick-up. These materials are rapidly removed in water, which results in film stiffening. Light exposure appears to help chemically break down surfactants and to make them less extractable with age.

We are only exploring the implications at this time but future aging and treatment studies will include:

[1] Use of different substrates
[2] Thicker paint samples
[3] In-situ cleaning
[4] Aging dependency on surfactant
[5] Greater use of TMA as well as DSC and TG-MS
[6] More surface studies using FTIR
[7] More complex extraction studies with LC-MS and GC-MS.

James Druzik is Senior Project Specialist in the Science Group of the Getty Conservation Institute. He joined the staff of the Getty in 1985 after five years at the Los Angeles County Museum of Art. From 1985 to 1994, he managed contract scientific research for the GCI and specialized in air pollution science within the museum environment. He is co-author of the ASHRAE Handbook Chapter 20 on air conditioning in museums, archives and libraries and presently is a member of the Conservation Advisory Committee of the Nation Archives and Records Administration. Since 1988, he has helped co-organize six symposia for the Materials Research Society entitled Materials Issues in Art and Archaeology. In January 2000 he joined the analytical chemistry section of the GCI Science Group and specializes in thermal analysis. He has a B.S. in Chemistry.

Dr.Tom Learner received an M.A. in chemistry from Oxford University in 1988 and a Diploma in the conservation of easel paintings from the Courtauld Institute of Art, University of London in 1991. He spent a year as a Getty Intern in the painting conservation and scientific research departments at the National Gallery of Art, Washington DC. Since 1992, he has been a conservation scientist at Tate Gallery, principally researching analytical techniques for the characterization of twentieth century painting materials. He received his Ph.D. in chemistry (thesis entitled 'the characterization of acrylic painting materials and implications for their use, conservation and stability') from Birkbeck College, University of

London in 1997. Since then, he has combined his research as a conservation scientist with practical conservation work on the Tate's newly acquired modern paintings. He was a co-author of 'The Impact of Modern Paints' (Tate Gallery Publishing Ltd.), published in 2000.

Michael Schilling earned his B. S. (1983) and M.S. (1990) in chemistry from The California State Polytechnic University, Pomona. He has worked at the Getty Conservation Institute since 1983, and presently holds the position of Senior Scientist in charge of analytical research. His present interests include thermoanalytic characterization of mortars and plasters, and the identification of organic materials by gas chromatography-mass spectrometry, with particular interests in contemporary art materials. He has been involved in the examination of painted museum objects using various instrumental techniques, and in the analysis of volatile organic compounds in the museum environment. He has participated in collaborative projects to study and preserve wall paintings in Egypt and China, and was part of a research team that studied the Dead Sea Scrolls.

NOTES

THURSDAY MARCH 7, 2002

MANUFACTURERS PRESENTATIONS

REFLECTANCE ACCESSORY FOR SPECTROSCOPIC ANALYSIS OF SCROLLS, PAINTINGS, WORKS OF ART AND ARCHAEOLOGICAL OBJECTS

Milan Milosevic and Denis Yang

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A reflectance accessory has been developed to allow non-contact spectroscopic analysis of large-size scrolls, paintings and other objects generally found in museums. This accessory is designed to work in a commercial FTIR spectrometer. The spectroscopic technique employed is external reflection. Incorporated into the accessory are a video camera and a small LCD display to enable viewing of the spot sampled.

There are two major features of this accessory. One is that the sampling point extends outside of the spectrometer sample compartment. The other is that the accessory is designed to pivot around the spectrometer beam without misaligning the optics. Since the sampling point is outside of the spectrometer, the accessory body can be positioned to look downward to sample a surface of a partially unrolled scroll, lying on a flat table. Alternatively, the accessory can be swung upward 90 degrees to sample a vertical surface, be it a painting or the surface of a clay vessel. In either case, the sample is moved about until the area of interest is in the sampling position of the accessory. All this is done with the aid of a small video camera and its display screen.

With an appropriate positioning aid, this accessory can examine the majority of objects found in museums. In addition, for those objects that can be touched, an optional ATR element can be attached to this accessory allowing it to be used in ATR mode.

Denis Yang was, prior to his retirement, a design engineer at Harrick Scientific Corporation. He has been involved in the design of many well-known Harrick accessories. While still at Harrick, Denis satisfied his great love of and interest for art by volunteering at Metropolitan Museum of Art. When his work at Harrick became a hindrance to his volunteering at the Met, Denis retired from Harrick and focused on his work of photographing seals in the Met's Chinese and C.C. Wang collections. However, he kept strong ties to Harrick and when, in his work at Met, he encountered a situation where he saw that a spectroscopic analysis of scrolls could be helpful, he came to Harrick and offered to help design and build an accessory described in this work.

Milan Milosevic is the president of Harrick Scientific Corporation. In addition to working at Harrick, Milan has worked for Spectra-Tech and ASI/SensIR, and has been involved in the development of many products.

NOTES

A NEW APPROACH TO INFRARED MICROSPECTROSCOPY INSTRUMENTATION – AN FT-IR FOR YOUR LIGHT MICROSCOPE

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By reducing the size of the FT-IR spectrometer, an attachment to infinity corrected light microscopes is now available which transforms it into an infrared microspectrometer system. The new spectrometer accessory, the IlluminatIR, produces a beam of infrared radiation that matches both the optics of the microscope and the spectral resolution needed to analyze either solid or liquid samples. The IlluminatIR is very efficient; it is controlled by a personal computer and the software used simplifies spectral collection and analysis. The software provides spectral collection, library searching and reporting. Spectral library searching can happen automatically and library spectra can be immediately compared. Users can easily generate libraries or add spectra to existing libraries. Spectra collected with the IlluminatIR can be directly moved into Grams or Spectrum One spectral analysis software for advanced operations.

With a new diamond internal reflection objective for ATR spectral measurements, this system is both simple to use and robust. This objective employs SensIR Technologies' patented diamond internal reflection element, combining a zinc selenide (ZnSe) paraboloid with a diamond sample-contacting surface. This element provides an indestructible surface for contacting the sample and an optically efficient means to concentrate the infrared radiation onto the sample. When this new diamond ATR objective is used with the IlluminatIR, it is unsurpassed in either its image or spectral quality.

Thin film samples are analyzed by reflection-absorption spectroscopy using a new all-reflecting objective. This objective has all-reflecting elements that concentrate the infrared on to a diffraction limited 100-micrometer spot and a refracting element that produces a visual image. This combination gives the best infrared and imaging quality.

The IlluminatIR and the new diamond ATR objective will be presented with application to the analysis of cultural materials. In addition, a portable FT-IR spectrometer that can be taken into the field will be discussed.

Dr. John A. Reffner received his Doctoral degree from the U. of Connecticut (Storrs, CT). His earlier education includes an M.S. from the Illinois Institute of Technology (Chicago, IL), and a B.S. from the U. of Akron (Akron, OH). Upon completing his B.S. degree, Dr. Reffner joined B. F. Goodrich, working with

Dr. R. P. Allen in their microscopy lab. In 1958, he joined W. C. McCrone Associates, a microscopy consultant firm in Chicago. In 1966, he became the Assistant Director of the Institute of Materials Science (U-Conn.) and later a member of the chemistry faculty. Leaving IMS in 1977, Dr. Reffner became a Principal Scientist at American Cyanamid. He joined Spectra-Tech Inc. in 1986 and retired in 1998. He is now unretired, working with SensIR Technologies. For over 25 years, Dr. Reffner has served as a forensic consultant to the Connecticut State Police. While working in industry, Dr. Reffner continued to teach. In addition to numerous short courses and workshops, he was an adjunct faculty member at U. Conn., John Jay College of CUNY, U. of New Haven and The Fashion Institute (NY). He is on the Graduate Faculty of John Jay College (CUNY). He is a member of the Coblentz Society, the Society of Applied Spectroscopy (SAS), the American Chemical Society, Microscopical Society of America, New York Microscopical Society and several other scientific and professional societies. He is a Fellow of the Academy of Forensic Science and serves on the editorial board of the Journal of Forensic Science.

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USE OF THE RAMAN MICROPROBE FOR ART CONSERVATION

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Several characteristics of the Raman Microprobe make it an ideal tool for the art conservator:

- It provides identification and characterization of both inorganic and organic materials.
- It provides better than 1μm spatial resolution.
- No sample preparation is required other than that for optical microscopy under ambient conditions.
- Macro and remote samples can be accommodated with special chambers and fiber-optically coupled probe heads.
- A special adaptation for horizontal illumination enables in-situ examination of large artifacts.

Because this technology is new to the art conservation community, the functionality of the instrumentation will be described. Examples will be shown where pigments have been identified. In particular, a sub millimeter-sized plug could be removed from a statue or painting and probed on edge to determine the artist's techniques or subsequent conservation treatments.

In a recent collaboration with the Los Angeles County Museum of Art, the presence of PbS in laser-treated pigments has been identified. This was part of an ongoing project to study the behavior of pigments after laser treatment. Since PbS is normally not used as a pigment, but other forms of lead are (oxides, sulfates, carbonates), this proves the conjecture that these pigments can be converted to the sulfide. Ongoing modeling studies of laser treatments are aimed at determining if significant previous chemical adsorption is necessary; or if ambient, atmospheric sulfates are adequate for the chemical transition. Ultimately this will impact the understanding of normal weathering of lead (and other metal) pigments that exhibit electrochemical potential for conversion to the sulfide.

Dr. Fran Adar is Worldwide Raman Applications Manager at Jobin Yvon Horiba, Inc. Dr. Adar completed degrees in physics at the University of Pennsylvania. She subsequently spent five years with the RW Johnson Foundation at the University of Pennsylvania Medical School before taking a position in the Raman Microprobe Applications Laboratory with Jobin Yvon Horiba. In that capacity, she has been instrumental in pioneering applications of Raman microprobe technology in North America.

Dr. Andrew Whitley is Director of the Raman Group, Jobin Yvon Horiba, Inc. Dr. Whitley completed degrees in Chemistry at the University of Durham. He subsequently worked for Bruker Instruments with their vibrational spectroscopy products; and Renishaw as the US Product Manager providing insights for instrument developments for new applications of the Raman microscope.

NOTES

Far Red/UV Laser
Microprobe
Resonant conditions
Spatial res. better in Raman than IR
in wavelength of light
spectra down to 100cm^{-1}
Delhaye 1974, 1975 J Raman Spectroscopy 3, 33-43
filters reduce Rayleigh light

Gems
Alterations of pigments by laser cleaning

SADVANCEMENTS IN INFRARED AND RAMAN MICROSPECTROSCOPY

Bonnie Leimer and Jesse Gallop

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Fourier Transform Infrared (FTIR) microspectroscopy is a versatile tool for analyzing a variety of samples from a very large size to as small as 10 microns. A number of options have been added to the infrared microscope to aid in analyzing many sample types. See how the latest infrared microscope designs will quickly solve analytical problems and help to evaluate complex sample matrices.

Raman Spectroscopy provides vibrational information that is complimentary to data obtained by infrared techniques. Micro sampling can be performed on either the FT-Raman system or the dispersive Raman providing spot sizes, from 50 μm to 1 μm respectively. Depth profiling and mapping can now be done with the dispersive Raman technique.

Bonnie Leimer is currently an Applications Chemist for the Western Region of the United States. She started off her career in spectroscopy as an applications specialist in the marketing department at Thermo Nicolet. Here, she analyzed customer samples using various techniques including IR and IR microscopy, FT-Raman and FT-Raman microscopy, TGA-IR, GC-IR and Photoacoustic spectroscopy. Bonnie earned her Bachelor of Arts and Science degree from the University of Wisconsin, Madison in 1994.

Jesse Gallop is currently a Senior Sales Engineer at Thermo Nicolet in Southern California. Jesse earned his B.S degree in Biology from CSU Fullerton in 1978.

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INFRARED IMAGING:
APPLICATIONS IN CONSERVATION SCIENCE

Norman A. Wright

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The infrared array detector coupled to a FTIR spectrometer has created a powerful analytical tool with which to simultaneously collect spatially distinct high quality spectra. The benefits of this instrument are seen in the analysis of heterogeneous sample systems where the power of parallel detection provides data of sufficient fidelity to be able to determine small differences or trends in the chemical information extracted from the infrared spectra of neighboring pixels.

Since the introduction of array detection on an FTIR spectrometer, applications have been reported in a variety of applications including biomedical [1]; biomineralized tissue—bone [2], polymer extrusions [3] and polymer curing reactions [4]. One of the early adopters of infrared imaging technology has applied this technique in a variety of art restoration applications as well as drug release studies [5]. In this presentation, some applications to demonstrate the utility of the technique will be discussed, as well as an analysis of a paint chip to resolve and identify the layers.

The ability to use infrared imaging to contribute to difficult analyses has led to improvements in the technology, particularly in the last year, that have allowed successful application to some traditionally difficult sample types. The instrumental challenges will be reviewed, including what specific improvements, including durability, ease of use, sensitivity, and spatial resolution.

Imaging Spectroscopic analysis is a technique that provides chemical specific infrared images. With the analytical resolution achieved using an interferometer, specific chemical information becomes available. Slight band shifts now can be routinely detected and used as an aid in complex problem solving. From the images, precise information about the chemical composition and material structure of a sample is obtained. This information is significant as it allows the investigator to understand more fully the chemically diverse sample, which is the rule rather than exception, when studying real world and samples in the art evaluation and restoration field. Advances in both the technology and the data analysis tools have produced an analytical system that now can become a routine part of an analytical toolbox.

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Dr. **Norman Wright** is currently the Worldwide Applications Manager for Digilab LLC. He received a Ph.D. in Chemistry from the University of California, Riverside under the direction of Peter Griffiths. He first joined Digilab as a product development engineer working on various large accessories including FT-Raman, TGA and GC hyphenated interfaces; and most recently, the Infrared imaging products for which he was also the product manager.

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MICROSCOPIC INFRARED REFLECTANCE IMAGING

S. E. White and R. A. Spragg

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The combination of infrared spectroscopy with imaging is clearly a very powerful tool for characterizing the distribution of materials in complex matrices. It is only in the last five years that it has become possible to generate images rapidly, with the use of array detectors. We will describe a novel FTIR imaging system that provides improved performance and versatility at significantly lower cost than earlier systems. This improved performance facilitates the measurement of samples in reflection as well as in transmission, which greatly broadens the potential applications.

The early imaging systems used a square detector array, in conjunction with a step-scan spectrometer. The sample was imaged onto the detector to produce an image that typically had 64 x 64 pixels. The step-scan spectrometer was necessary because of the rather slow rate at which the detector signals could be read. The PerkinElmer Spotlight system is radically different. It uses a small linear array and builds up an image by moving the sample on a motorized microscope stage. The size and shape of the image can be matched to the area of interest. The linear array has inherently better performance in terms of sensitivity and range than square arrays. It also has much faster readout, allowing the use of a simpler rapid-scanning spectrometer. This results in speed comparable to that of systems that combine more expensive detectors with more complex spectrometers. For example, an image of an area 2 mm square can be obtained in 2 minutes. The pixels can be 6 or 25 microns square, with the image size limited only by the memory available. The system also has a single point detector so that it can be used as a conventional IR microscope, including ATR measurements at single points. ATR spectra can be especially useful in confirming the interpretation of the sometimes complex spectra obtained in reflectance.

A major consideration in IR imaging is sample presentation. The most favorable samples are thin sections measured in transmission, and almost all published IR images have been obtained in this way. However, in many situations samples must be measured in reflectance. There are two problems that are usually cited. One is that reflectance signals are generally weak so that the signal-to-noise ratio may be unacceptably poor. The other is that extremely flat samples are needed because of the limited depth of focus in IR microscopes. We have found that samples prepared for light microscopy, such as embedded and polished paint cross-sections, do not require any further treatment before imaging. The spectra have the characteristics of specular reflection from the surface. They can be compared with normal reference spectra after applying Kramers-Kronig transformation.

In other situations, such as paper surfaces, the spectra correspond to diffuse reflectance. Such spectra resemble transmission spectra with distorted intensities, and can be compared directly with reference spectra.

In the example shown here an embedded paint cross-section approximately 1.0 x 1.5mm was measured with 6.25 micron square pixels at $8 cm^{-1}$ resolution in less than 20 minutes. Below the visible image is an IR image based on the intensity of the carbonate absorptions. After K-K transformation, the 35,000 individual spectra are of excellent quality.

The sample was provided by courtesy of Boris Pretzel of the Victoria and Albert Museum, London.

Samuel White has been with PerkinElmer Instruments since 1978. He sold chromatography and infrared spectroscopy products until 1984, when he became an Infrared Product Specialist. He currently is based in the Chicago Customer Center where he provides applications support and conducts training courses for PerkinElmer customers. He has vast experience in the field of infrared microspectroscopy, and gives papers and technical talks at major IR training courses such as Bowdoin College and Miami University.

Richard Spragg has been with PerkinElmer Instruments since 1970. He is currently Principal Applications Scientist in the Molecular Spectroscopy product department in England, where the Spotlight Imaging system was developed. His major interests are analytical applications of vibrational spectroscopy and chemometrics.

NOTES

POSTER PRESENTATIONS

FROM CLASSIC ANTIQUITY TO CONTEMPORARY ART: SOME APPLICATIONS OF REFLECTION FTIR MICROSPECTROSCOPY DISCLOSING THE COMPOSITION OF MULTILAYERED ARTIFACTS

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Reflection FTIR microspectroscopy is a powerful analytical technique for the characterization of artworks, involving dramatic minimization of loss of valuable sample material. The method proves to be very effective in characterizing the inorganic constituents of a wide variety of polychrome artifacts, providing also an indication of the chemical class of organic materials present. Therefore, the instrumental analysis provides an insight not only of the constituent materials, but also of the techniques of execution of the artifacts. Analytical data are pinpointed within a precise layer of the stratigraphy of the cross-sectioned samples under study, and unambiguous identification coupled to individual characterization of all the different components of paint mixes is also possible. Reflection FTIR microspectroscopy is also a valuable tool for in situ studies of manuscripts and illuminated documents on parchment and paper (whose sampling is almost never allowed), providing complementary information with respect to micro-Raman results (especially when Raman bands are hindered by excessive fluorescence of the binding medium) [1,2].

A thorough study of potentials and limitations of reflection FTIR microspectroscopy was carried out by the authors examining a wide variety of artifacts; and a few examples of possible applications of this technique on materials of polychrome works of art and archaeology are reported [3,4]. Polished epoxy-resin cross-sections of the samples were placed on the microscope stage and analyzed. For illuminated parchment analysis, a specially devised microscope stage and polymethylmethacrylate holding device were used. Samples were analyzed between 4000 and 800 cm^{-1} with a JASCO WS-IR 100 infrared spectrophotometer, equipped with nitrogen cooled MCT detector and Olympus optical microscope (total magnification 360x): masking blades can be interposed in the beam path in order to further limit the target area up to a minimum of approximately 10 x 30 mm, thus achieving a very high degree of selectivity and spatial resolution. Insufficient energy throughput is recovered below that limit.

Examples include the analysis of the vividly colored groups of terra cotta life-size sculptures that decorate the Chapels of the Sacromonte in Ossuccio (Como, Italy), manufactured at the beginning of the 17th century, and subjected to extensive restoration in the following epochs [5]. The samples consisted of an articulate succession of different layers made of mixtures of various pigments. Interestingly, every repainting was made using different pigments as well as different media, and not always respecting the original artist's intentions. It was found that layers painted in malachite and azurite in tempera were painted over with cheaper, more modern pigments such as Prussian blue and Chrome yellow (i.e. Chrome green) in oil.

Archaeological samples coming from the wall decoration of buildings dating back to the Roman age and located in northern Italy are also discussed. In these cases, reflection FTIR microspectroscopy was capable of unambiguously resolving different components of the various layers (characterized by a range of pigments such as green earth –*creta viridis*-; green frit; Egyptian blue - *caeruleum aegyptium*-; red ochre - *rubrica* -, yellow ochre -*sil atticum*-), without the need of complex manual separation. In these instances also, the analysis gave a piece of information on the technique of execution of the mural painting. In fact, absence of any trace of organic binding medium coupled to detection of calcite only, besides the coloring agents, led us to infer that the wall paintings were executed with actual "buon fresco" technique.

Reflection FTIR spectroscopy was also employed non-destructively and *in situ* in order to determine the palette used to illuminate a 15th century Milanese court document on parchment [6]. Even though the surface analyzed wasn't microscopically homogeneous and flat, it was nevertheless possible to record significant spectra useful for the identification of the different pigments used by the illuminator. Moreover, reflection FTIR examination of the document gave preliminary indications on the nature of the binding medium used in the illuminated areas (actually egg albumen).

Finally, results obtained on the analysis of a monochrome Blue bas-relief by conceptual artist Yves Klein (dating from the 1950's), painted with the renowned patent-pending International Klein Blue (IKB), are reported [7]. The pigment used was actually identified as artificial ultramarine blue, dispersed in a little quantity of polyvinylacetate binder, which helped in retaining the textural and visual qualities of the loose pigment powder.

The few case studies reported above provide an insight in the research work performed on a variety of different polychrome artifacts in order to evaluate potential and limitations of reflection FTIR spectroscopy in the field of art conservation. It was found that different painting techniques, as well as different grounds and supports used by the various artists, can actually affect the sensitivity of the analytical technique towards a particular compound. In general, better results are obtained on frescoes, where coarser pigment particles are customarily used and no organic binding media are present. Nevertheless, even though organic binding media produce poorer quality spectra in reflection than in transmission mode, preliminary information about the general chemical class of the binder is obtainable.

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NOTES

THE SCROVEGNI CHAPEL AT PADOVA: CHEMICAL INVESTIGATIONS ON THE POLYCHROMY OF WOODEN FURNISHINGS

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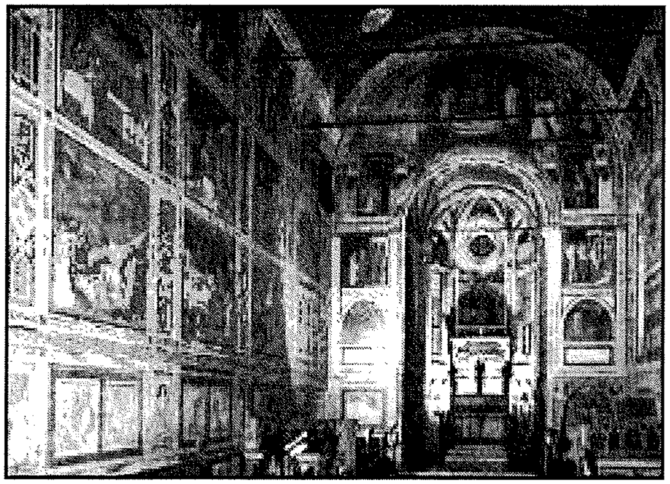


The Scrovegni Chapel is famous for its frescoes by Giotto, a complete cycle by the great Florentine painter.

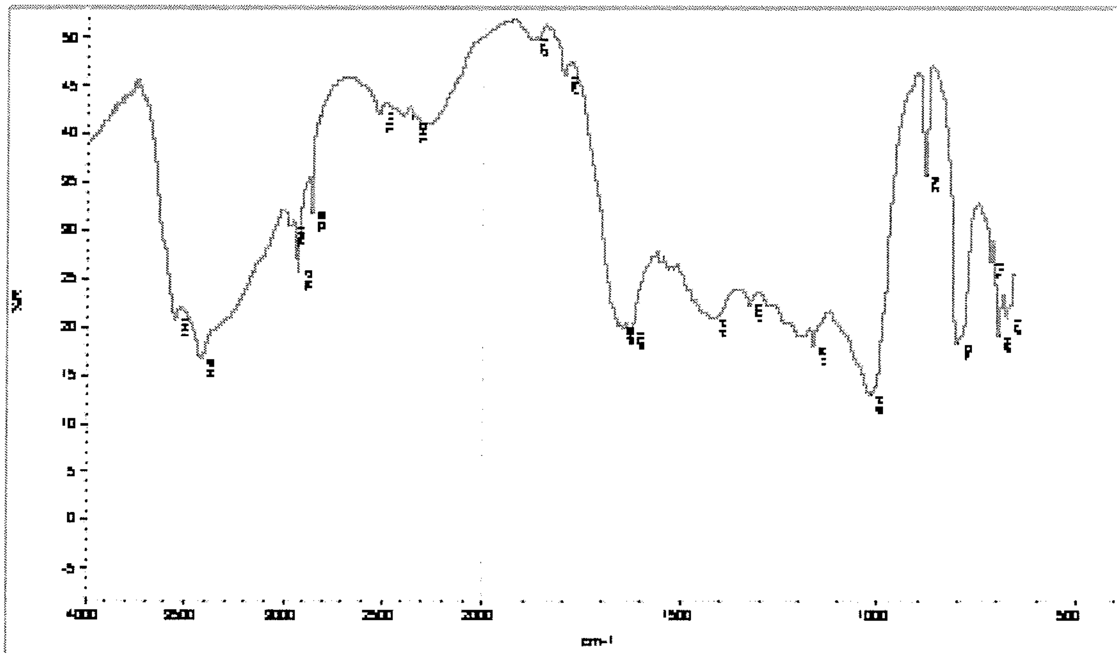
Parts of the wooden furniture present in the Scrovegni Chapel in Padova were at one time painted. The pews against the walls of the Chapel and a wardrobe and kneeler in the vestry have either floral motifs or geometrical designs. Their general state of degradation, however, required attention and accurate restoration with preliminary diagnostic studies of the varnish and paint layers (once again visible). The designs are datable to between the 14th-15th centuries. Coins of that period were also found while removing pews in the apse.

The paintings on wood were done after traditional preparation of the wood by leveling and preparing the surface with a clear protective coat of chalk and glue. Precious pigments amalgamated with an oily-protein type binding were used with a final coat of paint.

The original designs have undergone subsequent interventions; indeed, on certain samples, touch-ups are evident. These covered up the loss of color that occurred with the detachment of the protective coat of chalk and glue. To give the paintings a more uniform appearance, a brown plastering was applied; this covered most of the floral designs. There is a superficial coat of varnish on both the benches and on the other furniture (wardrobe and kneeler).

We used several analytical techniques to obtain precise identification of the pigments, ligands, varnishes and preparation layer. The micro-infrared analysis carried out with a Nicolet Magna 560 spectrophotometer connected to a Continuum Spectra-Tech microscope proved indispensable. This technique led to the exact identification of the various organic components of the layers of paint. The superficial layer is made up of beeswax, while the preparatory coat was carried out traditionally, with the addition of animal glue to chalk. The brown plastering is based on brown earth mixed with an oily-protein binding. Calcium oxalate, often in consistent amounts, is present on the surface. One of the bindings for the pigments was identified as mastic resin. The analysis revealed the presence of casein in the green pigment of the cupboard.

For a more thorough analysis of the blue pigment, which under the electronic microscope proved to be made up of lapis lazuli, a few dark crystals were analyzed under a micro-FTIR. The spectrum obtained revealed typical bands of lapis lazuli, like those found in literature. The presence of a small but clear band of 2349 cm^{-1} provides information as to where the material might have come from. The study ended with the identification of the various pigments used. The red pigments were obtained from Cinnabar, Hematite and Red Earth; the yellow with Orpiment and Yellow Earth. The color white is essentially made up of White Lead, while in the touch-ups, Titanium White and Zinc White were found. The greens were obtained with Green Earth and a mixture of Orpiment and Ultramarine Blue. The blue is mainly made up of lapis lazuli, even if in more recent touch-ups there is also a bit of Smalt.



The FTIR spectrum of the blue pigment

Rossana Arbizzani earned her degree in chemistry from the University of Venice. She has over ten years experience in chemical analysis in the field of the *Beni Culturali,* winning scholarships and research funds while working in the scientific laboratory of the Soprintendenza dei Beni Artistici, Venice and for ICTIMA C.N.R. (Italian National Research Council), Padova, where she continues to work. She has specialized in the conservation of wooden materials, attending courses organized by the European Community; and has contributed to the chemical diagnosis of various materials in numerous works of restoration, in Venice, Padova, Pisa, Feltre, Florence and in Croatia.

Umberto Casellato graduated in chemistry and is a researcher at ICTIMA-CNR (Italian National Research Council), Padova. He has taught chemistry at the University of Padova for ten years and has acquired considerable experience in the field of the characterisation of materials by crystallographic and diffractometric studies. For the last four years he has headed a Research Unit (of about ten people) on the target Project *Beni Culturali* for the CNR. The Unit deals with "Physico-chemical and analytical methodologies on the determination of the correlated parameters on the degradation level of historical and artistic heritage" for the CNR Target Project *Beni Culturali.*

NOTES

APPLICATIONS OF FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR) TO THE STUDY OF ANCIENT CHINESE JADES

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Fourier-transform infrared spectroscopy (FTIR) has several applications in the study of ancient Chinese jades dating from the Neolithic period (ca. 5000 to ca.1700 BC) through the Han dynasty (206 BC to 220 AD). First, basic mineral identification of jade materials can be done easily and rapidly using FTIR. The Chinese word for jade, *yu*, refers to the beautiful, polished appearance of a stone rather than its mineral content. Although various stone materials were used by early Chinese cultures, "nephrite" *yu* was clearly the material of choice. The term "nephrite" refers to the fine-grained, compact variety of two solid solution end-members of the amphibole group of minerals: tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, and actinolite, $Ca_2MgFe_4Si_8O_{22}(OH)_2$. Other jade-like materials were used in antiquity including serpentine (antigorite and lizardite), diopside, quartz (chalcedony), marble, prehnite and talc. FTIR permits rapid identification of these materials.

The second application of FTIR is the determination of iron content within the tremolite – actinolite solid solution. The iron to magnesium ratio of nephrite has been used to characterize jade materials used by various ancient Chinese cultures (Wen and Jing, 1992) and may be indicative of the geological source of the nephrite. The iron to magnesium ratio in nephrite can be determined by examination of the O-H stretching vibrations in the range of 3700-3600 cm^{-1}. The low-iron tremolitic nephrite are shown to produce spectra which have one sharp peak (A) near 3669 cm^{-1}, and often a small peak (B) near 3654 cm^{-1}. Seventy-three of the ninety-four ancient jades from the Freer and Sackler collections that have been studied by this technique were of this low-iron tremolitic nephrite type. The medium-iron nephrites have spectra with three peaks with a third peak (C) occurring near 3639 cm^{-1}. Twelve of the jades analysed by this technique were of this type. The high-iron actinolitic nephrite display four characteristic peaks with a fourth peak (D) occurring near 3619 cm^{-1}. Nine of the jades analyzed by this technique were of this type.

Detection of heating is another important application of the study of Chinese jades using FTIR (Douglas, 2001). Some art historians and archaeologists believe that jade workers in ancient China may have used heat to soften jade to make it easier to work. Other jades might have been heated sometime after they were worked, such as during burial rituals involving cremation. Heat-treatment may also be used in the production of modern-day forgeries to give the appearance of naturally weathered and altered jades.

Slices of a pale green low-iron nephrite pebble from Hetian (Khotan), Xingjiang province of China, were heated from 500 to 1100° C for 24 hours to determine the visual changes that occur due to the heating process. The samples became more white and opaque with heating. Vickers hardness measurements on the heated samples showed that nephrite becomes slightly harder, rather than softer, up to 800° C. After this temperature, the material becomes brittle and tends to fracture more easily. No firm evidence was found to support heat-treatment as a means to soften jade for working.

In addition to X-ray diffraction (XRD), FTIR was investigated as a method to detect heating of ancient Chinese jades. Both techniques were found useful for detection of heat-treatment of nephrite, but only when the material is heated above 800° C. Visual observations coupled with XRD and FTIR were used to examine ten ancient Chinese jades whose physical appearance suggests they may have been heated in antiquity. Two jades, a bowl and bracelet, were found to have been heated to above 800° C based on XRD and FTIR results.

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Janet G. Douglas is a Conservation Scientist in the Freer and Sackler's Department of Conservation and Scientific Research. Her area of research involves the analysis of a variety of inorganic materials relating to Asian art such as bronze, mineral pigments, stone, and jade. She is a geologist by training, and received a Master's Degree from Bryn Mawr College in 1980. Subsequently, she was involved in the study of mineral particulates at the U. S. Bureau of Mines. At the Freer and Sackler Galleries, her work involves study of conservation-related materials and research on Asian art and archaeological materials to answer questions relating to their authenticity, cultural context and method of manufacture. Recent projects involve the mineralogical study of ancient Chinese jades and characterization of glass and stone gokok beads from Korea.

NOTES

RAMAN SPECTROSCOPY OF BRAZILIAN CULTURAL HERITAGE MATERIALS

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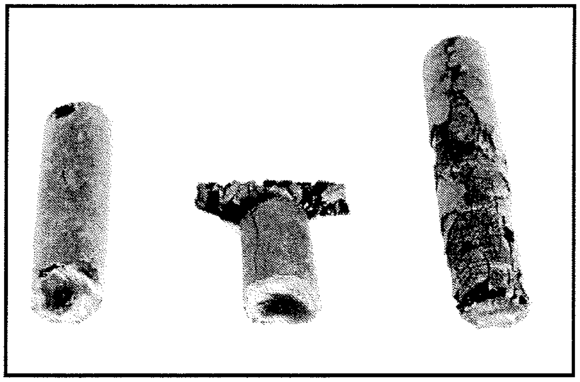
Raman spectroscopy is attracting the attention of the scientific community involved with conservation and restoration problems, since it is a non-destructive analytical technique requiring no or minimal pre-treatment of specimens. Other spectroscopic advantages lie (i) in the coverage of a large wavenumber range (typically from 100 to 4000 cm^{-1}) in one instrumental scan, accessing simultaneously the vibrational modes of inorganic and organic compounds; and (ii) the existence of enhancement effects such as resonance Raman and surface-enhanced Raman scattering (SERS).

In the past few years we have been applying Raman spectroscopy in art and archaeology; the investigations involving Brazilian cultural heritage are particularly interesting. The studies embrace the identification of pigments in paintings [1] rock art and Indian pottery [2] and the analyses of archaeological biomaterials [3].

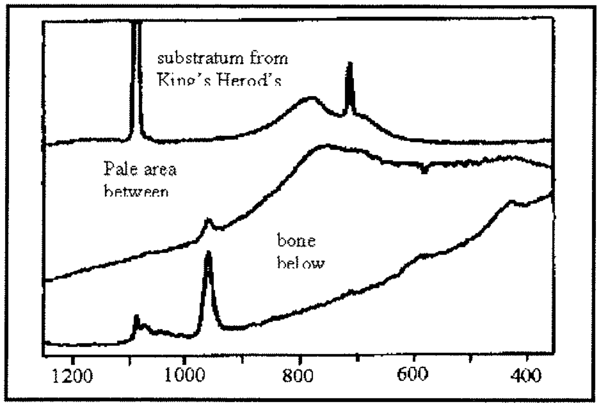
Here we report the results of Raman spectroscopic analyses of two types of objects belonging to the Museum of Archaeology and Ethnology of the University of São Paulo and found in archaeological excavations recently undertaken in Brazil: a tembetá, (lip-plug) found at Iepê (São Paulo State); and an ochred bone from a sambaqui (mould) excavation in the south of Brazil (Santa Catarina State).



The tembetá, in a very fragile and fragmented state (figure left), is ca. 1,600 years old and presents a rusty-brown coating, whereas its core has a red glassy aspect. The conservators were in urgent need of information concerning the nature of the object in order to define the best procedure to preserve it. Raman investigation carried out with excitation in the NIR (FT-Raman) and visible proved that the tembetá is made of resin and as such is a very rare example of this type of artifact, which is more often made of wood or stone. The coating proved to be composed of a degraded resin, rather than a mineral oxide or pigment. From the Raman spectra it was possible to classify the resin as a triterpenic one, and some possibilities for its identification have been suggested from the data analysis and from a database of gums, resins and waxes.

The *ochred bone* from the Jaboticabeira II archaeological site (burial no. 32 at Locus 2.16, tench 15) dates from about 3,000 BC and corresponds to the skeletal remains of a young adult of indeterminate sex. Almost all the bones and bone fragments found in this trench exhibited pronounced ochre coloration and marks which were particularly thickly layered on the humerus studied here.

The Raman spectra revealed that the ochred bone specimens consisted of degraded hydroxyapatite/collagen composition with a surface coating of pure hematite, which has not been processed or treated thermally. Between the hematite coating and bone was found a layer of pale yellowish material which provided a spectrum similar to "limewash", partially hydrated calcium oxide/hydroxide (the upper spectrum in the figure left—substratum from King's Herod's palace—shows the "limewash" band at ca. 780 cm^{-1} for comparison purposes). It is possible that the "limewash" had been applied to the remains but it is also likely that it corresponds to the cation exchange reaction product, involving the hydroxyapatite (mostly calcium phosphate) and hematite (a-Fe_2O_3). Investigations are in process to address this question.



Another point worth mentioning is that although there is no limestone in this region of Brazil, mounds of seashells and hearths were found in the excavations. Raman analysis of concretion deposits from the hearths show evidence of fragmented seashells (aragonite) and limewash, suggesting the possibility that the hearths could be better described as kilns. These examples demonstrated the viability of Raman spectroscopy for the analysis of museum specimens, involving rarity, no preparation of the sample and studies which involved inorganic and organic compound mixtures.

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Dr. Dalva Faria has been a lecturer at the Dept. of Chemistry of the University of São Paulo (Brazil) since 1990, where she studied chemistry (1982) and obtained her M.Sc. (1985, Raman spectroscopy of charge transfer complexes) and Ph.D. (1991, spectrochemical investigation of antimalarial drugs). Among her scientific interests is the application of Raman spectroscopy in art and archaeometry, particularly focusing on Brazilian cultural heritage materials. These studies include cave paintings, pottery, biomaterials (teeth and bones), painting pigments and varnishes, with the aim of reaching a better understanding of cultural and technical aspects of ancient Brazilian cultures and contemporary practices. Such interdisciplinary investigation largely benefits from collaborations with researchers from museums (particularly Museu de Arqueologia e Etnologia and Museu Paulista, both linked to the University of São Paulo) and conservators from other institutions.

Dr.Marisa Coutinho Afonso works as an archaeologist at the Museum of Archaeology and Ethnography/University of São Paulo (Brazil). She completed her B.A. (1979) in Geology, and her M.A. (1988) and Ph.D. (1995) in Geography (Geomorphology) at the same University. She is responsible for the Graduate Program in Archaeology at the University of São Paulo and is Secretary of the Society for Brazilian Archaeology (Sociedade de Arqueologia Brasileira). She was curator of the Museum of Archaeology and Ethnography (1991-1992 and 1995) and assistant curator (1993-1995), responsible for the documentation, conservation and laboratory areas. Her scientific interests include archaeological projects about human prehistoric occupations in Southeast-Southern Brazil; and the study of archaeological collections from the Museum. She has conducted fieldwork focusing on the prehistoric peoples of Brazil, with interdisciplinary teams, specialized in geoarchaeology and archaeometry.

Dr. Howell G. M. Edwards is Professor of Molecular Spectroscopy in the Department of Chemical and Forensic Sciences at the University of Bradford, UK . He studied Chemistry at the University of Oxford and took his M.A. there in 1965; he then earned his B.Sc. and D.Phil. research degrees at the University of Oxford under the supervision of Dr. Leonard Woodward on Raman spectroscopy. Following a Science Research Council Fellowship at the University of Cambridge, he then took a Lectureship at Bradford, being promoted to Reader in 1989. During his academic career, Howell Edwards has published more that 470 papers on Raman spectroscopy and its applications to molecular structure problems; and has supervised 40 research students successfully through to Ph.D. degrees. In recent years, he has been investigating the application of Raman spectroscopy and Raman microscopy to archaeological and art historical problems. Support for this research has come from organizations such as the British Antarctic Survey, NASA , the European Space Agency, EPSRC, NERC, and companies such as ICI, BP, Elf Aquitaine, Castrol and Regenysis Technologies.

NOTES

QUANTITATIVE MEASUREMENTS OF THE GELATIN CONTENT OF HISTORIC PAPERS USING MID-IR AND NIR

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Gelatin was commonly used as a paper sizing material from the 1400's to the 1800's. Previous research by Barrett and Mosier, and Barrett, Lang and Waterhouse, has indicated a possible relationship between the gelatin content of historic papers and their resistance to long-term natural aging. In this project, this relationship is studied further using nondestructive mid-IR and NIR techniques and statistical analysis methods. The gelatin content of historic specimens had previously been measured by a destructive chemical assay (TAPPI 504 om-89); and values were in the range 0 - 7%. This method measures the concentration of hydroxyproline, an amino acid component of gelatin. Controls with various gelatin concentrations were also made from Whatman chromatography paper and handmade flax paper. The percent weight change of the controls before and after sizing was used to measure their gelatin content. Some controls were also analyzed using the TAPPI method.

Mid-IR reflection spectra of the papers were made with a microscope. The sampling area was approximately 0.05 mm^2. Spectra were taken at six locations and averaged. Strongly absorbing cellulose peaks dominate in the mid-IR range, but these peaks are weaker in NIR spectra. To investigate this range, NIR spectra of some papers were collected using a diffuse reflectance accessory.

A partial least squares calibration was performed to correlate the size of the gelatin amide peaks with the previously determined values for gelatin content. In the analysis program, the pathlength was assumed to be constant or estimated by normalizing to a cellulose peak. First or second derivative spectra gave better results and helped to reduce the effects of baseline drift without making baseline corrections. Correlation coefficients were typically in the range 0.8 - 0.9, and the repeatability was acceptable. The analysis was generally more successful using the percent weight change data rather than the hydroxyproline measurements, which had relatively large uncertainties at higher gelatin concentrations.

Based on these results, it appears that both mid-IR and NIR techniques can provide a non-destructive method that can categorize the gelatin content of historic papers as low, medium, and high over the range of 0 - 10%. Further research may help to make the model more precise. This method can then be used to study a much wider range of historic papers and to better understand the relationship between gelatin content and paper degradation.

Mark Ormsby has worked as a conservation scientist at the National Archives and Records Administration since 1990. He graduated from Grinnell College, Iowa, with a degree in physics and earned a Master's in physics at the University of Maryland.

Timothy Barrett is the Director of the Center for the Book at the University of Iowa. He has authored two books, six videotapes, and over 20 articles on the history, technique, and aesthetics of hand papermaking.

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