

Liquid Chromatography Workshop and Meeting

**National Gallery of Art
Washington DC, USA**

April 5 - 9, 2004



Preface

On behalf of the Trustees of the National Gallery of Art, welcome to the first official meeting of the Users' Group for Mass Spectrometry and Chromatography (MaSC).

It has been a year since MaSC was founded at the 'Discussion Meeting on Binding Media Identification in Art Objects' at the Netherlands Institute of Cultural Heritage in Amsterdam. Our original mission was to explore the possibility for creating a mass spectral database and to establish a forum for encouraging information exchange among those using these techniques in the field of conservation science.

Since then, the co-ordinating committee has been discussing and working on various topics to reach consensus about the direction our group should be taking. At our October meeting at the National Gallery London we decided on a number of issues:

- The website, which is now up and running (www.mascgroup.org)
- The adoption of the JCAMP-DX file format for mass spectral data exchange, and the NIST library formats
- The organization of the present meeting and Liquid Chromatography workshop

A number of issues are still under discussion:

- Legal and quality control issues regarding the mass spectral database
- Future meetings and workshops
- Exchange of sample material
- Degree of formality of our organizational structure
- Composition of the membership

At the conclusion of this meeting there will be an opportunity to discuss these issues and we encourage your input.

We hope you find the meeting stimulating and enjoy your stay in Washington!

Christopher Maines

North American Co-ordinator

Klaas Jan van den Berg

European Co-ordinator

Ester Ferreira

Catherine Higgitt

Ken Sutherland

Organizing Committee

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

Meeting Schedule

Thursday, April 8, 2004

GC-MS in the Analysis of Cultural Heritage

- 9:00a Opening Remarks
- 9:15 **A Sampling of Current Projects Involving Gas Chromatography Mass Spectrometry at the Canadian Conservation Institute**
Jennifer Poulin, Canadian Conservation Institute
- 9:45 **GC-MS Analysis of John Singer Sargent's Mural Cycle "The Triumph of Religion"**
Glenn Gates, Harvard University Art Museums

Advances in GC and GC-MS Analysis Methodologies

- 10:15 **GC-MS Analysis of Amino Acids Using Ethyl Chloroformate**
Jens Glastrup, National Museum of Denmark
- 10:45 Coffee Break
- 11:15 **Characterization of Alkyd Paint Media by Gas Chromatography-Mass Spectrometry**
Michael Schilling, Getty Conservation Institute
- 11:45 **Curie Point Py/GC-MS at AMOLF: Old Knowledge, New Set-Up**
Ester Ferreira, AMOLF -FOM Institute for Atomic and Molecular Physics
- 12:15p Lunch
- 2:00 Opening Remarks, Announcements
- 2:15 **GC analysis of aged oil paint: some comments on the significance and reproducibility of molecular markers**
Klaas Jan van den Berg, Netherlands Institute for Cultural Heritage (ICN)

Mass Spectrometry in the Analysis of Artists' Materials

- 2:45 **Aging of Triterpenoid Resin Varnishes**
Patrick Dietemann, Bavarian State Office of Historic Monuments (BLFD)
- 3:15 Coffee Break
- 3:45 **The Identification of Synthetic Organic Pigments by DTMS**
Suzanne Lomax, National Gallery of Art, Washington

4:15 **Building and Using Mass Spectral Reference Libraries**
Stephen Stein, NIST Mass Spectrometry Data Center

4:45p End

Friday, April 9, 2004

LC and LC-MS in the Analysis of Cultural Heritage

9:00a Opening Remarks

9:15 **The Characterization of Polysaccharide Binders by Chromatographic Analytical Procedures**
Maria Perla Colombini, University of Pisa

9:45 **LC and LC-MS in Natural Dye Projects Involving the National Museums of Scotland (NMS): Flavonoids and MODHT**
Anita Quye, National Museums of Scotland

10:15 **Analysis of Natural Organic Red Dyestuff with HPLC**
Ioannis Karapanagiotis, "Ormylia" Art Diagnosis Centre

10:45 Coffee Break

11:15 **A Non-Hydrolytic Method of Dyestuff Extraction from Lake Pigments in Paint Samples: Pros and Cons**
Catherine Higgitt, National Gallery, London

11:45 Summary of LC Workshop and Discussion of Future Workshops

12:30p Lunch

Discussion Meeting

2:00 Opening Remarks, Announcements

2:15 Panel Discussion on MaSC Spectral Database

3:00 Coffee Break

3:30 "Business Meeting" – continuation of mass spectral database discussion, plans for next meeting, general floor discussion of needs/concerns/suggestions/problems

5:00p End

Abstracts

A Sampling of Current Projects Involving Gas Chromatography Mass Spectrometry at the Canadian Conservation Institute

Jennifer Poulin

Canadian Conservation Institute, Ottawa, Canada

The Analytical Research Laboratory at the Canadian Conservation Institute (CCI) undertakes material analysis on a wide range of objects, including paintings, archeological and ethnographic objects, works on paper, furniture and architectural interiors. This talk will outline several recent examples where gas chromatography-mass spectrometry was used in the detection and identification of organic materials.

The on-going archaeological excavation of a 16th century waste deposit in Gothenburg, Sweden recently uncovered a wooden bowl containing seeds from fruits and berries, nuts, insects and soft residues. The conservator requested analysis to determine the nature of the residues and if they originated from food substances. Analysis of the trimethylsilyl derivatives by gas chromatography mass spectrometry (GC-MS) identified compounds formed through the microbial reduction of cholesterol in the human digestive tract. Analysis of the inorganic components was also consistent with human waste matter.

A recent survey of ethnographic collections at the McCord Museum, Montreal was undertaken in order to ascertain the possible contamination of artifacts with organic pesticides. The conservator at the museum had information which suggested prior applications of DDT on some artifacts; however, the documentation was not complete and there were doubts of its validity. The on-site analysis using a portable X-ray fluorescence (XRF) system indicated that the majority of the collection was not contaminated with inorganic pesticides. However, samples collected and analysed by GC-MS revealed that many objects in the collection contained trace to high levels of several different organo-chlorine pesticides, including DDT, DDD, perthane and methoxychlor.

Other examples that will be discussed include: the identification of 2,4,6-trinitrotoluene (TNT) amongst surface accretions on a newspaper recovered from the WWI battlefield at Vimy Ridge, France; the identification natural resins in varnishes and paint media in an early 20th century painting by Charles Comfort; and the characterisation Canadian amber from a number of geological deposits.

GC-MS Analysis of John Singer Sargent's Mural Cycle *The Triumph of Religion*

Glenn Gates

Harvard University Art Museums, Cambridge, Massachusetts

In 1893, John Singer Sargent started work on a mural cycle entitled *The Triumph of Religion* for a long and narrow barrel-vaulted hall within the Boston Public Library. A conservation examination in 1999 detected a carbohydrate surface coating on several painted canvases on one side of the hall. During the 2002-2003 conservation campaign, cross-sections revealed this was an original surface coating. However, it was disfiguring and obscured much detail. The conservation decision was made to reduce, but not remove the original coating. To determine what the carbohydrate-containing material was, quantitative gas chromatography-mass spectroscopy (GC-MS) was employed, using procedures and databases developed at the Getty Conservation Institute. Nine different sugars were used to create calibration curves relating response to sugar concentrations in the range from 50 to 1 ppm. Five sugars were used to compare the results of the analyses to standards in the GCI database and identify the carbohydrate coating. The results of the GC-MS analyses showed that the carbohydrate material was a cellulose-ether, most likely carrageen, and was probably applied as a matting agent. This surface treatment contrasts with the proteinaceous surface coatings detected on other walls of the rectangular hall. The analyses provide evidence for Sargent's aesthetic sensitivity to the lighting characteristics of the Library's hall.

GC-MS Analysis of Amino Acids Using Ethyl Chloroformate

Jens Glastrup

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The ethyl chloroformate derivatization of amino acids, and analysis using GC-MS, has been reexamined. After derivatization of the amino acids, the derivatives are extracted directly, using Solid Phase Micro Extraction (SPME) and after a 30 sec. extraction, injected into the GC port (on-column). The derivatives are analyzed on a relatively thick phase OV-1701 – a semi-polar stationary phase. In contrast to previous results, the stationary phase of this column proves to be stable after repeated (more than 75 analyses) injections using the SPME needle. The needle does last for at least 50 analyses.

The sensitivity and linearity range in full-scan MS mode lies in general from 0.1 to at least 3 nmol. Data for the linearity of the data will be presented as will tuning options for the mass spectrometer.

Characterization of Alkyd Paint Media by Gas Chromatography-Mass Spectrometry

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Tom Learner
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Alkyd resins, manufactured from polyols, polybasic acids, and monobasic fatty acids, may be categorized as oil-modified polyesters. Resin formulators customize the drying and performance properties of alkyd paints either by varying the type and/or stoichiometric proportions of the reactants, or by adding modifiers (e.g., styrene, acrylics, and isocyanates) during the manufacturing processes. Alkyd resins have been widely used as binding media in virtually all types of paints since the 1940s, having replaced drying oils in many industrial applications. Identification of alkyd paint media is most often accomplished using Fourier-transform infrared spectroscopy or pyrolysis-gas chromatography-mass spectrometry, yet these techniques are semi-quantitative at best. Two GC-MS procedures have been developed to quantitatively analyze polyol, dibasic acid, and fatty acid components. Results from the analysis of various alkyd paints and unpigmented media demonstrate the utility of the procedures in characterizing alkyd paint media.

Curie Point Py/GC-MS at AMOLF: Old Knowledge, New Set-Up

Ester S.B. Ferreira

AMOLF -FOM Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands

Flash pyrolysis mass spectrometry has a long history of development in AMOLF and it was shown to be a revolutionary technique in the analysis of organic complex systems. In particular Curie point Py/GC-MS is an important technique for the analysis of paint samples.

A commonly employed method of sample preparation in Curie point Py/GC-MS is online TMAH (tetra methyl ammonium hydroxide) derivatisation, which has significant advantages. However, one of the problems associated with this methodology is the gradual degradation of the analytical column's stationary phase on the course of several heating-cooling cycles, compromising performance and increasing column bleeding. The destruction of the excess reagent did not prove successful therefore a new set-up was developed. This, whose principles were based from those of large volume sampling, intends to remove a significant percentage of the un-reacted TMAH thus minimising the damage to the column. For this a retaining pre-column and a reagent vent module were installed between the flash pyrolysis unit and the analytical column.

Description of the set-up and the experimental parameters will be presented.

This method has been used for the survey of binding media in a set of 17th century paintings with a limited and well-known restoration and display history. Some of the first results will be discussed.

GC analysis of aged oil paint: some comments on the significance and reproducibility of molecular markers

Klaas Jan van den Berg, Meryem Tsouli, Leslie A. Carlyle
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Organic analysis of traditional oil paints with gas chromatographic methods may provide the scientist, restorer or art historian with information on the nature, extent of drying, and the preparation of the oil medium. The reliability of the analytical information, however, can be questioned. The so-called 'P/S ratio' of a paint, for example, is normally determined on the basis of one measurement of a very small paint sample and this raises questions about the reproducibility. In addition, migration of fatty acids through layers and mixtures of paint media influence the significance of the measurement.

One of the potential sources of information least discussed is the ratio of the dicarboxylic acids, e.g. the suberic to azelaic (C9/C8) dicarboxylic acid ratio. It has been established that this ratio is determined or at least influenced by the degree of heating of the oil prior to paint manufacture (Mills and White 1982, Schilling 1997).

The availability of a large set of well-defined paint samples, which were made in 1999 according to 19th century recipes (Carlyle 2001) enabled us to study the significance and reproducibility of molecular markers in more detail. In this presentation we attempt to relate the composition and preparation of oil paints with a number of oil paint markers in gas chromatograms, with an emphasis on the relation of the dicarboxylic acid composition to the heat preparation of the oil medium.

References

- Mills, J.S. & White, R., Organic Mass-Spectrometry of Art Materials: Work in Progress, National Gallery Technical Bulletin, 6, p.3-18, 1982.
- Schilling, M.R., Khanjian, H.P. and Carson D.M., Fatty acid and glycerol content of lipids; effects of ageing and solvent extraction on the composition of oil paints, *Techne*, 5, 71-78, 1997.
- Carlyle, L.A., Historical reconstructions of artists' oil paint: an investigation of oil processing methods and the use of selected artists' mediums. In Phenix, A. (ed.), Extended abstracts of the presentations at Deterioration of Artists' Paints: Effects and Analysis. Interim meeting of the ICOM-CC Working Groups Paintings 1 & 2 and The Paintings Section, UKIC. London: ICOM and UKIC, pp. 6-8, 2001.

Aging of Triterpenoid Resin Varnishes

Patrick Dietemann

Bavarian State Office of Historic Monuments (BLFD), Munich, Germany

Dammar and mastic, natural resins used as varnishes on paintings, are well known to oxidize and yellow with time. In this study, oxidation was followed by graphite-assisted LDI-MS, and it could be shown that considerable oxidation takes place within weeks after application as a varnish. Up to 7 oxygen atoms or more can be incorporated into a single triterpenoid molecule. These compounds can not be seen with GC-MS. Commercial resins, usually considered “fresh”, are found to be in advanced stage of oxidation and deterioration. With GC-MS, only weakly oxidized compounds can be detected. These develop within a few months or are already contained in the fresh resin. Progressive oxidation only lowers the absolute amount of these compounds, but does not lead to a qualitative change in the chromatogram.

Radicals, intermediates in the autoxidation process, are found in significant amounts in all resins, regardless of age and storage conditions. It is concluded that the main aging process in both light and darkness is (radical) oxidation. Yellowing, one of the main problems of resin varnishes on paintings, is readily explained by alternating thermal and oxidative radical reactions. This leads to the conclusion that yellowing is not a dark-reaction as often believed, but is only more pronounced in darkness due to simultaneous bleaching in light.

A kinetic study of radical formation/termination showed that radical content of varnishes change within hours after change of illumination conditions: the amount of radicals in dark-aged varnishes is doubled after 1.5 h of (moderate) light exposure, and radical contents in light-aged varnishes drop within ca. 5 h after relocation into darkness. Heavy oxidation within a short time and very fast change of radical content show that the aging of resin varnishes is a very dynamic and drastic process, and aged varnishes are still very sensitive to environmental changes.

The Identification of Synthetic Organic Pigments by DTMS

Suzanne Quillen Lomax

National Gallery of Art, Washington, District of Columbia

Michael Schilling

Getty Conservation Institute, Los Angeles, California

Synthetic organic pigments are widely used in artists' paints. These pigments encompass many different chemical structures and polarities. Their identification by techniques such as polarized light microscopy, infrared spectroscopy, or x-ray diffraction is often complicated by their particle size, the presence of fillers and extenders, as well as in the structural similarity of many of the pigments.

A group of 119 dry pigments and eight paints were taken to the Getty Conservation Institute for examination by mass spectrometry. Initially, pigments were examined by pyrolysis-mass spectrometry using a direct insertion probe. Azo pigments of relatively low molecular weight were successfully pyrolyzed, but other pigments were not able to be characterized. It was decided to switch to direct temperature resolved mass spectrometry (DTMS), re-examining the pigments studied with pyrolysis and looking at others. Total ion chromatograms (TIC) were obtained for 106 pigments, with mass spectra collected at 70 eV.

The pigments that were non-organometallic and non-lake (e.g. not salts) gave excellent TIC's and mass spectra. The 70 eV ionizing voltage gave spectra which were a good balance of molecular ion and fragmentation. The technique worked well even for pigments that are inherently extremely stable due to extensive conjugation, such as the quinacridones.

Four of the eight paints were examined. These included two acrylic (with pigments PY74 and PY3) and two water-miscible oils (pigments PB15 and PY65). In all of the cases it was possible to identify the pigment from the paint. It was also possible, in the case of the acrylics, to determine the copolymer mixture.

Building and Using Mass Spectral Reference Libraries

Steve Stein

NIST Mass Spectrometry Data Center, Gaithersburg, Maryland

Electron ionization mass spectra serve as fingerprints for volatile compounds, and when allied with retention time matching in GC-MS, provide what has been called the 'gold standard' for compound identification. Yet spectral variations do occur, compounds may be missing from the library and extracting good quality spectra from complex matrices can present problems, especially when a high level of confidence is demanded. This presentation will examine these and related issues.

Variability: Even for electron ionization mass spectra, peak abundances in the spectrum of a compound can depend on instrument conditions and chemical reactivity. Spectral variations are compensated for by inclusion of replicate spectra and use of robust algorithms for matching.

Matrix Effects: A sufficiently complex or unlucky analysis can produce spurious peaks that prevent a clear identification. Practical methods for extracting "purified" spectra will be discussed.

Retention Times: Retention index requirements, even using estimates, can greatly add to the confidence of identification. The development and use of a comprehensive collection of retention indices and estimation methods will be discussed.

Multiple Ion Monitoring: For detection of compounds at very low levels, methods may monitor just a few peaks. Our recent studies show that the risk of misidentification by this method may be larger than commonly realized.

Reference Spectrum Reliability: A variety of computer methods are used to find suspect spectra. Mass spectra are full of surprises and a skilled evaluator is required in the discovery of errors. Illustrations of these difficulties will be presented.

Compounds not in the Library: When a detected compound is not represented in the library, other means can be used for establishing its identity. These include spectra similarity searching, substructure/hit-list analysis and trial-and-error methods assisted by spectrum/structure analysis tools.

The Characterization of Polysaccharide Binders by Chromatographic Analytical Procedures

Maria Perla Colombini, Vincenzo Restivo

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Identifying plant gum in painting samples is still a difficult task due to the complexity of the matrix, the small amount of material available for the analysis and the degradation of the original material.

In this work, two analytical chromatographic procedures are described for the characterisation of plant gums in paint samples. The sample is submitted to microwave-assisted hydrolysis with trifluoroacetic acid, and is then cleaned up on an cationic exchange resin. Two analytical instrumental procedures for their detection may be adopted:

- One is based on the direct analysis of the hydrolysate by Anion Exchange Chromatography with Amperometric Detection;
- The other is based on the mercaptalation and silylation of the hydrolysate, and analysis by GC-MS.

Both methods allow the separation of seven monosaccharides and two uronic acids with detection limits of 0.1-0.3 ng/ μ l.

The analytical procedures were tested with reference samples prepared according to ancient recipes at the Opificio delle Pietre Dure of Florence (Italian Ministry of Cultural Heritage - Italy) and applied to the characterisation of paintings from Macedonian tombs (4th – 2nd centuries BC). All the data collected, expressed in relative sugar percentage contents, were submitted to cluster analysis and principal components analysis for gum identification: several groups were spatially separated, which enabled the identification of arabic, tragacanth, karaya, cherry, ghatti, guar and locust bean gum. Wall painting samples from Macedonian tombs (Greece) of the 4th–3rd Centuries B.C., processed by the suggested methods, showed the presence of a complex paint media mainly consisting of tragacanth and fruit tree gums. Moreover, starch had probably been added to plaster as highlighted by the presence of a huge amount of glucose.

LC and LC-MS in Natural Dye Projects Involving the National Museums of Scotland (NMS): Flavonoids and MODHT

Anita Quye

National Museums of Scotland, Edinburgh, United Kingdom

The NMS routinely uses photodiode array high-performance liquid chromatography (PDA HPLC) to analyse organic natural dyes in historical textiles. Interpreting the results relies on both the chemical characterisation of reference dyes, and identification of chemical differences between reference and historical dyes. Several collaborative projects have been developed by the NMS with the School of Chemistry, University of Edinburgh to identify unknown dye components and degradation products observed in PDA HPLC results, with flavonoids in natural yellow dyes being of special interest. The successful application of LC and LC-ESI MS n (electrospray ionisation with mass spectrometry “to the n ”) for characterising flavonoids and their photo-degradation products to improve the interpretation of results in the routine analysis of historical samples will be shown.

The NMS and UoE are now applying the analytical approach from the flavonoid research to a multidisciplinary scientific project funded by the European Union called ‘Monitoring of Damage to Historical Tapestries’ (MODHT)*. MODHT seeks to improve the care and protection of tapestries through a better understanding of the materials and techniques used in their construction as well as identifying degradation processes at the molecular level. The project is taking an integrated analytical approach to these aims by correlating the chemical composition (bulk and surface) of dyed and undyed wool and silk fibres with changes in their physical properties, e.g. viscoelasticity and tensile strength. Ultimately the project will lead to scientific ‘indicators of damage’ being developed so that the risk of damage when moving, treating or displaying an historic tapestry can be analytically assessed. An overview of the chromatographic and mass spectrometric methods being used in MODHT will be presented.

**MODHT is funded in the EU’s 5th Framework Programme for ‘Improved damaged assessment on cultural heritage’, contract number EV4K-CT-2001-00048.*

Analysis of Natural Organic Red Dyestuff with HPLC

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Different variations of High Performance Liquid Chromatography with a diode-array-detector (HPLC-DAD) based methods have been successfully applied to the identification of natural organic dyes in art objects, proving that HPLC is a powerful tool to detect dyestuffs that are present even in tiny quantities. Recently, more elaborate analytical methods employing mass spectrometric (MS) detection have been introduced for investigation of natural dyes. LC-MS has potentially enhanced analytical capabilities, but of course with increased analysis costs.

Red natural organic colorants, extracted from samples that were derived from Byzantine Icons, were identified utilizing a reversed-phase HPLC-DAD. Standards of alizarin, purpurin and carminic acid were used for standard solution preparations, and reference materials of madder, cochineal, Brazil wood, dragon's blood and lac dye were utilized for method development. Standards and reference materials were used for preliminary HPLC investigations to develop a method that enables adequate separation and accurate identification. A library with retention times and corresponding spectra was developed.

Reference and real sample quantities on the order of 1mg were treated with a solution of H₂O:MeOH:37% HCl (1:1:2, v/v) for 15 minutes at 100° C. After filtering, the solutions were evaporated by heating (50-60° C) under gentle nitrogen flow. The dry residues were reconstituted in 0.5ml of a mixture of H₂O:MeOH (1:1, v/v) and submitted for HPLC analysis performed with a gradient elution program utilizing two solvents: solvent A: H₂O-0.1%TFA and solvent B: CH₃CN-0.1%TFA and a flow rate of 0.6ml/min. Retention times and UV-Vis spectra were acquired in the wavelength range of 191-799nm and were used for identification.

Samples from five Byzantine Icons were analyzed. Carminic acid, the main component of cochineal was detected in three of the samples. Brazil wood appeared to be present in the other two.

A Non-Hydrolytic Method of Dyestuff Extraction from Lake Pigments in Paint Samples: Pros and Cons

Catherine L. Higgitt, Jo Kirby
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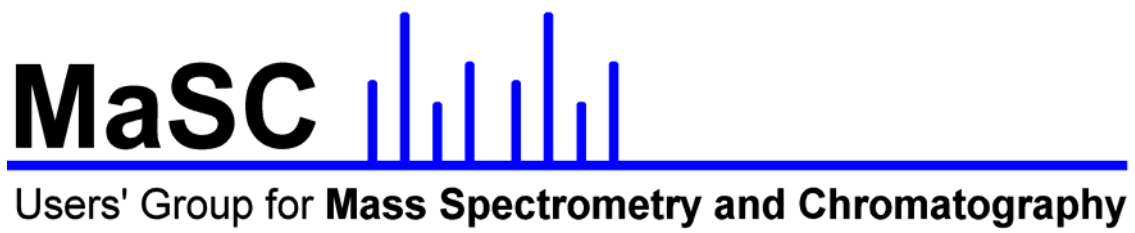
Acid hydrolysis is commonly used to extract dyestuffs from samples for analysis. Where the dyestuff is present on a substrate in the form of a pigment and bound in a paint medium, this method is not always efficient. A methylation method was developed at the National Gallery in London originally for TLC and is now employed for HPLC–DAD examination of red and yellow dyestuffs in lake pigments used in easel paintings.

BF₃/MeOH is recommended for use as a reagent for the conversion of fatty acids into methyl esters and thus is able to break up the polymerised oil paint film, releasing the pigments. In addition, it releases the dyestuff from the lake pigment, taking it into solution. It has been found by LC–MS that, under the conditions employed, carboxylic acid groups in certain anthraquinone dyestuffs are partially methylated, but no other changes have been observed. Samples are treated with a 4% solution of BF₃/MeOH, left overnight at room temperature and analysed within 24 hours.

The advantage of the method is that, apart from this methylation, the dyestuff pattern observed is a good reflection of what is present in the pigment. Where the glycosides of dyestuff constituents could be present, as in the case of yellow lake pigments, they are seen and not lost as the result of hydrolysis. Carboxylic acid-containing constituents, such as the madder constituent pseudopurpurin, are methylated, but remain distinguishable. The ability to recognise such components is useful to provide information on the pigment manufacture.

The principal disadvantage of the method is that the results are difficult to quantify. The action of the reagent is not quantitative and side reactions may occur. Because this is a non-hydrolytic method, the advantage of the relatively simple chromatograms given by hydrolysis is lost.

The use of the method is illustrated with examples.



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Proposed JCAMP-DX Guidelines for Mass Spectral Database Submissions

The MaSC Organising Committee has adopted the JCAMP-DX file format as the basis for *submissions* to its future Mass Spectral Database.

1. Official JCAMP-DX format versions, label names, label definitions and other labeling/naming conventions will be used whenever possible as established by the IUPAC JCAMP Working Party (<http://www.jcamp.org>) and IRUG (<http://www.irug.org>).
2. JCAMP-DX files will only be used for mass spectral data. A JCAMP-DX protocol has not been defined by the JCAMP Working Party for chromatographic data and there are no plans to do so.
3. Version 5.01 of the file format, the most recent official version, will be used as it contains label names for mass spectral data.

JCAMP-DX 5.01 File Format Requirements

Basic structure:

1. A JCAMP-DX file consists of a series of linked data records (fields).
2. Data records are stored in one of three types: a *labeled data record* (LDR), a *data-type-specific record*, or a *user-defined labeled record*. Only the *user-defined labelnames* are modifiable by MaSC.
3. General JCAMP: The *labeled data records* have the format: `##labelname= dataset`
MS specific: The *data-type-specific records* have the format: `##.labelname= dataset`
MaSC specific: The *user-defined labeled records* have the format: `##$labelname= dataset`
4. The first three data records must be `##TITLE=`, `##JCAMP-DX=`, and `##DATA TYPE=` in that order. The file must terminate with `##END=`

General remarks:

1. Data records may be no longer than 80 characters per line, but are allowed to continue on subsequent lines.
2. Comments, which are ignored by data importers and translators, begin with `$$` or `##=`, and must finish at the end of the line on which they start.
3. Data records can be in any order with the exception of `##TITLE=`, `##JCAMP-DX=`, `##DATA TYPE=`, and `##END=` as described above.

Proposed MaSC JCAMP-DX File Format

##TITLE= [first 8 characters assigned by MaSC]; [Sample name]
##JCAMP-DX= 5.01 \$\$[Name and Version number of the JCAMP-DX program]
##DATA TYPE= MASS SPECTRUM
##DATA CLASS= PEAK TABLE (for single spectrum), XYDATA (for raw data),
NTUPLES (for spectral series)
##ORIGIN= [Institution name, analyst name, address, phone, fax, e-mail]
##OWNER= COPYRIGHT (C) [Year] by [Institution Name]
##\$License= [a licensing statement to be determined at a later date]
##\$Institution Filename= [originating institution's filename]
##SAMPLE DESCRIPTION= [composition or origin, collection date, state (solution/solid), etc.]
##SAMPLING PROCEDURE= [no derivatisation, pyrolysis, derivatisation (diazomethane,
BSTFA, Methprep I/II, TMAH, BF3, etc.)]
##TEXT= YES/NO (future plans: complete bibliographic information
available on www.mascgroup.org)
##LONG DATE= [YYYY/MM/DD HH:MM:SS.SSSS ±UUUU] (defined in 5.01
version)

\$\$ Equipment
##.INLET= GC (gas chromatograph), LC (liquid chromatograph), DIRECT
##INSTRUMENTAL PARAMETERS= [For GC: column brand, stationary phase, i.d., o.d., film
thickness, column length, pressure/flow control, temperature
program, carrier gas, flow rate, injection parameters (pyrolysis,
split/splitless, on-column), etc.]
##SPECTROMETER/DATA SYSTEM= [Manufacturer and Model of Mass Spectrometer and of GC
or LC, software system and version]
##RESOLUTION= [mass resolution]
##.SPECTROMETER TYPE= Q (quadrupole), TRAP (ion trap), TOF (time-of-flight), B, BE, EB,
etc.
##.SOURCE TEMPERATURE= [temperature of ion source]
##.IONIZATION MODE= EI+/-, CI+/-, FAB+/-, TSP+/-, ESI+/-, APCI+/-
##.IONIZATION ENERGY= [ionization energy in eV]
##.AQUISITION RANGE= [first mass, last mass in amu]
##.SCAN RATE= [scan rate in masses/second with units defined]

\$\$ Compound Information
##CAS NAME= [if known]
##NAMES= [common names]
##MOLFORM= [molecular formula]
##CAS REGISTRY NO= [CAS number]
##MW= [molecular weight]

\$\$ Spectrum
##.SCAN NUMBER=
##.RETENTION TIME= [retention time in seconds or Kovats Index]
##.BASE PEAK=
##.BASE PEAK INTENSITY= [unscaled Y-value of the base peak] COUNTS
##.RIC= [relative ion count as recorded by instrument software]
##DATA PROCESSING= AVERAGE or BACKGROUND SUBTRACTION
##XUNITS= [m/z]
##YUNITS= [Relative Abundance]
##NPOINTS= [Total number of x,y pairs]
##XYDATA=(XY..XY)
##END=

Example

##TITLE=MaSC0001 - Methyl hexadecanoate
##JCAMP-DX=5.01 \$\$Information entered manually, no JCAMP export available
##DATA TYPE=MASS SPECTRUM
##DATA CLASS=XYDATA
##ORIGIN=National Gallery of Art, Christopher Maines, Scientific Research Department, 6th and Constitution Ave. NW, Washington DC USA, tel: +1 202 842 6055, fax: +1 202 842 6886, email: c-maines@nga.gov
##OWNER=COPYRIGHT (C) 2004 by National Gallery of Art, Washington DC
##\$License=to be determined
##\$Institution Filename=Mitchell-WhiteFluffyCrystals.sms
##SAMPLE DESCRIPTION=White crystals from painting
##SAMPLING PROCEDURE=TMAH in-situ, pyrolysis, splitless
##TEXT=NO
##LONG DATE=2004/04/09 16:00 -5:00

\$\$ Equipment

##.INLET=GC
##INSTRUMENTAL PARAMETERS= Varian VF-5ms,30m x 0.32mm o.d. x 0.25mm i.d., 0.25u film, VF-5ms, Helium, 1.2 ml/min, flow control, 5min at 40C then 10C/min to 300C for 5min
##SPECTROMETER/DATA SYSTEM=Varian Saturn 2000 GC/MS, Saturn GCMS Workstation v.5.51
##RESOLUTION=1 m/z
##.SPECTROMETER TYPE=TRAP
##.SOURCE TEMPERATURE=220
##.IONIZATION MODE=EI-
##.IONIZATION ENERGY=
##.AQUISITION RANGE=45, 600
##.SCAN RATE=1 sec/scan

\$\$ Sample Information

##CAS NAME=Hexadecanoic acid, methyl ester
##NAMES=Methyl palmitate
##MOLFORM=C17H34O2
##CAS REGISTRY NO=112-39-0
##MW=270

\$\$ Spectrum

##.SCAN NUMBER=1478
##.RETENTION TIME=1478
##.BASE PEAK=74
##.BASE PEAK INTENSITY=1947 COUNTS
##.RIC=12581
##.DATA PROCESSING=BACKGROUND SUBTRACTION
##XUNITS=m/z
##YUNITS=Relative Abundance
##NPOINTS=196
##XYDATA=(XY..XY)
45 56
50 22
.....
##END=

