MaSC

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

MaSC 2024 Meeting Programme

The National Gallery of Art
Washington DC, USA

19-20 September 2024

Preface

The Committee of the Users' Group for Mass Spectrometry and Chromatography (MaSC) is pleased to welcome you to the eleventh MaSC Meeting, to be held in the West Building Lecture Hall of the National Gallery of Art, Washington DC.

This meeting is of particular significance to the group since it takes place twenty years after the inaugural meeting of MaSC in 2004, also hosted by the National Gallery of Art. Over the intervening two decades, MaSC has provided an essential forum that has facilitated discussion and collaboration among scientists using chromatographic and mass spectrometric techniques for the study of art and historical artefacts. The Group currently has over 100 members, representing 85 institutions – primarily cultural and academic organisations – in 26 countries.

While the 2004 Meeting was combined with a workshop on liquid chromatography mass spectrometry, the current meeting was preceded by a three-day workshop concerned with analytical strategies for the characterisation of volatile organic compounds (VOCs) in studies of cultural heritage artefacts, and for the evaluation of exhibition and storage materials. Workshop sessions were hosted by the National Gallery of Art, the Library of Congress and the National Archives, and we are immensely grateful to the invited workshop instructors, Mark Ormsby and Lindsay Oakley (National Archives) and Eric Monroe and Kelli Stoneburner (Library of Congress), for sharing their expertise.

As in previous years, the 2024 Meeting has a varied programme reflecting the current activities and research interests of MaSC members, with sessions focussed on the workshop topic of analysis of VOCs, as well as new developments and strategies for data treatment and interpretation, and the characterisation of diverse materials in works of art: from naturally sourced coatings and pigments to synthetic polymers and plastics.

Since the foundation of MaSC, there has been an enormous evolution and diversification in chromatography and MS techniques and the possibilities for their application to cultural heritage studies, as well as in the specialisation of users, and so we look forward to your feedback and input on how MaSC can continue to serve as a resource and support a cooperative spirit within this active and growing community.

We would like to extend our thanks to the National Gallery of Art's Conservation Division for their efforts in organising and hosting this event. We hope you enjoy the Meeting, and your visit to Washington DC!

The MaSC Committee:
Christopher Maines, Ken Sutherland, Klaas Jan van den Berg, Ester Ferreira, David Peggie, Catherine Higgitt

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

Meeting schedule

Meeting Schedule

Thursday, 19 September, 2024

8:00	**Welcome & Registration in West Building Garden Court** *Entrance at 6th St. NW & Constitution Ave. NW*
9:10	**Introductory remarks** Christopher Maines, North American MaSC Coordinator Lena Stringari, Chief of Conservation, National Gallery of Art
Session 1: Volatiles and Thermal Desorption Techniques Chair: Christopher Maines, National Gallery of Art	
9:30	A review of sampling techniques and lessons learned for thermal desorption GCMS in application of cultural heritage *Kelli Stoneburner, Eric Monroe, Fenella France*
10:00	Characterization of VOCs emitted from heritage objects using TD-GC-MS-O *Emma Paolin, Fabiana Di Gianvincenzo, Irena Kralj Cigić, Cecilia Bembibre, Matija Strlič*
10:30	Coffee break & posters
11:00	Untargeted DTD-GC-MS Analysis for Materials Testing *Julia Bakker-Arkema, Rose King, Eric Breitung*
11:30	Lightning poster presentations
12:10	Lunch break on your own
Session 2: Volatiles and Solid Phase Microextraction Techniques Chair: Ken Sutherland	
13:30	Investigating efflorescence found in exhibition cases with SPME sampling to evaluate volatile contaminant mitigation and object cleaning methods *Erin R. Birdsall, G. Asher Newsome, Susan Heald, John George, Gwénaëlle Kavich*
14:00	A Detailed Examination of the Volatiles Produced from 150-year-old Cetacea using SPME and HS-SMPE-GCMS *Wren Montgomery, Fabiana Portoni, Jonathan Watson, Mark Sephton, Richard Sabin*

14:30	HS-SPME-GCMS to identify the materials used to create House of Hope by Montien Boonma *Catherine H. Stephens*
15:00	Coffee break & posters
Session 3: Plastics and Pyrolysis-GCMS Techniques Chair: Eric Monroe	
15:30	ESCAPE: save time, be precise, acquire knowledge in interpreting analyses of modern materials of cultural heritage *Nathalie Balcar and Michael Schilling*
16:00	Multi-functional pyrolysis applications for colored p-PVC – advantages and limitations *Teodora Raicu, Katja Sterflinger, Valentina Pintus* *(Pre-recorded presentation followed by live Q&A via Zoom)*
16:30	Meeting ends
17:00	National Gallery of Art closes
17:30 – 19:30	Reception for MaSC members at Cuba Libre Restaurant *801 9th St NW, Washington, DC*

Friday, 20 September, 2024

8:30	West Building 6th St Entrance open for attendees
Session 4: Data Processing Workflows Chair: Mark Ormsby	
9:00	The past, present, and future of ESCAPE *Michael Schilling, Henk van Keulen, Nathalie Balcar, Jenny Poulin, and Mike Szelewski*
9:30	NIST Mass Spectrometry Data Center and the NIST mass spectral libraries *Edward P. Erisman*
10:00	New approaches to non-targeted EI-GC-MS data analysis *Rose King, Julia Bakker-Arkema, Eric Breitung*
10:30	Coffee break & posters
Session 5: Characterisation of Natural Coatings and Pigments Chair: Klaas Jan van den Berg	
11:00	Identification of polysaccharides in thermoset *Anacardiaceae* (Asian Lacquer) polymers using thermal degradation and gas chromatography based techniques *Jonas Veenhoven, Steven Saverwyns, Henk van Keulen, Frederic Lynen, Maarten van Bommel*
11:30	Composition of lacquers on *lacca povera* objects *Ursula Baumer, Charlotte Höpker and Patrick Dietemann*
12:00	Lunch break on your own
13:30	Investigating Ancient Egyptian Mortuary Practices: GC-MS Analysis of Black Organic Coatings on Funerary Objects *Hitomi Fujii, Alicia McGeachy, Olawunmi Akinlemibola, Rachel Aronin, and Isabel Schneider*
14:00	Animal, vegetable, mineral: Characterization of distinctive painting materials on a group of Bwa masks from Burkina Faso *Clara Granzotto and Ken Sutherland*

Session 6: Determination of Molecular Markers Chair: Klaas Jan van den Berg	
14:30	Detection of Gum Benzoin in Historical Varnishes Using THM-GC/MS *Louise Decq, Steven Saverwyns*
15:00	Molecular markers for heat pretreatment of drying oils: dicarboxylic acids (re-)revisited *Ken Sutherland*
15:30	Coffee break & posters
16:00	MaSC Business Meeting
16:30	Meeting ends
17:00	National Gallery of Art closes

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Oral Presentation Abstracts

A review of sampling techniques and lessons learned for thermal desorption GCMS in application of cultural heritage

Kelli Stoneburner, Eric Monroe, Fenella France

Library of Congress

The release of volatile organic compounds (VOCs) from materials can present a risk of accelerated degradation to library and heritage collections. These materials can range from the supplies used to build exhibit cases, storage spaces, and housing for collection objects, to the actual collection objects themselves, which can off-gas compounds that may potentially damage nearby objects or themselves. Therefore, compounds from collections may provide insights into a collection object's condition. With this range of materials and not always being able to take a physical sample, a variety of techniques are required to meet specific analytical needs. To examine the VOCs being emitted from materials of interest, we have developed a suite of sampling techniques utilizing semi-quantitative thermal desorption gas chromatography mass spectrometry (TD-GCMS). This set of methods includes several techniques to prepare materials for direct thermal desorption but also a range of techniques for active air sampling of collection spaces, housings, or objects. This presentation will explore the knowledge we have acquired using this technique for eight years and the different methodologies developed via several case studies. In addition, the presentation will explore some of the biases from both sampling methods and direct thermal desorption.

Characterization of VOCs emitted from heritage objects using TD-GC-MS-O

Emma Paolin[1], Fabiana Di Gianvincenzo[1], Irena Kralj Cigić[1], Cecilia Bembibre[2], Matija Strlič[1]

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[2]Institute for Sustainable Heritage, University College London, London, UK

The analysis and characterization of volatile organic compounds (VOCs) emitted from objects in heritage environments have mostly focused on assessing the risk these compounds may pose to the surrounding collection and people. In our work, we investigate not only the typical emissions of different museum object materials, but also the relationship between the VOCs emitted by the objects and their perceived smell [1].

In our innovative non-invasive approach, we introduce the analysis of volatile compounds with thermal desorption gas chromatography coupled with mass spectrometry and olfactometry (TD-GC-MS-O) to identify the olfactory profile of heritage objects [2]. This determines, which compounds contribute to the smell of the object and helps to explore its historical value and cultural significance [3].

We have applied this methodology to various case studies, ranging from objects directly related to olfaction, like a historical perfume flask, to objects that are not usually considered of value due to their smell, such as ancient Egyptian mummified bodies or a historical snuffbox. These studies demonstrate the potential to investigate the characteristic emitted volatiles and their relevance to conservation assessment. However, they also highlight the importance of olfactory analysis and olfactory exhibitions, which lead to a more comprehensive understanding of cultural heritage.

Keywords: VOCs, GC-MS-O, olfactory analysis

[1] E. Paolin and M. Strlič, "Volatile Organic Compounds (VOCs) in Heritage Environments and Their Analysis : A Review", Applied Sciences, 2024.

[2] M. A. A. Mahmoud and Y. Zhang, "Enhancing Odor Analysis with Gas Chromatography-Olfactometry (GC-O): Recent Breakthroughs and Challenges," *J. Agric. Food Chem.*, vol. 72, no. 17, pp. 9523–9554, 2024, doi: 10.1021/acs.jafc.3c08129.

[3] C. Bembibre and M. Strlič, "Smell of heritage: A framework for the identification, analysis and archival of historic odours," *Herit. Sci.*, vol. 5, no. 1, pp. 1–11, 2017, doi: 10.1186/s40494- 016-0114-1.

Untargeted DTD-GC-MS Analysis for Materials Testing

Julia Bakker-Arkema, Rose King, Eric Breitung

The Metropolitan Museum of Art

The Oddy Test is used at many cultural heritage institutions around the world to evaluate materials for their use in collections care. These tests act as a screening tool to detect reactive volatile emissions from materials before they can negatively impact collections. While progress in testing protocols has been made over the years, the interpretation of Oddy Test results lacks fundamental chemical information about the identity of the volatile emissions, and the chemical mechanisms of degradation that occur on the surfaces of the metal substrates.

Direct Thermal Desorption coupled to Gas Chromatograph-Mass Spectrometry analysis has been employed at many institutions as a complement to, and in some cases, an alternative for the Oddy Test. While DTD-GC-MS analysis as a materials testing tool lacks an easily observable damage threshold, it does allow for specific chemical measurement and identification. At The Metropolitan Museum of Art, we are conducting untargeted DTD-GC-MS measurements on materials in conjunction with Oddy Testing to learn about the volatile emissions responsible for the observed corrosion during Oddy Testing. In this work, we present our methods and considerations when performing DTD-GC-MS materials testing, including sampling, data processing, and interpretation, with the goal of developing a chemically informed approach to materials testing for collections care.

Investigating efflorescence found in exhibition cases with SPME sampling to evaluate volatile contaminant mitigation and object cleaning methods

Erin R. Birdsall[1,2], G. Asher Newsome[1], Susan Heald[2], John George[2], Gwénaëlle Kavich[1]

[1]*Smithsonian Museum Conservation Institute*
[2]*Smithsonian National Museum of the American Indian*

Organic salts of the base 2,2,6,6-tetramethyl-4-piperidinol (TMP-ol) have been observed in recent years at many museums in tightly sealed glass cases. The volatile TMP-ol is emitted from the glass-metal adhesive in cases and then is deposited on museum works. The molecular structure of TMP-ol, the adhesive location in an example case, and the resulting efflorescence is shown in figure 1. Efforts have been made to clean objects and prevent future growth in the display cases, including active air filtration as investigated here.

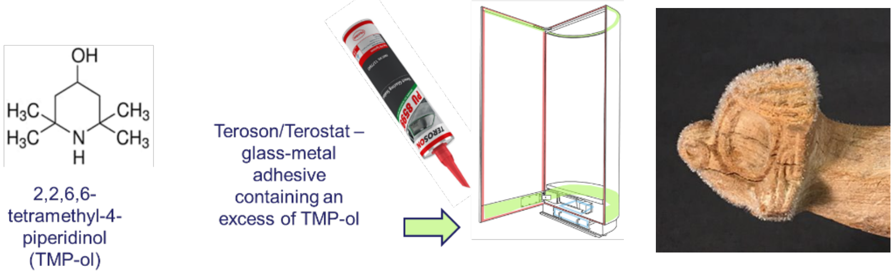

Figure 1. A) Structure of 2,2,6,6-tetramethyl-4-piperidinol (TMP-ol), B) Graphic showing the location in green of the adhesive in an example case C) Photo of object 4/2409, Bowl with human head handle with white efflorescence on the surface of the handle.

Solid-phase microextraction gas chromatography mass spectrometry (SPME-GCMS) was used to evaluate the efficacy of fan filtration techniques at the National Museum of the American Indian in New York (NMAI-NY) over 18 months. Major compounds found in the cases include toluene, acetic acid, naphthalene and TMP-ol. Other major compounds identified were alkylbenzene derivatives (common indoor pollutants). Representative chromatograms are shown in Figure 2. Work was aided by implementing SPME-direct analysis in real time mass spectrometry using a multi-shot sampling protocol. In total, over 27 cases at NMAI-NY were sampled along with cases at four other peer museums. The presence and signal intensity from TMP-ol and other compounds were observed over time. In display cases with a fan-filtration unit installed, TMP-ol and other tracked compounds gave weaker signal, and some fell below detection limits. However, there was no noticeable change in a case where passive filtration was used. The results in a single case led the museum to install fan filtration units in all cases that have adequate decks to house the units.

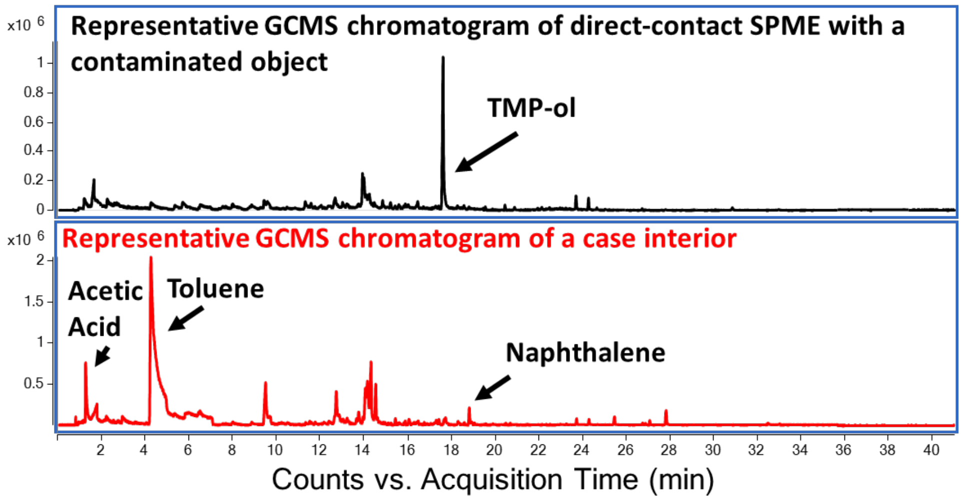

Figure 2: Representative chromatogram of a direct-contact sample with an impacted object showing the retention time of TMP-ol (black). Representative chromatogram of a headspace-style experiment in a display case noting typical compounds (red).

Direct contact SPME-GCMS was also used to evaluate dry versus damp cleaning methods.

Direct-contact sampling with SPME fibers was used before and after object cleaning to qualitatively assess cleaning efficacy. Two methods of object cleaning were used: 1) dry brush and vacuum and 2) damp cosmetic sponge. The cleaning method used was chosen based on conservator expertise and material type. Before cleaning, direct-contact SPME-GCMS detected TMP-ol on selected objects. After just dry brush and vacuum, TMP-ol was still detected. After cleaning an object that could tolerate dry brush and vacuum and damp cosmetic sponge, no TMP-ol was detected. The results suggest that damp cleaning should be used where tolerated. This result is consistent with the slight solubility of the TMP-ol crystals in water. Now, damp cleaning is included in the cleaning protocol for appropriate objects after a dry brush and vacuum. Over the course of five months after cleaning, no crystal growth was visually observed and no TMP-ol was detected by SPME-GCMS where a fan-filtration unit was installed. Chromatograms showing the direct-contact SPME-GCMS results after different cleaning methods are seen in figure 3.

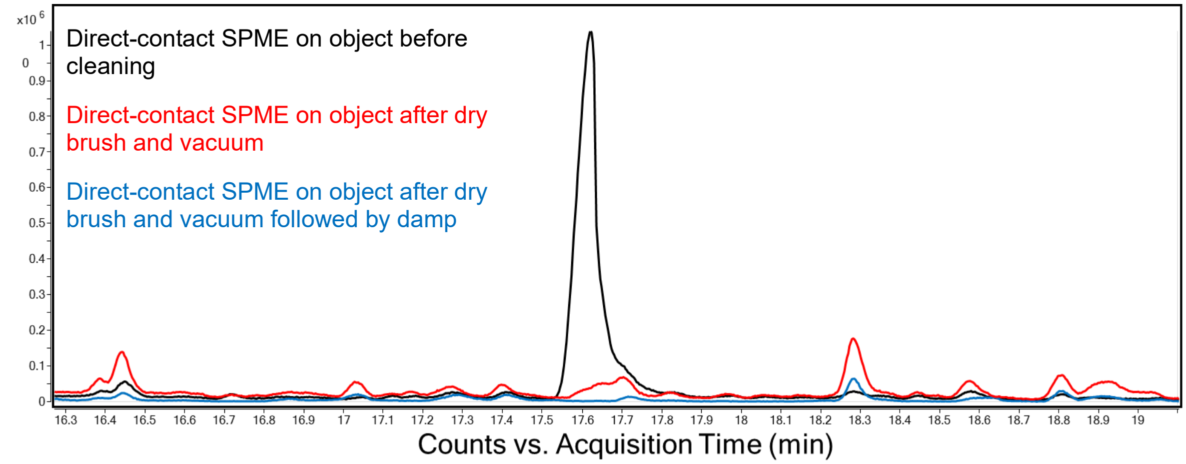

Figure 3. Total ion chromatogram of an object before cleaning (black), after dry brush and vacuum (red), and after a direct brush and vacuum followed by damp cosmetic sponge (blue). Sampling was performed by direct-contact SPME-GCMS

A Detailed Examination of the Volatiles Produced from 150-year-old Cetacea using SPME- and HS-SMPE-GCMS

Wren Montgomery[1], Fabiana Portoni[1], Jonathan Watson[2], Mark Sephton[2], Richard Sabin[1]

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We have used the combination of solid phase microextraction (SPME) coupled with gas chromatography mass spectrometry (GC-MS) and headspace (HS)-SPME-GC-MS to characterize a collection of historic (~150-year-old) Cetacea skins held by the Natural History Museum, London, including *Delphinus delphis*, *Cephalorhynchus heavisidei*, and *Globicephala macrorhynchus*.

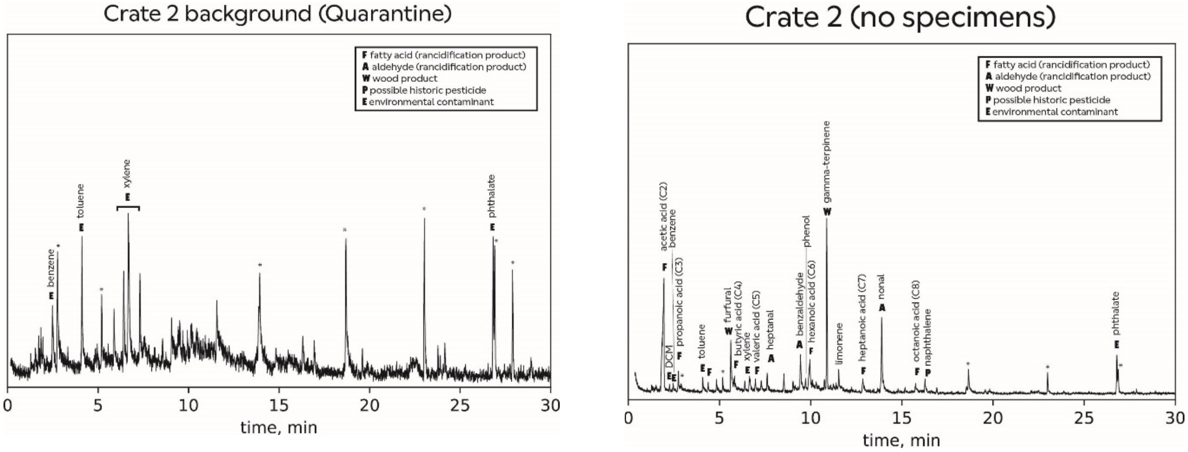
Some of these specimens were prepared for display for the International Fisheries Exhibition of 1883 or for public display in the NHM galleries; however, by the end of the 19th century, the NHM publicly stated that it would move away from the use of taxidermized cetacean specimens in the galleries and use models instead due to the rapid rate of deterioration, resulting pest infestation, and ongoing maintenance required. Samples collected and preserved for scientific research were prepared differently. Thus, the preparation methods for these display specimens have been lost.

Table 1 provides examples of specimens in life, pre-, and post-conservation. Cetacea were not traditionally prepared using the same methods as mounted taxidermy due to material limitations that made them unsuitable for standard mounted preservation techniques; therefore, these skins are likely to be some of the only preserved mounted Cetacea taxidermy left in the world. This is a chance to understand not only the lost preparation methods but also any present safety issues the specimens pose.

Organic chemical analysis can determine the oxidation and rancidification of the specimen, providing a qualitative understanding of the degradation of the specimen. Rancidification products, such as fatty acids and aldehydes, as well as historic pesticides and conservation treatments, were detected through SPME-GC-MS of the historic storage crates, an example of which is given in Figure 1. Material removed during stabilization was compared with oil secreted from a whale jawbone of a similar age, which has received relatively little conservation treatment. HS-SPME-GC-MS of samples from all specimens showed C6-C9 aldehydes, C4-C9 fatty acids, and C8-C11 ketones similar to the reference material.

Table 1

Delphinus delphis Common dolphin	*Grampus griseus* Risso's dolphin
Living	
 Credit: Patrick Le Mao	
Pre-conservation	
	 Credit: Lauren Burleson
Post-conservation	
	 Credit: Lauren Burleson



Crate 2 background (Quarantine)

Crate 2 (no specimens)

Figure 1: SPME-GCMS chromatograms from storage area and inside crate that had contained specimens for decades. Note that the quarantine area is adjacent to the parking lot. Athough it had been emptied, Crate 2 displayed identifiable amounts of volatile components.

HS-SPME-GCMS to identify the materials used to create *House of Hope* by Montien Boonma

Catherine H. Stephens

Museum of Modern Art

Analysis of the scented components of the art installation *House of Hope* by Montien Boonma, including bags of powder used to make a mural and strands of aromatic beads to construct a structure, was completed to facilitate its display at the Museum of Modern Art. Though an olfactory experience is central to experiencing the piece, limited information was known about the materials. The powders and beads, some nearly 30 years old, were identified through static headspace solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME-GCMS) and confirmed using controls. Challenges included deterioration of scents over time and cross-contamination. The contents of five bags of powder were successfully identified as black pepper (two bags), clove, turmeric, and white sandalwood. All beads contained nutmeg, peppermint, ginger, and turmeric, while some contained licorice root, thyme, cardamom, and clove. The beads were bound using pine honey. Following this initial phase of this work, two things happened: a notebook written in the artist's hand was discovered that included notes about spices, and 11 more bags of unlabeled powders were found. Research continues and may move to pyrolysis techniques to identify materials not successfully identified with HS-SPME-GCMS.

ESCAPE: save time, be precise, acquire knowledge in interpreting analyses of modern materials of cultural heritage

Nathalie Balcar[1] and Michael Schilling[2]

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[2] Getty Conservation Institute, Los Angeles, California, USA

Py-GCMS analysis is a powerful technique for identifying the organic content of a sample from a modern and contemporary artwork, given that 20th and 21st century artists have a wide variety of synthetic materials in their palette, just like the conservators in their toolbox. Pyrolysis-derived compounds are chemical markers that can be traced back to the material from which they are formed, provided these markers are correctly identified and sufficient knowledge is available to associate them with the materials. Both these tasks are handled by the ESCAPE tool.

Today, the focus is on acrylic and vinyl materials used in paints, varnishes and adhesives. Their chemistry is varied and changes from period to period. Fortunately, the chemical markers of these materials are highly characteristic and formed according to a similar fragmentation pathway. This enables us to increase the AMDIS library with many acrylics markers and to build an Excel report to help the user identify the material, so that novices quickly become experienced.

The power of these tools will be demonstrated through case studies that will provide insight into the use of synthetic materials by artists, the evolution of conservation treatments and a better understanding of the world of coating materials.

Multi-functional pyrolysis applications for colored p-PVC – advantages and limitations

Teodora Raicu[1,*], Katja Sterflinger[1], Valentina Pintus[1,2]

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p-PVC is prevalent in modern and contemporary art museum collections and it is well known to suffer from discoloration and migration of plasticizers, causing a sticky surface and loss of mechanical properties [1,2]. While uncolored p-PVC has already been extensively studied and its degradation patterns are well-documented, colored p-PVC still needs to be fully explored. For this work, and to address the knowledge gap in colored p-PVC, the colored vinyl sheets *"Hanging"* used by Kiki Kogelnik (1935-1997), an Austrian pop-artist, were considered and investigated using a multi-functional pyrolysis methodology. This approach encompassed SS Py-GC/MS, DS Py-GC/MS, EGA-MS, and HC-EGA-GC/MS, highlighting their advantages and limitations. Moreover, MFS (Multi-Functional Splitless) Py-GC/MS, a recently developed sampling technique, was newly employed. This technique allows high sensitivity analyses of trace samples (~1 µg, in contrast to ~100 µg for the others). The results obtained revealed the complex PVC formulation, including plasticizers (DEHP, DBP, DEP, triethylcitrate), lubricants (e.g. polydimethylsilane oil), flame retardants (e.g. TPP), and pigments (e.g. β-naphthols). Considering the required small sample amount compared to the other techniques, MFS Py-GC/MS was highly efficient in characterizing both polymer matrix and additives at lower concentrations, such as lubricants and flame retardants.

[1] King R., Grau-Bové J., Curran K., Plasticiser Loss in Heritage Collections: Its Prevalence, Cause, Effect, and Methods for Analysis, Heritage Science 8 (2020), 123, doi:10.1186/s40494-020-00466-0.

[2] Bart J.C.J., Polymer Additive Analytics: Industrial Practice and Case Studies; Manuali – Scienze; 1st ed.; Firenze University Press: Firenze, 2006; Vol. 3

The past, present, and future of ESCAPE

Michael Schilling[1], Henk van Keulen[2], Nathalie Balcar[3], Jenny Poulin[4], and Mike Szelewski[5]

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[2] *Cultural Heritage Agency, Amsterdam, Netherlands*
[3] *Centre de Recherche et de Restauration des Musées de France, Paris, France*
[4] *Canadian Conservation Institute, Ottawa, Ontario, Canada*
[5] *Winterthur Museum, Winterthur, Delaware, USA*

ESCAPE (Expert System for Characterization using AMDIS Plus Excel) was originally developed at the Getty Conservation Institute as a two-step data processing tool used with pyrolysis-gas chromatography/mass spectrometry for identifying various organic materials in Asian lacquerware. In ESCAPE, AMDIS is used with the ESCAPE library and a retention index calibration file to generate a report of compounds identified in a sample. A custom Excel report template sorts the marker compounds listed in the AMDIS report by material category and presents the results as diagnostic graphs and tables that aid users in confirming materials present in the sample. Over the years, partnerships with Py-GC/MS experts in cultural heritage led to an expansion in the ESCAPE library and the development of custom report templates for identifying natural resins, natural dyes, synthetic paint media, synthetic organic pigments, and plastics. Of the 1660 mass spectra in the current version of the ESCAPE library, 717 originate from cultural heritage research, with the remainder copied from the NIST library. In-person workshops have been the primary mechanism for introducing new users to ESCAPE, and the largest workshop was held at the 2017 MaSC meeting in Portugal.

The MaSC community would derive a number of benefits by adopting ESCAPE: ready access to a mass spectral library relevant to cultural heritage, retention index data that impart greater confidence in compound identification, access to specialized knowledge and a systematic approach to data processing that enables material identification, and standardized report formats that facilitate information sharing. Moreover, MaSC support would be incredibly beneficial in promoting and providing broader access to ESCAPE, expanding the range of materials through partnerships (especially in the areas of archaeological materials and treatment materials), conducting round robin studies to aid in learning, and preparing instructional videos and user guides. With MaSC involvement, the future of ESCAPE looks bright indeed.

NIST Mass Spectrometry Data Center and the NIST mass spectral libraries

Edward P. Erisman

National Institute of Standards and Technology

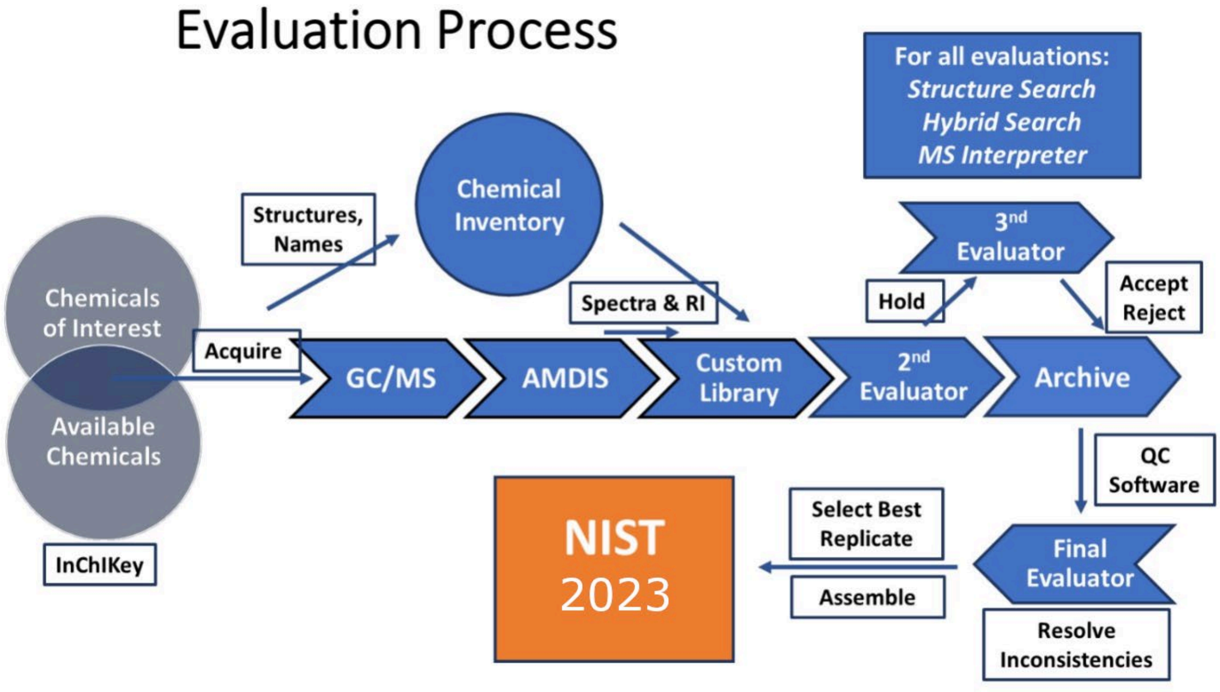
The NIST Mass Spectrometry Data Center (MSDC) maintains several mass spectral libraries. These libraries include the electron ionization (EI) library (collected at 70 eV), the tandem (electrospray) spectral library, and the DART library. The EI and tandem libraries are commercial products distributed through vendors and are on a three-year update cycle with 2026 being the next release. The MSDC has an extensive compound selection process to ensure new additions to the library are relevant. The libraries are carefully curated by a professional staff to ensure the spectra are of the highest quality. The MSDC has developed data processing software tools to aid the extraction, search, and evaluation of spectra and the tools are freely available. The software available includes Automated Mass Spectral Deconvolution and Identification System (AMDIS) for mass spectral deconvolution, MS Search for spectral searching, and MS Interpreter (to aid in interpretation).

The NIST23 EI mass spectral library contains 394,000 spectra of which 347,100 are unique compounds. The library has 492,000 experimentally determined retention index values for a variety of column polarities (either collated from literature or measured in-house). Each library entry also has an artificial intelligence predicted as well as a group additivity model predicted retention index value for a semi-standard non-polar column (e.g. DB-5 type column). Each library entry contains meta data which includes, common name, molecular formula, molecular mass, chemical structure, InChIkey, Chemical Abstract Service registration number (when available) and a link to search the internet for more information.

The 2023 tandem mass spectral library contains 2.4 million spectra from 51,501 compounds. The library contains ESI high resolution accurate mass spectra for 49,590 compounds, ESI low resolution spectra for 49,865 compounds and high resolution APCI spectra for 561 compounds.

The DART mass spectral library is a freely available library. Each of the 1,371 compounds in the library consists of a set of three different in-source collision induced dissociation mass spectra. The DART Data Interpretation Tool (DIT) utilizes an inverted library search algorithm (ILSA) to look for confirmation in higher fragmentation energy spectra of a component found in low fragmentation energy spectra.

The MSDC is in the process of creating a pyrolysis-GCMS library. Currently this is in proof-of-concept stage with a unique search algorithm. The library contains a small number of polymers (with more to be added) and in conjunction with the Getty Conservation Institute data will be added for various paints, lacquers, and natural resins. The library search is a R-shiny script that utilizes the *.ELU output from AMDIS in conjunction with NIST MS PepSearch (for batching searching) with retention index constraints. Each pyrolysis library spectrum is annotated with the material(s) that it came from and each query pyrolysate is searched against the library. The average match factor of the pyrolysates found multiplied by the ratio of pyrolysates found to pyrolysates in the library gives a final material match score.



New approaches to non-targeted EI-GC-MS data analysis for preventive conservation

Rose King, Julia Bakker Arkema, Eric Breitung

The Metropolitan Museum of Art

The identification of VOCs/SVOCs emitted from conservation materials is an ongoing research priority and semi-routine preventive conservation task at The Metropolitan Museum of Art.

Utilizing direct thermal desorption gas chromatography-mass spectrometry (DTD-GC-MS) for non-targeted screening, we routinely analyze samples that generate over 100 chromatographic peaks. To optimize data analysis and identify compounds with corrosion potential, we evaluated the performance of proprietary software (Agilent MassHunter, Cerno MassWorks) and open-source alternatives.

We will present a custom script that automatically flags analytes containing functional groups of interest, enabling rapid visual comparison of emissions profiles between preferred and alternative materials in exhibit design. This approach supports the efficient selection of low-risk materials for use in conservation and display environments.

Identification of polysaccharides in thermoset *Anacardiaceae* (Asian Lacquer) polymers using thermal degradation and gas chromatography based techniques

Jonas Veenhoven[1,2,3], Steven Saverwyns[1], Henk van Keulen[4], Frederic Lynen[2], Maarten van Bommel[3]

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The identification of polysaccharides in *Anacardiaceae* (Asian lacquers) is relevant in the process of polymerisation, in the fully cured polymer and during ageing. The literature on Asian lacquer polymerisation consists for a large part on reports of laccase catalysed mechanisms for phenolic compounds in the lipid phase. Polysaccharides, however, play a pivotal role in keeping these laccase enzymes active by preventing rapid water loss, thereby keeping the laccase enzymes dissolved in water, promoting continues coupling of the lipid phase compounds. In the fully polymerised network, which is composed of lipid phase phenolic agglomerates, the polysaccharides are dispersed within the lacquer macromolecules and act as adhesives between the agglomerates. With this typical grain structure the carbohydrate polymers also limit oxygen diffusion, thereby protecting the phenolic macromolecules from degradation through light exposure.

Identifying polysaccharides in fully crosslinked *Anacardiaceae* polymers is a difficult procedure due to the thermoset nature of the materials. This is probably a reason why these compounds are to date understudied. The results we obtained showed modification of the carbohydrates through complex pathways of in vivo metabolism and biosynthesis. By using thermal degradation, and gas chromatography based techniques we will discuss our recent developments in identifying the lacquer carbohydrates from polysaccharides in fully thermoset samples.

Composition of lacquers on *lacca povera* objects

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Lacca povera or decoupage is a baroque decoration technique where coloured print motives on paper are cut out, pasted onto a prepared surface and then varnished with gloss lacquer. In the early 18th century, *lacca povera* was quite widespread and used for embellishment of various objects and furnishings, often serving as a substitute for japanning. Today, only a small number of *lacca povera* objects are preserved and even less were scientifically examined.

In an art technological study several *lacca povera* objects dating around 1750, were investigated and analysed. The decorated objects comprise a small box, a shrine, a writing cabinet as well as doors of three different cabinets. The study revealed that the cut-out motives were glued to the surface with starch and / or animal glue. To cover these projecting motives, transparent lacquers were applied to produce even and glossy surfaces. Similar to European gloss lacquers of that time, the most important natural resin in the *lacca povera* lacquer formulations is sandarac. However, the studied *lacca povera* objects showed a higher amount and broad range of natural softeners.

Only few art historical sources mention the art of *lacca povera*, even scarce offer precise recipes and instructions. With the analyses presented here this information can now be evaluated.

Investigating Ancient Egyptian Mortuary Practices: GC-MS Analysis of Black Organic Coatings on Funerary Objects

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Anointing mortuary objects with black coatings, composed of mixtures of organic materials, was a practice employed in certain periods of Egyptian history[1]. Thought to reflect functional and/or ritualistic purposes, these coatings have not been fully understood historically, and investigating their composition is essential to develop effective conservation strategies.

The present study constitutes the first in-depth analysis of black coatings found in twenty funerary objects dated to the Third Intermediate and Late Periods in the collection of the Brooklyn Museum, including mummiform figures, canopic jars, and Egyptian coffins. Analysis of these materials by gas chromatography-mass spectrometry was challenging due to the limited sample size. A comprehensive organic profile of these coating materials was achieved using various extraction methods targeting bitumen, resin, oil, wax, and gum. Results revealed the presence of bitumen markers such as alkanes, hopanes, and steranes by the asphalt separation method[2]. Natural resins (Pinaceae and Pistacia), oil, natural gum, and beeswax were also found.

The final goals of determining the bitumen provenance and categorizing objects across time and typology based on the composition of their black coatings offer insights into curatorial and conservation practices, enriching our understanding of ancient Egyptian mortuary rituals and guiding preservation efforts.

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[1] Clark, Katherine A., Salima Ikram, and Richard P. Evershed. "The significance of petroleum bitumen in ancient Egyptian mummies." *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 374.2079 (2016): 20160229.

[2] Fulcher, Kate, et al. "Molecular analysis of black coatings and anointing fluids from ancient Egyptian coffins, mummy cases, and funerary objects." *Proceedings of the National Academy of Sciences* 118.18 (2021): e2100885118.

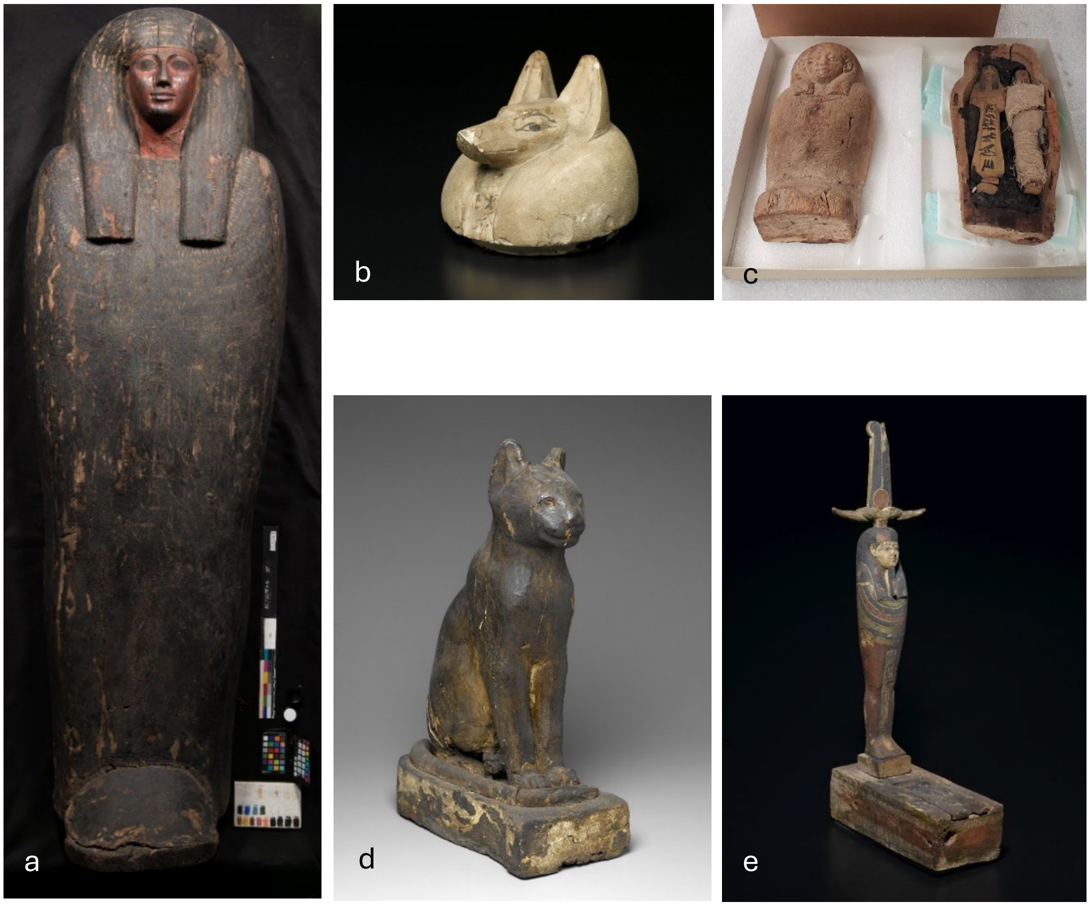

Figure 1. Subset of funerary objects studied in the collection of the Brooklyn Museum (Brooklyn, New York, USA) including **a)** Large Anthropoid Sarcophagus **37.1927Ea-b**, date 945-740 B.C.E., **b)** Jackal-Headed Cover of Canopic Jar **37.1905E**, date 1075-332 B.C.E., **c)** Small Model of a Coffin with Two Ushabti of Seba **37.126Ea-b**, date 1075-945 B.C.E., **d)** Cat Coffin **37.1946Ea-b**, date 664–332 B.C.E., and **e)** Mummiform Figure of Osiris **37.1481E**, date 664-332 B.C.E.

Animal, vegetable, mineral: Characterization of distinctive painting materials on a group of Bwa masks from Burkina Faso

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Wooden masks associated with the Bwa culture in Burkina Faso, West Africa, are carved into different shapes and display various geometrical patterns according to diverse usage. One of their characteristic features is the use of the colors black, red, and white, which evoke the three major rivers crossing the country: the Black, Red, and White Voltas [1]. While materials and the process of painting these masks have been reported in some detail by scholars working within the community, scientific analysis is critical to investigate material preferences in individual cases, and possible changes in traditions over time. A group of four Bwa masks in the Arts of Africa collection of the Art Institute of Chicago, dated from the late 19th-mid 20th century, was investigated using a complement of spectroscopic, chromatographic and mass spectrometric analytical techniques to characterize the nature of both inorganic and organic constituents [2].

The materials used for the colored paints were identified as gypsum, kaolinite and, in one case, reptile excrement for the whites; red iron oxide in an egg-based medium for the red; and a tannin-rich extract of boiled Acacia seed pods for the black. This presentation will focus on the analytical strategy employed for characterization of the organic constituents. In particular, Py- GCMS was essential to support and complement spectroscopic data on the black material, while mass spectrometry-based proteomics has proven again to be crucial to determine with precision the nature of unfamiliar materials and their sources, as demonstrated in the analysis of red and white paint. Discussion with an artist from Boni, Burkina Faso, with experience in mask making following traditional methods, was also critical to inform this study.

The results obtained corroborate published accounts of scholars who have worked directly with artists, while also providing new insights into the nature of the coloring materials and the selection and substitution of pigments and binders, generating a more nuanced understanding of this traditional practice.

[1] Roy, C.D. Art of the Upper Volta Rivers; Alain et Françoise Chaffin: Meudon, France, 1987.
[2] Granzotto, C.; Sutherland, K. Black, Red and White: Characterization of Painting Materials on a Group of Bwa Masks from Burkina Faso. Appl. Sci. 2023, 13, 12240.

Detection of Gum Benzoin in Historical Samples Using THM-GC/MS

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Gum benzoin, a fragrant resin derived from the Styrax plant, is valued for its medicinal and cosmetic properties, as well as its role as a minor ingredient in varnishes. Commonly used in combination with other resins, gum benzoin serves as a plasticizer and gloss agent in coatings. Although resin can be harvested from several Styrax species, two primary types are of interest in cultural heritage: Siam benzoin (Styrax benzoides Craib) and Sumatra benzoin (Styrax benzoin Dryand). These resins are characterized by their phenolic composition, including ester derivatives of benzoic and cinnamic acids.

In the context of Py-GCMS (pyrolysis-gas chromatography-mass spectrometry) analysis of historical varnish samples, detecting benzoin can be challenging. Many markers are not specific enough; for example, benzoic acid and 3,4-dimethoxybenzoic acid can originate from other sources, and some signals may be confused with homologous molecules at shifted retention times. As a result, identifying benzoin in varnishes and mixtures can be subtle and complex.

This presentation explores several Py-GCMS measurements aimed at finding more reliable indicators of gum benzoin's presence in historical varnishes and other complex mixtures. To enhance benzoin identification, reference samples of both Sumatra and Siam varieties of gum benzoin were analyzed using Py-GCMS with TMAH derivatization. The study reveals that while detection of a range of markers, including cinnamic and benzoic acids and their derivatives, is influenced by the presence of other resins and degradation processes, their ratios are useful for identifying gum benzoin. Additionally, the study examines triterpenoids as potential biomarkers for confirming Styrax resins; however, the weak triterpenoid signal of Styrax can be easily lost in the presence of other triterpenoids.

In summary, this presentation gives an overview of the possibilities and limitations associated with identifying benzoin in historical varnishes by THM-GC/MS.

Chiavari, G.; Montalbani, S.; Otero, V. Characterisation of Varnishes Used in Violins by Pyrolysis-Gas Chromatography/Mass Spectrometry. *Rapid Commun. Mass Spectrom.* 2008, *22* (23), 3711–3718. https://doi.org/10.1002/rcm.3785.

Courel, B.; Adam, P.; Schaeffer, P. The Potential of Triterpenoids as Chemotaxonomic Tools to Identify and Differentiate Genuine, Adulterated and Archaeological Balsams. *Microchem. J.* **2019**, *147*, 411–421. https://doi.org/10.1016/j.microc.2019.03.035.

Echard, J. P.; Benoit, C.; Peris-Vicente, J.; Malecki, V.; Gimeno-Adelantado, J. V.; Vaiedelich, S. Gas Chromatography/Mass Spectrometry Characterization of Historical Varnishes of Ancient Italian Lutes and Violin. *Anal. Chim. Acta* **2007**, *584* (1), 172–180. https://doi.org/10.1016/j.aca.2006.10.048.

Langenheim, J. H. *Plant Resins: Chemistry, Evolution, Ecology, and Ethnobotany*; Timber Press, 2003.

Modugno, F.; Ribechini, E. GC/MS in the Characterization of Resinous Materials. In *Organic Mass Spectrometry in Art and Archaeology*; Colombini, M. P., Modugno, F., Eds.; Wiley, 2009; pp 215–235.

van Keulen, H. The Analysis and Identification of Transparent Finishes Using Thermally Assisted Hydrolysis and Methylation Pyrolysis-Gas Chromatography-Mass Spectrometry. In *Furniture Finishes*; Proceedings of the Twelfth International Symposium on Wood and Furniture Conservation; Stichting Ebenist: Amsterdam, 2015; pp 134–141.

van Keulen, H.; Schilling, M. AMDIS & EXCEL: A Powerful Combination for Evaluating THM-Py-GC/MS Results from European Lacquers. *Stud. Conserv.* **2019**, *64* (sup1), S74–S80. https://doi.org/10.1080/00393630.2019.1594580.

Webb, M. *Lacquer: Technology and Conservation: A Comprehensive Guide to the Technology and Conservation of Asian and European Lacquer*; Butterworth-Heinemann: Oxford, 2000.

Molecular markers for heat pretreatment of drying oils: dicarboxylic acids (re-)revisited

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Since their introduction as binders for painting, drying oils such as linseed oil have been treated in various ways to improve their visual and working properties and ageing characteristics. In particular, partial pre-polymerisation of the oil can be effected by various means: with exposure to heat, sunlight, oxygen, driers, or combinations of these; to produce viscous media that provide several advantages when used in a paint, as compared to the raw oil. Heat-bodied oils – that is, oils that undergo initial polymerisation primarily as a result of heating, with little or no exposure to oxygen – are particularly valued for their tendency to form durable, glossy paint films with reduced yellowing. The modified drying and ageing characteristics of heat-bodied oils (nowadays generally referred to as polymerised or stand oils) are a consequence of the distinct chemical reactions induced by anoxic heating, in contrast to the free radical chain reactions that lead to the formation of a cross-linked polymer network in the presence of oxygen under typical ambient conditions.

The possibility of differentiating between raw and heat-bodied oils in a dried paint by GC or GCMS analysis, based on the relative proportions of dicarboxylic acids of different chain lengths, was first noted in the 1980s [1], and numerous researchers have since adopted parameters such as the suberate:azelate ratio to make such distinctions. Subsequent studies of paints made with oils prepared following historic recipes cast doubt on the reliability of this approach, however [2,3]. The aim of the current study was to test the validity of molecular markers for the discrimination of heat bodied drying oils in aged paints, using GCMS analysis of a diverse range of reference samples from various museum collections dating from the 1920s to 1990s. This well-documented sample set allowed a thorough investigation of the influence of factors such as ageing and pigmentation, as well as the oil pretreatment. Furthermore, discussions of dicarboxylic acid ratios in the published literature have been reexamined, including selected studies in which the use of these ratios was a key aspect of the interpretation, to provide a more holistic view of their application and value.

[1] J. Mills, R. White, “Organic mass spectrometry of art materials: work in progress”, National Gallery Technical Bulletin 6 (1982) 3-18
[2] K. J. van den Berg, M. Tsouli, L. Carlyle, “GC analysis of aged oil paint: some comments on the significance and reproducibility of molecular markers”, MaSC Meeting, Washington DC (2004)
[3] I. Bonaduce, L. Carlyle, M. P. Colombini, C. Duce, C. Ferrari, E. Ribechini, P. Selleri, M. R. Tiné, “New insights into the ageing of linseed oil paint binder: A qualitative and quantitative analytical study”, PLoS One 7 (2012) e49333

MaSC

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

Poster Abstracts

Enhanced detection of orchil and crottle lichen dyes from textiles through optimized liquid chromatography and related separation techniques

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Analysing lichen dyes from textiles is complex due to the unique chemistry of lichen chromophores. These dye compounds, in lichens purples (orchil lichens) are not in the lichen composition as such. The dye compounds in orchil lichens form after treatment in alkalic media followed by environmental exposure. For lichen browns (crottle lichens) the dye compounds can be extracted in boiling water. The chromophores, found in orchil and crottle lichens, are unstable in acidic conditions. This poses a challenge for liquid chromatography (LC) analysis, which typically involves acid hydrolysis for preparative extraction and an acidified mobile phase in reversed-phase LC (RPLC) analysis. The acidity can cause in situ degradation the chromophores, complicating dye identification. With this poster we present our results, primarily focused on using RPLC-DAD analysis of unaged orchil and crottle lichen dyes. We aimed to enhance the detection of lichen chromophores by reducing acidity in both the sample pretreatment step and the RPLC mobile phase. Initial findings are promising, suggesting improved stability and detectability of lichen chromophores or marker molecules thereof. Further studies, including artificial aging of lichen dyed reference yarns and comparisons with other analytical methods, are planned as part of the ongoing Colour4CRAFTS project.

(https://www.helsinki.fi/en/researchgroups/bio-based-colourants/about-colour4crafts)

Science Communication in Belgium: The NERDLAND Festival

Louise Decq, Jonas Veenhoven

Royal Institute for Cultural Heritage (KIK-IRPA)

Belgium is a federal country with two major regions: a Dutch-speaking north and a primarily French-speaking south, sharing the capital, Brussels. Some authorities are managed at the national level while others are regional.

Our research institution, KIK-IRPA (Koninklijk Instituut voor het Kunstpatrimonium in Dutch, Institut royal du patrimoine artistique in French), is a Belgian royal institute operating under Belgium's relatively small science policy. Culture and education, including universities and most museums, fall under regional policy, where culture serves as a narrative for regional identity. This places KIK- IRPA, positioned at the intersection of science and culture, in a challenging position in a country with two very distinct regions.

At the federal level, which has seen a decrease in authority since the foundation of the institute, KIK-IRPA researches heritage objects and responds to inquiries from historians, owners, and restorers in both regions, as well as in Brussels and abroad. An intense dialogue with these different levels is crucial.

In every situation, and particularly in this context, broad science communication is essential as science also plays a societal role. In this poster, we aim to visually highlight the science communication initiatives developed by KIK-IRPA.

The pros and cons of DART-MS for the analysis of art and archaeological materials: Insights from more than a decade of experience

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For the past 13 years, our laboratory has been exploring the use of direct analysis in real time mass spectrometry (DART-MS) for characterizing small molecules in art and archaeological materials. The method is fast, requires no sample preparation, and is exceptionally useful for screening of materials prior to doing more in-depth analysis with GC-MS or other methods. This poster will highlight the good and the bad of our experiences using DART-MS for characterizing rock paintings from Cuba, dyes in Peruvian textiles, and various different residues, from ancient Egyptian mummification balms to Greco-Roman perfumes to charred and absorbed cooking residues. In many cases, combining DART-MS and GC-MS has shown that understanding the chemistry of the systems we are studying is important in the interpretation of the results.

One of our early applications of DART-MS was to evaluate the organic content of rock paintings for radiocarbon dating. Identifying the presence of a binding medium in rock paintings is difficult, due to decomposition, contamination from biofilms, and the wide array of possible materials. In our study of the rock art of the Las Charcas region of Cuba (Armitage et al., 2021), initial DART-MS analysis suggested the carbon black pigments were combined with pine resin used as a binder. Based on this, radiocarbon dates were obtained on samples from two of the Las Charcas caves, with the results clearly indicating that some part of the paint contained ^{14}C-free carbon. Follow-up studies with GC-MS showed that the saturated hydrocarbons, not observed by DART-MS, were indicative of a solid hydrocarbon source for the black pigment, consistent with locally available gilsonite. This demonstrated the importance of combining techniques for a full understanding of the nature of the organic material in rock paintings for radiocarbon dating.

Much of our work has been in the identification of dyes in archaeological textiles, particularly those from pre-Columbian Peru. DART-MS proved valuable in confirming the presence of anthraquinone red dyes in yarn fragments from mummy bundles dating to the Paracas period in southern Peru (Armitage et al., 2015b). Combining DART-MS and paper spray ionization with HPLC, either with MS or diode array detection yields significantly more information about the composition of dyes prepared from known plants native to Peru (Armitage et al., 2019; Campos Ayala et al., 2021). Questions remain, however, about the presence of alizarin and/or xanthopurpurin in the *Relbunium* plant dyes; these structural isomers cannot be differentiated with mass spectrometry or by UV-vis spectroscopy. Given the capabilities of modern LC-MS/MS instrumentation, this is a good opportunity to reinvestigate past analysis of *Relbunium* and *Galium* dyes (Dutra Moresi and Wouters, 1997) to better characterize the full complement of anthraquinones, including the glycosides.

DART-MS is an important step in sequential analysis and dating of textiles, as the sample needed is so small and can be done so as to minimize damage to the yarn being analyzed. We first demonstrated using DART-MS to identify red dyes on yarns from the Seip Mound Group, now part of the Hopewell Ceremonial Earthworks UNESCO World Heritage site in Ohio (Armitage et al., 2015a; Armitage and Jakes, 2015). This identification was repeated on the wash solution remaining after the yarns were prepared for AMS radiocarbon dating. Though DART-MS cannot yet be used to identify all of the colorant molecules in a dyed sample, it can rapidly suggest a dye source that can be further confirmed with follow-up HPLC-MS/MS analysis. Just how much information can be squeezed out of one sample of textile yarn (1 cm or less in length) is the subject of much ongoing work in our laboratory, including fiber identification, dyes analysis, radiocarbon dating, and isotopic analyses.

Perhaps the most in-demand application of DART-MS for archaeological materials in our laboratory has been the identification of plant metabolite biomarkers in ceramic residues. This is often complicated by contamination from storage or handling of the objects, as in the case of a purported wine residue on a sherd stored directly in a plastic bag and handled repeated with bare hands. Not surprisingly, the residue in question appeared to mainly erucamide slip agent from the storage bag and a variety of compounds characteristic of human fingerprints, particularly squalene. In other cases, DART-MS analysis has initially supported intriguing uses of ancient ceramics, as when a student identified possible nicotine in Hopewell ceramics that was later identified with GC-MS as phthalate contamination (both with an m/z peak at 163 Da). Differences in the amount of sample used, how the sample is extracted and prepared for GC-MS, and the sensitivity of the two approaches has led us to dig deeper into combining the methods for confirmation of screening results. Ongoing studies include identifying metabolites of *Theobroma cacao* in residues scraped from a variety of Central American ceramic vessels and looking for entheogen markers like dimethyltryptamine in vessels either shaped like or decorated with motifs of plants and animals known to produce DMT and its derivatives. Structural identification of the possible traces of these biomarkers identified by mass using DART-MS is an important step in validating the results.

The same advantages GC-MS provides in structural identification can also complicate interpretation when comparing those results with what is obtained via DART-MS. Because there is no sample preparation, there is also no fractionation caused by the solvent used to extract the sample for derivatization prior to GC-MS (something not necessary in Py- or THM-GC-MS). This was particularly problematic when characterizing the composition of Egyptian mummification balms, where marked differences were observed in the dioic and hydroxy fatty acids identified by DART-MS and then GC-MS of both total lipid extracts and acid-extracted methyl esters. Many of the hydroxy fatty acids appear to undergo keto-enol tautomerization to form oxo fatty acids during acid extraction. Expecting these chemical transformations is an important step in interpreting the results and comparing them with the DART-MS results of the raw, unaltered samples.

Armitage, R.A., Arrazcaeta, R., Torres, S., Baker, S.M., Fraser, D., 2021. Chemical characterization and radiocarbon dating of the rock art of Las Charcas caves, Cuba. Archaeometry 63, 878–892. https://doi.org/10.1111/arcm.12639

Armitage, R.A., Day, C., Jakes, K.A., 2015a. Identification of anthraquinone dye colourants in red fibres from an Ohio Hopewell mound site by direct analysis in real time mass spectrometry. STAR: Science & Technology of Archaeological Research 1, 1–10. https://doi.org/10.1179/2054892315Y.0000000010

Armitage, R.A., Fraser, D., Degano, I., Colombini, M.P., 2019. The analysis of the Saltzman Collection of Peruvian dyes by high performance liquid chromatography and ambient ionisation mass spectrometry. Heritage Science 7, 81. https://doi.org/10.1186/s40494-019-0319-1

Armitage, R.A., Jakes, K., Day, C., 2015b. Direct analysis in real time-mass spectroscopy for identification of red dye colourants in Paracas Necropolis Textiles. STAR: Science & Technology of Archaeological Research 1, 60–69. https://doi.org/10.1179/2054892315Y.0000000009

Armitage, R.A., Jakes, K.A., 2015. Sequencing Analytical Methods for Small Sample Dating and Dye Identification of Textile Fibers: Application to a Fragment from Seip Mound Group, Ohio. Midcontinental Journal of Archaeology 20, 1–15. https://doi.org/10.1179/2327427115Y.0000000009

Campos Ayala, J., Mahan, S., Wilson, B., Antúnez de Mayolo, K., Jakes, K., Stein, R., Armitage, R.A., 2021. Characterizing the Dyes of Pre-Columbian Andean Textiles: Comparison of Ambient Ionization Mass Spectrometry and HPLC-DAD. Heritage 4, 1639–1659.

Dutra Moresi, C.M., Wouters, J., 1997. HPLC analysis of extracts, dyeings and lakes, prepared with 21 species of Relbunium. Dyes in History and Archaeology 15, 85–97.

Identifying oil binders in viceregal Mexican lacquerware by targeted and untargeted proteomics

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In Mesoamerica, chia (*Salvia hispanica*) seed oil has been used by Indigenous populations as a binding medium since as early as 1200 CE.[1] It is known to be the primary binder in pre-Hispanic and viceregal (16th to 19th century) Mexican lacquerware (*maque*). However, its use in oil paintings is not fully understood, though records suggest chia oil may have been used as an alternative to imported linseed oil in the viceregal era.[2] Analytically identifying the use of chia oil is a challenge. The standard pyGC-MS method for distinguishing European oils relies on ratios of specific fatty acids. This method falls short here, as chia and linseed oils have similar fatty acid profiles and therefore are indistinguishable by their ratios. We present an alternative for species-specific identification of minimally processed oil binders based on proteins. This is achieved through an optimized enhanced filter-aided sample preparation (eFASP) protocol[3,4] to extract and digest seed proteins from the complex oil network. Resulting peptides are then analyzed using untargeted and targeted data-dependent acquisition methods and searched against relevant plant protein databases.

Our approach supposes that the traditional production of chia oil (toasting, grinding, wetting, pressing) may allow seed proteins to transfer to the oil and, by extension, to the oil-based paint or lacquer. Beginning with reference materials produced at The Met, as well as materials provided by currently practicing Mexican lacquerware artisans, we established the validity of extracting seed proteins from chia seeds, oils, semi-cured films, and replica paints (Figure 1). The required oil volumes were as low as 10 µL, and sample sizes of model paints were comparable to those obtained from objects by conservators.

Numerous chia proteins were detected with high sequence coverage, and several species-specific peptides were identified. In the chia oil paints, primarily seed storage proteins (11S globulins and 2S albumins) were identified, consistent with expectations given that globulins comprise approximately half of proteins in chia seeds.[5,6] Homogenization proved crucial for protein extraction from the semi-cured oils and paints, which takes on added importance in historic samples, where aging can contribute to further cross-linking of the oil and chemical derivatization of the proteins.

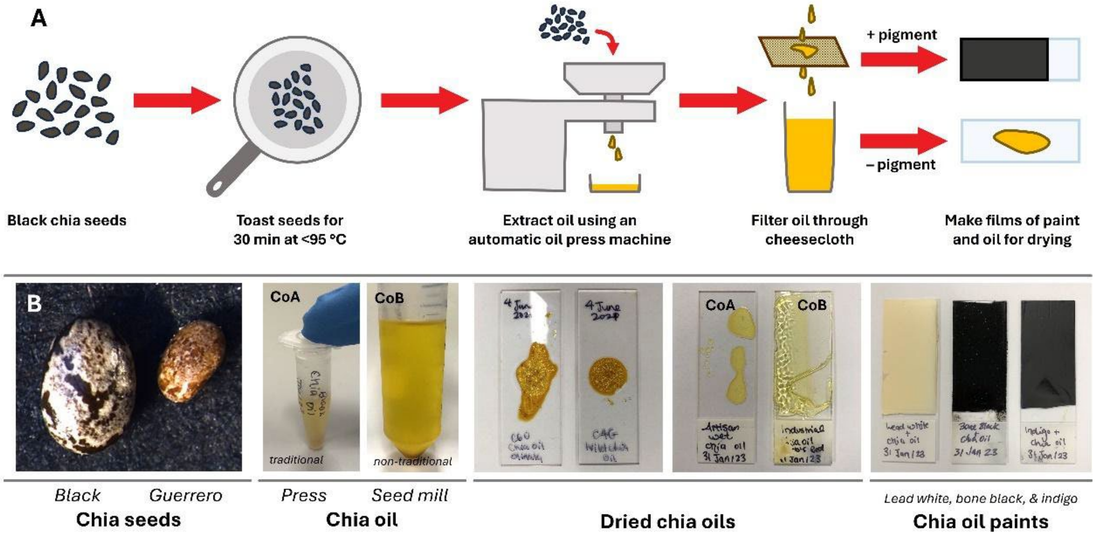

Figure 1 A) Schematic of a production process for reference materials at The Met, shown here using a seed mill (non-traditional). B) Photographs of reference materials.

In order to improve sensitivity of the method moving into historic art samples, we also explored targeted analysis of chia-specific peptides. Black and Guerrero chia seeds were used to produce a target peptide MS/MS inclusion list, derived from three seed-storage proteins. To maximize information, samples were analyzed using untargeted and targeted methods for comparison.

With our success in reference materials, three historic (18-19th century) and one contemporary Mexican lacquerware object were analyzed, and traces of seed proteins were detected in all. We discuss these object results along with the challenges of applying our bottom-up proteomics approach to aged historic samples. This work provides an initial foundation for future identification of not only chia oil, but other understudied biological materials used in artworks around the world.

References

1. Katz, M. Colonial Spanish American Lacquered Objects in the Collection of the Hispanic Society of America. In *AIC Wooden Artifacts Group Postprints*; *44th Annual Meeting American Institute for Conservation*, Montreal, Quebec; Storti, C., Deurenberg-Wilkinson, R.M.H., Eds.; The American Institute for Conservation of Historic & Artistic Works: Washington, DC, 2016; pp 37–47.
2. Arroyo Lemus, E.; Amador Maerrero, P.F. Aproximación a los materiales y las técnicas del pintor Juan Correa. In *Juan Correa: Su vida y su obra Tomo I*; Universidad Nacional Autónoma de México, Instituto de Investigaciones Estéticas, Mexico, 2017; pp 205–239.
3. Erde, J.; Loo, R. R. O; Loo, J. A. *Methods Mol. Biol.* **2017**, *1550*, 11–18.
4. Pozzi, F.; Arslanoglu, J.; Galluzzi, F.; Tokarski, C.; Snyder, R. *Herit. Sci.* **2020**, *8*, 1–14.
5. Sandoval-Oliveros, M.R.; Paredes-López, O. *J. Agric. Food Chem.* **2013**, *61*, 193–201.
6. Alejo-Jacuinde, G.; Nájera-González, HR.; Chávez Montes, R.A. *et al. Commun. Biol.* **2023**, *6*, 820.

Investigation of Talens emulsion paint colour charts by ASAP-HRMS

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Royal Talens, the Dutch manufacturer of paints and art supplies, was founded in 1899 as a manufacturer of stationery and artists' materials. Talens products were sold widely; ledgers in the Talens archives show that already in 1902, the company sold oil and water colour paints to USA and Russia. The casein/oil emulsion paint 'ETA' was produced from 1932 until 1980. Artists' quality tempera paints of varying composition were produced for a longer period.

Talens and RCE together own a vast collection of original colour charts and remnants of ETA paints from old tubes, tins and flacons. Paint samples from five Talens emulsion paint colour charts from various periods have been sampled for a pilot study, using an atmospheric solids analysis probe combined with high-resolution mass spectrometry (ASAP-HRMS), to investigate binding media and synthetic organic pigments (SOPs) used in these paints.

Several SOPs have been identified in ETA and aquarelle yellow and red paints. In 'Rembrandt' fine art tempera paints, diterpenoid resins were observed but no pigments.

MaSC

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