MaSC

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

MaSC 2009 Meeting

ABSTRACTS

Clore Education Centre, British Museum
London, UK

2–3 April 2009

Preface

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

Since its establishment in 2003, MaSC has grown as an international forum for interaction and discussion among scientists using chromatographic and mass spectrometric applications in conservation, preservation, cultural heritage and archaeological science studies. The Group has over 100 members, representing over 70 institutions – primarily cultural and academic organisations – in 25 countries. MaSC aims to run a combined workshop and discussion meeting about every 18 months, and the 4th Workshop and Meeting follows those held at the National Gallery of Art, Washington DC, in 2004; at the FOM Institute AMOLF and the Van Gogh Museum, Amsterdam, in 2005; and Philadelphia Museum of Art, Winterthur Museum and Agilent Technologies in 2007.

As in previous years, the 2009 Meeting again has a diverse programme reflecting the varied specialities and current research activities of MaSC members, and includes sessions on the characterisation of paints, varnishes, coatings and objects; archaeological materials; analysis of organic colourants using LC, GC and MS; and sample preparation/derivatisation and new analytical techniques in museum and preservation studies. A special session this year is linked to the theme of the GC-MS Data Treatment Workshop, held at the National Gallery, London immediately prior to the Meeting, and focuses on data processing and analysis, spectral deconvolution and interpretation and the application of chemometric methods. This session is in addition to a programmed discussion of the Workshop. We are also delighted to have a large number of poster presentations and to welcome a number of external organisations or companies to present at the meeting.

Additional activities of MaSC to be discussed in the next two days will include the development and distribution of a second Round Robin sample and summary discussion of the first sample (coordinated by Henk van Keulen of the Netherlands Institute for Cultural Heritage, Amsterdam); developments of the MaSC database of mass spectra and the use of the freely available AMDIS software for the preparation of high quality mass spectra suitable for submission to the database.

We would like to acknowledge the support of the National Gallery and the British Museum in providing venues and facilities for hosting the 4th MaSC Workshop and Meeting and would particularly like to thank colleagues at the National Gallery and the British Museum for all their support and assistance in organising and hosting these events – in particular the local organising committees at both venues, colleagues in the Scientific Department (National Gallery) and Department of Conservation and Scientific Research (British Museum) and Audiovisual, Information Services and box office staff.

The printing of this book of abstracts and the delegate packs were produced with generous support from Jaytee Biosciences Ltd, Whitstable, Kent.

We hope you enjoy the Meeting, and your visit to the British Museum and, as ever, we hope to create an informal atmosphere for the exchange of ideas and discussion.

The MaSC Committee:

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

Local organising committees

Catherine Higgitt, Rebecca Stacey, Marei Hacke, Janet Ambers, Tony Simpson, Larry Carr and Duncan Hook (British Museum)

David Peggie and Rachel Morrison (National Gallery)

The organising committee gratefully acknowledges
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Users' Group for **Mass Spectrometry and Chromatography**

Abstracts

The application of the micro-cryotrap to thermal desorption-gas chromatography-mass spectrometry for the study of conservation and art materials

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Thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) techniques simplify and clarify conservation and art material analysis by thermally separating volatile and semi-volatile components from a sample before pyrolysis. However these compounds can still be difficult to detect because they spread on the column resulting in peak broadening and peak overlap in the chromatogram. Micro-cryo-focusing can vastly improve the chromatography of volatile and semi-volatile components and consequently improve their chromatographic quality and therefore, their identification. This technique, coupled with pyrolysis-GC-MS (py-GC-MS) can lead to more confident material identification of complex mixtures. This paper will describe two areas of research where we have found the micro-cryotrap, coupled with a Frontier vertical furnace pyrolyzer, to be a critical accessory. The first area is the evaluation of conservation materials and residues from conservation treatments. This approach is ideal for the assessment of the presence of volatile and semi-volatile residues on substrates: TD-GC-MS allows the selective desorption of materials absorbed on a substrate and the addition of micro-cryo-focusing enables their improved characterisation. The second area of investigation is the detection of characteristic low molecular weight markers in art and conservation materials for their characterisation and for the evaluation of their potential for off-gassing. Again, the sensitivity of TD-GC-MS coupled with the micro-cryotrap enables the identification of compounds that are not be well visualized with traditional TD-GC-MS or py-GC-MS.

Modern oil paints – an analytical challenge

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At the previous MaSC meeting in Philadelphia in 2007, and at the Workshop on Binding Media Identification in Amsterdam in 2003 [1], discussions took place on the usefulness of the ´P/S ratio', which is still widely used by GC-MS operators to assign a certain type of drying oil to a paint medium. The question was raised whether the P/S ratio is of little or no diagnostic value in many circumstances.

The presence of mixed oils, migration between layers in dry paints and addition of non-drying fatty or waxy material all influence the measured P/S ratio. The use of other drying oil media than linseed, walnut and poppy in the twentieth century as well as the addition of metal stearates and fatty acids furthermore compromise the use of the P/S ratio for a convincing conclusion as to the type of oil medium.

Especially the analysis of twentieth century oil paints is problematic but there are improved strategies that may be helpful. This paper discusses fractionation of oil paints before GC-MS as a technique to improve analytical information. In addition, preliminary results of a novel direct temperature-resolved mass spectrometry approach using a time-of-flight mass spectrometer (DT-TOF-MS) are presented.

Results are discussed in the light of historic developments in the production of oil paint, as taken from technical sources, archives and interviews with artists´ oil paint manufacturers.

Reference

[1] K. Sutherland, 'Issues in the quantitative GC analysis of fatty acids for binding medium identification', *Workshop on Binding Media Identification in Art Objects*, ICN, Amsterdam, March 24-28, (2003) (abstract). http://www.mascgroup.org/Amsterdam2003.html.

A GC-MS analytical procedure for the characterisation of organic materials in paint samples: determination of lipids, waxes, resins, proteinaceous and polysaccharide materials in the same micro sample and in the presence of interfering inorganic pigments

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Samples from painted works of art are characterised by the presence of several different organic materials together with pigments, fillers and dryers. A GC-MS analytical procedure for the characterisation of lipids, waxes, resins, pitch, tar and proteinaceous material in the same paint micro-sample has been described [1]. By this procedure polysaccharide materials required analysis of a different sample aliquot [2]. High amount of inorganic pigments, dryers and fillers are known to give rise to strong analytical interferences in the determination of proteinaceous binders and recently a clean up procedure has been proposed for the elimination of these interferences [3,4].

On the basis of the previous studies, this paper presents a novel GC-MS analytical procedure for the determination of lipids, waxes, resins, proteins and polysaccharide materials in the same paint micro sample in the presence of interfering inorganic pigments. With this analytical procedure the separation between polysaccharide and proteinaceous materials is achieved, and purification of proteinaceous binders is simultaneously performed. This analytical procedure achieves:

- the identification of the proteinaceous binder (egg, collagen, casein) on the basis of the quantitative determination of the amino acid profile processed by principal component analysis;
- the identification of lipids (linseed oil, poppy seed oil, walnut oil and egg), plant resins (Pinaceae resins, sandarac, mastic and dammar), animal resins (shellac), tar or pitches and natural waxes (beeswax, carnauba wax) on the basis of the quantitative determination of fatty and dicarboxylic acids, and molecular pattern recognition of alcohols, hydrocarbons and terpenic molecular markers;
- the identification of the polysaccharide binder (starch, tragacanth, arabic, fruit tree, guar, and karaya gums) on the basis of the quantitative/qualitative determination of occurring sugars and uronic acids, processed both with a decisional scheme and principal component analysis.

Examples from paintings will be presented, and the identification of organic components will be discussed.

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Application of mass spectrometry-based protein sequencing to mummified remains and associated artifacts

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In most cases, proteins are the most abundant organic material surviving in mummified tissues; specifically collagen, present in bone and skin, and keratins, in hair. In the last twenty years sequencing of ancient DNA has expanded, while ancient protein research has languished, arguably due to the lack of an adequate sequencing technology equivalent to the polymerase chain reaction. In the past few years, protein sequencing by mass spectrometry however has been successfully applied to paleontological, archaeological and artistic materials.

We used a soft-ionization mass spectrometry approach to analyse a small leather sample from a plaited Iron Age armband. The armband was found on an Irish human bog body (362–175 BC) conventionally denominated Oldcroghan Man, found during drain clearance operations in the townland of Oldcroghan, Co. Offaly. Peptide sequencing allowed confident attribution of several collagen peptides consistent with bovine skin collagen, revealing that the plaited armband was made from cattle leather.

Despite the presence of interfering compounds present in the bog, it was possible to successfully sequence collagen from an Iron Age sample and identify its origin. Thus, while DNA recovery in contexts like this is limited due to diagenetic processes, protein mass spectrometry can provide useful information about exploitation of natural resources by ancient human communities. Investigation on other skin and hair mummy tissues is in progress at the moment, to better characterise the biomolecular preservation of the proteinaceous remains.

Exploiting the synergy of molecular structures and isotopic compositions in the study of cultural artifacts

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Analysis of medical moulages – skin diseases in wax

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Medical moulages made of wax were used for the education of physicians (mainly dermatologists) prior to the development of reliable colour picture reproductions in medical books, but also in popular health education. The Deutsches Hygiene-Museum Dresden (DHMD) nowadays owns a large collection of moulages, which were produced in the museum's workshop in large numbers from its foundation in 1912 until the 1980s. Moulages are made by taking a gypsum negative of the body part showing the disease, into which wax is then poured. The wax replica is finally painted in front of the patient to yield an extremely precise and naturalistic three-dimensional copy of the disease.

Today, many moulages show severe colour changes, efflorescence, or are broken in pieces. In collaboration with the DHMD the wax mixtures of a representative selection of moulages were analysed by GC-MS. A very broad variety of materials was identified: beeswax, montan wax, paraffin wax, Japan wax, carnauba wax, and spermaceti wax. The analyses always revealed a certain amount of dammar or colophony which were added to improve the reproduction of small details in the moulage. A French moulage of 1944 that came into the collection as a gift consists of animal fat and dammar. The basis of most moulages produced in the DHMD is montan wax due to import restrictions on more suitable materials (beeswax) in the former German Democratic Republic.

Montan wax is extracted from brown coal and is of brown to black colour. Therefore it needs to be cleaned and bleached. There are many technological processes involving treatment with chromic acid or distilling at very high temperatures, both changing the composition considerably. Hence, montan wax is not well suited for moulages, and is probably a main cause for severe discolouration.

Some moulages show severe efflorescence, which were surprisingly found to consist of long-chain phthalate plasticisers. Montan wax is a natural product with very variable composition, and the moulage makers often complained about batches of wax that did not show the claimed properties. We therefore assume that the plasticisers were added by the factories producing montan wax in order to adjust its physical properties. However, other plasticisers were also detected: dibutyl phthalate was found in an early Dresden moulage, and phosphate plasticisers in the French moulage.

Tryptic peptide analysis applied on proteins in cultural heritage

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A proteomics approach is presented to identify proteinaceous materials in cultural heritage objects. The proteins were digested enzymatically into peptides using trypsin before being separated and detected by liquid chromatography–electrospray ionisation tandem mass spectrometry (LC-ESI-MS-MS). Mascot (Matrix Science), a search engine that uses mass spectrometric data to identify proteins from primary sequence databases, was used to analyze the resulting data, identify the tryptic peptides and the proteins from which they originate. By these means, amino acid sequences could be studied that retain much more specific information about the proteins in comparison with the traditional amino acid analysis: egg yolk and glair can be distinguished based on their different protein content, binary (and complex) mixtures can be identified unambiguously and animal sources of glues can be differentiated, consuming as little as 10 µg or less sample. Moreover, this technique opens perspectives for the study of degradation effects and pigment-binder interactions. This novel methodology was successfully applied for the analysis of proteinaceous binding media and adhesive layers in several paintings.

Investigation of laser-cleaned marble by pyrolysis GC-MS

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The yellowing of marble during laser cleaning is a common phenomenon and has received some attention in conservation science. Pre-existing yellow layers, iron contamination, light scattering or substrate damage have all been proposed as possible causes.

This yellowing has also been experienced in the British Museum stone conservation studio; however, when a Greek marble sculpture depicting Europa and the Bull with particularly severe surface dirt was cleaned with a laser (Nd:YAG 1064 nm), the resulting discolouration was quite different – the marble took on a deep shade of orange. The orange discolouration was removed by poulticing with Laponite followed by steam cleaning. It was suspected that an organic coating may have been present under the heavy layer of dirt and that this coating caused the orange discolouration.

Analyses by pyrolysis GC-MS of the dried steam cleaning run-off, the black crust pre-laser cleaning and black dirt from an outdoor brick wall all showed a variety of sulphur-containing organic compounds. Many of these compounds were aromatic or related cyclic structures indicative of sulphurous coal soot. Samples of the black surface crust from the marble sculpture were also analysed by FTIR, XRF and SEM but no indication was found for an applied organic coating. Black dirt from another marble relief was analysed by pyrolysis GC-MS but no sulphur-containing compounds were identified. Instead, the surface dirt from this marble contained various long chain hydrocarbon series, perhaps resulting from grease from handling or remnants of a wax coating. The marble relief did not turn orange during laser cleaning but showed the commonly achieved hue of yellow. The results of the investigation suggest that a heavy soiling with sulphur-containing compounds caused the unusual orange discolouration during laser cleaning and that the sulphur-containing soiling was likely due to contamination from coal soot.

Volatile organic compounds from books: characterisation using novel mass spectroscopy techniques

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The UK's six legal deposit libraries (LDLs) and two archives are examining their collections' state comparing traditional and novel techniques. Identical editions of *c*. 370 books were picked in each LDL and compared using visual examination, visible and infra-red spectra, pH, molecular weight (MW), fibre composition and volatile organic compounds (VOCs) profile.

VOCs in store rooms and from individual books were collected and quantified using a variety of traditional and novel techniques. Comparative trials of contrasting collection methods from a small number of individual books were carried out. VOCs absorbed onto SPME fibres and elastomer strips placed between the pages in books were analysed by desorbing onto a GC-MS system. The headspace concentrations of VOCs developed in sealed containers over the same books was measured by collecting on tenax tubes which were analysed by desorbing onto a GC-MS system. The headspace concentrations were measured directly by two novel techniques, both of which sample and quantify the VOCs in the gas phase: Field Asymmetric Ion Mobility Spectrometer (FAIMS) system, Lonestar, developed by Owlstone Technologies [1] and Selective Ion Field Tube mass spectroscopy (SIFT), developed by SYFT-MS [2].

The two new methods provide near instantaneous results of identification and vapour concentration (30–120 seconds) with no sample preparation. The standardisation process for these VOCs is underway by correlation with established methods. The identification and quantification of the analytes is therefore only partial at present. The results of the FAIMS and SIFT techniques will be compared with those of the standard absorption/GC-MS methods.

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[2] http://www.syft.com

The identification of the red organic pigment in Piet Mondriaan's *Victory Boogie Woogie* with THM-py-GC-MS and HPLC

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Organic pigments in paint and textile samples can often be identified successfully using HPLC with which the ultraviolet (UV) absorption spectrum and retention time are used for the identification of the pigment. No match was found in retention time and UV spectrum for the red organic pigment used by Piet Mondriaan for his painting *Victory Boogie Woogie* (Gemeentemuseum, Den Haag). Pyrolysis-GC-MS, used for the identification of the binding medium of the paint sample showed pyrolytic fragments originating from the organic pigment. Experiments showed that some pigments produce different pyrolysis products when pyrolysed as they are (pure and without derivatisation), pyrolysed in the presence of tetramethylammonium hydroxide (TMAH), when analysed (with TMAH) together with a dried oil sample or when analysed (with TMAH) as a pigmented paint sample. It was not clear if the difference in pyrolysis products was caused by alteration of the pigments in the linseed oil, or was caused by the thermally assisted hydrolysis and methylation (THM) reaction during pyrolysis.

For the identification of the red organic pigment a selection of pigments were prepared as an oil paint with linseed oil. The paint samples were analysed with thermally assisted hydrolysis and methylation-GC-MS in combination with pyrolysis. Pyrolytic fragments originating from the selected pigments were used to indicate the identity of the pigment present in the *Victory Boogie Woogie* sample.

HPLC dyestuff analysis of the same paint samples confirmed the assumption that the chemical structure of the organic pigments can be altered as a consequence of the drying process of the linseed oil binding medium. UV spectra and retention times of the paint sample reconstructions were used to identify the organic pigment in the *Victory Boogie Woogie* sample as lithol red (Pigment Red 49).

Analysis of modern paints and pigments with LDMS: what we have learned since MaSC 2007

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Our laboratory has continued developing and exploring the use of Laser Desorption Mass Spectrometry (LDMS) for the characterisation of modern paints and pigments, particularly for the analysis of samples from works by modern artists including Cy Twombly, Mark Rothko, Roy Lichtenstein and James Castle, among others. Application for a wide variety of samples has demonstrated that the technique is well suited for the identification of organic pigments regardless of matrix, and is especially effective with mixtures of colourants. In addition to organic pigments, we can identify many inorganic species present in the samples either as colourants or other matrix components. We will show examples that illustrate our experiences.

Results to date show that LDMS used alone is a valuable tool for the conservation scientist, but we believe its greater strength resides in its use in combination with complementary techniques, especially Raman and FTIR spectroscopies. In order to gain a clear overview of how these three techniques overlap and support one another, and to better understand the sample-dependent strengths and weaknesses of each, we have begun the systematic characterisation of a large set of samples from works by Cy Twombly and James Castle. Initial results from these studies will be presented.

Finally, although some LDMS pigment spectra are quite simple and readily lead to identifications, a large number are relatively complicated and require time consuming comparison with reference spectra. To alleviate this ‘log jam’, we have begun creating a searchable database of our collection of reference pigments and will demonstrate its use in this presentation.

Analysing Mantegna's binding media by HPLC and GC. New data for the understanding of an Italian Master

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In the light of the great exhibition held in the Musée du Louvre, Paris, during fall 2008, an extensive study of several paintings by Andrea Mantegna (1431–1506) has been undertaken at the C2RMF. Among many masterpieces, either on wood panel or canvas, three were selected in regards of the specific problems encountered. Indeed, in the case of paintings on canvas, the certain identification of the binding media could not be achieved despite the many studies they have undergone previously [1]. Three renowned paintings, *Saint Sébastien* (Louvre), the *Vierge de la Victoire* (Louvre) and the *Ecce Homo* (Jacquemard-André), were thus re-examined in the light of new analytical developments, particularly the implementation of protein analysis by HPLC and specific oil media analysis by GC-MS.

As the main result, we were able to demonstrate the use of egg tempera for the painting of the *Ecce Homo*, whereas until then, it was believed to be painted with glue and moreover presented as one of the best example of the so-called glue technique [2]. This result emphasizes the need for molecular analysis in the complete understanding of painting techniques, especially for those tumultuous ages where painters tested different techniques, using different media and mixtures of natural compounds.

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Characterisation of archaeological waterlogged wood by mass spectrometric techniques

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In underwater environment, waterlogged archaeological wooden objects, such as shipwrecks, can slowly be degraded by the action of water and anaerobic erosion bacteria. This generally causes the loss of cellulose and hemicellulose, and of extractable compounds, leading to the formation of pores and cavities filled with water. During this degradation processes, lignin can be altered, and the result is soft and fragile structure, mainly composed of residual lignin, that can easily collapse when drying if proper consolidation/conservation treatments are not applied [1,2].

The chemical characterisation of archaeological lignin is therefore an aspect of primary importance in the diagnosis and conservation of waterlogged wood artifacts because of such degradation processes. To date, the knowledge of lignin degradation processes in historical and archaeological wood is scarce, and further studies are required.

In this study archaeological wood samples of different species and age have been examined by mean of analytical techniques based on mass spectrometry. The majority of them were collected during the excavations at the Ancient Harbour of San Rossore (Pisa, Italy), where several shipwrecks dating from second century BC to fifth century AD have been discovered over the period from 1998 until the present. The chemical composition of archaeological waterlogged wood, with particular attention to lignin, has been investigated by employing direct exposure electron ionisation - mass spectrometry (DE-MS) as well as using by analytical pyrolysis-gas chromatography-mass spectrometry (py-GC-MS).

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LC-MS (Ion Trap) as tool for the characterisation and identification of natural dyes in historic textiles

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Identification of natural dyes of vegetal and animal origin can provide useful information about the period and geographic area in which a particular object was made and may contribute to the object's conservation.

Liquid chromatography with mass spectrometric detection (LC-MS) has been increasingly used in the last years for dye characterisation and identification, either as an independent tool or to complement the "traditional" diode array detection methods.

The present work discusses the experiments performed by LC-MS (Ion Trap) to develop an analytical protocol capable of identifying the biological sources responsible for the colour in textiles of artistic, historic and archaeological interest. Experiments were performed on a collection of standard dyes and standard dyed wool fibres (prepared within the Eu-ARTECH and COST G8 European projects) and include the use of MS in Full Scan (FS), Single Ion Monitoring (SIM) and Single Reaction Monitoring (SRM).

Although the sensitivity of MS detection in FS mode is comparable with that resulting from diode array detection, the increased selectivity achieved in the SIM and SRM modes confirm mass spectrometric detection as a valuable tool in the identification of natural dyes in historic textiles.

Organic patinas on Renaissance and Baroque bronzes – interpretation of compositions of the original patination by using a set of simulated varnished bronze coupons

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In the frame of an on-going research projected dealing with the identification of “organic patina” on small indoor bronzes from the collection of the Kunsthistorisches Museum, Vienna, a set of model varnishes on bronze coupons prepared at the Metropolitan Museum of Art, New York, was subjected to GC-MS analyses. The study of the model varnishes answered and clarified various uncertainties in the identification and interpretation of the natural materials previously detected in the authentic varnishes of Renaissance and Baroque bronze sculptures. The alterations in the composition of the oil-resinous coatings noted in the authentic varnishes can now been explained not only by ageing processes but also to the methods by which the varnishes were originally applied to the surface of the bronzes, e.g. the varnishes were often directly baked on the surface of the statues at temperatures exceeding 100 °C.

The GC-MS results relating to the compositions of the model coatings helped to better understand some of the difficulties in the detection and identification of original oil-resinous varnish components. In particular, the study allowed the low abundance of the mastic resin in the varnishes to be explained, specific markers to distinguish particular resins within a *Pinaceae* family to be proposed and, furthermore, a more cautious interpretation of drying oils mixtures is now advised.

The identification of bleached shellac picture varnishes using GC-MS and py-GC-MS with AMDIS mass spectral deconvolution software

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Reference samples of bleached and unbleached shellacs from a number of commercial artists' and industrial suppliers and museum collections were characterised using GC-MS and py-GC-MS, following treatment with MethPrep II and TMAH, respectively. These techniques proved effective for the separation and identification of the characteristic aliphatic and cyclic (sesquiterpene) hydroxyacids that compose the shellac resins. Furthermore, the bleached shellacs could be differentiated from unbleached shellacs by the detection in the former of trace levels of chlorinated compounds, discernible from the characteristic chlorine (Cl) isotope peak ratios in their mass spectra. The presence of Cl in the bleached shellacs was also confirmed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis. The molecular masses and fragmentation patterns of the chlorinated compounds suggest that they may be modified hydroxyacids, produced as artifacts of the chemical bleaching process, which typically involves treatment of the shellac with sodium hypochlorite [1].

Detection of the chlorinated marker compounds was challenging because of their occurrence at very low levels, and because of the complexity of the shellac chromatograms, with peak overlaps in some cases. However, treatment of the GC-MS data with AMDIS mass spectral deconvolution software proved to be a valuable tool to overcome the sensitivity and separation issues. GC-MS and py-GC-MS in combination with AMDIS were applied successfully in the identification of bleached shellac ("white lac") varnishes on paintings by the American artists George Inness (1825–94) and William Merritt Chase (1849–1916) [2] in the collection of the Philadelphia Museum of Art. Bleached shellac was also identified in a sample from a bottle of "Soehnée Frères" varnish, dating from the early twentieth century, part of the collection of studio materials of the American Impressionist painter William Chadwick (1879–1962) at the Florence Griswold Museum, Connecticut. This study is part of ongoing research to characterise bleached shellac and investigate its use in works of art.

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Heritage ‘degradomics’: an introduction

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Heritage ‘degradomics’ [1] can perhaps be best defined using similarities with the well known field of metabolomics. Metabolomics is the analysis, both qualitative and quantitative, of the arrays of metabolites produced in biological systems, their dynamics, composition, interactions, and responses to changes in environmental conditions [2-4]. While metabolism is a process in living organisms that have the power to adapt and renew, if one treats a heritage object as a pseudo-organism, then immediate parallels can be drawn between the ‘degradome’ –the sum of the products of various degradation processes– and the metabolome of an organism.

The suffix “-omics” designates a particular methodology for experimental design, data generation, and data handling. Because little is known about the system initially, a hypothesis-driven, reductionist cycle of knowledge is better substituted with a holistic and inductive approach to experimentation [5]. Typically very large sample sets of hundreds to thousands of replicated samples are used to generate a statistically significant sample space and distinguish interesting sample variability from obscuring variability by application of various data processing methods, descriptive statistics and visualisation, and supervised and unsupervised multivariate techniques [2-4,6,7]. Hypotheses are then generated and tested *in silico*, and the cycle repeats. This experimental methodology is well suited to dealing with the complexities of heritage objects whose ‘degradomes’ are the product of a system of chemical reactions that are influenced by the original composition of the object, the sum of its “biography” including any interventions, and its past and present local environment.

‘Degradic’ fingerprinting and footprinting methods can be used respectively to identify residual degradation marker compounds in or on an object, or off-gassed into the microenvironment surrounding the object. Once the markers have been identified, ‘degradic’ profiling can be performed to quantify the markers, explore the ‘degradic’ system and to evaluate a particular conservation technique, storage/display method, or stability of a class of objects. A ‘degradic’ footprinting experiment to test the effect of anoxic display and storage on watercolours by J.M.W. Turner will be discussed as a proof of concept for the field of heritage ‘degradomics’.

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Volatile ‘degradic’ fingerprinting of historical paper

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Volatile compounds, emitted by materials during degradation, have been shown to be both numerous and informative. Donetzhuber et al. identified more than 200 volatiles emitted by paper and paper products [1]. On the other hand, the emission of furfural during degradation of historic paper has been correlated with its pH [2], which is one of the most important parameters defining the lifetime of paper.

Therefore, we investigated whether volatile ‘degradic’ fingerprinting, i.e. unbiased screening to classify materials based on patterns of volatile degradation products, may reveal qualitative and quantitative information on historic papers and on the degradation processes. In order to perform such a study, a collection of well characterised papers is needed. In our research, 72 samples from the SurveNIR historic paper collection [3] were used. A 10 mg paper sample was pre-heated in a closed vial and extraction of headspace volatiles was performed using a solid-phase micro-extraction (SPME) fibre. Following the extraction, separation and detection of volatiles was performed using GC-MS.

The subsequent data analysis is a multi-stage process: (i) pre-processing of raw data, (ii) data reduction, and (iii) hypothesis generation. The first two steps were performed manually in order to obtain high quality data. The compound peak areas were then compared with the measured historic paper properties, such as lignin content, gelatine content, carbonyl group content, pH etc.

Among the advanced statistical methods we used: (i) principal component analysis for reduction of multidimensional data sets to lower dimensions, (ii) cluster analysis for partitioning of a data set into clusters sharing a common property, (iii) discriminant analysis to find the linear combination of features which best separate two or more classes of objects, (iv) partial least squares (PLS) to model predicted variables in terms of observed variables, i.e. historic paper properties.

Using non-supervised methods, it is possible to hypothesize on the source of particular volatiles and on the possible degradation pathways. In addition, PLS correlations were obtained between chromatographic data and paper properties, demonstrating that volatile degradome is an important source of information on the composition of historic papers. Considering that such analysis can in principle proceed non-destructively, it could also be used for historic objects.

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Poster Abstracts

Qualitative and quantitative analyses of proteinaceous binders in rock paintings

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Thermally-assisted hydrolysis/methylation-gas chromatography-mass spectrometry (THM-GC-MS) has proven useful for characterising the organic material present in rock paint samples, information that is particularly important for dating such paintings by radiocarbon analysis. THM-GC-MS results have indicated that amine compounds, likely derived from proteinaceous binders, may be present in some of these paint samples. Extraction, hydrolysis, and derivatisation of the resulting amino acids to their N(O,S)-ethoxycarbonyl ethoxy esters and analysis by GC-MS were used to further characterise the nature of the proteinaceous materials and to determine their relative concentrations in the paint and substrate rock. Preliminary studies were carried out on known binders, including egg, blood, and saliva that were applied to limestone and allowed to age at ambient laboratory conditions for several years. Further analyses on paint from the Pecos River area of Texas, which have been previously dated to *c*. 4000 years old, will help to clarify the nature of the material that was dated. Samples of paint from a handprint and a linear figure from Cueva La Conga, the only known painted cave in Nicaragua, are also being characterised prior to dating using the plasma-chemical oxidation and accelerator mass spectrometry method. These are the first scientific studies of the rock paintings in that country.

One significant problem in dating rock paintings is that organic material not related to the paint may be present. Ideally this contaminating material, presumably present as humic substances from soil, should be removed selectively prior to dating. Several pre-treatments have been proposed, all of which have the potential to remove the water-soluble protein components along with the contamination. Quantitative comparisons of the effect of these treatments will be presented. The results of this work will help to clarify the nature of what has been dated using the plasma-chemical oxidation and accelerator mass spectrometry technique and to develop pre-treatments that allow for removal of contaminants while still preserving the diagnostic material. Ultimately, this work will aid archaeologists who study rock paintings in understanding both the age and composition of these unique artifacts.

The chemical characterisation of ambers of European provenance by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS)

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The availability and unique physical properties of amber have made it one of the materials of choice since antiquity for the fabrication of jewels, tools, ornaments and works of art. Amber belongs to the class of fossil resins formed by polymerization and maturation reactions over geological timescale. In Europe, these kinds of fossil resins are found particularly in the Baltic area and are generally called Baltic ambers. Nevertheless, deposits of ambers of different geological eras can be found all over Europe including Italy, Spain, Germany and Romania.

This paper presents the most significant results of a systematic study aimed at the chemical characterisation of ambers of different European provenance, including succinite, simetite, zigburnite, glessite, gedanite and Italian Apennine ambers. The aim was to improve knowledge of these materials and of their chemical characteristics and composition so that they may be effectively used as references in provenance studies both of geological and archaeological finds. Because of the chemical complexity of these organic substances, an analytical approach based on the use of analytical pyrolysis in the presence of hexamethyldisilazane followed by gas chromatographic-mass spectrometric analysis (py-GC-MS) has been used in this study. This technique was found to be a fast technique and a versatile fingerprinting tool for the analysis of ambers. Moreover, the use of hexamethyldisilazane as an on-line derivatising agent avoided the problems due to the formation of non-volatile products during pyrolysis.

Py-GC-MS enabled the chemical composition of ambers to be reliably studied and allowed us to obtain for each fossil resin a characteristic pyrogram that can be used as fingerprint for identification purposes. Finally, on the basis of the chemical composition (pyrolytic molecular markers), it was possible to construct a decisional scheme which can help us in the identification of ambers and of their provenance.

Mass spectrometric studies of pollutant-aged varnishes to assess the protective effect of varnishes on paintings in microclimate frames

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To preserve paintings as close as possible to the artists' original expression is a central focus for museum conservators. An important part of this work is to protect the paintings against the degrading influences of various indoor environments. The main aim of the PROPAINT project (EU project FP6, 044254), is to develop innovative protection treatments used as a preventive conservation measure for paintings during exhibition, storage and transit.

Within this context, one of the important aims is to investigate the quality and protective effect of varnishes used as remediation treatment for paintings when exposed to pollutant and climatic factors generally, and in microclimate frames particularly.

This paper presents results which demonstrate the deteriorating effects on painting varnishes of specific pollutants. Ageing studies were performed on varnish replicas in climatic chambers under various concentrations of pollutants (NO_2, O_3 and acetic acid). Prepared samples of dammar, mastic, MS2A and Paraloid B72 resins were used, with the addition of Tinuvin 292 in the dammar and MS2A samples. To understand the changes at the molecular level, pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), gas chromatography-mass spectrometry (GC-MS) and Matrix Assisted Laser Desorption Ionization-Mass Spectrometry (MALDI) techniques were used.

All of the ageing regimes affected the varnish compositions to varying degrees; the presence of Tinuvin 292 reduced cross linking and polymerisation reactions in dammar resin and is extremely efficient in preventing the oxidation of free terpenoids. This finding is significant for conservation because the use of such a stabiliser can avoid the need for frequent removal and replacement of the varnish layer. It has also been shown that trapping of aromatic compounds which are used in the preparation of MS2A varnish occurs. These compounds could migrate towards the paint films and act as solvents for some of the paint constituents, and this could contribute to the well known phenomenon of the formation of ghost images.

GC-MS investigations on gold varnishes from historical gilt leather wall hangings

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Three different varnishes for leather wall hangings (so called gold lacquers), reconstructed following historical recipes, have been investigated together with several original samples. GC-MS analysis was carried out after derivatisation or transesterification.

The analytical results are compared and the findings discussed.

An analytical study of organic components of decoration of painted pottery from the Neolithic site of Polivanov Yar (Cucuteni-Tpipolye)

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This paper represents the results of a study of binding media and organic coatings from decorated ceramics of the Neolithic site of Polivanov Yar (Cucuteni-Tpipolye culture in the Carpatian-Dnieeper region). Polychrome painted ornament in the beginning of Tripolye BI- Cucuteni A stage (the middle fourth millennium BC in uncalibrated dates) was innovative in ceramic decoration. Red, black and white colours were used. The chemical characterisation of samples from the exterior surface and inside of vessels from the 1949-1951 excavation (currently housed in the Department of Archaeology of Eastern Europe and Siberia of the State Hermitage Museum) was performed through an analytical procedure based on GC-MS. The proteinaceous materials of Tripolian paints were determined using GC-MS analysis after extraction, acid hydrolysis and derivatisation using MTBSTFA. The lipid components were analyzed after saponification and silylation using BSTFA.

The chromatographic profiles of lipid and proteinaceous components for samples of the paint medium from the exterior surfaces of the vessels indicate that egg was used as one component of the binding medium. The identification of cholesterol confirmed this conclusion. The presence of beeswax relied upon the detection of two classes of biomarkers. These are the odd-numbered hydrocarbons and even-numbered fatty acids. Perhaps, egg was used as the binder, and after that the decorated ornament was covered with a coating of wax. In addition, sucrose was observed in all of investigated samples.

The revealed organic binders associated with the archaeological pottery led to the conclusion that decoration was applied on the surface of Tripolian vessels predominantly after firing.

Py-GC-MS analysis of dyes and inks

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The py-GC-MS laboratory at the CNR-Rome undertakes analyses of different objects, including paper, inks and pigments. Over the last few years particular attention has been dedicated to the analysis of iron-gall inks to investigate their effects on the degradation of paper. Mainly spectroscopic techniques devoted to the determination of the iron content have been used, while less attention has been dedicated to the organic components.

In this study we propose pyrolysis with and without thermally assisted hydrolysis and methylation (THM) as a rapid tool for the characterisation of the organic components of inks. The method was applied to several standards and on original samples showing that it is suitable for the characterisation of iron-gall inks. Moreover information on the organic binder may also be achieved at the same time.

The same technique has been used to study different natural dyes such as cochineal, indigo, saffron, etc. The pyrolysis of cochineal at 500 °C with THM results in the formation of methyl esters of 1,2-benzenedicarboxylic acids and methyl esters of benzoic acids for example. Results from a range of samples will be discussed in this presentation.

The isotopic analysis of north-western European forest glass: working towards an independent means of provenancing

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Glass is one of several early modern industries where the development from small-scale workshop to large-scale industry offers a valuable insight into wider socio-economic trends. Previously, medieval and early modern forest (wood ash) glass has been studied using a range of analytical techniques. However, characterisations of production centres and exchange systems for forest glasses are difficult to verify, in part because very few examples of raw glass from furnace sites have been investigated. The necessity for an independent means of provenancing glass used in the study of exchange systems is clear.

Compositional analysis can provide evidence for the raw materials used and can sometimes provide compositional groupings specific to sites. Furthermore, strontium, neodymium and oxygen isotope determinations can actually provenance the glass by linking the geological ages, or sources, of raw materials to production sites. The potential of using Sr and O isotopes in the study of plant ash glasses has recently been established [1].

Using EPMA-WDS we have analysed over 220 raw glass samples from sixteen European production sites in operation between the fourteenth and seventeenth centuries. These analyses have shown surprisingly distinct compositional groupings which are relatable to the region or, in some cases, the period of production. We have analysed over 70 glass and raw material samples from these sites using TIMS to determine strontium and neodymium isotope ratios. The isotopic analyses have also been very effective in showing differences between sites, even those within the same region. Moreover, we have been able to define specific raw material types and shown that mixing of seaweed-ash and wood-ash raw glasses has occurred. The combination of these techniques offers a promising new way of provenancing archaeological glass.

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Discovering the colours of Portuguese Arraiolos carpets

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The Arraiolos carpets are an important and unique Portuguese textile tradition, with a great resemblance to Persian carpets in its structure and decoration. The materials used on their manufacture could be locally provided, like sheep wool, or could have come into the village from Portuguese colonies, like indigo or brazilwood dyes. The colour palette of these textiles in the seventeenth century was composed usually of six colours as reported in the historic nineteenth century Arraiolos dyeing recipes [1]. The blue colour was obtained with indigo; the reds could be obtained with brazilwood or brazilwood and spurge flax; yellows were obtained with weld or weld and brazilwood; the greens were dyed with indigo and weld; the purple was dyed with brazilwood, and the browns were obtained with brown natural wool dyed with spurge flax.

The natural dyes in two mid seventeenth century Arraiolos carpets from the National Museum of Machado de Castro were analysed by high-performance liquid chromatography with UV-Vis diode array detection (HPLC-DAD) and HPLC- tandem mass spectrometry (LC-MS^n), along with reference dye samples. Extraction of the dyes in the Arraiolos carpet samples was performed using mild conditions to preserve the glycoside linkages. For the blues a dimethylformamide (DMF) solution proved to be efficient for indigotin recovery. For all the other colours, an improved mild extraction method (with oxalic acid, methanol, acetone and water) was used, enabling the full yellow dye source fingerprint to be obtained.

Using this approach, weld (*Reseda luteola* L.), indigo and spurge flax (*Daphne gnidium* L.) were found to be the dye sources, in accordance with the original nineteenth dyeing recipes collected in the Portuguese Arraiolos village.

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Shedding light on the compositions of artists' alkyd paint resins using py-GC-MS and THM-GC-MS

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Alkyd paints produced specifically for artists have been commercially available since the 1970s. Being relatively 'new' materials little is known about their properties, both chemical and physical, and there is very little information concerning them in the literature. All of the information available focuses on the most popular brand: Griffin Alkyds, from Winsor & Newton [1-5], and does not discuss the other brands that are available, or that were available in the past. This paper will focus on py-GC-MS and THM-GC-MS (using tetramethylammonium hydroxide, 25 wt% in water) results for the identification of the types of alkyd resins for six different artists' alkyd paint products, three of which are no longer on the market. Also, other major paint components identified with THM-GC-MS will be discussed. It was observed that there were two different types of alkyd binders used in the six artists' alkyd products. A GC-MS technique with derivatisation is recommended for the correct identification of an alkyd paint [6-8].

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Gas chromatography–mass spectrometry analysis of products from on-line pyrolysis-derivatisation of polysaccharide binding media in watercolours

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In watercolour paints the binding media traditionally used are plant gums, in particular gum arabic.

Plant gums are complex polysaccharides and their classification may be achieved on the basis of monosaccharide composition after cleavage of glycosidic bonds. Characterisation of plant gums in works of art is complicated by the necessity of using a minimally invasive method and requiring a small mount of sample. Pyrolysis is a useful method to obtain polysaccharide decomposition and generally pyrolysis products can be identified by the use of gas chromatography–mass spectrometry. Derivatisation is necessary because the presence of hydroxyl groups gives rise to excessive interactions in the chromatographic column, with peak broadening and loss of resolution.

This work describes methods where gum arabic, gum tragacanth and some watercolour samples were pyrolysed in presence of two kind of derivatising agents using an on-line py-GC-MS apparatus. The derivatising agents used were HMDS (hexamethyldisilazane) with TMCS (trimethylchlorosilane) as catalyst, and TMAH (tetramethylammonium hydroxide).

The silylating mixture of HMDS and TMCS gives good diagnostic results, allowing differentiation of gum arabic and gum tragacanth and the identification of gum arabic in watercolour samples. However in this method some products are underivatised and different molecules are eluted together giving mixed mass spectra. The difficulty of identifying minor pyrolysis products may hinder accurate classification of plant gums, especially in a complex sample or in a mixture of different carbohydrate materials. Therefore the attention was focused on methylation through the use of TMAH. Previous studies on mono- and polysaccharides have shown that the combined effects of reagents and high temperatures give a number of characteristic markers useful in the identification of monosaccharides in gum and watercolour samples.

Characterisation of additives in synthetic binders used in modern paintings by pyrolysis-silylation-gas chromatography-mass spectrometry

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Commercial paint formulations for modern paints include a number of compounds in addition to pigments and synthetic binders in order to improve the physical and chemical properties of the paint. In the case of polyvinyl acetate polymers (PVAc), addition of plasticizers provides improved mechanical properties making them suitable as binding media for paints. Nevertheless, the ageing of films prepared with this type of binder has been reported to produce the loss of mechanical strength and flexibility and to increase yellowing [1], and this is often related to the migration of additives such as plasticizers. Acrylic paint formulations also include additives that detrimentally influence the chemical and physical properties of the paint films. One of the additives most frequently present in these paint formulations is the surfactant, which is responsible for stabilizing the polymer and the pigment(s) in the aqueous phase.

A new method is proposed for identifying the additives present in both PVAc and acrylic commercial formulations based on the “on-line” silylation using hexamethyldisilazane (HMDS) as a derivatisation reagent in py-GC-MS.

Interestingly, the proposed method allows the evaluation of the changes of the plasticizer content in PVAc paint films subjected to UV light aging. The proposed method is based on the use of 1,4-dibromebenzene as an internal standard.

Two series of specimens of Mowilith 50 (PVAc pure resin) containing diethylphthalate and dibutylphthalate prepared as thin films were analyzed. The plasticizer content was determined before and after ageing. Changes in the content of plasticizer and changes in the mechanical properties determined by tensile strength testers were investigated.

Analysis carried out on titanium white paints prepared by adding plasticizer at 5% demonstrate that diethyl phtalate is lost to a larger extent that dibutyl phtalate when the paint film is subjected to aging. This is also confirmed by the increased stiffness in the stress-strain curves obtained for the PVAc samples.

Reference
[1] J.L. Down, M.A. MacDonald, J. Tetreault and R.S. Williams, ‘Adhesive testing at the Canadian Conservation Institute--an evaluation of selected poly(vinyl acetate) and acrylic adhesives’, *Studies in Conservation* **41** (1996) pp. 19–44

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Pitch, tar and resinous materials in 18th century nomenclatures

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Pitch may be considered a collective term for several products originating from resins. Different ways of heating the resin or resin mixed with wood result in variation in the chemical composition. Aside from differences between northern and southern Europe, methods differ also by the temperature, the apparatus used and botanical species. Historical sources can give assistance but often they miss exact details which could reconstruct the applied process. The different chemical compounds can be identified with chromatographic and mass spectrometric methods. Modern “Burgundy Pitch”, a tar made by methods bequeathed by Pliny and fresh balm from different botanical sources of the family of Pinaceae were analysed to investigate the differences. A ‘Pix Burgundica’ (Burgundy Pitch) from a 300 year old English material collection was analysed in this context in order to determine the production process and the botanical species used. Related sources were consulted to investigate details of the production process. The colophony-like material could be identified as the residue of a low heating process in the presence of oxygen and not of smouldering.

Application of TD-GC-MS and FT-IR in chemical characterisation of Romanian amber

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The composition of fossil resins is a complex and active area of research, as evidenced by the number of written scientific papers, the number of analytical techniques involved as well as the multitude of resin types investigated. In the frame of ROMANIT National Research Project (www.romanit.ro), coordinated by the Romanian National History Museum (MNIR), a multidisciplinary team was involved in characterisation of fossil resins with a particular focus on Romanian amber (rumanite). The project aims to use and develop analytical methods capable of distinguishing rumanite from other fossil resins. One of the primary aims of the research is the authentication of rumanite in archaeological jewelleries from the MNIR collection.

Thermal desorption coupled with GC-MS in different instrumental configurations has been used for characterisation of volatile constituents of fossil resins. By eliminating complicated solvent extraction and concentration steps, it has been proved as a powerful analytical technique for investigating the chemical structure of fossil resins.

Direct thermal desorbtion coupled with GC-MS was used to extract, concentrate and identify volatile organic compounds from amber in one single automated analysis. A chromatographic method together with a specific data analysis method based entirely on AMDIS software were developed for semi-quantitative and qualitative identification of biomarkers specific to amber specimens. Results show some hundreds of volatile organic compounds, part of them previously found by other laboratories specialized in characterisation of fossil resins and many without an assigned chemical structure. A mass spectra database was created for all characterised volatiles. Although a large volume of work was involved, mainly regarding data analysis, preliminary results are promising and suggest that TD-GC-MS has good potential for fossil resins fingerprinting especially used in conjunction with FT-IR spectroscopy.

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AnalyzerPro software

A commercial data mining software package for GC-MS and LC-MS data processing is used to perform targeted and non-targeted analysis of samples. Proprietary algorithms are shown to detect a number of components which are obscured under closely eluting chromatographic peaks. Semi quantitative results can be represented in a sample/ component matrix and are also readily exported to allow additional data processing such as PCA.

Introducing a new bench top time of flight mass spectrometer (***BenchTOF-dx***), with automated dynamic baseline compensation and new deconvolution/ chemometric based target compound identification software (***TargetView***)

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ClearView and *TargetView* software and *BenchTOF-dx* bench top (reflectron) time of flight mass spectrometer

BenchTOF-dx is a new high performance bench top (reflectron) time of flight mass spectrometer developed by ALMSCO International (UK). Its design uses sophisticated electronics with innovative ion optics to create a system ideally suited to the analysis of volatile and semi volatile organic compounds.

BenchTOF-dx is approximately the width of a conventional GC (~64cm) with high performance characteristics which include fast spectral acquisition (10k scans/second full mass range 1–1000 amu), enhanced spectral quality and sensitivity with on line automated background ion compensation and data reduction algorithms. Excellent sensitivity is achieved with full mass range acquisition using a direct extraction technique from the ion source.

The system will interface with most leading GC instruments providing a generic TOF detection system. GC control and data analysis is achieved using existing vendor GCMS software (Agilent Chemstation, Thermo Fisher Excalibur, Shimadzu Solutions), enabling users to control the GC and process data in a familiar software environment. Alternatively data analysis is possible with ALMSCO proprietary software (dx-VIEW) which is based on the Microsoft SQL data base.

Performance characteristics for the instrument – sensitivity, linearity etc – will be reviewed and a range of real world samples will be shown to demonstrate the system performance. This will include examples of conventional high speed chromatography and GC x GC separation for complex samples. In addition, the unique ability to dynamically compensate for baseline anomalies in real time will be demonstrated for all speeds of chromatography providing flatter baselines, minimal noise and enhanced spectral purity.

Finally new target compound identification software will be shown which will process both BenchTOF-dx and conventional Quad type data. This combines a process of spectral deconvolution with multivariate analysis (PCA) to identify multiple known compounds within a sample mixture. The software is ideally suited to the performance characteristics of BenchTOF-dx.