MaSC

Users' Group for **Mass Spectrometry and Chromatography**

MaSC 2007 Meeting Program

Philadelphia Museum of Art
Philadelphia, PA, USA

14-15 September 2007

Preface

The MaSC Committee would like to welcome you to the third Meeting of the Users' Group for Mass Spectrometry and Chromatography (MaSC) at the Philadelphia Museum of Art.

Since its establishment in 2003, MaSC has grown as an international forum for interaction and discussion among scientists using chromatographic and mass spectrometric applications in conservation and preservation studies. The Group currently has over 90 members, representing 56 institutions – primarily cultural and academic organisations – in 21 countries.

The 2007 Meeting has a diverse programme reflecting the varied specialities and current research activities of MaSC members, and includes sessions on the characterisation of artists' paints and varnishes; sample preparation methods; archaeological organic materials; dye analysis; and new mass spectrometric techniques in museum studies.

The programme also includes a discussion of the GCMS Workshop, held at the Philadelphia Museum of Art, Winterthur Museum and Agilent Technologies, immediately prior to the Meeting. Previous MaSC Conferences in this format – comprising a Workshop and Meeting – were held at the National Gallery of Art, Washington DC, in 2004; and at the FOM Institute AMOLF and the Van Gogh Museum, Amsterdam, in 2005.

Additional activities of MaSC to be discussed in the next two days will include the Round Robin sample (coordinated by Henk van Keulen of the Netherlands Institute for Cultural Heritage, Amsterdam); the incorporation of MaSC as a not-for-profit organisation; and developments of the MaSC database of mass spectra.

We would like to thank the staff of the Philadelphia Museum of Art for their support and assistance in organising and hosting this event – in particular Beth Price, Andrew Lins, Chris Wasson, Jay Martin, Erin Soper, Michelle Bach, and the staff of Audiovisual and Information Services.

The Meeting was made possible with generous support from the Samuel H. Kress Foundation, Agilent Technologies Inc., Milestone Inc., and Grace Davison Discovery Sciences.

We hope you enjoy the Meeting, and your visit to the Philadelphia Museum of Art!

The MaSC Committee:

Ken Sutherland
Christopher Maines
Klaas Jan van den Berg
Ester Ferreira
Catherine Higgitt

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Meeting Schedule

MaSC Meeting, Philadelphia Museum of Art, Seminar Room
14-15 September 2007

Friday 14 September

9.00 Registration, coffee

Workshop discussion

10.00 Welcome and opening remarks; review of workshop by demonstrators, chaired by Klaas Jan van den Berg, Netherlands Institute for Cultural Heritage

11.00 Discussion of Round Robin sample, chaired by Michael Schilling, Getty Conservation Institute; and Henk van Keulen, Netherlands Institute for Cultural Heritage

12.00 Lunch/registration

1.30 General Meeting: opening remarks

Chair: Ken Sutherland

Session 1: sample preparation/derivatization for GCMS

1.45 **H. van Keulen, Netherlands Institute for Cultural Heritage**
Simultaneous GCMS Analysis of Amino Acids and Carbohydrates as N,O-Acetate Methyl Esters

2.10 **M. Ormsby, National Archives**
Analysis of Paper Degradation Products by Solid-phase Microextraction

2.35 **M. Silva, Universitat Politècnica de València, *et al*.**
A Study of Acrylic Resins Used in Artworks by Pyrolysis-Silylation GCMS

3.00 Coffee

Chair: Christopher Maines

Session 2: characterization of paints, varnishes, coatings

3.30 **P. Dietemann, Doerner Institute, *et al*.**
The Binding Media of Max Beckmann: Case Studies of the Munich Collection and Observations on the Formation of Protrusions on the Triptych “Temptation”

3.55 **A. Rizzo, Metropolitan Museum of Art, *et al*.**
An Analytical Study of Chemical Components in Replicas of 18th Century Oil-copal Varnishes

4.20 **K.J. van den Berg, Netherlands Institute for Cultural Heritage**
Beeswax in Artists’ Oil Paints, 1830-1930: Quantification of Wax Content Using DTMS

4.45 **V. Pitthard, Kunsthistorisches Museum, Vienna, *et al*.**
A Study of the Organic Coatings on Metal Museum Objects

5.10 Closing remarks
5.30 Drinks reception at PMA

Saturday 15 September

9.00 Opening remarks

Chair: Klaas Jan van den Berg

Session 3: new analytical techniques in museum and preservation studies

9.20 **D. Kirby, Straus Center, Harvard University Art Museums, *et al*.**
Applications of Laser Desorption Ionization Mass Spectrometry in the Conservation Laboratory

9.45 **G. Frysinger, US Coast Guard Academy, *et al*.**
Comprehensive Two-dimensional Gas Chromatography with Mass Spectrometric Detection (GC×GC-MS) and its Application to the Separation and Identification of Organic Compounds in Some Natural Resins and Waxes

10.10 **J. Adams, Library of Congress**
Direct Analysis in Real Time Mass Spectrometry (DART$^{\text{TM}}$-MS): A New Tool for Addressing Preservation Issues at the Library of Congress

10.35 Coffee

Chair: Catherine Higgitt

Session 4: archaeological materials

11.05 **H. Barnard, Cotsen Institute of Archaeology at UCLA**
Suggestions for the Analysis of Archaeological Proteinaceous Residues

11.30 **A. Chudolij, Vassar College, *et al*.**
Characterization of *Pistacia* Resins in Archeological Samples Using GCMS, Py-GCMS and Thermal Desorption Py-GCMS Techniques

11.55 **R. Armitage, Eastern Michigan University**
Characterization of Binder Materials in Rock Paintings by GCMS

12.20 **J. Poulin, Canadian Conservation Institute, et al.**
The Identification of a Hafting Adhesive Residue on a Slotted Antler Point from the Southern Yukon Ice Patch Collection

12.45 Lunch

Chair: Ester Ferreira

2.00 **I. Bonaduce, University of Pisa, *et al*.**
The Binding Medium of the Polychromy of Qin Shihuang's Terracotta Army

Session 5: dye analysis by LC and MS

2.25 **R. Laursen, Boston University, *et al*.**
The Use of LCMS for the Analysis of Dyes in Objects of Historical Interest

2.50 **Y. Sasaki, Kyoto Institute of Technology, *et al*.**
ESI Mass Spectrometric Analysis of the Dyestuff Used in 17th Century Mughal Carpets

3.15 **C. Grzywacz, Getty Conservation Institute, *et al*.**
LC-PDA-MS Analysis of Asian Organic Colorant Reference Samples: The Beginning of a New Research Project

3.40 Coffee

4.10 Members' meeting, database discussion
5.10 Closing remarks
5.30 Close of session

Posters

K.B. Kalinina, E.P. Renne, V.A. Korobov
Examination of Binding Media in British Paintings of the 18th Century Using GCMS

M.E. Freund, R.A. Armitage
The Use of THM-GCMS for the Evaluation of Chemical Pretreatments for Removing Humic Substances from Archaeological Artifacts

S. Mirabaud, J. Langlois, M. Regert
Development of Analytical Strategies for Investigating Varnishes on Old Master Paintings

E. Karpova, G. Balakina, V. Vasiliev, V. Mamatyuk
Determination of Haematein and Brazilein in Historical Textiles

A. Schönemann, M. Eisbein, W. Frenzel, A. Unger, M. Dell'Mour, E. Kenndler
A GCMS Study of Wooden Art Objects Treated with Chinese Tung Oil

J.L. Mass, M. van Bommel, W.C. Petersen, C. Matsen
HPLC-PDA Analysis of Atypical Mahoganizing Stains in an Eighteenth Century Connecticut High Chest Finish

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Abstracts

Simultaneous GCMS Analysis of Amino Acids and Carbohydrates as N,O-Acetate Methyl Esters

Henk van Keulen
Netherlands Institute for Cultural Heritage, Amsterdam, The Netherlands

Samples obtained from works of art for instrumental analysis are often small and complex in composition. It is not uncommon to find several organic materials such as drying oil, resin, polysaccharide, protein, or wax in a single sample. For this reason it is advantageous to use GCMS protocols which allow the simultaneous detection and identification of several classes of organic material. Although methods have been developed for the simultaneous analysis of oils, resins and waxes, protocols typically employed for proteins and polysaccharides require separate derivatization procedures. This paper discusses the development and optimization of a method for the simultaneous analysis of proteins and polysaccharides in samples from artworks.

In published GCMS methods for the simultaneous analysis of amino acids and carbohydrates, derivatization procedures include silylation of functional groups following oximation of the carbohydrates [1]. Methods for the separate analysis of amino acids and carbohydrates also include esterification with an alcohol (methanol, isopropanol or butanol), followed by acetylation with (trifluor)acetic acid [2,3].

An important factor for the analysis of samples containing protein and/or polysaccharide is the initial hydrolysis step, often not discussed in published methods for simultaneous analysis. A standard hydrolysis procedure for proteins using 6M HCl will destroy carbohydrates, whereas a milder treatment with trifluoracetic acid as used for the hydrolysis of carbohydrates [4] will not efficiently hydrolyze proteins.

In our laboratory, a mixture of amino acids and carbohydrates was used for an initial evaluation of different derivatization methods. Silylation was not always a success. Although silylation reagents theoretically can be used for a wide range of functional groups, the results of derivatization differ from type to type and application.

However, a combination of methylation and acetylation produced stable and reproducible derivatives for both the amino acids and the carbohydrates in the standard sample, which are analyzed as N,O-acetate methyl esters.

Hydrolysis procedures using different concentrations of hydrochloric and trifluoracetic acids, temperatures and times of hydrolysis, were tested on a mixture of protein and polysaccharide. From these experiments, a procedure was developed by which it was possible to hydrolyze both polysaccharides and proteins with a good compromise between loss and efficiency. This paper will outline the preparation procedure, and examples of applications to the study of artworks will be discussed.

References:
[1] U. Roessner, C. Wagner, J. Kopka, R.N. Trethewey, L. Willmitzer. Simultaneous analysis of metabolites in potato tuber by GCMS. *The Plant Journal* 2000 23(1), pp.131-142.
[2] A. Casoli, G.Palla, J. Tavlaridis. GCMS of works of art: Characterization of binding media in post-Byzantine icons. *Studies in Conservation* 43 (1998) pp.150-138.
[3] R. Stenutz, P.E. Jansson and G. Widmalm, "A practical guide to structural analysis of carbohydrates" http://www.casper.organ.su.se/sop
[4] M. Schilling. Procedure for GCMS analysis of plant gums and sugars, Revised Oct. 8, 2000

Analysis of Paper Degradation Products by Solid-phase Microextraction

Mark Ormsby
National Archives and Records Administration, College Park, MD, USA

As paper-based materials degrade they emit a wide range of volatile compounds that produce the characteristic “old book” odor. Recent studies have identified more than 70 volatiles that make up this smell. Some compounds are produced by the acid-catalyzed hydrolysis of cellulose, while others are by-products of oxidation. Lignin-containing papers produce additional compounds.

This presentation discusses the use of solid phase microextraction (SPME) in combination with gas chromatography mass spectrometry as a convenient method for the analysis of paper degradation products. SPME is a simple, sensitive, and economical technique that utilizes polymer-coated fibers to collect the sample and transfer it to the instrument without the use of solvents. The reusable fibers are housed within a syringe-like device and are exposed by extending the fiber tip outside of a protective steel needle. Various polymer coatings are available in a range of polarities.

To analyze volatiles in archival storage areas air samples were collected in gas sampling bulbs that had been deactivated to reduce adsorption on the glass surface. After sampling, the bulbs were returned to the laboratory, and a SPME fiber inserted through the bulb’s septum and exposed for a set time (usually 30 minutes). The fiber was then immediately desorbed in the injection port of the GCMS. The method using the glass bulbs was selected because researchers in other fields studying similar matrices of compounds have carefully evaluated the linear ranges, effects of competitive adsorption, and other factors that may influence quantitative measurements.

Qualitative SPME analysis has shown that acetic acid, furfural, benzaldehyde, benzyl alcohol, toluene, phenol, and other compounds associated with paper degradation are present in various storage areas. In addition, phthalates have been found in some stacks. These plasticizers are most likely given off by photographic film and laminated documents. Preliminary quantitative measurements have been made by calibration of the system using permeation tubes. Results indicate that the limit of quantitation for acetic acid is 1-2 ppb. Future work will use mixtures of compounds to study possible interferences from competitive adsorption. The quantitative data will be used to study the relationship between the concentration of volatiles in storage rooms and the air exchange rate for the area. Previous research showed that lowering the exchange rate produced considerable energy savings, without a significant change in the pollutant concentrations in the stacks.

In addition to evaluating air samples, SPME can be used to analyze solvent extracts from paper to study less volatile deterioration products. Polar compounds such as formic acid, for example, may be strongly bound to the cellulose. Formic acid has not been detected in air samples, but significant amounts have been found in ethanol extracts after derivatization to form ethyl formate, prior to headspace SPME sampling. Consequently, SPME shows great promise for providing a more complete picture of paper deterioration products.

A Study of Acrylic Resins Used in Artworks by Pyrolysis-Silylation GCMS

María Teresa Doménech-Carbó, Laura Osete-Cortina, Giovanna Bitossi, Dolores Julia Yusá-Marco, Miguel F. Silva
Institut de Restauració del Patrimoni, Universitat Politècnica de València, Spain

The use of acrylic resins as binding media and varnishes for paintings has increased in recent decades. The mechanical and optical properties conferred to coating and paint layers by acrylics have encouraged contemporary artists to use these polymers as varnishes and paint binders in place of other organic media traditionally used for this purpose. Nevertheless, these resins have not been systematically studied from the point of view of their stability and behaviour when they are subjected to the degradation effects of environmental agents.

A study was carried out in order to characterize different acrylic resins used in artworks. A derivatization method was employed for Py-GCMS based on “on line” silylation-pyrolysis with hexamethyldisilazane (HMDS). Pyrograms were obtained with this method exhibiting a well resolved peak for the trimethylsilyl ester of acrylic acid, instead of the strongly fronting peak of acrylic acid typically observed with direct pyrolysis or “on line” methylation with tetramethylammonium hydroxide. Peaks are also obtained corresponding to monomers, dimers, trimers and sesquimers. The method has been successfully applied in the identification of binding media found in a 20th century painting by an unknown artist, as well as in graffiti on a mediaeval bridge in the city of Valencia.

As a second part of the study, an investigation of the ageing of acrylic resins was carried out. A series of samples were subjected to three different accelerated ageing treatments and analyzed in order to determine the main chemical changes. The acrylic resins were applied as thin films and exposed to different environmental agents: a) thermal ageing (55ºC and 45% RH), b) UV light exposure, and c) ageing in SO2 polluted chamber. Initial results showed a decreased intensity of the plasticizer peak for two acrylic dispersions tested – Plextol D-498 and Primal AC-35; whereas no significant alterations of the ratios of monomers/dimers and monomers/trimers were observed.

Acknowledgements
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The Binding Media of Max Beckmann: Case Studies of the Munich Collection and Observations on the Formation of Protrusions on the Triptych "Temptation"

Patrick Dietemann, Heike Stege, Ursula Baumer, Irene Fiedler
Doerner Institut, Bayerische Staatsgemäldesammlungen, Munich, Germany

The large collection of paintings by Max Beckmann (1884-1950) is one of the highlights of the Pinakothek der Moderne in Munich. Recently it was possible to start a systematic study of the binding media used by Beckmann. The results from the study point to the conclusion that Beckmann used commercially available oil paints almost exclusively, most of them based on linseed oil. A similar pattern of additives was found in most of the paint samples studied, consisting of minor amounts of non-drying oils, animal fats, traces of proteins and drying additives. This is interpreted as the typical pattern of commercial artists' oil paints around 1920-1940, a conclusion supported by written sources which state that Beckmann did not prepare his paints himself, but rather used commercial tube paints.

Beckmann's famous triptych "Temptation", painted in Berlin in 1936/37, exhibits an interesting phenomenon: extensive protrusions are observed on both side paintings, but not on the central painting, even though all three parts have a similar storage, display and conservation history. The paint compositions on both the central and the side pieces were therefore studied using GC, GCMS, AAA and FTIR.
Similar materials, including support and preparation layers, were found on the central and side paintings. Our studies revealed that the protrusions originate from the commercial ground layer of the paintings and consist of zinc soaps. The ground layer with protrusions contained a larger amount of oil binding medium, a factor that could be connected with the formation of the protrusions.
By comparison with detailed photographs from 1969 we could deduce that the protrusions must have formed within the first 30 years after the painting was finished. Since then, the protrusions have not developed further. This is probably due to storage of the triptych in stable climatic conditions and careful handling (the triptych is no longer loaned).

An Analytical Study of Chemical Components in Replicas of 18th Century Oil-copal Varnishes

Adriana Rizzo[1], Julie Arslanoglu[1], Joy Mazurek[2], Michael Schilling[2], Anna Schönemann[3]
1 The Metropolitan Museum of Art, New York, NY, USA
2 Getty Conservation Institute, Los Angeles, CA, USA
3 University of Vienna, Institute for Analytical Chemistry, Vienna, Austria

The use of copal resin as an ingredient in the manufacture of oil-resin varnishes has been widely documented. In particular, French and German 18th century treatises mention copal in the preparation of varnishes with a glossy finish, to be used to imitate Oriental lacquers and porcelain finishes on light colored grounds for furniture, interiors and carriages. The choice and proportions of the ingredients in copal varnishes varied according to the function of the varnish. The high temperatures necessary for the melting of the copal resin, and its inhomogeneous incorporation in mixtures with the different additives, result in variations in the distribution and intensity of characteristic biomarkers from the original materials. Such chemical variance can compromise the identification of the resin and other varnish components. This paper presents the results of a collaborative project between the Getty Conservation Institute in Los Angeles and the Goering Institut für Restauratorenausbildung in Munich, Germany. 18th century recipes for oil-copal varnishes were replicated in Munich using Congo copal as the semi-fossil resin. Formulations included linseed oil, larch turpentine and essential oils. Starting ingredients and samples from each preparatory step in the varnish making process were analyzed to systematically follow chemical changes and distribution of components with heat treatment and filtrations. Analyses were carried out using THM-Py-GCMS with TMAH methanolic solution. The survival of resin biomarkers was followed throughout the varnish making process and accelerated aging of selected cast films. The concomitant survival of copal biomarkers and the presence of pyrolysis fragments of the polymer skeleton allowed for identification of these classes of copal resins in old oil-varnish samples. However, it is shown here that high temperatures during the varnish making process, and the presence of additives, affect the detection of these copal biomarkers even before aging.

Acknowledgements
The project was carried out at the Getty Conservation Institute during the authors Rizzo, Arslanoglu and Schönemann's former tenure in the Museum Research Laboratory of the J. Paul Getty Museum in Los Angeles. Thanks are due to The Getty Grant Program, which supported the project and A. Rizzo's graduate internship, and to Bernhard Kügler and Christian Stadelmann at the Goering Institut, Munich, for their contribution in evaluating the historic literature and preparing the oil-copal varnishes.

Beeswax in Artists' Oil Paints, 1830-1930: Quantification of Wax Content Using DTMS

Klaas Jan van den Berg
Netherlands Institute for Cultural Heritage, Amsterdam, The Netherlands

In the development of artists' oil paints and painting techniques in the 19th Century, beeswax has played an important role. Artists would sometimes add beeswax to their paints to give a silkier, more matte appearance. Tube oil paint manufacturers frequently used beeswax as an additive to prevent the oil paint from "running", a practice gradually replaced by the use of aluminium, zinc and other metal stearates in the early 20th Century.

Beeswax is thus frequently detected in 19th and early 20th Century paintings. In studying artists' paints, the question often arises whether beeswax was added by the artist, or was already present in the paint obtained by the manufacturer. In addition to its use as a constituent of the oil paint, in some cases it may also have been introduced through a conservation treatment.

This paper focuses on the analysis of beeswax in oil paint using Direct Temperature-resolved Mass Spectrometry (DTMS). Examples will be shown of tube paints, paint reconstructions, artists' palettes, and paintings containing beeswax in proportions from 0-20 %. Quantification of the beeswax/oil ratio is discussed in the light of a study of a specific wax painting technique introduced by Ernst Ludwig Kirchner (1880-1938), which was also employed by his colleagues of the artists' societies *Die Brücke* (Germany) and *De Ploeg* (Groningen, the Netherlands).

A Study of the Organic Coatings on Metal Museum Objects

Václav Pitthard[1], Sabine Stanek[1], Martina Griesser[1], Helene Hanzer[1], Claudia Kryza-Gersch[1], Tatjana Bayerová[2], Martina Griesser-Stermscheg[2]
1 Kunsthistorisches Museum, Vienna, Austria
2 Institute of Conservation Science and Restoration Technology, University of Applied Arts, Vienna, Austria

This presentation summarizes the first results of an ongoing three-year project to characterize the organic coatings on various historical metal objects. This systematic study should help to better understand the condition of the objects, to assist in their art historical interpretation, and to enable the development of appropriate conservation treatments. Two parts of the project will be discussed: the investigation of “organic patinas” on indoor Renaissance and Baroque bronzes in the collections of the Kunsthistorisches Museum; and the study of natural and synthetic organic coatings on lead-tin sarcophagi in the Imperial Crypt, Vienna. The coatings on the artefacts were studied using microscopy, GCMS and Py-GCMS.

The Kunsthistorisches Museum holds a precious and important collection of Renaissance and Baroque bronze sculptures. The sculptures appear to have been treated using coloured organic coatings (“varnishes”). These treatments were meant to enhance certain aspects of the design, but also to hide technical defects from the casting process. In addition, organic coatings may have been applied to the bronzes in later centuries during conservation treatments to prevent the development of corrosion. Microscopic examination of cross-sections revealed multilayer structures of coatings on the bronze surfaces, and GCMS analysis determined the presence in the coatings of mixtures of natural resins, drying oils, bitumen and waxes, in distinct compositions. These results, discussed in the context of art historical and provenance studies, will facilitate future investigations concerning origins, workshops (“schools”) and production methods of the sculptures studied.

The Imperial Crypt is famous for its ensemble of sarcophagi containing the bodies of over 150 members of the Austrian Imperial Habsburg family. For decades, the high relative humidity in the Imperial Crypt has been a major problem for the preservation and conservation of these lead-tin cast objects. In previous restoration campaigns, the sarcophagi were coated with epoxy resin containing tin grains, possibly also wax, or with nitrocellulose lacquers followed by acrylic-based resins with additions of shellac. Many damages have since occurred in areas where the previous restoration coatings had been applied. The pilot analysis of the coating materials has confirmed the presence of the various materials, and more detailed investigations will provide information that will be useful to help formulate further conservation treatments.

Applications of Laser Desorption Ionization Mass Spectrometry in the Conservation Laboratory

Dan Kirby, Narayan Khandekar
Straus Center for Conservation, Harvard University Art Museums, Cambridge, MA, USA

Different mass spectrometric techniques have been used in the field of conservation science for many years; their value is well known. More recently, Laser Desorption Ionization (LDI) mass spectrometry has been adopted from the biotechnology community, and multiple groups have demonstrated its application for the analysis of art objects, especially with modern pigments. Generally conducted in analytical laboratories by experienced mass spectrometrists, LDI studies of model paint systems, as well as authentic samples, have clearly established the value of this technique to the conservation scientist. The purpose of this presentation is to show the utility of LDI as a routine tool in the environment of a small conservation laboratory.

First we will discuss basic instrumental requirements, sampling considerations, data collection, analysis and interpretation, and background effects. These aspects of LDI will be illustrated with results from standards and model systems. Then, results from studies of modern works by Mark Rothko, Barnett Newman and Donald Judd, as well as paintings attributed to Jackson Pollock, will be used to illustrate how LDI has been used in our laboratory, either alone or in conjunction with other standard analytical techniques, to obtain information about these artists' choice of pigments.

Finally, we will discuss additional uses of LDI that have the potential to broaden the scope of its application in the conservation laboratory. Specifically we will discuss plans and progress for the analysis of proteinaceous materials in art objects, and approaches to obtaining MS information from cross sections.

Comprehensive Two-dimensional Gas Chromatography with Mass Spectrometric Detection (GC×GC-MS) and its Application to the Separation and Identification of Organic Compounds in Some Natural Resins and Waxes

Glenn Frysinger[1], Gregory Hall[1], Richard Gaines[1], Ken Sutherland[2]
1 US Coast Guard Academy, Department of Science, New London, CT, USA
2 Philadelphia Museum of Art, Philadelphia, PA, USA

Comprehensive two-dimensional gas chromatography (GC×GC) is a high resolution, multidimensional gas chromatographic method in which the entire sample is subjected to two independent chromatographic separations. The high resolving power of GC×GC produces a powerful capability to separate, identify, and quantify compounds in complex mixtures. The GC×GC chromatogram is a plot of two-dimensional retention time and detector signal. In volatility-by-polarity separations, compound peaks are ordered and grouped in the retention time plane by similar molecular weight and polarity. Coupling GC×GC with a fast mass spectrometer produces a third dimension of data so each compound peak in the GC×GC chromatogram has a full-scan, low-noise, mass spectrum for identification. Trace compounds are more easily identified because chromatographic co-elution is greatly reduced with the two-dimensional separation. The presentation will discuss GC×GC instrumentation and practice. Chromatograms for several natural resin and wax samples including dammar, seedlac and beeswax will be presented.

Direct Analysis in Real Time Mass Spectrometry (DART^{TM}-MS): A New Tool for Addressing Preservation Issues at the Library of Congress

Jeanette Adams
Library of Congress, Washington, DC, USA

The Library of Congress recently purchased a JEOL AccuTOF-DART^{TM} mass spectrometer. The DART^{TM} (Direct Analysis in Real Time) ion source operates at atmospheric pressure and is physically distant from the TOF (time-of-flight) mass analyzer by approximately 1.5 cm of open space. The DART^{TM} emits a thermal stream of excited-state (metastable) helium atoms, which interact with water in ambient air to produce protonated water clusters $[(H_2O)_nH^+]^+$. Penning ionization gives rise to thermal electrons that result in oxygen radical anions ($O2^{\cdot -}$). These gas-phase ionic reactants then collide with analyte molecules present on the surface of a sample that is inserted between the DART^{TM} and the mass analyzer. The protonated water reactant cations undergo proton transfer to produce protonated $(M + H)^+$ ions, whereas the oxygen reactant anions either undergo proton abstraction to produce $(M – H)^-$ ions or give $(M + O_2)^{\cdot -}$ adduct ions. The analyte ions are then swept into the TOF through a pin-hole leak. The TOF operates at a mass resolving power of 6000 (m/Δm), and the software provides for matching both accurate mass measurements and experimental isotope abundances to theoretical elemental formulas, which inform ion identification. The temperature of the stream of helium exiting the DART^{TM} can be varied to produce different results. Ambient (50 °C) temperature provides for non-invasive direct analyses of highly volatile indicator compounds from collection materials, such as formic acid from aged paper and acetic acid from magnetic media that have “vinegar syndrome”. Higher temperatures used with micro-samples (micrometer in size, microgram in mass) provide “fingerprint” analysis of additives (such as paper size) and plastics used in collection housings, and provide for detection of “sticky shed syndrome” in magnetic media. Pyrolysis of micro-samples results in “fingerprint” analysis of different paper types, such as cotton vs. hardwood vs. high-lignin papers.

Suggestions for the Analysis of Archaeological Proteinaceous Residues

Hans Barnard
Cotsen Institute of Archaeology at UCLA, Los Angeles, CA, USA

The increasing numbers of publications on organic residues in archaeological materials are testimony to the fact that analysis of these residues has the potential to yield important information. The analysis of lipid residues and their association with food products is now relatively well established, although the interpretation of the results can still be problematic [1]. Organic compounds other than lipids that may survive in an archaeological context include polysaccharides, DNA and proteins. Ancient polysaccharides have been isolated from archaeological pottery, historical paints and the surfaces of stone tools. They could potentially serve as diagnostic markers, but will generally leach rapidly out of archaeological materials or be digested by microorganisms. The amount of residual DNA, theoretically the most informative biomolecule, is very low in most food products and even lower in archaeological food residues, again due to the loss of molecules by leaching and microbiological decay. Proteins are generally much more abundant in natural substances than DNA. They are likely to provide more specific information concerning their origin than lipids or polysaccharides because they are the direct products of the DNA of the plant or animal species in which they were synthesized.

On the basis of published studies, as well as my own research, I will present a short overview of the possibilities and problems associated with the various methods available for the identification of proteinaceous residues in archaeological materials [2].

References:

[1] H. Barnard, S.H. Ambrose, D.E. Beehr, M.D. Forster, R.E. Lanehart, R.E. Parr, M.E. Malainey, M. Rider, C. Solazzo and R.M Yohe II, "Mixed Results of Seven Methods for Organic Residue Analysis Applied to One Vessel with the Residue of a Known Foodstuff", *Journal of Archaeological Science* **34** (2007), pp. 28-37.
[2] H. Barnard, L. Shoemaker, O.E. Craig, M. Rider, R.E. Parr, M.Q. Sutton and R.M. Yohe II, "Introduction to the Analysis of Protein Residues in Archaeological Ceramics", in H. Barnard and J.W. Eerkens (eds.), *Theory and Practice of Archaeological Residue Analysis*, British Archaeological Reports International Series 1650, Oxford (Archaeopress), 2007, pp.216-231.

Characterization of *Pistacia* Resins in Archaeological Samples using GCMS, Py-GCMS and Thermal Desorption Py-GCMS Techniques

Anne Chudolij[1], Julie Arslanoglu[2], Adriana Rizzo[2], Curt Beck[1], Edith Stout[1]
1 Vassar College, Department of Chemistry, Poughkeepsie, NY, USA
2 The Metropolitan Museum of Art, New York, NY, USA

This paper presents the results of a collaborative project between Vassar College and The Metropolitan Museum of Art to characterize *Pistacia* resins from the Eastern Mediterranean using gas chromatography mass spectrometry (GCMS), pyrolysis gas chromatography mass spectrometry (Py-GCMS) and thermal desorption Py-GCMS (TD-Py-GCMS) techniques. *Pistacia* resins recovered as cargo in a Bronze Age shipwreck off the Turkish coast at Ulu Burun had been preserved in a dark, anaerobic environment. The remarkably well-preserved resins allowed an investigation into the determination of the species, subspecies and geographical origin of the resins. Previous research has focused on the larger, triterpenoid molecules – the main components of deciduous resins. However, this paper reports that differentiation between species and geographic origins of *Pistacia* resins appears to depend on variations in the lower molecular weight components. GCMS techniques with methylation by diazomethane and MethPrep II (Alltech) proved useful for the characterization of the monoterpenes. Py-GCMS (with and without derivatization with TMAH) and TD-Py-GCMS were employed as reliable and fast techniques for the assessment of the presence and identification of marker compounds in the *Pistacia* resins, providing additional information not obtained from GCMS analyses. Py-GCMS and TD-Py-GCMS were not only effective in the detection and identification of monoterpenes in the resins, but also revealed previously overlooked marker compounds in this region, whose identification was facilitated via analysis of thermal desorption data. These additional compounds proved to be critical for the distinction between *Pistacia* resins. The analyses have been helpful in identifying the botanical origin of the archeological resin. This information has also been useful in determining the possible place of origin and destination of the Ulu Burun shipwreck.

Acknowledgements
The project was initiated as a senior thesis under the guidance of Professor Curt Beck and Edith Stout, and was supported by funding obtained from Vassar College's Undergraduate Summer Research Institute. The work was continued and enhanced by the generosity of the resources made available at the Metropolitan Museum of Art.

Characterization of Binder Materials in Rock Paintings by GCMS

Ruth Ann Armitage
Eastern Michigan University, Department of Chemistry, Ypsilanti, MI, USA

Direct radiocarbon dating of rock paintings requires that there is an organic binder remaining in the paint samples. The nature of this binder is often unclear, as recipes for these paints are uncommon and likely depend on locally available and culturally relevant materials. Thus the composition of the paints is presumably not the same at different rock art sites. Radiocarbon dates have been determined for samples of rock paintings from sites around the world, based on the assumption that a binder was present, and the measured dates have typically fallen within the broad range of ages expected from archaeological inference. We have undertaken GCMS analysis of rock paintings from several sites to determine the nature of the organic material in the paint, and to compare the composition of the material to that found on unpainted substrate rock. We have utilized primarily thermally-assisted hydrolysis/methylation-GCMS, as it requires only minute samples, minimal sample preparation, and is appropriate for a broad range of possible binders (e.g., plant and animal materials). In some cases, especially at one site near Antigua, Guatemala where the paintings were exposed to the elements, few differences were observed in the composition of the paint samples and the organic material from the substrate rock. This indicates either that no organic binder was present in the paint, or that it had significantly decomposed since the paint was applied. These samples were therefore not ideal for radiocarbon dating. Results for two paintings from the Black Hills National Forest in North Dakota and Pecos River style paintings from Texas will also be discussed.

The Identification of a Hafting Adhesive Residue on a Slotted Antler Point from the Southern Yukon Ice Patch Collection

Jennifer Poulin[1], Kate Helwig[1], Valery Monahan[2]
1 Canadian Conservation Institute, Ottawa, Canada
2 Department of Tourism and Culture, Government of Yukon, Canada

Since their chance discovery in 1997, Yukon ice patches have been the focus of multidisciplinary research into Yukon's human and environmental past. The patches are ancient snow preserved in remote alpine areas of the Coast Mountains, Ruby Range and Southwestern Yukon Plateau. A pattern of hot summer weather over the past decade has caused rapid melting of the patches, exposing diverse biological materials and archaeological artefacts. Approximately 180 artefacts have been recovered from Yukon ice patches. They appear to have been frozen quickly and to have remained frozen until the recent melting of the ice. This has resulted in a remarkable preservation of their organic components.

This presentation describes the identification of hafting adhesive on an antler point, slotted for microblade insertion. The adhesive, found in the slots of the point, would have held the microblades in place. Radiocarbon dated to 7310 ± 40 BP (uncalibrated), the point is one of the oldest artefacts recovered from the ice patches.

Analysis of residues in the slots of the point was performed using two separate derivatisation techniques: methylation with TMTFTH, and trimethylsilylation with BSTFA. Modern resins from five trees common to southern Yukon were also analysed for comparison, and the presence or absence of chemical markers such as of 13-epi-manool, abienol, and epi-torulosol were used to aid in identification. Based on this comparison, the resin from the slotted point most closely resembles the chemical profile of a species of white spruce (*Picea glauca*).

This is the first time a North American hafting adhesive has been identified. It was found to be remarkably well preserved (showing approximately the same degree of oxidation as a two-year old reference sample of resin), likely because of its burial environment and subsequent storage. Additionally, the absence of retene and related compounds suggests another unique characteristic when compared to the existing identified hafting adhesives from Old World origins, which typically exhibit such compounds as evidence of heat treatment.

The Binding Medium of the Polychromy of Qin Shihuang's Terracotta Army

Ilaria Bonaduce[1], Catharina Blaensdorf[2], Patrick Dietemann[3], Maria Perla Colombini[1]
1 Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa, Italy
2 Technische Universität München, Munich, Germany
3 Doerner Institut, Bayerische Staatsgemäldesammlungen, Munich, Germany

The "Terracotta Army", one of China's most famous attractions, is well known for its legions of greyish brown soldiers arranged in long rows. The fact that the soldiers, chariots and weapons were originally painted in bright colours is still not widely known, although fragments of colour have been recorded since the very beginning of the excavations. The environmental conditions of the site, together with the particular painting technique used, have made the remaining polychromy extremely fragile [1]. The development of an appropriate conservation treatment for the polychromy has been one of the main aims of a joint German-Chinese project for more than ten years. Parallel to the conservation tests, scientific investigations of the paint layers have also been carried out. The inorganic pigments have been characterised successfully [2], but identifying the binding medium has proved more difficult, due to the high inorganic content, the effects of a fire started by a rebel army in 206 BC, followed by 2200 years in the soil. The original investigations performed in the 1990s did not provide conclusive results; it was assumed that there was not enough binding medium preserved to allow identification. Here we show a successful attempt to determine the binder of the polychromy through the use of a purification technique commonly used in the field of proteomics. In particular, the proteinaceous material was determined using GCMS analysis, after extraction, purification, acid hydrolysis and derivatisation steps. Principal Component Analysis of the relative percentage composition of amino acids was used for protein identification. Monolithic sorbent tips - micro-columns packed with reversed phase resins - were used for protein cleanup. The ability to obtain highly purified organic materials, although partially degraded and in very small amounts, allowed us to identify egg as the medium used. This result is interesting in terms of the historical significance of the work of art, and important to inform conservation methods. It also helps to understand and reconstruct the overwhelming visual impression of Qin Shihuang's army and other burial objects from his tomb.

References:

[1] C. Thieme, "The terracotta army of the first Chinese emperor Qin Shihuang", in Y. Wu, T. Zhang, C. Blaensdorf, E. Emmerling, and M. Petzet (eds.), Arbeitshefte des Bayerischen Landesamts für Denkmalpflege 83, Munich (Karl M. Lipp Verlag), 2001, pp.424-461.
[2] C. Blaensdorf, in Annual Report 2001 and 2002 for the Project "Testing and Optimising of Conservation Technologies for the Preservation of Cultural Heritage of the Shaanxi Province, PR China", Munich, 2001, pp.81-93.

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The Use of LCMS for the Analysis of Dyes in Objects of Historical Interest

Richard Laursen, Xian Zhang
Boston University, Department of Chemistry, Boston, MA, USA

Using high performance liquid chromatography (HPLC) with photodiode array and mass spectrometric detection, dyes extracted from objects of historical interest or from natural plant/animal dyestuffs can be characterized on the basis of three orthogonal properties: HPLC retention time, UV-Visible spectrum and molecular mass. In the present study, we have focused primarily on yellow dyes, the bulk of which are flavonoid glycosides, and which, without mass spectrometric detection, would be almost impossible to characterize. Also critical for this analysis is a method of mild extraction of the dyes from the objects without hydrolyzing the glycosidic linkages. This was accomplished using 5% formic acid in methanol rather than the more traditional 6M HCl. Mass spectrometry, besides providing the molecular mass of the dye molecule, sometimes yields additional structural data based on fragmentation patterns. In addition, co-eluting compounds can often be detected using ion extraction scanning. For this purpose, we used an Agilent Series 1100 VL on-line atmospheric pressure electrospray ionization mass spectrometer, usually in the negative ion mode. The utility of mass spectrometry will be demonstrated by discussion of the identification of yellow dyes detected in specimens of dyed silk exported to the Americas from China during the 19th century. In this study, we identified, in individual specimens, three distinct types of yellow dye: flavonoid glycosides from *Sophora japonica* (pagoda tree), curcumins from *Curcuma longa* (turmeric) and protoberberine dyes from a species of *Fibraurea* (Chinese *huangteng*). Besides the aforementioned dyed silks, we have used these techniques to identify the dye type, and sometimes the original dyestuff, in a variety of objects ranging in age from about 150 to 3000 years. So far we have accumulated a library of, and have analyzed, over 200 dyestuffs (mostly plants) and are creating a website that will make this information available to everyone.

ESI Mass Spectrometric Analysis of the Dyestuff Used in 17th Century Mughal Carpets

Yoshiko Sasaki[1], Nobuko Kajitani[2], Ken Sasaki[3]
1 The Museum and Archives, Kyoto Institute of Technology, Kyoto, Japan
2 Conservator Emerita, Metropolitan Museum of Art, New York, NY, USA
3 Kyoto Institute of Technology, Department of Biomolecular Engineering, Kyoto, Japan

Red dyes such as madder, kermes, cochineal and lac are frequently used in historical textiles. The colouring principles in these dyes have a common anthraquinone structure and therefore exhibit similar chemical and physical properties. For this reason, discrimination and/or identification by usual spectroscopy techniques can be difficult. The authors have developed an analytical protocol for accurate identification of dyestuffs in microsamples, by combining two or more instrumental techniques, and have shown the effectiveness of mass spectrometric analysis of the extracted dyes. In this presentation, we will discuss the identification of red dyestuffs from Indian carpets of the Mughal Dynasty (first half of the 17th Century) using Electrospray Ionization – Ion Trap (ESI-IT) mass spectrometry. One of the important features of the ion trap analyzer is the MS^n capability. The MS^n spectra can provide structural information on the dye molecules, and can also be used for molecular identification by comparison with MS^n spectra of reference compounds, even in the presence of significant levels of impurities. The structural information from MS^n analysis is important for correct identification of dyestuff molecules, especially using a protocol in which additional information from LC separation and DAD is not available. The MS^n analysis is also highly sensitive: by the application of this methodology, the sampling amount was decreased by a factor of 100 compared to typical LCMS conditions. (Analyses required roughly 3µg fibre in 100µl extract solvent.)

Visible absorption spectra of dye extracts from the carpets were almost identical with those of lac or cochineal. ESI-IT analyses indicated a molecular mass consistent with laccaic acid A, the main ingredient of lac dye. ESI-IT MS/MS and MS/MS/MS targeted for the molecular mass showed two successive decarboxylation processes by neutral loss, which are a structural indication of laccaic acid A with two carboxyl groups.

LC-PDA-MS Analysis of Asian Organic Colorant Reference Samples: The Beginning of a New Research Project

Cecily M. Grzywacz[1], Jan Wouters[2]
1 Getty Conservation Institute, Los Angeles, CA, USA
2 Royal Institute for Cultural Heritage (KIK/IRPA), Brussels, Belgium

The Getty Conservation Institute (GCI) launched a collaborative research project with Jan Wouters (KIK/IRPA) in June 2006 to investigate Asian organic colorants. This is the GCI's first organic colorant project. The objective is to develop analytical strategies for traditional Chinese organic colorants used as textile dyes and pigments.

Detection and identification of Chinese organic colorants presents many challenges. Not only have many of the biological sources used to create them not been well studied, they are often also present at relatively low concentrations within the textile or paint matrix.

A review of the literature identified over 100 biological dye sources as having been used in China. From these, a selection of twenty-four best-hit plant species and resins were made. These biological sources are being acquired from Chinese pharmacies and botanical gardens. Validation of the biological sources is made using LC-PDA-MS^n. Bulk reference samples have been prepared with the biological sources using historical recipes when available. Dyeings on wool and silk with and without mordanting with alum were performed. Pigments were prepared on a hydrated aluminum oxide base. Paints were prepared by suspending those pigments in a dilute animal glue medium or by concentrating the dye extract and adding glue. The reference samples will be used to develop the analytical strategy.

LC-PDA-MS^n (ESI-NIM) results from several reference samples will be presented. The ESI mass spectra and UV-Vis spectra will be submitted to MaSC databases.

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Poster Abstracts

Examination of Binding Media in British Paintings of the 18th Century Using GCMS

Kamilla B. Kalinina, Elizaveta P. Renne, Victor A. Korobov
The State Hermitage Museum, St. Petersburg, Russia

The collections of the State Hermitage Museum include significant examples of 18th Century British paintings. These paintings have not previously been the subject of a systematic study with regard to their binding media. It is known that some British artists of this period employed unconventional media and techniques. Especially famous for his use of idiosyncratic materials is Sir Joshua Reynolds (1723-1792), a fact that accounts for the unsatisfactory condition of a number of his paintings. Daniel Gardner (1750-1805) showed a similar experimental approach in his use of paint materials.

A study of the organic composition of the binding media used in paintings by British artists including Reynolds, Gardner, Joseph Wright of Derby (1734-1797) and Thomas Jones (1742-1803) was carried out using gas chromatography mass spectrometry (GCMS). Analyses revealed the presence in paint samples of linseed or walnut oil, sometimes in combination with additional organic components such as resins, waxes and sugars.

The paintings studied exhibited varying degrees of deterioration, and correlations could be observed between their current condition and the binding media used by the artists. In particular, deformation of the paint layers was found to be pronounced where megilp with a high concentration of mastic was used as binding medium.

The Use of THM-GCMS for the Evaluation of Chemical Pretreatments for Removing Humic Substances from Archaeological Artifacts

Mary Ellen Freund, Ruth Ann Armitage
Eastern Michigan University, Department of Chemistry, Ypsilanti, MI, USA

In order to radiocarbon date archaeological materials accurately, it is typically necessary to clean them chemically first. The standard pretreatment regime requires washing materials first in acid to remove carbonates, then in alkali to dissolve out humic acids – organic compounds that often saturate buried objects affected by groundwater permeation – and finally in acid again to neutralize the remaining alkali and prevent adsorption of atmospheric carbon dioxide. This process is destructive, often leaving only a residue of the original material. We are investigating less destructive pretreatment options that will be suitable for use with our plasma-chemical oxidation radiocarbon dating method, which itself is minimally destructive. Development of an alternative cleaning procedure is important to preserve culturally and historically significant objects.

Because of the nature of the plasma-chemical oxidation method, the acid steps in the standard pretreatment regime are unnecessary. The purpose of our work is to replace the alkali step with an equally effective, yet less harsh treatment. Modern materials representing those of most interest – including charcoal, cotton and linen – were selected for evaluation. The materials were soaked in a solution of humic acid standard. Fragments from two artifacts excavated from Little Lost River Cave in Idaho were also included in this study. Residues after treatments with NaOH, phosphate buffer (pH 8), and deionized water were characterized using thermally-assisted hydrolysis/methylation-GCMS. Preliminary results indicate that both NaOH and phosphate buffer are equally effective for the removal of humic acid, as indicated by a loss of several marker compounds from the humic standard. Additionally, the samples were less visibly changed after the phosphate treatment. Comparisons of the effects of the different chemical treatments on measured radiocarbon ages for the archaeological materials from Idaho will also be discussed.

Development of Analytical Strategies for Investigating Varnishes on Old Master Paintings

Sigrid Mirabaud, Juliette Langlois, Martine Regert
Laboratoire du Centre de Recherche et de Restauration des Musées de France, Paris, France

During the restoration of paintings, varnish layers often show variation in their solubility properties. Characterization of the different layers is therefore important to inform conservation treatments, as well as to understand the treatment history of the paintings.

A multi-step methodology was implemented in our laboratory for the analysis of varnishes. Depending on the state of restoration of the paintings, the varnishes were sampled either by cotton swabs impregnated with a solvent, or by removal of a microscopic flake using a scalpel blade. Solvent swabs were extracted with dichloromethane, in parallel to the extraction of an unused swab as an experimental blank. Both types of sample were first analyzed using direct-inlet mass spectrometry (DI-MS) to achieve a general characterization of the resin class, and determine the presence of additives. Subsequent analyses were aimed at obtaining a more precise identification of the resin and its stage of alteration, by silylation of an aliquot of the swab extract or scratched varnish sample, followed by analysis with high temperature gas chromatography mass spectrometry. To investigate the presence of additives to the resin such as drying oils that could explain the differences in solubility of the varnishes, an additional aliquot of sample was analysed by GCMS, following transesterification with BF_3-propanol.

By a combination of DI-MS and GCMS analyses using different modes of sample preparation it was possible to assess the resinous and oil components and the alteration state of varnish samples from paintings from the 15th to 18th centuries, in the collections of different French museums. These results will be discussed in the context of the restoration process, and the general artistic and technical knowledge of the works of art.

Determination of Haematein and Brazilein in Historical Textiles

Elena Karpova, Galina Balakina, Vladimir Vasiliev, Viktor Mamatyuk
Novosibirsk Institute of Organic Chemistry RAS (Sib. Br.), Novosibirsk, Russia

Redwoods – Brazilwood and logwood – were widely used in the Middle Ages for the dyeing of textiles. The wood of trees of the *Haematoxilon* genus (*H. brazilleto* Karsten, *H. campechianum* L., family Leguminosae) still has value as the source of dyes for obtaining black, dark blue and violet shades. Similarly, wood of trees of the *Caesalpinia* genus (*C. sappan* L., *C. echinata* Lam., *C. brasilensis* L., *C. crista* L.) finds continued use for dyeing fabrics in various shades of red.

A liquid chromatography mass spectrometry methodology was developed for the determination of dyestuffs of redwoods – brazilein and haematein – in Siberian indigenous ethnographic textiles. For chromatographic analysis, textile samples were treated with methanolic hydrochloric acid. Chromatographic analysis was conducted on a liquid chromatograph with diode-array and mass-selective detectors (Agilent 1100 Series LC/MSD). The diode-array detector records the UV-Vis spectra (240–700), and the mass-selective detector is used for molecular weight determination of the dyes analyzed.

It has been stated that the dyestuffs of Brazilwood and logwood undergo dehydration in an acid medium at high temperature, complicating their detection and characterization. However, the dehydration products can act as useful marker compounds for identification of the dyes. Redwood dyes were successfully identified in a number of samples from ethnographic textiles at the Institute of Archaeology and Ethnography, Siberian Branch of the Russian Academy of Science.

A GCMS Study of Wooden Art Objects Treated with Chinese Tung Oil

Anna Schönemann [1,2], Manfried Eisbein [3], Wolfgang Frenzel [4], Achim Unger [5], Madeleine Dell'Mour [2], Ernst Kenndler [2]
1 Academy of Fine Arts Vienna, Austria
2 University of Vienna, Institute for Analytical Chemistry, Vienna, Austria
3 State Office for the Preservation of Historical Monuments Saxonia, Dresden, Germany
4 Technical University of Berlin, Institute of Environmental Technology, Berlin, Germany
5 Rathgen Research Laboratory, National State Museums Berlin, Berlin, Germany

Materials traditionally used for the consolidation of wooden artefacts were often based on oil-resin or wax-resin combinations. In the first half of the twentieth century in Germany, wooden art objects were also treated with mixtures containing Chinese tung oil [1,2]. Although the treatments were intended to stabilize the wood, detrimental effects are frequently observed in objects impregnated with consolidation mixtures. To investigate the composition of historic consolidation mixtures, reference samples of tung oil (fresh, and subjected to accelerated ageing regimes) were studied. Chinese tung oil is a vegetable oil with a very strong drying behavior, derived from the fruits of the tung oil tree. It is characterized by a high proportion of unsaturated fatty acids, principally α-eleostearic (cis, trans, trans-9,11,13-octadecatrienoic acid), in the triglycerides [3]. Alteration of the fatty acid composition was followed using GCMS analysis. It was found that the main fatty acid components of tung oil are altered predominantly into two isomers, which were characterized by evaluation of their mass spectra. In addition, degradation processes leading to the formation of dicarboxylic acids were investigated, and interpreted in relation to studies of linseed oil [4].

Results obtained from the examination of reference materials were used in the characterization of samples taken from wooden art objects. Alterations such as softening of the wooden material and the presence of exudates on the surfaces could be correlated with the use of oil-resin mixtures, where tung oil was identified as oil component in most cases.

References:

[1] A. Unger, A.P. Schniewind, W. Unger, *Conservation of Wood Artefacts*, 2001, Springer Berlin, Heidelberg, New York.
[2] E. Fonrobert, *Das Holzöl*, 1951, Berliner Union, Stuttgart.
[3] A. Thomas, Fats and Fatty Oils, in: *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed., 2006, Editorial advisory Board: Matthias Bohnet et al., Wiley-Verlag Chemie Chemie GmbH&Co. KgaA, Weinheim, DOI: 10.1002/14356007.a10_173
[4] A. Schönemann, W. Frenzel, A. Unger, E. Kenndler, An Investigation of the Fatty Acid Composition of New and Aged Tung Oil, *Studies in Conservation*, 2006, 51, pp.99-110.

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HPLC-PDA Analysis of Atypical Mahoganizing Stains in an Eighteenth Century Connecticut High Chest Finish

Jennifer L. Mass[1], Maarten van Bommel[2], W. Christian Petersen[1], Catherine Matsen[1]
1 Winterthur Museum, Winterthur, DE, USA
2 Netherlands Institute for Cultural Heritage, Amsterdam, The Netherlands

The finish history of an eighteenth-century cherry Connecticut high chest was examined to determine the cause of its unusual degree of blackening and crazing. This type of appearance commonly results from the photo-oxidative degradation of high resin content finishes that were favored in the nineteenth century. FTIR and GCMS analysis of the high chest finish confirmed its unusually high resin content, with FTIR spectra that more closely matched pine resin references than oil-resin mixtures, and GCMS chromatograms displaying an unusually high ratio of 7-oxo-dehydroabietic acid to fatty acid methyl esters. However, cross-section microscopy revealed the presence of at least three finish campaigns on the high chest, two of these containing suspended red particles, suggesting that the finishes functioned as ‘mahoganizing’ stains, applied to redden the color of the cherry primary wood and make it appear to be the darker and more valuable mahogany. Traditional mahoganizing stains used in the eighteenth and nineteenth centuries were Brazilwood (*Caesalpinia braziliensis*) and logwood (*Haematoxylon campechianum*). However, HPLC-PDA analysis of the high chest finish revealed that the earlier mahoganizing campaign employed carminic acid (indicating cochineal dye from the female *Dactylopius coccus* Costa insect), and the later mahoganizing campaign predominately employed the synthetic azo dye Fast red AV. The cochineal finding is notable in that period references to this material mention its use for musical instrument finishes only. The Fast red AV finding is notable in that, to the authors’ knowledge, this is the first identification of this important nineteenth-century red azo dye as a mahoganizing stain. As Fast red AV was first synthesized in 1877, the identification of this compound provided a *terminus post quem* for this mahoganizing campaign and for the high resin content finish campaign above it.

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Meeting Participants

Jeanette Adams
Library of Congress
101 Independence Ave. SE
Washington DC 20540, USA
Tel: 1 202-707-1031
Fax: 1 202-707-1525
jead@loc.gov

Ruth Ann Armitage
Eastern Michigan University
Department of Chemistry
225 Mark Jefferson
Ypsilanti, MI 48197, USA
Tel: 1 734-487-0290
Fax: 1 734-487-1496
rarmitage@emich.edu

Julie Arslanoglu
The Metropolitan Museum of Art
Department of Scientific Research
1000 5th Avenue
New York, NY 10028, USA
Tel: 1 212-396-5534
Fax: 1 212-396-5466
Julie.Arslanoglu@metmuseum.org

Hans Barnard
Cotsen Institute of Archaeology at UCLA
PO Box 951510
Los Angeles, CA 90095, USA
Tel: 1 310-267-5550
Fax: 1 310-206-4723

Ursula Baumer
Doerner Institut
Barerstr. 29
80799 Munich, Germany
Tel: +49 89 23805-161
Fax: +49 89 23805-156
baumer@doernerinstitut.de

Klaas Jan van den Berg
Netherlands Institute for Cultural Heritage
Gabriel Metsustraat 16
1070 KA Amsterdam, The Netherlands
Tel: +31 20 3054710
Fax: +31 20 3054700
klaas.jan.vd.berg@icn.nl

Aniko Bezur
Art Institute of Chicago
111 S. Michigan Avenue
Chicago, IL 60563, USA
Tel: 1 312-443-3335
Fax: 1 312-541-1959
abezur@artic.edu

Christina Bisulca
Freer Gallery of Art
Smithsonian Institution
DSCR, 1150 Independence Ave. SW
Washington DC 20560, USA
Tel: 1 973-668-8616
bisulcac@si.edu

Ilaria Bonaduce
Dipartimento di Chimica e Chimica Industriale,
Universita’ di Pisa
Via Risorgimenta 35
56126 Pisa, Italy
Tel: +39 0502219252
Fax: +39 0502219260
ilariab@dcci.unipi.it

Oscar Chiantore
University of Turin
Dept of Chemistry
Via Giuria 7
10125 Torino, Italy
Tel: +39 011 6707558
Fax: +39 011 670 7855
oscar.chiantore@unito.it

Maria Perla Colombini
Dipartimento di Chimica e Chimica Industriale,
Universita’ di Pisa
Via Risorgimenta 35
56126 Pisa, Italy
Tel: +39 0502219305
Fax: +39 0502219260
perla@dcci.unipi.it

Connell Cunningham
Rohm and Haas Company
Research Laboratories
727 Norristown Road, PO Box 904
Spring House, PA 19477, USA
Tel: 1 215-619-5623
Fax: 1 215-619-1607
CCunningham@rohmhaas.com

Patrick Dietemann
Doerner Institut
Barerstr. 29
80799 Munich, Germany
Tel: +49 89 23 805 158
Fax: +49 89 23 805 156
dietemann@doernerinstitut.de

Peter Eastman
Rohm and Haas Company
Research Laboratories
727 Norristown Road, PO Box 904
Spring House, PA 19477, USA
Tel: 1 215-684-5229
Fax: 1 215-619-1607
PEastman@rohmhaas.com

Ester Ferreira
Schweizerisches Institut für
Kunstwissenschaft,
Zollikerstrasse 32
CH-8032 Zürich, Switzerland
Tel: +41 44 388 5151
ester.ferreira@sikart.ch

Mary Ellen Freund
Eastern Michigan University
Department of Chemistry
225 Mark Jefferson
Ypsilanti, MI 48197, USA
Tel: 1 734-487-0290
Fax: 1 734-487-1496
mefreund78@yahoo.com

Glenn Frysinger
U.S. Coast Guard Academy
Department of Science, 27 Mohegan Ave.
New London, CT 06320, USA
Tel: 1 860-444-8656
glenn.s.frysinger@uscg.mil

Gwénaëlle Gautier
Art Institute of Chicago
111 S. Michigan Avenue
Chicago, IL 60603, USA
Tel: 1 312-443-7290
Fax: 1 312-541-1959
ggautier@artic.edu

Jennifer Giaccai
Walters Art Museum
Conservation Division
600 North Charles Street
Baltimore, MD 21201, USA
Tel: 1 410-547-9000 x633
Fax: 1 410-837-1274
jgiaccai@thewalters.org

Cecily M. Grzywacz
Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6260
Fax: 1 310-440-7711
cgrzywacz@getty.edu

Eric Hagan
Tate
Millbank
London SW1P 4RG, UK
Tel: +44 78 75 83 51 80
Fax: +44 20 7887 8051
eric.hagan@tate.org.uk

Gregory Hall
U.S. Coast Guard Academy
USCGA (ds-1), 27 Mohegan Ave.
New London, CT 06320, USA
Tel: 1 860-444-8624
Fax: 1 860-701-6147
Gregory.hall@uscga.edu

Gretchen Hall
University of Pennsylvania Museum for
Archaeology & Anthropology,
3260 South St.
Philadelphia, PA 19104, USA
Tel: 1 215-573-3214
ghall2@comcast.net

Catherine Higgitt
The British Museum
Department of Conservation,
Documentation and Science,
Great Russell Street
London WC1B 3DG, UK
Tel: +44 20 7323 8679
Fax: +44 20 7323 8276
chiggitt@thebritishmuseum.ac.uk

Kamilla Kalinina
The State Hermitage Museum
34 Dvortsovaya nab.,
St. Petersburg, Russia 190000
Tel: 7 812 710 95 49
Fax: 7 812 710 95 49
Kkalinina@mail.ru
Kkalinina@hermitage.ru

Elena Karpova
Novosibirsk institute of organic chemistry
RAS (Sib. Br.)
Lavrentiev ave. 9
Novosibirsk, 630090, Russia
Tel: +007 383 3307864
Fax: +007 383 3309752
karpovae@nioch.nsc.ru

Henk van Keulen
Netherlands Institute for Cultural Heritage
Gabriel Metsustraat 16
1070 KA Amsterdam, The Netherlands
Tel: +31 203054736
Fax: +31 203054700
henk.van.keulen@icn.nl

Narayan Khandekar
Straus Center for Conservation
Harvard University Art Museums
32 Quincy Street
Cambridge, MA 02138, USA
Tel: 1 617-495-4591
Fax: 1 617-495-0322
narayan_khandekar@harvard.edu

Daniel P. Kirby
Straus Center for Conservation
Harvard University Art Museums
32 Quincy Street
Cambridge, MA 02138, USA
Tel: 1 617-495-2392
Fax: 1 617-495-0322
dpkirby@fas.harvard.edu

Richard Laursen
Boston University
590 Commonwealth Ave.
Boston, MA 02215, USA
Tel: 1 617-353-2491
Fax: 1 617-353-6466
Laursen@bu.edu

Tom Learner
Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6132
Fax: 1 310-440-7711
tlearner@getty.edu

Lynn Lee
Straus Center for Conservation
Harvard University Art Museums
32 Quincy St.
Cambridge, MA 02138, USA
Tel: 1 617-384-8717
Fax: 1 617-495-0322
LfLee@fas.harvard.edu

Andrew Lins
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19101, USA
Tel: 1 215-684-7540
Fax: 1 215-684-7550
alins@philamuseum.org

Suzanne Quillen Lomax
National Gallery of Art
DCL-SR, 2000B South Club Drive
Landover, MD 20785, USA
Tel: 1 202-842-6763
Fax: 1 202-842-6886
s-lomax@nga.gov

Russ Lorber
Segment Leader, Consumables
Grace Davison Discovery Sciences
7500 Grace Drive
Columbia, MD 21044, USA
Tel:1 410-531-4702
Fax: 1 410-531-4301
russ.lorber@grace.com

Christopher Maines
National Gallery of Art
DCL-SR, 2000B South Club Drive
Landover, MD 20785, USA
Tel: 1 202-842-6055
Fax: 1 202-842-6886
c-maines@nga.gov

Jennifer Mass
Winterthur Museum and Country Estate
Conservation Department
Winterthur, DE 19735, USA
Tel : 1 302-888-4808
Fax: 1 302-888-4838
jmass@winterthur.org

Catherine Matsen
Winterthur Museum and Country Estate
Conservation Department
Winterthur, DE 19735, USA
Tel: 1 302-888-4918
Fax: 1 302-888-4838
cmatsen@winterthur.org

Joy Mazurek
Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6850
Fax: 1 310-440-7711
jmazurek@getty.edu

Chris McGlinchey
The Museum of Modern Art
11 West 53rd Street
New York, NY 10019, USA
Tel: 1 212-708-9821
chris_mcglinchey@moma.org

Melissa Meighan
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19101, USA
Tel: 1 215-684-7566
Fax: 1 215-684-7550
mmeighan@philamuseum.org

Sigrid Mirabaud
Centre de Recherche et de Restauration
des Musées de France C2RMF,
Palais du Louvre
14 quai Francois Mitterrand
75001 Paris, France
Tel: +33 1 40 20 84 34
Fax: +33 1 47 03 32 46
Sigrid.mirabaud@culture.gouv.fr

Sarah Nettleton
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19101, USA
Tel: 1 215-764-0613
senettle@yahoo.com

Bronwyn Ormsby
Tate
Millbank
London SW1P 4RG, UK
Tel: +44 20 7887 3980
Fax: +44 20 7887 8982
Bronwyn.ormsby@tate.org.uk

Mark Ormsby
National Archives
8601 Adelphi Road, Room 1800
College Park, MD 20740, USA
Tel: 1 301-837-2026
Fax: 1 301-837-0665
mark.ormsby@nara.gov

David A. Peggie
The National Gallery
Trafalgar Square
London WC2N 5DN, UK
Tel: +44 20 7747 2825
Fax: +44 20 7839 3897
david.peggie@ng-london.org.uk

W. Christian Petersen
Winterthur Museum and Country Estate
Conservation Department
Winterthur, DE 19735, USA
Tel: 1 302-888-4920
wcptrsn@aol.com

Alan Phenix
Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6282
Fax: 1 310-440-7711
aphenix@getty.edu

Vaclav Pitthard
Kunsthistorisches Museum
Burgring 5, A-1010 Vienna, Austria
Tel: +43 1 52525 5702
Fax: +43 1 52525 4398
vaclav.pitthard@khm.at

Rebecca Ploeger
University of Turin
Dept of Chemistry
Via Giuria 7
10125 Torino, Italy
Tel: +39 0116707554
Fax: +39 0116707855
rebecca.ploeger@unito.it

Jennifer Poulin
Canadian Conservation Institute
1030 Innes Rd.
Ottawa, ON, Canada, K1A 0M5
Tel: 613 998 3721 x145
Fax: 613 889 4721
jennifer_poulin@pch.gc.ca

Beth Price
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19101, USA
Tel: 1 215-684-7552
Fax: 1 215-684-7550
bprice@philamuseum.org

René de la Rie
National Gallery of Art
DCL-SR, 2000B South Club Drive
Landover, MD 20785, USA
Tel: 1 202-842-6669
r-delarie@nga.gov

Rachel Rivenc
Getty Conservation Institute
1200 Getty Centre Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6877
rrivenc@getty.edu

Adriana Rizzo
The Metropolitan Museum of Art
Department of Scientific Research
1000 5th Avenue
New York, NY 10028, USA
Tel: 1 212-396-5494
Fax: 1 212-396-5466
adriana.rizzo@metmuseum.org

Ken Sasaki
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku
Kyoto 606-8585, Japan
Tel: +81 75 724 7827
Fax: +81 75 724 7827
ysasaki@kit.ac.jp

Yoshiko Sasaki
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku
Kyoto 606-8585 Japan
Tel: +81 75 724 7827
Fax: +81 75 724 7827
ysasaki@kit.ac.jp

Steven Saverwyns
Royal Institute for Cultural Heritage
Jubelpark 1
1000 Brussels, Belgium
Tel: +32 2 739 68 46
Fax : +32 2 732 01 05
steven.saverwyns@kikirpa.be

Michael Schilling
Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049, USA
Tel: 1 310-440-6811
Fax: 1 310-440-7711
mschilling@getty.edu

Gundel Schmidtbauer
University of Fine Arts Dresden
Günzstraße 34
01307 Dresden, Germany
Tel: +49 351 4402 106/107
Fax: +49 351 4402 250
schmidtbauer@serv1.hfbk-dresden.de

Anna Schönemann
Academy of Fine Arts Vienna
Schillerplatz 3
1010 Vienna, Austria
Tel: +43 1 588 16 223
Fax: +43 1 588 16 224
A.Schoenemann@akbild.ac.at

Nobuko Shibayama
The Metropolitan Museum of Art
Department of Scientific Research
1000 5th Avenue
New York, NY 10028, USA
Tel: 1 212-396-5139
Fax: 1 212-396-5494
nobuko.shibayama@metmuseum.org

Miguel F. Silva
Institut de Restauració del Patrimoni
Universitat Politècnica de València
Camino de Vera 14
46022 Valencia, Spain
Tel: +34 963879312
Fax: +34 963877836
correio_do_mike@hotmail.com

Gregory Dale Smith
Buffalo State College
1300 Elmwood Ave, RH230
Buffalo, NY 14222, USA
Tel: 1 716-878-4646
Fax : 1 716-878-5039
smithgd@buffalostate.edu

Ken Sutherland
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19106, USA
Tel: 1 215-684-7559
Fax: 1 215-684-7550
ksutherland@philamuseum.org

Mike Szelewski
Agilent Technologies
2850 Centerville Rd
Wilmington, DE 19808, USA
Tel: 1 302-633-8275
mike_szelewski@agilent.com

Chris Wasson
Philadelphia Museum of Art
Box 7646
Philadelphia, PA 19101, USA
Tel: 1 215-684-7542
Fax: 1 215-684-7550
cwasson@philamuseum.org

Shuya Wei
Institute for Natural Sciences and
Technologies in Art,
Academy of Fine Arts
Kleine Neugasse, 20/35
1040 Wien, Austria
Tel: +43 699 1132 5978
Fax: +43 1 58801 15199
sywei66@hotmail.com

Tianlan Zhang
Rohm and Haas Company
Research Laboratories
727 Norristown Road, PO Box 904
Spring House, PA 19477, USA
Tel: 1 215-684-5373
Fax: 1 215-619-1607
TZhang@rohmhaas.com

Xian Zhang
Williamstown Art Conservation Center
225 South St.
Williamstown, MA 01267, USA
Tel: 1 413-458-5741 x433
Fax: 1 413-458-2314
xzhang@williamstownart.org