8th MaSC

MEETING PROGRAMME

28-29th September 2017

Fórum Eugénio de Almeida, Auditorium
Évora - Portugal

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

8th MaSC

MEETING PROGRAMME

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LABORATORIO HERCULES
HERANÇA CULTURAL, ESTUDOS E SALVAGUARDA

UNIVERSIDADE DE ÉVORA

The Committee of the Users' Group for Mass Spectrometry and Chromatography (MaSC) welcomes you to the eighth MaSC Meeting at the HERCULES Laboratory at the University of Évora, Portugal. Since its foundation in 2003, MaSC has established itself as a vital international forum for interaction and discussion 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.

The 2017 Meeting has been preceded by two days of a workshop on sample introduction techniques for GCMS – pyrolysis and solid-phase microextraction (SPME) – hosted at HERCULES and the Enology Lab at the Mitra Campus of the University of Évora. There will be third workshop day on data treatment given by our colleagues Michael Schilling and Henk van Keulen using AMDIS and Excel to which all are invited. In the afternoon, Michael and Henk will demonstrate the ESCAPE method for GCMS data treatment developed at the Getty Conservation Institute. We are very grateful to the workshop lecturers for sharing their expertise and discussing new research: Cristina Barrocas Dias, Ester Ferreira, Maria Helena Florêncio, Henk van Keulen, Michael Schilling and Christopher Maines. We're also most grateful to hands-on instructors Ana Manhita and Dora Teixeira (HERCULES Laborary), Michael Schilling (Getty Conservation Institute), and Henk van Keulen (Cultural Heritage Institute of the Netherlands) for pyrolysis – GCMS natural and synthetic materials, and to Maria João Cabrita (Mitra Campus), Marco Gomes da Silva (New University of Lisbon), and Christopher Maines (National Gallery of Art) for SPME-GCMS of exhibition and storage materials.

The 2017 Meeting in keeping with past meetings covers a broad range of materials, techniques and topics ranging from archaeological materials to modern paintings, and from organic binding media to gold coins using techniques including MALDI-MS, SPME-GCMS, Py-GCMS, and LA-ICP-MS. Materials covered will be inks, dyes, natural resins, East Asian lacquer, pollutants.

We would like to thank the local committee staff of Laboratorio HERCULES and the University of Évora for their support and assistance in organising and hosting this event –in particular: António Candeias, Cristina Barrocas Dias, Ana Manhita, Dora Teixeira, Maria João Cabrita, Marco Gomes da Silva, Ana Teresa Caldeira, Rosário Martins.

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ABSTRACTS

Mass spectrometry for the characterization and identification of proteins in samples from artistic and archaeological objects

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Proteins are the building blocks of cells in all living species, and they carry the information necessary for life, replication, defence and reproduction. It has recently been proven that proteins are much longer preserved than DNA, as they have been found in paleontological findings dating back to the Pleistocene. Proteins are also important components of archaeological findings, including bones, textiles, food and cosmetic residues of vases and amphorae, as well as fundamental constituents of works-of-art, used to paint or to decorate objects.

Many analytical methods for the identification and characterization of proteins in samples from cultural heritage, such as paintings and works-of-arts and archaeological findings have been presented in the literature, based on staining, immunological, spectroscopic, chromatographic, and proteomics techniques [1-3]. Each of these techniques has shown the potential of being able to successfully detect, and in some cases, identify, proteins in selected samples, but all of them present more or less drawbacks, which are seldom discussed and rarely put in relation to degradation mechanisms. In the course of ageing, though, proteins are subject to significant changes, including amino acids modifications (such as deamidation, hydroxylation and oxidation) and structural modifications (such as hydrolysis, aggregation, cross-linking and formation of strong complexes with cations), which are not all well understood [4-8]. Aggregation, cross-linking and complexation, may hamper the access of cleavage enzymes, and may also strongly affect the protein solubility, making the protein extraction necessary for wet chemical methods a difficult task. Our research in the last years has been devoted at developing analytical methodologies based on mass spectrometry for the detection and identification of proteins in samples from cultural heritage, which can be reliably used to characterise objects with a high inorganic content, in the presence of other organic materials, and highly degraded. These include gas chromatography/mass spectrometry (GC/MS), evolved gas analysis coupled with mass spectrometry (EGA/MS), pyrolysis coupled with gas chromatography/mass spectrometry (Py/GC/MS), double shot pyrolysis gas chromatography/mass spectrometry (DSP/GC/MS), and, most recently, bottom-up proteomics based on tandem mass spectrometric analysis of peptide solutions obtained with non-enzymatic proteolytic digestion [8-10].

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Something is eating your object? Application of SPME-GC-MS method for the detection of active moulds on the historic objects

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Historical objects and art items have usually very high material, cultural, social and historic value, and some of them are just priceless. Thus, the early detection of their degradation, especially biodeterioration, is of high importance to museums, archives or libraries, the owners of the collections. Historic objects are mostly made of organic materials, proteins or cellulose, which are very susceptible to many destructive processes. These are mainly due to the influence of environmental factors: temperature, humidity and UV light. The permanent exposure to unstable environmental conditions affects the structure and properties of historical objects. As a result of this natural ageing, the objects become more susceptible to biodeterioration. The biodeterioration of historical objects may be caused by bacteria or moulds. Nevertheless, bacteria need high water activity in the materials to develop when compared to fungi. Thus, biodeterioration is initiated more frequently by moulds. Many authors have found that there are many species of moulds that can deteriorate naturally aged historical objects. However, when there are any visible alterations on the surface of a historical object that suggest the presence of moulds, first of all, it should be investigated if the moulds are actively growing. This information is crucial for conservators because, based on that, they decide on the disinfection of objects, which is required only if the results confirmed that the fungi are vital. This decision is especially important in the case of naturally aged historical objects, which are fragile and very sensitive to many physicochemical factors acting during disinfection processes.

Thus, the confirmation that the moulds are indeed active is required. This may be investigated with classical microbiological methods, but they are time-consuming, labour-intensive and require a contact with the surface of objects. The results of these analyses give information rather about the microbial contamination of the surface than the presence of active moulds. They also exclude the possibility of active moulds detection when fungi are growing inside the structure of objects. An alternative method of active moulds investigation may be the analysis of volatile metabolites that are emitted by moulds at every stage of their development. These metabolites are called microbial volatile organic compounds (MVOCs). They can be detected when moulds grow both on the surface and inside the material as they easily diffuse of the objects.

The main goal of this study was to assess the possibility of using the solid phase microextraction GC-MS method for detection of active moulds, based on MVOCs measurements. The analysis was carried out for selected moulds that were inoculated on the model samples of silk, cellulose, parchment and wool placed on microbial broths prepared in closed vials. One additional experiment was carried out for a historical sample of leather inoculated with *Aspergillus niger* prepared in a Petri dish without a broth (open system). After six days of incubation the MVOCs acquired inside the vials and emitted by *A.niger* growing on leather were sampled on SPME fibre and then analysed in GC-MS system. The obtained chromatograms were analysed qualitatively and quantitatively in order to determine whether among the identified compounds are indicators of moulds activity that may be used for their detection in case they develop on the real historical or art objects. The results showed that there are three groups of volatiles that can be used for the detection of active forms of moulds on historical objects.

Figure 1: Sampling of MVOCs on SPME fibre in a 19th century book with a visible alteration on the surface of the first page, which suggests the presence of the active mould.

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Binding media of Antique Mummy Portraits

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In the context of a research project on the development of painting in the Mediterranean area from Antiquity to Middle Ages (c. 200-1250) [1], 13 mummy portraits in various German museums have been investigated. In addition to technical studies, it was possible to sample four portraits for binding medium analyses. All four portraits were painted with wax, no tempera paintings were sampled due to their small size and thin paint layers. Because long brushstrokes can be observed on many mummy portraits, it is obvious that at least these paints were applied with a brush. It has been assumed that it is not possible to paint mummy portraits with molten beeswax, and it has long been proposed that the Egyptians had found a way to apply liquid wax paints at temperatures much below the melting point of beeswax. It was suggested that addition of resins or oil, as well as partial saponification and emulsion formation due to boiling with lye were used to liquefy the beeswax. The main question was to confirm or refute these suggestions.

Reconstructions of Antique recipes by Pliny or Disoscorides demonstrated that boiling of beeswax in seawater only results in cleaning and bleaching of the wax. After addition of a small amount of lye (e.g. sodium or potassium carbonate), an emulsion is formed during boiling, however. Nevertheless, below the melting point of normal beeswax, the wax solidifies and the emulsion turns into a suspension. In a suspension, the wax forms small particles that have no ability to bind the pigments but work as a filler, which increases the amount of binder needed to bind the paint. Emulsions at low temperatures cannot be obtained, even after boiling with concentrated lye.

Paint samples were analysed by FTIR as well as by GC/MS after extraction with isooctane, methanol, chloroform/methanol (7:3) and methanol with 10% oxalic acid, proteins in the residue were analysed with amino acid analysis after hydrolysis with HCl [2].

Not surprisingly, beeswax was identified as main binder in all four paintings. Due to the long storage in Egyptian climate, the more volatile alkanes of the beeswax have evaporated, as has been reported before [3]. The binders of two mummy portraits were pure beeswax. However, the samples of two portraits showed additional components.

The flesh tones of one mummy portrait contained lumps of a yellow transparent material. Analysis by FTIR showed that the lumps did not consist of undissolved resin, as might have been expected, but lead soaps. Therefore, these might be the oldest known protrusions. Analysis of this paint revealed large amounts of lead soaps by FTIR and large amounts of free fatty acids in addition to the beeswax components by GC/MS. In addition, relatively large amounts of myristic acid were identified, which is untypical of beeswax but a clear marker for animal fat. In contrast, all other samples from mummy portraits did contain lead soaps as well, but only in rather small quantities, and they did not contain large amounts of free fatty acids. It is concluded that triglycerides in mixtures with beeswax are not stable with regard to hydrolysis and lead soap formation in paints containing lead white pigment occurs, as is well known from oil paintings. On the other hand, beeswax seems to be rather stable with regard to hydrolysis. If this assumption is correct, it might be concluded that addition of significant amounts of fat or oil to beeswax should always lead to a significant amount of lead soaps and protrusion formation. However, this has not been observed in any other mummy portraits studied so far. Accordingly, it seems very unlikely that the addition of fat or oil for painting mummy portraits has been a common procedure. Additions of resins have not been identified at all in any wax paints from mummy portraits.

The samples of a fourth mummy portrait contained proteins in addition to beeswax. The lower preparatory layer contained animal glue, the upper paint layer mainly egg, with a bit of animal glue, presumably from contamination. The composition of the beeswax was remarkable: the alkanes were completely sublimated, and even the lighter wax esters were reduced. Therefore, it seems that this wax was exposed to very high temperature because even very long ageing in Egyptian climate cannot explain the detected composition.

It is unclear how the combination of proteins and beeswax should be explained. Staining of cross-sections with the protein-selective fluorescent stain SYPRO Ruby indicated a homogenous distribution of the proteins in the paint layers, which excludes contamination with materials from conservation treatments or retouchings. Maybe the portrait was painted with tempera paints and then soaked with beeswax. It is not possible, however, that the beeswax was emulsified in an aqueous solution containing egg or animal glue, because the beeswax is only liquid at temperatures where egg denatures and coagulates. Further possibilities of mixing protein and wax binders and how to paint with beeswax below its melting point will be discussed during the MaSC conference.

Keywords

Mummy portraits, beeswax, encaustic, Punic wax, saponification, protrusions

Acknowledgements

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Mixed binding media in Reverse glass paintings of Heinrich Campendonk

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Two interdisciplinary research projects are dedicated to reverse glass paintings created during the Classical Modernism (1905-1955). The technique of reverse glass painting (*Hinterglasmalerei*) is well-known in folk art for a long time, in 1908/09 this technique was introduced by Gabriele Münter to the group of *Der Blaue Reiter* and its members Wassily Kandinsky, Franz Marc, Paul Klee and later Heinrich Campendonk (1889-1957). As reverse glass painting was not an established technique at that time, its experimental character opened a new field for artistic development and was passed on to other artists in Germany.

The presentation will focus on the oeuvre of Heinrich Campendonk [1]. Campendonk created more than 70 reverse paintings on glass throughout his lifetime and experimented with a variety of techniques. He was among the many modernists condemned as degenerate artist during Nazi time. That is why he moved to the Netherlands, where he was working at the Rijksakademie in Amsterdam, first teaching Decorative Art then as Academy Director.

Here, the analyses of six reverse glass paintings by Campendonk, dated between 1917 and 1946 will be presented. All samples were extracted with the help of a multistep-extraction and derivatisation system, comprising analysis of lipids, resins, proteins as well as saccharides [2]. The analyses show that Campendonk was working with well-known media of that time, both oil- as well as aqueous media. Skillfully he used the various characteristics of the different binding media. For his early self-portrait in 1917 he applied a gouache system based on gum arabic to create bright paints with very fluidic transitions (Fig.1a and 1b). The analyses show that from the nineteenth-twenties onward he was primarily working with commercial oil tube paints. His technique changed and he created multi-layered works with oil- and gum-based paints on top of each other (Fig.2a and 2b) [1].

The presented results show analogy with a research project on reverse glass paintings by Paul Klee. Early works of Klee - dated between 1905 to 1908 - reveal similar binding media (gum arabic, starch, protein and oil), but Klee used them in a rather different artistic manner for his paintings [3].

Figure1a: *Selbstbildnis in Oberbayern* (Selfportrait in Upper Bavaria), Clemens-Sels-Museum, Inv. No. 1964Ma073, dated 1917.

Figure1b: Detail *of Selbstbildnis* (transmitted light) showing very fluid, converging paints, bound with a gouache-system.

Figure 2a: *Zwei schwarze Asse*, private collection, dated 1926.

Figure 2b: Detail of *Zwei schwarze Asse*, reverse side with multilayered build-up. The white paint is rolling off - a phenomenon showing that an aqueous paint is applied on top of an oleaginous.

Keywords

Classical Modernism, reverse glass painting, analysis, binding media

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Specific and micro-scale identification of plant gums in works of art using saccharide mass fingerprinting with MALDI-MS

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While matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) has become an established tool in the cultural heritage field for protein analysis (proteomics), it has only recently proved to be valuable also for plant gum identification. The analytical strategy involves partial enzymatic digestion of the polysaccharide fraction of the gum followed by analysis of the released oligosaccharides. Due to significant differences in their polysaccharide structure, gums from different plant sources can be discriminated according to their unique saccharide mass fingerprint [1]. The analytical strategy allows unambiguous identification of plant gums in aged microsamples, even in the presence of inorganic (e.g. pigment) and other organic components (e.g. resin, oil) [2, 3].

Gum arabic is the most widely encountered gum in museum artefacts. It can be obtained from different *Acacia* species, the most important being *A. senegal* and *A. seyal*. In the art technical literature the selective use of gums from specific Acacia species is suggested but to our knowledge it has never been analytically confirmed. In this study a variety of botanical reference samples of known provenance have been collected and studied both by MALDI-MS and MS/MS analysis in order to develop a strategy for their discrimination.

Results indicate that *A. senegal* and *A. seyal* can be distinguished from the presence of specific oligosaccharides and MALDI-MS/MS analysis allowed determination of the exact composition of the most intense ions observed in the mass spectrum of *A. seyal* gum. In addition, other *Acacia* species showed distinctive and characteristic MS fingerprints. This analytical strategy has been used in the present work to elucidate the nature of organic materials in objects in the collections of the Art Institute of Chicago and the Metropolitan Museum of Art ranging from ancient Egypt to the 20th century, supplementing information gained by more established techniques such as Fourier transform infrared (FTIR) spectroscopy and pyrolysis gas chromatography mass spectrometry (Py-GCMS).

Continuing research will lead to a library of MALDI mass fingerprints that can be shared among the MaSC and cultural heritage research communities, in order to improve differentiation and facilitate reliable identification of plant gums. The ability to discriminate gums from different Acacia species is potentially valuable to answer questions of trade and provenance in the use of gums in ancient and modern artefacts.

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The characterisation and identification of shellac resin by liquid chromatography techniques coupled with electron spray ionisation and mass spectrometry

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Shellac resin is a complex mixture of different mono- and polyesters of hydroxyaliphatic acids, i.e.; 9,10,16-trihydroxyhexadecanoic (aleuritic acid) and 6-hydroxytetradecanoic acids (butolic acid), and sesquiterpenoid acids, i.e.; jalaric and laccijalaric acids [1].

Gas chromatography mass spectrometry (GC-MS) techniques have been widely applied both to the characterisation and identification of shellac resin in art samples, and to the study of their degradation [2-6]. Due to the macromolecular nature of shellac, GC-MS requires chemical or thermal pre-treatment (pyrolysis), in order to obtain the constituting shellac acids suitable for GC analysis. As a result, information on the macromolecular composition of the resin is inevitably lost.

High pressure liquid chromatography mass spectrometry (HPLC-MS) is a powerful state-of-the-art technique suitable for the analysis of large and polar molecules. A minimal sample pre-treatment is sometimes required. In this work electron spray ionisation (ESI) in negative mode coupled with quadrupole-time of flight (Q-ToF) detection techniques were used to characterise some samples of shellac resin, with the aim of obtaining information on the polyester components of the resin.

Flow injection analysis (FIA) revealed the distribution of the shellac components. Eight groups of compounds with increasing masses were detected and assigned to free acids, esters and polyesters with up to eight units. HPLC enabled the compounds to be chromatographically separated and identified by the measurement of their accurate molecular masses and their tandem mass (MS/MS) spectra. In some cases, highly detailed information about the ester linkages was provided by the MS/MS spectra, enabling the different isomers to be distinguished. Oxidation products were also identified in the samples and differences were observed in terms of hydrolysis and oxidation.

The techniques were then applied to two historic shellac samples (early 19th century) from the Salvemini collection (Florence, Italy). The results revealed that the macromolecular components are significantly affected by ageing, mainly in terms of hydrolysis of ester bonds.

Finally, this work enabled the identification of some shellac components in archaeological samples taken from a polychrome Hellenistic terracotta oinochoe from the British Museum's collection. Analyses by HPLC-ESI-Q-ToF were initially performed to investigate the pink colourant used in mixture with Egyptian blue to obtain a purple pigment present on the surface of the figurine. It is generally accepted that these pink colourants are derived from *Rubiaceae* plant sources, to form madder lakes [7]. However, recent reports have shown that insect sources, namely Armenian cochineal (*Porphyrophora hamelii* Brandt), were also used in mixtures with madder [8]. Molecular markers for madder (purpurin, pseudopurpurin, xanthopurpurin, munjistin and rubiadin) and for cochineal (carminic, kermesic and flavokermesic acids) were identified, as well as laccaic acid A, erythrolaccin and deoxyerythrolaccin, all considered molecular markers for lac dye. In addition to these dye molecules, the main constituting acids of shellac (jalaric, laccijalaric, aleuritic and butolic acids) were detected together with three main esters. Initial thoughts centered on the presence of these compounds as indicative of the use of shellac as a past conservation treatment for consolidation of the surface. However, the lack of shellac polyester components compared to the data obtained from the reference and aged samples was more consistent with the effects of hydrolysis, as might be produced by alkaline extraction of a source of lac (sticklac) to produce a lake pigment. Although further studies are required, this evidence may point to the first known use of lac dye as a colorant in a lake pigment from Antiquity.

Keywords

Shellac, flow injection, HPLC-ESI-Q-ToF, MS/MS spectra, lac dye, Hellenistic polychromy

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Xanthene dyes: a study on fragmentation patterns and degradation pathways in textiles

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Artist's approach towards painting radically changed with the introduction of ready-to-use synthetic tube colours. Starting from the second half of the 19th century, hundreds of synthetic organic pigments (SOPs) started to be produced quickly replacing the traditional natural organic dyes due to their cheapness, great range of bright nuances and wide availability [1]. Xanthene dyes and pigments are aromatic compounds derived from the molecule of 9H-xanthene and characterized by intense fluorescence and photosensitivity. Rhodamine B and Eosin Y are two molecules belonging to this class. The former was firstly synthesized by Cérésole in 1887 [2] and widely exploited ever since to dye in violet. In fact, the addition of substituents gives rise to a complete class of red and violet pigments [3]. The latter was synthesized by Caro in 1873 [4], and was usually precipitated with lead and aluminum salts and employed for brilliant pink-scarlet coloration. Both colours were also used as dyes in textile industry.

This work aims at investigating the degradation pathways of Rhodamine B and Eosin Y due to the aging and fading of the dyes within textile matrices. The study of the degradation mechanism and mass fragmentation of the starting molecules, their intermediates and end products have been carried out thanks to the analysis of artificially aged reference wool yarns, provided by the IPERION network [5]. Based on the various products and their relative amount detected in samples subjected to increasing irradiation times, the kinetics of degradation of the dyes has been also outlined.

An ultra-sensitive analytical method based on HPLC-DAD-FD and LC-ESI-Q-ToF techniques was developed and optimized. In order to select the best chromatographic conditions suitable for both DAD and mass spectrometric detection, different chromatographic columns have been tested revealing that the novel C18 solid silica core column (Poroshell 120 EC-C18) is the best choice compared to the traditional TC-C18 and Poroshell 120 SB.

Tandem mass and UV-Vis spectra allowed us to demonstrate that Rhodamine B incurs in subsequent functional groups losses and in a blue shift of the maximum absorbance of the degradation products. Interestingly, the ageing pathway has been confirmed by the analysis of a restored Florentine velvet cope dated to XV century and belonging to the Musée des Tissus de Lyon (France).

With regard to eosin, a radical degradation pathway has been hypothesized. The mechanism implies the formation of yellow-coloured intermediates, leading to a final stable, not coloured compound. The evidences have been supported by previous data collected on aged paint model samples.

The analytical method optimized allowed us to characterize Rhodamine B and Eosin Y and their degradation pathways. The present work demonstrated that molecules belonging to the same chemical class of Xanthenes incur in completely different ageing patterns leading to specific end products. This approach was successfully adopted to study β-naphtols, mono-azo and tryarilcarbonium organic pigments and dyes.

Keywords

Synthetic Organic Pigments, Degradation, HPLC-DAD-FD, LC-ESI-Q-ToF, Poroshell C18 column

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Mass spectrometry to investigate molecular degradation phenomena of modern oil paintings

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This study is aimed at advancing our knowledge on the molecular causes and mechanisms related to the condition of unvarnished modern oil paintings.

Until the 18th century, oil paints were made in artists' ateliers: raw materials were purchased and paints were prepared according to traditional and sometimes secret recipes. The industrial revolution brought technological changes that affected the production and quality of artists' materials and consequently the deterioration of painting made using them. In the twentieth century synthetic polymers became available as paint binders, however artists continued to use oil paints that were by this time manufactured and supplied in tubes. Manufacturers' paint formulations also developed to include a range of formulations incorporating a range of pigments and oil binders together with other additives to produce paint with consistent drying time and rheology. These paints included traditional drying oils, new drying and semi-drying oils and industrial oleo-chemicals such as hydrogenate or partially transterified drying oils. Metallic salts, metal soaps, and a variety of dispersion agents, plasticizers, fillers, surfactants, free fatty acids, waxes, proteins and other materials could also be added to paint formulations to achieve and modulate different properties such as viscosity, drying rate, colour, production stability, rheology, working properties and shelf-life, which became important to manufacturers of artists' oil paints within a highly competitive market.

Modern paintings made in oil media present conservation problems due to physical and chemical degradation of the paint. This includes colour change, formation of medium skins on paint surfaces, efflorescence, protrusions, dripping paint and paint delamination. During surface cleaning by conservators, these paintings can also exhibit water- and solvent-sensitivity.

The present study aims to provide further information about the organic composition of modern oil paint samples. A new analytical procedure employing both GC/MS and LC/MS has been developed that allows the characterization of the molecular composition of oil fraction of paint samples including the degree of hydrolysis, degree of saponification and crosslinking of the oil. These procedures were then used to investigate the oil binders of a range of reference materials, some paints sampled fresh from the tube and as prepared films that have been naturally aged for 10 years and artificially aged. Thermoanalytical techniques were also used on simplified model systems to aid data interpretation and to provide information on other aspects of the paint.

Keywords

GC/MS, LC/MS, free fatty acids, metal soaps, unvarnished modern oil paintings

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Modern paints : archives versus analyses

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Archives such as photography, letters, invoices, interviews reveal sometimes the name of the materials used by the artists and this documentation could be consider as precious source of information for the conservation of modern and contemporary artworks. Unfortunately this cited name is sometimes only a trademark without any relation with the chemical composition of the paint or of the varnish. Then begins a long investigation with manufacturers to collect more information on the chemical composition of their products.

These contacts are often fruitless for different reasons: the manufacturers fail to respond to the information request, the product and its data sheet are no longer available, the documentation contains too vague information or the mentioned trademark corresponds to a variety of products.

The analyses of micro-samples from artworks are the only solution to have access to the chemical composition of the materials. For the characterization of the paint binder, the Py-GCMS is the most powerful analytical technique, especially when the sample is unique: no preparation is required and with the same pyrolysis temperature and chromatography parameters, as a screening method, it’s possible to identify many kind of paints: oils, alkyds, vinyls, acrylics, epoxy, urethane etc , some organic pigments and to detect additives in most cases present in trace quantities.

The results improve the knowledge of artist’s practices but more significantly could inform us on the state of preservation of the artwork and they are important tools for the conservation treatments. The following case studies demonstrate sometimes the necessity of analyses to modulate what it can be read, hear or see.

In this way, a photography showing Keith Haring preparing the paint for the mural at the Hopital Necker in Paris indicates the use of a paint named Pantex 1300®, a product for interior and exterior decoration. This paint is no longer produced in France and it’s possible to read on the can "acrylic". The analyses, from mural samples and from old Pantex 1300 cans, allow today to establish that it was a vinyl paint made with a PVAc copolymerised with a vinyl ester of fatty acid.

For the conservation of the painting le bain turc (1973) by Phlippe Artias [1], his wife has been interviewed. She explained that her husband begun to use vinyl paint in the 1970’s and acrylic at the ends of this decade. She specified that he used Caparol®, a vinyl dispersion for decorative purposes. Analyses confirmed the presence of this vinyl paints but revealed that some colours are made with an acrylic paint: it seems that Artias experimented acrylic sooner. The copolymer identified, a styrene-acrylic, suggests that it refers also to a decorative paint.

In the same manner, the soon of Jurg Kreienbuhl explained that his father made his paints by mixing pigments to a product called Elotex 55 TW 25®. The technical data sheet detailed that it’s a homopolymer dispersion with two external plasticizers : dibutyle phtalate and tri-o-cresyl phosphate. The results obtained from samples of the painting Secteur d’Argenteuil(1965) [2], confirm the use of Elotex 55 TW 25® as binder for coloured layers but also for the varnish. They indicate that fifty years later both plasticizers are still presents in the binder, so the paint is still flexible.

Thank to the analyses of micro-samples of various colors from Le Grand serpent (1976) de Bernard Bazille,[3], a concomitant use of acrylic and vinyl paints also has been demonstrated while the artist mentioned to the curator only the use of Flashe paints. For the yellow color, in the same analyse, the PVAc binder and the azo pigment (PY3) could be identified. By comparison with our older (1980's) Flashe paints references conserved at the C2RMF[4] it's possible to specify that the hue of the yellow sampled is probably Lemon Yellow and not Senegal (PY1+PY3) or Gold (PY1) yellow.

In all these examples, it is evident that collect reference materials allows us to have more accurate information that the ones available on archives (labels on tubes, catalogs or color chart). As a result, a series of paint samples (artist grade, household and industrial paints) from 1985 to nowadays is evolvingat the C2RMF (around 500 references) available in various amount from small samples (microscope slide) to original cans or tubes.

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A methodological approach for the investigation of modern inks

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Analysis of inks may be important for the investigation of modern art, design and architectural sketches with the purpose of establishing the optimal conservation conditions and/or restoration treatments [1-4]. Moreover, in the specific case of graffiti, the analysis of marker pen inks is mandatory for the set-up and application of removal methods such as chemical, bio- and laser cleaning [5].

Here, the investigation of different classes of modern inks is illustrated. Both permanent and washable inks, often referred to as marker pen and felt-tip pen inks, respectively, were analysed with a multi-technique approach: (pyrolysis-) gas chromatography-mass spectrometry (Py-GC-MS), Fourier transform infrared (FT-IR) spectroscopy, thin layer chromatography (TLC), µ-Raman spectroscopy, surface enhanced Raman spectroscopy (SERS) and spectrophotometry. Since permanent and washable inks have dissimilar compositions, different analytical pathways were used. In particular, Py-GC-MS provided highly detailed information on binders and additives, and in some cases revealed to be essential for the identification of the pigments and dyes [6]. A series of synthetic dye's and pigment's standards (triarylmethanes, xanthenes, azo-dyes, indigoids, phthalocyanines) was subjected to analytical pyrolysis to obtain useful data for comparison [7].

Marker and felt-tip pens of various commercial brands and colours were selected, among which pens used by contemporary artists and architects (Fig. 1).

The marker pens revealed to contain a wide range of binders comprising not only alkyd, and styrene-acrylic polymers, but also phenolic, ketone and polyvinylacetate resins. In the felt-tip pens styrene-acrylic resins or natural gums were found. Phthalocyanine, dioxazine and azo pigments were detected in the marker pens and some felt-tip pens, whereas the majority of the washable inks contain mixtures of dyes such as triarylmethanes, xanthenes, azines, indigoids and azo-dyes.

Preliminary data on the assessment of fading of a selection of modern inks in relationship to their chemical composition (pigments vs dyes; styrene acrylic binder vs plant gum) are also presented.

Figure 1: *Somme*, Anne Flore Cabanis, felt-tip pen ink on paper.

Keywords
Ink, felt-tip pen, marker pen, TLC, GC-MS, pyrolysis, spectroscopy

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A New Approach to an Old Problem: Evaluating Pollutant Off-Gassing from Museum Construction Materials Using Evolved Gas Analysis with GC-MS

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The rapid and reliable vetting of museum construction materials for potential pollution off-gassing remains a grand challenge of preventive conservation. The preservation of cultural heritage in museums requires that only non-corrosive, non-polluting materials be used in proximity to artwork. Materials suitability testing in museums has historically used subjective microchemical and/or accelerated corrosion methods to determine the hazardous off-gassing potential of construction materials. A faster and more reliable approach to materials testing has been a goal of museum professionals for more than a decade. This lecture will summarize the results of a two year NEH-funded research project to develop further an alternative sampling strategy based on evolved gas analysis (EGA) to monitor volatile organic compounds (VOCs) emitted from materials [1]. The goal of this work is to link the identity (and possibly the quantity) of VOCs generated by a material under accelerated emission conditions to visual evidence of material suitability provided by Oddy tests and microchemical reactions. The results generated in this project indicate that EGA-GC-MS can provide a fast and comprehensive assessment of pollution off-gassing of a material prior to - or sometimes in lieu of - a 28 day Oddy test (Figure 1).

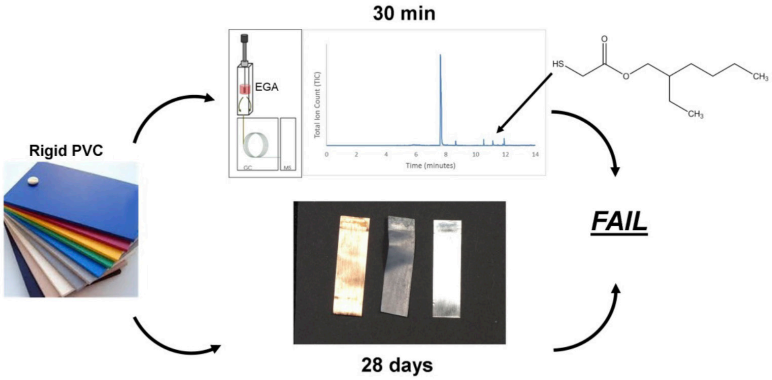

Figure 1: EGA-GC-MS offers a rapid route for screening construction materials prior to or perhaps in lieu of a traditional month long Oddy Test.

For this research, a group of 35 materials commonly used in museums was assembled for in-depth study. Materials included various plastics, fabrics, woods, adhesives, and sealants. The EGA analysis of these materials was conducted alongside traditional chromatographic analysis techniques for volatiles such as static headspace (HS) and solid-phase microextraction (SPME). EGA compares well to these techniques with the ability to concentrate VOCs using cryotrapping while avoiding the selectivity of an intermediate adsorbent phase. The EGA technique was optimized by varying the thermal extraction temperature and time, as well as the sample size and the surface area, which could be increased through cryomilling. The final approach uses a few mg of material with a 30 second thermal extraction at 115ºC and a short chromatographic run for a total analysis time of 30 minutes.

Relying on published data and general chemical intuition, the EGA pollution profiles for each material were used to predict the result of an Oddy test. The same materials were then repeatedly analyzed using the traditional Oddy test in order to generate a visual indication of the potential pollutants' effects on artwork surrogates. Fig. 2 presents the correlation between the predicted result (red = Unsuitable, yellow = Temporary, green = Pass) versus the average result of the actual Oddy tests (histogram height) for the plastics in the sample set. A good correlation exists between the 30 min instrumental assessment and the 28 day corrosion test, with only a few mistaken predictions. It is anticipated that misclassifications will be reduced as more is learned about the corrosive effects, particularly adverse effect levels, of the numerous VOCs identified in these studies.

Other experiments explored the use of EGA-GC-MS to quantify pollutants emitted by construction materials as a means of selecting the best performer among a group of similar materials and to estimate the adverse effect level for particular pollutants. The performance of rigid PVC board will be used as a case study of a pollutant that until now has gone unrecognized in our field. In conclusion, the EGA sampling approach for assessing material suitability for museum use serves as an extremely rapid, comprehensive, reliable, and potentially quantitative method for overcoming many of the shortcomings of traditional Oddy testing.

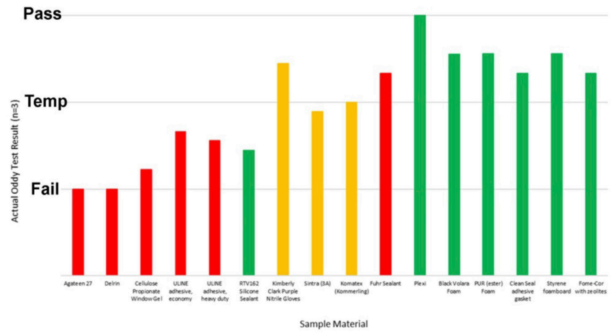

Figure 2: Correlation of material suitability determined by EGA (colors) and Oddy Test result.

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Mass spectrometry in the study of archaeological materials - selected case studies

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Archaeological artefacts usually yield very complex samples for analysis. In the making of the artefacts, an array of materials is used alongside ancient and sometimes unknown recipes and manufacture technologies. Moreover, their chemical analysis is generally further complicated by the chemical changes induced by the ageing of the materials. The questions that need to be answered vary depending on the object to be studied, but are usually related either with the history and the manufacture of the object (where and how it was produced, how was it used throughout times, or about the decay processes of their constituent materials (crucial in terms of their conservation). Mass spectrometry can be a powerful technique to uncover the secrets behind the archaeological objects. Both the organic and inorganic materials can be analyzed using mass spectrometry techniques.

In this presentation, two case studies will be presented to show the wide range of questions and analytical methodologies need to address them. The identification of the previous contents of archaeological ceramics is usually done using GC-MS, and this will be exemplified in the identification of the illuminant used in Roman oil lamps from two archaeological sites from the south of Portugal [1]. The study of paleodiets is done throughout the analysis of the stable isotopic ratios for carbon and nitrogen of collagen extracted from osteological remains. These analyses are done by isotopic ratio mass spectrometry coupled with elemental analyser (EA-IRMS), and this will be exemplified with the study of the paleodiet of the Late Antiquity population of Monte da Cegonha (Vidigueira, Beja) [2].

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Assessing by Py-GC/MS the decontamination of archaeological bones cleaned using supercritical fluids prior to radiocarbon dating

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Radiocarbon dating is the principal method for building chronologies in archaeology. However, for radiocarbon results to be accurate, samples must be free of contamination to a minimal level. This is even more crucial when dating material approaching the radiocarbon age limit of ~50,000 BP, because trace amounts of contamination at this age will drastically affect the accuracy of the results. Contamination can originate from a wide range of sources in the post-depositional environment but may also occur during excavation and post excavation activities (i.e. with the application of conservation materials) or during laboratory handling [1]. Efficient procedures to remove these contaminants are therefore crucial in the process of radiocarbon dating. This work describes the results obtained in developing innovative sample pretreatments that can be as effective as routine pretreatments in the radiocarbon dating of bone samples. In addition, data from novel methods based on analytical pyrolysis for the quality control of the cleaning procedure are also reported.

We compared two different pre-treatments for the decontamination of archaeological bones (Figure 1). The first treatment, routinely used in radiocarbon laboratories, includes the use of organic solvents for the removal of consolidants. The second one investigated here is based on the use of supercritical fluids which present unique solvation properties. The two treatments were performed on the same set of samples including reference samples intentionally contaminated with conservation materials such as Paraloid B72, Butvar B98 and polyvinyl acetate as well as archaeological bone samples from a Palaeolithic site.

In order to test the effectiveness of the cleaning procedures and to compare the two different pre-treatments, the chemical composition of the samples at each stage of the two procedures was checked using analytical pyrolysis based techniques: EGA-MS (Evolved Gas Analysis -Mass Spectrometry) and Py-GC/MS (Pyrolysis - Gas Chromatography coupled with Mass Spectrometry). By monitoring the intensity of the pyrolysis product signals before and after the different steps, it was possible to compare the effectiveness of the two pre-treatments used for the decontamination of archaeological samples. These samples, prepared with the two protocols, were also dated by Accelerator Mass Spectrometry (AMS).

All the results of this study show that SFE is an efficient alternative method to remove contaminants such as conservation materials from bone samples with a minimum of handling and could be used routinely in radiocarbon dating laboratories. This work also demonstrates that pyrolysis is a very efficient method to assess the decontamination of bone samples.

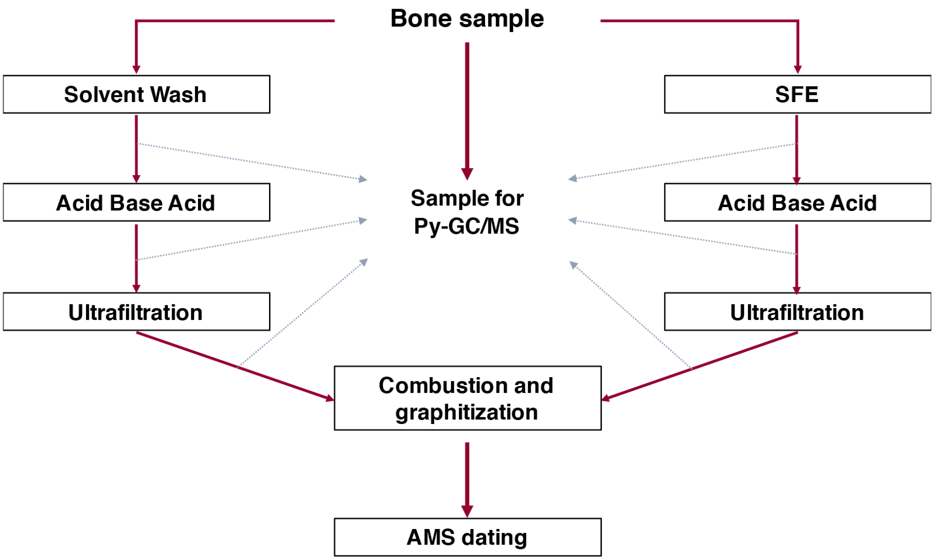

Figure 1: Two pretreatment procedures applied on bone samples and sampling strategy for pyrolysis analyses

Keywords

Archaeological bones, radiocarbon dating, supercritical fluids, pyrolysis, mass spectrometry

Acknowledgements

This work has been financially supported by the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° [324139] "PalaeoChron" awarded to Professor Tom Higham.

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The application of LA-ICP-MS in the fingerprinting of raw materials: the examples of gold coinages and prehistoric ceramics

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To better understand economic and paleo-economic problematics based on the exchanges of objects, is it necessary to determine the links between them and identify the origins of the raw materials. This paper aims to present methodological approaches by LA-ICP-MS of the fingerprinting of raw materials in the field of the arts of fire: the analysis by the depth profile of gold coinage in the AUREUS program, and the sourcing of raw material from ceramics, by the analysis of the mineral inclusions.

The AUREUS program directed by Pr. Arnaud Suspène aims to understand the establishment of the first unitary gold coinage of the occidental Europe: the Roman gold coinage. This multidisciplinary program, joining numismatists and analysts will allow us to establish the evolution of the gold coinage between the end of the IVth century BC and the Ist century AD. AUREUS will provide information about the supply of gold; the control of stock. Almost 1000 coins from the main gold coinage area (Africa, Greece, Italy, Celtic world, Spain) and pieces of jewellery from French patrimonial collections will be analysed to determine the gold fingerprint used by the artisans. The method [1] used is based on several micro sampling by DPA-LA-ICP-MS (Depth Profile Analysis) at the IRAMAT-CEB laboratory (UMR 5060, IRAMAT-CEB, CNRS/University of Orléans). In this way, it is possible to determine the variations of the concentrations of the major, minor and trace elements from the surface of the coin to a depth ranging from tens of micrometres to more than 1mm.

The second approach concerns the problematic of the raw materials sourcing of ceramics. The traditional analytical methods used for determining the origin of archaeological ceramics (such as petrographic study in thin sections, the global chemistry...) attain their limits for differentiating bodies of similar composition. This happened especially when clay derive from the alteration of plutonic rocks. This method is based on the chemical analysis of mineral inclusions in ceramic bodies using a LA-ICP-MS [2, 3]. It allow us to identify the geological origin of the clay used. By scanning the whole inclusions of a given nature contained in ceramics, made from clay derived from the alteration of rocks, the raw material used to shape the pottery can be linked to the original mother-rock. Thus, it is possible to establish a link between a magmatic rock formation and ceramics in order to propose a circumscribed production area. We have developed this approach at the Archéosciences laboratory (UMR 6566, CReAAH, CNRS/university of Rennes 1 & 2) for several minerals, such as biotite, amphibole and opaque minerals.

This paper will be the occasion to present the application and the contributions of LA-ICP-MS analysis on heritage artefact research, through several specific examples such as the coinage (AUREUS program) and the ceramics [4]. This makes it possible to underline the decisive contribution of these analyses, and to highlight important methodological developments that are under way thanks to the LA-ICP-MS. Exchanges with other specialists in this type of analysis could be enriching for the continuation of work in progress.

Keywords

LA-ICP-MS, Depth profile analysis, Gold coinage, Ceramics

Acknowledgements

The AUREUS program has been financially supported by the Centre-Val de Loire region (France) in the framework of the calls for Regional Projects of Academic Initiative (AUREUS program) and is developed at the IRAMAT-CEB laboratory (UMR 5060, IRAMAT-CEB, CNRS/ university of Orléans). The research on the analysis of mineral inclusions in ceramics was developed in the scope of a PhD research [4] financially supported by the Bretagne region at the Archéosciences laboratory (UMR 6566, CReAAH, CNRS/university of Rennes 1 & 2).

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Slow Pyrolysis: Py-GC-MS Analysis Using a Lower Pyrolysis Temperature and a Slower Heating Rate

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Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) is an invaluable tool in the analysis of cultural materials, particularly those containing complex polymerised components, whether natural or synthetic in origin. This presentation will show how a relatively inexpensive accessory can be utilised with Agilent GC-MS systems to provide laboratories with the ability to perform Py-GC-MS analyses. Examples of both natural and synthetic reference materials, as well as case studies, will be presented to demonstrate this adapted analytical technique. This will include the analysis of the round robin sample that was produced and distributed prior to the 2007 MaSC meeting in Philadelphia [1].

There are several commercial pyrolysers available for sample introduction into GC-MS systems. These include flash filament-, furnace-, and Curie-point types, where the sample is instantaneously pyrolysed, with or without reagents under a flow of inert carrier gas. At the Canadian Conservation Institute (CCI) from 2008 until 2012, a CDS 5000 Pyroprobe® (filament type) pyrolyser was used with an Agilent instrument to perform Py-GC-MS on synthetic modern materials and amber. However, since 2012, all pyrolysis has been carried out using an Agilent thermal separation probe (TSP) accessory for sample introduction. The TSP is largely marketed and utilised as a thermal desorption device, and published applications generally use inlet temperatures below 300 °C. However, the TSP is seated in a multi-mode inlet that is capable both of cryogenic cooling and of heating to 450 °C. Instantaneous heating of the inlet is not possible, but it is programmable for rates of up to 900 °C/minute. One clear advantage of the technique is sample size. Analysis can be made in splitless mode using just one or two micrograms of sample. At a time when much effort is being expended to develop non-destructive and micro-destructive analyses, this is an important benefit.

At the CCI, the probe was first tested as a pyrolyser for Class Id amber, a Canadian amber that contains succinic acid and has a polymeric structure based on ozic acid and ozol. The results were promising, producing peaks for succinic acid and monomer pyrolysates that were comparable to those achieved using the Pyroprobe®. However, additional peaks, identified as ozol pyrolysates crosslinked with succinic acid, eluted late in the run and were not observed using the traditional flash pyrolysis method. Similar peaks were also identified for succinic acid-crosslinked communol pyrolysates in Baltic amber [2]. Utilising pyrolysis with a slower heating rate, lower final temperature, and longer isothermal dwell time allowed larger fragments of the amber polymers to remain intact and provided a more accurate depiction of how the macromolecules were constructed. Since this initial research, self-crosslinking in Class Ib and Class Ic amber has been identified, also using TSP Py-GC-MS [3,4].

As traditional Py-GC-MS analyses of synthetic polymers are often optimised at much higher pyrolysis temperatures than the TSP can obtain, testing the effectiveness of the TSP for the analysis of modern materials was the next phase in the development of the methodology. Testing has included many synthetic polymers, including acrylics, vinyls, urethanes, epoxies, rubbers and ketones. In general, the components identified using TSP Py-GC-MS were found to be consistent with those expected from flash pyrolysis at higher temperatures. The same holds true for natural polymers and macromolecules such as proteins, carbohydrates, and natural fibres. In some cases, similar to what was observed for amber, peaks of greater relative abundance are produced for some larger polymer fragments than were obtained for the same sample using the flash pyrolysis. This phenomenon is shown in Figure 1, for a reference sample of Winsor & Newton acrylic gloss varnish, based on a copolymer of styrene, methyl methacrylate, ethyl acrylate, and n-butyl acrylate.

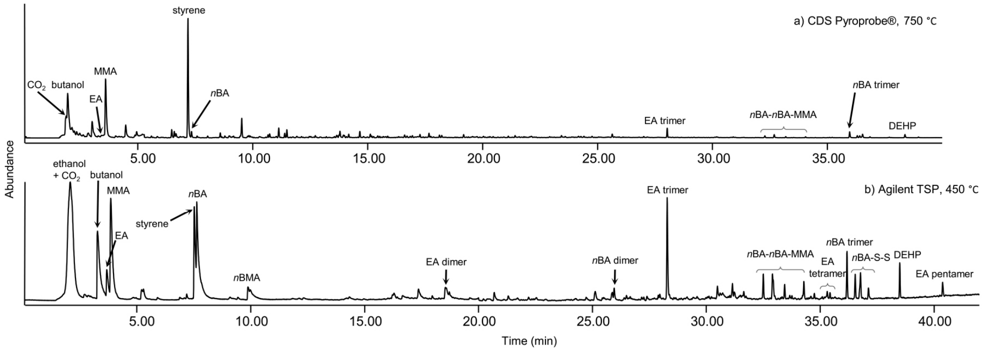

Figure 1: Total ion chromatograms of Winsor & Newton acrylic gloss varnish; no reagents. (a) Flash pyrolysis with a CDS Pyroprobe® at 750 °C, and (b) slow pyrolysis with an Agilent TSP at 450 °C.

TSP Py-GC-MS has proven to be an essential technique at the CCI. The advantages include the relatively low cost of the accessory, minimal maintenance, comparable pyrolysis results to traditional flash pyrolysis methods, small sample size and the ability to easily switch columns between the two GC inlets resulting in a single instrument that can be used for both GC-MS and Py-GC-MS. But, in addition to this, testing Py-GC-MS with a slower heating rate has shown that slow pyrolysis may provide more information about certain polymers and how they are constructed.

Keywords

Slow pyrolysis; pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS); thermal separation probe (TSP); modern materials; natural polymers

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An untargeted search for markers using AMDIS: Construction of a structured library of components present in artificially aged lacquer ingredients

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The "European Lacquer in Context" project (ELinC), studies the technological history of European lacquers. The project focuses on a number of lacquered objects from Western Europe originating mainly from the collections of the Royal Museums of Art and History (KMKG/MRAH) in Belgium, aiming to improve the understanding of the materials used and the way they were applied [1]. European lacquers are mainly complex, layered combinations of various natural materials, including resins, oils and solvents. With their diverse constitution and important impact of aging on the molecular composition, analysis can be challenging. More chromatographic markers could be useful to detect small amounts of ingredients or to differentiate between two similar ingredients. In this study, a marker database was created in a semi-automated way starting from chromatograms of different ingredients before, during and after artificial aging.

A total of 32 ingredients, frequently used in the production of European lacquer, was used in this study. 24 of them were selected for aging: colophony, spruce resin (*Picea abies*), fir resin (*Abies alba*), shellac, sticklac, buttonlac, seedlac, mastic, elemi, copaiba balsam, sandarac (as sold today), larch resin (also known as Venetian turpentine), Sumatra benzoin, Gamboge, Kauri copal, South American copal (fresh and fossile), Congo copal, Madagascar copal, Manila copal, East African copal, tung oil, boiled linseed oil and tragacanth gum. Black and transparent films of these were continuously exposed to ultraviolet light in an Atlas Weatherometer at constant relative humidity, and removed after 0-2-4-8-16-32-64 days. These films were analysed with thermally assisted hydrolysis and methylation-gas chromatography-mass spectrometry (THM-GC/MS) in full series after aging was complete [2]. In most cases only the black series were analysed to limit the scope.

Additionally, chromatograms of some materials that for practical reasons could not be artificially aged were added to the data: Zanzibar copal (4 samples), Baltic amber (3), sandarac as found in historical collections (4), historical turpentine (*Pistacia therebinthus*; 2), Strassbourg turpentine (2), oil of spike (1), Siam benzoin (4) and pine turpentine (2). Finally, also the blanks recorded during analysis of all previously described samples were added to the dataset. In total 419 chromatograms were used to compile the marker library.

Four steps were followed to obtain a structured list of markers out of the raw data:

1. Deconvolution in AMDIS

After deconvolution, a long list of mass spectra was generated. The data were calibrated using Kováts retention indices.

2. Group identical library items

After conversion to a NIST library, MSPepsearch was used to search within itself for identical mass spectra

(MF at least 600). Fine-tuning within the output was executed with a homemade script, in order to group spectra with identical mass spectra and retention index.

3. Filter to remove unwanted noise peaks
All markers occurring only once were left out, as well as markers in which the intensity of m/z 207 was at least 90% of highest peak (supposed column bleeding).

4. Construction of a new AMDIS library
Sum spectra of the remaining markers were calculated, taking into account their signal strengths. Each marker is tagged with the name of the ingredient(s) it has been found in, as well as the amount of artificial aging applied. The final result is a library of markers that can be used in AMDIS to help interpret chromatograms of historical lacquered (or varnished) objects. Targets are not chemically elucidated but possible related resins are listed.

In this presentation, the construction method of this library will be discussed. Afterwards, application will be illustrated with some examples of the analysis of real European lacquer objects.

Keywords

THM-GC/MS, AMDIS, European lacquer, target library, artificial aging, natural resins.

Acknowledgements

The authors would like to express their gratitude to Hans Beeckman (Royal Museum for Middle Africa – KMMA, Tervuren, Belgium), Viviane Leyman (Botanic Garden Meise, Meise, Belgium), Annegret Fuhrman (Hochschule für Bildende Künste, Dresden, Germany) and Ursula Baumer (Doerner Institute, Munich, Germany) for providing us with natural resins from their collections. The research leading to these results has been financially supported by the Belgian Science Policy through the contract no. BR/121/A3/ELINC within the BRAIN project "European Lacquer in Context" (ELinC).

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8th MaSC

POSTER ABSTRACTS

Study of illusionistic restoration painting of ancient pottery restored in the 19th century

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The State Hermitage Museum owns an impressive collection of ancient painted pottery. The core of the collection had been formed to 1862, it consisted of the vases from the collections of Giuseppe Antonio Pizzati, Alexandra Laval and Giovanni Pietro Campana. Later the Hermitage collection of ancient classical pottery was enriched with some smaller collections purchased from different owners and with big number of the vases and fragments from the excavations in South Russia.

Being found during archaeological excavations many vases have been extracted from graves or houses in broken condition, thus it is logical that they were assembled from pieces, missing parts were made of some proper materials and some badly preserved parts of the vase-painting were covered by restoration painting imitating the original one both because of practical and esthetic reasons. Both applied materials and esthetic changed with time passing: in the first half of the 19th century the prevailing concept was ‘illusionistic’ restoration, while in the second half of the 19th century it became more fashionable to conserve the vases without overpaint and modern additions.

The studies on the history of collecting allowed us to trace back the way of some vases, which are now in the Hermitage Museum and to make guesses concerning the place of their find and restoration. The studies of the publications of the 19th century and archive documents go hand in hand with the studies of the vases by different kinds of analytical techniques, including PY-GC/MS, PLM and SEM-EDS. Our results allowed us to collect information concerning with the organic and inorganic materials, applied for the illusionistic restoration of the Hermitage vases, in some cases it allowed even to guess concerning more or less precise chronology of the restoration.

Investigations by means of optical and scanning electron microscopy, energy dispersive spectroscopy and PY-GC/MS helped to identify both the stratigraphy and the composition of the studied restoration coating.

Data from thermally assisted hydrolysis and methylation (THM-PY-GC/MS) point to oil and resin binding media, which were testified by the presence of pyrolysis shellac markers, by the azelaic/palmitic acid (A/P) values and by pine resin biomarkers.

Scientific upcycling – Developing a SPME GC/MS methodology using anoxic chambers, for the monitoring of VOCs emitted from polymeric artworks

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Modern and contemporary objects of art and design are commonly constructed, either partially or exclusively, from polymeric materials. As these objects have grown in cultural significance they have entered museum collections, however their preservation within collections has not been without issue. Currently, there are few options for in-situ decay monitoring of polymeric materials.

My poster will report on the development of a non-destructive and non-invasive solid phase micro extraction gas chromatography mass spectrometry (SPME-GC/MS) methodology for the analysis of polymer objects under laboratory conditions. Monitoring the types of volatile organic compounds (VOCs) emitted from an object or present in its vicinity is a novel way to identify compositional or decay markers from the polymer.

The impetus for developing this methodology originates with limitations identified during previous analysis which aimed to 'upscale' the methodology proposed by Curran *et al.* (2016) and move from the destructive analysis of VOC emissions for polymer samples to a non-destructive approach, analyzing whole objects. These limitations originated from the use of Tedlar® bags; a number of VOCs, known to be emitted from the bag, cross-over with VOCs of interest to our research. There is also a limitation in pre-concentration time-length due to the permeability of the bag itself.

Samples of naturally aged cellulose acetate (CA) will be used to test the length of time needed for pre-concentration before SPME analysis. CA has been chosen due to its known VOC profile, containing acetic acid and the plasticizers diethyl phthalate and dimethyl phthalate, and its high emission rate. Cleaning regimes will be investigated in order to develop fast and efficient cleaning protocols between sample analysis. Oven heating to drive off VOCs along with solvent cleaning will be investigated. Finally, SPME exposure time inside the chamber will be investigated to determine the time required for equilibration of the fibre.

A successful methodology will be one where reliable capture of relevant VOCs from a sample, within a useable timeframe, is achieved, and cleaning between samples is efficient and relatively easy.

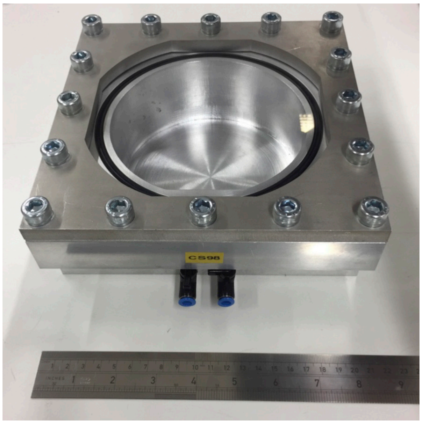

Figure 1: Anoxic chamber developed by Tate, London. This will be examined for its suitability for VOC capture from polymer objects. The chambers measure 21 cm by 21 cm overall with a useable volume of approx. 923 cm^3.

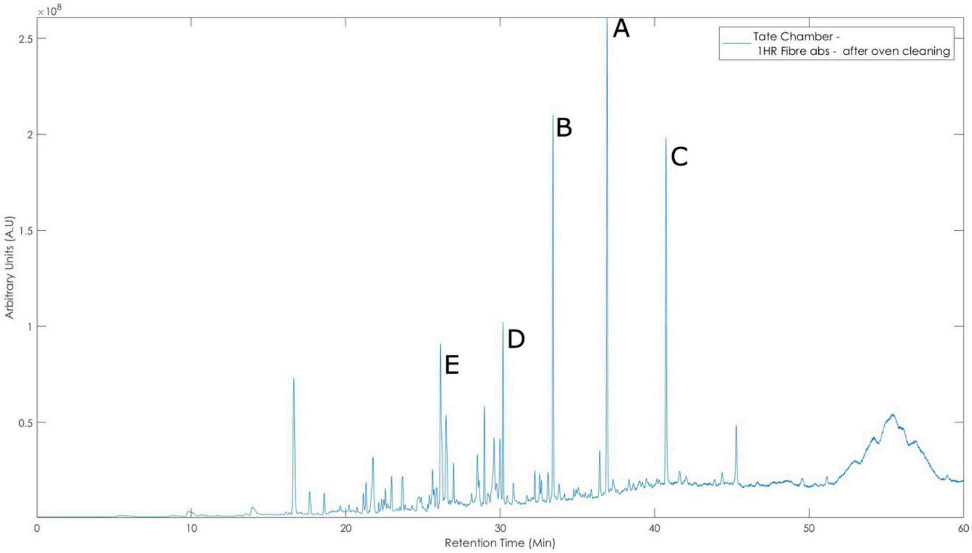

Figure 2: Initial chromatogram of the background from chamber after oven heating to drive off VOC's. VOCs found within the chambers (from o-rings, inlet valves, etc.) will be identified, taking particular note of any crossover with VOCs of specific interest to key degradation signs. Peaks relating to: *A* – Tetradecane, *B* – Trideccane, *C* – Pentadecane, *D* – Dodecane, *E* – 2-Ethyl-1-Hexanol.

Acknowledgements

This work has been financially supported by the European Union's Horizon 2020 project Nanorestart.

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Comparative study of sample preparation methods for tryptic peptide analysis

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In the last decade the analysis of tryptic peptides has become a mainstream analytical technique for the characterisation of proteins in art and archaeology. This usually achieved by either matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) or liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Although the technique is borrowed from proteomics, these existing procedures could not be simply copied: in age-old objects, the proteins that survived the ravages of time are incorporated in complex matrices, preventing and suppressing trypsin activity. For these reasons, each laboratory has independently implemented its own procedures for the sample preparation [1].

In this preliminary study a limited selection of the published and unpublished sample preparation procedures for proteinaceous paint samples were critically evaluated and compared. The procedures were dissected into individual steps and the influence of each step was examined. The influence was evaluated not only based on the quality of the results, expressed in protein scores, protein coverage, number of non-identical peptides or number of matched sequences (figure 1), but also on practical and economical parameters such as cost and time.

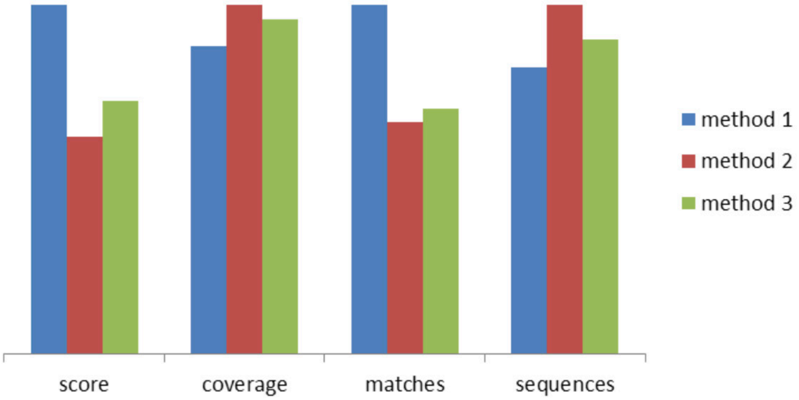

Figure 1: Comparison of three sample preparation methods on a fresh paint sample with rabbit skin glue, showing significant differences in protein scores, protein coverage, number of matched spectra and number of non-identical peptide sequences for collagen type 1 alpha 1.

All variants of the sample preparation procedures were evaluated on a small set of fresh and artificially aged paint samples. Herein, the most common proteinaceous paint binders, animal glue, egg white, egg yolk and milk casein are included: analysis shows that the matrix has a significant influence on the results of the tested sample preparation methods. All measurements were done with the same state of the art LC-MS/MS instrument: a nano-HPLC coupled with electrospray ionisation to an ion mobility spectroscopy – time of flight mass spectrometer (Waters Synapt G2-Si).

The aim of this ongoing study is a critical review of the various sample preparation steps, discussing their advantages, disadvantages, trade-offs and possible optimisations: guidelines for both existing and new users in optimising the sample preparation for their specific objects. This is also a call to cooperate and expand this study to include more sample preparation methods.

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Pyrolysis-gas chromatography/mass spectrometry analysis of a pair of 19th century Chinese lacquered wardrobes owned by the Philadelphia Museum of Art

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Extensive analytical studies were carried out on a pair of Qing dynasty (1644-1911) lacquer clothes wardrobes (PMA Acc# 1940-7-1,2), long considered a highlight of the Chinese Art Collection at the Philadelphia Museum of Art. The wardrobes' large size, over 9 feet (2.9 meters) in height, and their elaborate gilt application over a red and black lacquer background suggest these pieces would have belonged to an imperial household in China during the first half of the Qing dynasty (1644-1911), Figure 1. In preparation for the re-installation of the Chinese galleries at the museum, the wardrobes were brought to the Conservation Division for conservation, allowing for a technical study of both pieces. Analysis of the decorative finishes on the museum's lacquer compound wardrobes was undertaken in order to determine the geographical source of the lacquer.

Over 40 samples were taken from both wardrobes in preparation for analysis. A portion of each sample was prepared and examined as cross-sections to study the stratigraphy of the decorative surfaces; the cross-sections also were utilized for elemental analysis by scanning electron microscopy (SEM-EDS). The remaining portion of each sample was separated discretely by layer for media analysis by pyrolysis-gas chromatography mass spectrometry (Py-GCMS). Examination of the upper cabinets from both of the wardrobes reveals two campaigns of decoration (Figure 2). Each lacquer layer, from the earliest to the later layers was identified as a mixture of drying oil (likely tung oil as suggested in several layers) mixed with urushiol, based upon two of the major biomarkers: C8 acid catechol and C15 catechol. The identification of urushiol in the first and second generations is consistent with the wardrobes history of being made in China.

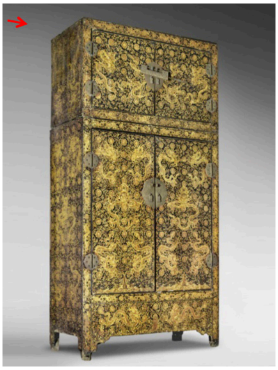

Figure 1: Chinese lacquer wardrobe from the Philadelphia Museum of Art, acc# 1940-7-1. Cross-section location notated with arrow.

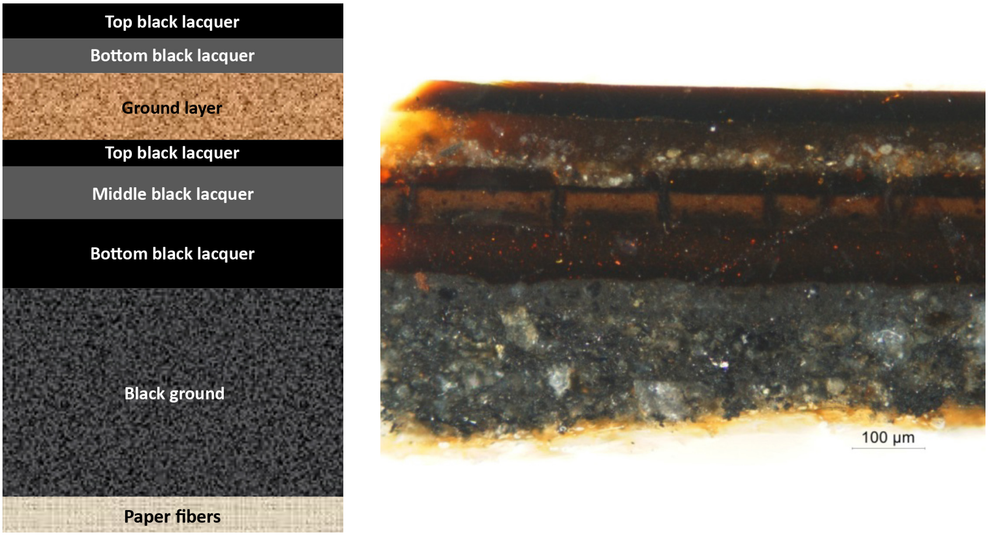

Figure 2: A cross-section taken from the exterior of the upper cabinet of the lacquer wardrobe. Two campaigns of lacquer decoration are visible in the cross-section.

Sticky situations: Identifying hafting adhesives in the South African archaeological record by mass spectrometry

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In South Africa, the use of hafting adhesives, the glue of composite technologies, is a well-established means to create reliable multi-component tools. The main organic components used in adhesives from this region are sourced from plant exudates, including resins, gums, and latexes derived from several plant families. Chemical characterisation by mass spectrometry of southern African exudates in archaeological contexts is a relatively recent field of research, providing insight into the sources of these materials and their manufacture processes [1-2]. This poster will present the analytical results obtained from gas chromatography- mass spectrometry (GC-MS) and pyrolysis-GC-MS of hafting adhesives found on implements housed in the Iziko South African Museum (Cape Town, South Africa) and Albany Museum (Grahamstown, South Africa)

The application of pyrolysis-gas chromatography mass spectrometry (py-GC-MS) provided a means to identify the breadth of organic materials present in each sample and guided downstream pre-treatment protocols. After saponification, hydrolysis and derivatization, gas chromatography mass spectrometry (GC-MS) [3] enabled for the characterization of the botanical sources of these adhesives. The chemical signatures of the archaeological material, particularly the di- and triterpenoid constituents, were compared to reference exudates from the families *Celastraceae, Euphorbiaceae*, and *Podocarpaceae*. The presence of phenolic diterpenoids and their oxidization products consistent with markers from members of the *Podocarpaceae* family, supports the current view of the longstanding use of these trees in the production of adhesives [4]. However, the appearance of triterpenoids in some material, absent in the *Podocarpaceae* family, suggests that these were not the only utilized sources.

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To be, or not to be (an acrylic)? Unraveling binding media in paintings by Carmen Herrera dated to 1948-1952

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Carmen Herrera: Lines of Sight (September 2016 - January 2017) was a partial retrospective of the Cuban-American female artist Carmen Herrera (aged 102 years) hosted at the Whitney Museum of American Art, New York. Focusing on the years 1948 to 1978, the period during which Herrera developed her signature style, the show featured more than fifty works, including paintings, three-dimensional objects, and works on paper [1]. Interestingly, binding media for all the paintings in the exhibition were listed by the artist as "acrylic" even though the earliest works date from the late 1940s to early 1950s, when Herrera was in Paris, and acrylics did not yet have widespread use. Questioned about those conflicting media entries, Herrera recalled purchasing early acrylic paints manufactured by a German company in an art supply store beneath her studio in the French capital.

In this study, a selected body of paintings by Carmen Herrera dated to 1948-1952 was analyzed with a variety of non-invasive and micro-invasive instrumental techniques to characterize the paints and ascertain whether early experimental solvent-based acrylic formulations that pre-date the 1950s might have been used. Fourier-transform infrared (FTIR) spectroscopy and pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS) with and without sample derivatization with tetramethyl ammonium hydroxide (TMAH) provided insight into the chemical composition of the binding media. In addition, complementary analyses by X-ray fluorescence (XRF) spectroscopy, Raman spectroscopy and scanning electron microscopy coupled with energy-dispersive X-ray (SEM/EDX) spectroscopy were conducted to gather information on the pigments and colorants.

Results obtained from scientific analysis show that the paints examined are composed of a relatively limited range of both traditional and modern pigments and colorants, including: calcite, gypsum, barite, and titanium white in the form of both rutile and anatase; cadmium yellows, oranges and reds; Pigment Red 83 - the synthetic counterpart of natural dye alizarin (1,2-dihydroxyanthraquinone) – precipitated onto an alumina substrate; viridian and emerald green; cerulean blue, cobalt blue, as well as Prussian blue; iron-containing earths and umber-based pigments; and bone and/or ivory black. More remarkably, a complex progression of organic binders was revealed: mixtures of modified oils, detected in paintings dated to 1948 and 1949, were gradually replaced or combined with other binding media, such as solvent-based acrylics - mostly N-butyl methacrylate -, polyvinyl acetate (PVAc) and oil-based alkyds (based on ortho-phthalic acid), in works painted during the following three years.

These results open questions about whether Herrera made a conscious choice to use a variety of paints with different material properties or, perhaps, she simply employed the same brand name of paints that changed formulation over the years. The present study clearly illustrates the importance of corroborating artists' memories with systematic materials identification by means of instrumental analysis, and not simply discounting memories that run counter to accepted doctrine.

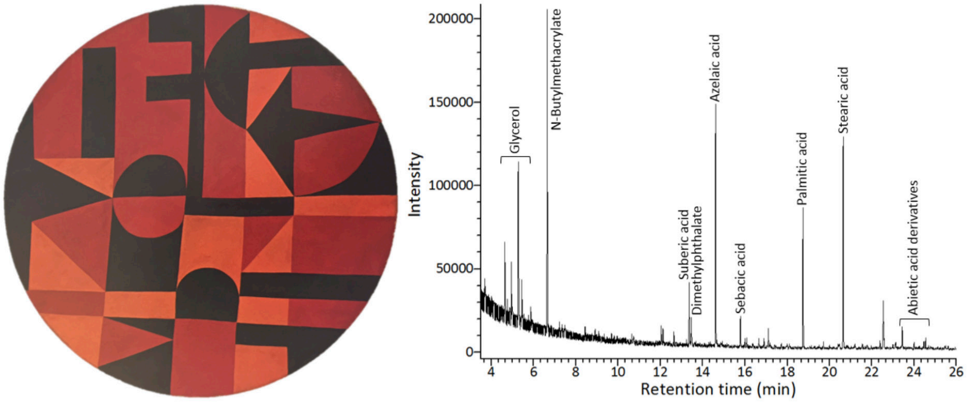

Figure 1: On the left, Carmen Herrera (born 1915), *Iberic*, 1949. Acrylic on canvas on board, diameter: 40 inches (101.6 cm). Courtesy of the artist and Lisson Gallery © Carmen Herrera. On the right, Py-GC/MS chromatogram of a black paint sample removed from the painting acquired upon derivatization with tetramethyl ammonium hydroxide (TMAH).

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