

## **MaSC 2011 Meeting Program**

Harvard Art Museums  
Cambridge, MA USA

12–13 May 2011

# Harvard Art Museums

Fogg Museum  
Busch-Reisinger Museum  
Arthur M. Sackler Museum

Dear MaSC Meeting participants,

On behalf of the Straus Center for Conservation and Technical Studies at the Harvard Art Museums, welcome to the Fifth Meeting of the Users' Group for Mass Spectrometry and Chromatography. We are very happy to be able to host this year's meeting and we hope your visit to Cambridge is enjoyable and informative. Thank you in advance to the presenters for their willingness to share and discuss their work, and to Narayan Khandekar, Dan Kirby, and Erin Mysak, who with Kathleen Kennelly have contributed much time and effort to plan and produce this event.

With warm regards,



Henry Lie

Director

Straus Center for Conservation and Technical Studies



## Preface

We would like to welcome you to the Fifth Meeting of the Users' Group for Mass Spectrometry and Chromatography (MaSC) at the Harvard Art Museums, Cambridge, MA.

This is the first time a MaSC Workshop and Meeting has been organized by an institution outside of those represented by the committee members and shows the importance and growth of the work begun by the Group in 2003. The Workshop that preceded this meeting focussed on the analysis of synthetic organic pigments and proteins by MALDI-TOF-MS. We are very grateful for the support of Waters Corporation who donated the instrument, and who provided expert staff for the three days of the Workshop. The techniques presented are relatively new in the museum world, and it is exciting that we are able to share these recent developments with the participants.

As always the Meeting has a diverse programme reflecting the wide range of research of MaSC members and includes keynote presentations by Marvin L. Vestal, who has extensive experience in proteomics and instrument development, and John M. Asara, who worked on the protein sequences from Mastodon and Tyrannosaurus Rex. The sessions cover direct mass spectrometry methods; museum applications of chromatography and MS; protein analysis; and resin and polysaccharide analysis. A summary of the workshop will give some insights to those who were unable to attend the workshop itself.

We would like to acknowledge Waters Corporation and the Andrew W. Mellon Foundation for their support of the Workshop, and Harvard Art Museums for providing venues and facilities for hosting the Fifth MaSC Workshop and Meeting, and we would particularly like to thank colleagues in the Straus Center for Conservation and Technical Studies for all their support and assistance in organising and hosting these events.

We are sure that you will enjoy the Meeting and hope that you will also have a chance to explore the many collections and history of the Boston area.

Local Organising Committee:

**Kathleen Kennelly**  
**Narayan Khandekar**  
**Daniel P. Kirby**  
**Erin Mysak**

The MaSC Committee:

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

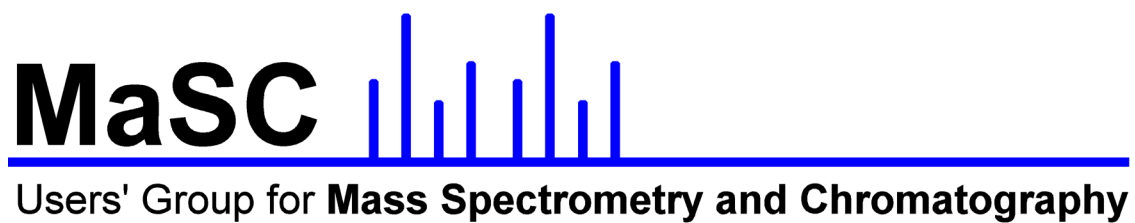


The organising committee gratefully acknowledges  
the support of our sponsors:

The Andrew W. Mellon Foundation







## Meeting Schedule





## MaSC Meeting, Harvard Art Museums, Sackler Auditorium

Thursday, 12 May

9.00 am      **Registration**

9.15          **Welcome and Introduction**

Henry Lie, Director, Straus Center for Conservation and Technical Studies  
Narayan Khandekar, Senior Conservation Scientist

9.30          **Keynote Speaker: Marvin L. Vestal**  
**Chair: Daniel P. Kirby**

10.30        Coffee

11.00        **Session 1: Direct MS Methods**  
**Chair: Klaas Jan van den Berg**

**Ilaria Bonaduce, Francesca Modugno, Sibilla Orsini,**  
**Jeannette Jacqueline Lucejko\*, Maria Perla Colombini**  
Characterisation of synthetic varnishes and paint binders by DEMS  
and Py-GCMS

**Lisa E. Gulian\*, Shawn Owens, Sarah Muliadi,**  
**Michael Callahan, Nathan Svadlenak, Mattanjah de Vries,**  
**Patrick McGovern, Karen Trentelman**  
Application of REMPI laser mass spectrometry to art

**Stepanka Kuckova\*, Marie Styblova, Tomas Matys Grygar,**  
**Radovan Hynek**  
Identification of natural organic dyes by mass spectrometry

**Pedro Caetano Alves\***  
The influence of different processing methods on the TAG profile of  
oils by MALDI-FT-ICR-MS

12.30 pm    Lunch

2.00        **Session 1: Direct MS Methods continued**

**Klaas Jan van den Berg\*, Aviva Burnstock, Frank Hoogland,**  
**Francesca Izzo, Henk van Keulen, Katrien Keune,**  
**Thomas Learner, Michael Schilling**  
Analysis of 20<sup>th</sup> century tube oil paint media and additives –  
Recent highlights

**Session 2: Analytical challenges in museum applications, part I**  
**Chair: Narayan Khandekar**

**Patrick Dietemann\*, Wibke Neugebauer, Irene Fiedler, Ursula Baumer**  
Mixtures of egg and oil: Fat tempera or oil paint?

**Joy Mazurek\***  
Characterization of free and total fatty acids in oil:  
Clyfford Still's painting materials

**Steven Saverwyns\*, Delphine Steyaert, Ingrid Geelen,  
Jana Sanyova, Cécile Glaude, Wim Fremout**  
Study of 15<sup>th</sup> and 16<sup>th</sup> century applied brocades of the Southern  
Netherlands

3.30 Coffee

4.00 **Session 3: Analytical challenges in museum applications, part II**  
**Chair: Christopher Maines**

**M.P.Colombini\*, F. Modugno, M.C. Gamberini**  
Quality assurance in archaeometry: a round robin test of a XVII  
century pharmaceutical formulation replica

**Clara Granzotto, Adriana Rizzo\*, Masahiko Tsukada,  
Daniel Hausdorf**  
Novel efflorescence on museum objects in relation to off-gassing of  
polyester polyurethane foams

**Masahiko Tsukada\*, Clara Granzotto, Adriana Rizzo**  
Organic off-gas analysis in the Oddy test vessel with SPME-GCMS

5.30 Drinks, Harvard Faculty Club, 20 Quincy Street, Cambridge

7.30 Dinner, Harvard Faculty Club (prepayment required)

## **Friday, 13 May**

9.30 am **Keynote Speaker: John M. Asara**  
**Chair: Daniel P. Kirby**

10.30 Coffee

11.00 **Session 4: Protein analysis/LC methods**  
**Chair: David Pegg**

**Katherine Phillips\*, Daniel P. Kirby**  
Peptide mass fingerprinting for protein identification in artificially  
aged egg film

**Wim Fremout\*, Maarten Dhaenens, Steven Saverwyns, Jana  
Sanyova, Peter Vandenabeele, Dieter Deforce, Luc Moens**  
Towards a dedicated peptide LC-MS/MS library for conservation  
science

**Mehdi Moini\***  
Application of capillary electrophoresis mass spectrometry to the  
analysis and dating of museum biological specimens

**I. Degano\*, M.P. Colombini, M. Biesaga, M. Trojanowicz**  
Analytical challenge and conservation: the case of the early  
restoration of a medieval tapestry

12.30 pm Lunch

2.00pm **Session 5: Characterisation of natural resins & polysaccharides**  
**Chair: Ken Sutherland**

**Ilaria Bonaduce, Maria Perla Colombini Joy Mazurek,  
Anna Lluveras Tenorio\***

Two analytical procedures for the GCMS analyses of saccharide binding media in paintings

**Richard Newman\*, Emily Kaplan, Charlotte Taylor**

The source for the natural resin used by the Inka to decorate qero cups

**Gundel Steigenberger\*, Christoph Herm**

GCMS investigations of natural resins from a 300 years old material collection (Vigani Cabinet, Cambridge).

**Michael R. Schilling\*, Herant Khanjian, Arlen Heginbotham**

Development of a pyrolysis-GCMS procedure for characterizing Asian and European furniture lacquers

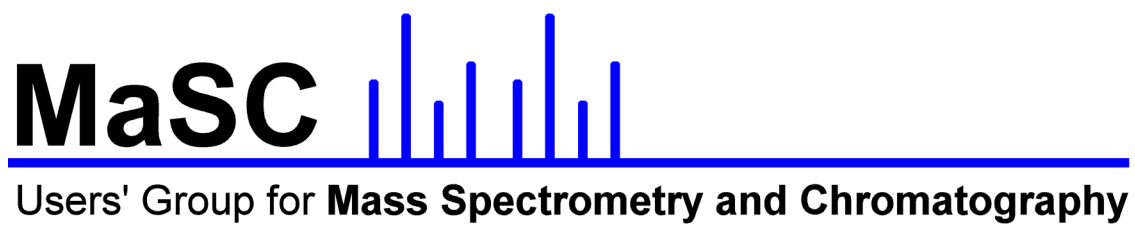
3.30 Coffee

4.00 **Session 6**  
**Workshop Summary: Daniel P. Kirby**

MaSC business meeting

\* designates author to whom correspondence should be addressed.





## Abstracts

## **Characterization of synthetic varnishes and paint binders by DEMS and Py-GCMS**

Ilaria Bonaduce, Francesca Modugno, Sibilla Orsini, Jeannette Jacqueline Lucejko, Maria Perla Colombini

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

Direct exposure mass spectrometry (DEMS) was used to characterize a series of synthetic resins used as varnish and paint binders in contemporary art and in restoration. The materials analyzed were acrylic resins (Paraloid B67, Acril 33), alkyd resins (Winsor & Newton Griffin and Ferrario alkyd paint), and materials more recently introduced in restoration practices as varnishes or consolidants, namely a hydrocarbon resin (Regalrez 1094) an aldehyde resin (Laropal A81), and a polyethyl-oxazoline resin (Aquazol 500). We characterized the raw materials and reference films, before and after natural ageing (1-4 months). The mass spectral interpretation was supported by the analysis of the same materials by Py-GCMS with hexamethyldisilazane. Principal component analysis was performed on the DEMS spectra and proved to be a useful tool for a fast and efficient comparison of the results obtained on reference materials and samples collected from works of art.

## **Application of REMPI laser mass spectrometry to art**

Lisa E. Gulian<sup>1</sup>, Shawn Owens<sup>1</sup>, Sarah Muliadi<sup>1</sup>, Michael Callahan<sup>1</sup>,  
Nathan Svadlenak<sup>1</sup>, Mattanjah de Vries<sup>1</sup>, Patrick McGovern<sup>2</sup>, Karen Trentelman<sup>3</sup>

1 Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, USA

2 Biomolecular Archaeology Laboratory for Cuisine, Fermented Beverages, and Health, University of Pennsylvania Museum of Archaeology and Anthropology, Philadelphia, PA, USA

3 Getty Conservation Institute, Los Angeles, CA, USA

REMPI laser mass spectrometry is a combination of resonance-enhanced multi-photon ionization spectroscopy and time of flight mass spectrometry. This technique enables the collection of mass specific optical spectra as well as of optically selected mass spectra. Analytes are jet-cooled by entrainment in a molecular beam before being resonantly ionized, and this low temperature gas phase analysis provides excellent vibronic resolution. Employing this method, mass spectrometric analysis of unique samples can be simplified and improved: optical selection of targets eliminates the need for chromatography, while highly resolved gas phase spectroscopy allows for specific identification. These two factors allow smaller sample sizes than commercial MS instruments, which in turn will require less damage to objects of cultural heritage. We have explored methods to optimize REMPI laser MS as an analytical tool for the art field to examine laccaic acids in shellacs and flavonoid derivatives used as yellow pigment in paintings and textiles.



## Identification of natural organic dyes by mass spectrometry

Stepanka Kuckova<sup>1,2</sup>, Marie Styblova<sup>2</sup>, Tomas Matys Grygar<sup>3</sup>, Radovan Hynek<sup>1</sup>

<sup>1</sup> Department of Biochemistry and Microbiology, Institute of Chemical Technology, Prague, Czech Republic

<sup>2</sup> Charles University, Department of Chemistry and Chemical Education, Prague, Czech Republic

<sup>3</sup> Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Řež, Czech Republic

Characterization of the majority of natural organic dyes has not been satisfactorily solved, mainly because of similarities in their elemental composition and structure, their presence in low concentrations, immobilization by chemisorption on substrates, and difficulty of extraction from complex matrices of color layers of artworks. Such complications hinder the use of common analytical methods such as gas and liquid chromatography, capillary electrophoresis, FTIR and Raman spectroscopy. We report the application of laser desorption mass spectrometry to the direct identification of natural dyes in their pure forms, as precipitates on inorganic substrates, in mixtures with organic binders, and in real samples of color layers and textile fibers. The method enables fast and reliable identification without any chemical and time consuming preliminary treatments. Additionally, the method could be considered non-destructive since the sample size required is extremely small.

## **The influence of different processing methods on the TAG profile of oils by MALDI-FT-ICR-MS**

Pedro Caetano Alves

Faculdade de Ciências da Universidade de Lisboa, Portugal

Currently, two important “soft-ionization” techniques are available that induce only negligible fragmentation of the analyte, namely electrospray ionization (ESI) and MALDI (matrix-assisted laser desorption ionization) MS. Triacylglyceride (TAG) spectra were among the very first lipid MALDI-TOF mass spectra to be analyzed quantitatively [1]. Although vegetable oil analysis by LCMS provides good results, the technique is quite time consuming when compared, for example, with MALDI-TOF-MS [1-7]. The composition of an oil can be calculated directly from the spectrum since TAGs yield exclusively Na<sup>+</sup> adducts and intense oxidation products are easily detectable by the characteristic mass difference of 16 Da corresponding to the incorporation of oxygen. Studies to address TAG profiles as characteristic features in ageing of oils and in paints made with them are underway. In this paper, preliminary results on oils used in painting formulations, and their processing methods, using MALDI-FT-ICR-MS, are presented.

### References:

1. G.R. Asbury, K. Al-Saad, W.F. Siems, R.M. Hannan, H.H. Hill, *Journal of the American Society for Mass Spectrometry* 10 (1999) 983-991
2. C.D. Cosima, F. Palmisano, C.G. Zambonin, *Rapid Communications in Mass Spectrometry* 19 (2005) 1315-1320
3. B. Fuchs, R. Süß, J. Schiller, *Progress in Lipid Research* 49 (2010) 450-475
4. F.O. Ayorinde, K. Garvin, K. Saeed, *Rapid Communications in Mass Spectrometry* 14 (2000) 608-615
5. G. Stubinger, E. Pittenauer, G. Allmaier, *Phytochemical Analysis* 14 (2003) 337-346
6. C. Hlongwane, I.G. Delves, L.W. Wan, F.O. Ayorinde, *Rapid Communications in Mass Spectrometry* 15 (2001) 2027-2034
7. J. Schiller, R. Süß, M. Petkovic', K. Arnold, *Journal of Food Lipids* 9 (2002) 185-200

## **Analysis of 20<sup>th</sup> century tube oil paint media and additives – recent highlights**

Klaas Jan van den Berg<sup>1</sup>, Aviva Burnstock<sup>2</sup>, Frank Hoogland<sup>1</sup>, Francesca Izzo<sup>3</sup>,  
Henk van Keulen<sup>1</sup>, Katrien Keune<sup>1</sup>, Thomas Learner<sup>4</sup>, Michael Schilling<sup>4</sup>

1 Netherlands Cultural Heritage Agency (RCE), Amsterdam, The Netherlands

2 Courtauld Institute of Art, London, UK

3 Ca' Foscari University, Venice, Italy

4 Getty Conservation Institute, Los Angeles, CA, USA

Modern oil paints are known to show degradation problems such as efflorescence and solvent sensitivity that relate to specific lipidic media and additives in the paint. A combination of analytical techniques is required to obtain information on mixtures of lipidic components in oil paints, the state of ageing or degradation through oxidation, hydrolysis and soap formation [1]. This paper presents some new analytical approaches to the analysis of 20<sup>th</sup> Century oil paints, using extraction procedures of paints and pre-separation of surface layers from bulk paint combined with GCMS, ESI-MS and evolved gas analysis MS (EGA-MS). The results show degrees of hydrolysis of metal soaps and oil media on the surface and bulk, depending on the pigments, inorganic additives and ageing conditions. EGA-MS allows for detection of free fatty acids, metal soaps and the polymeric network as distinct fractions.

### References:

1. K. Keune, F. Hoogland, J.J. Boon, D. Peggie, C. Higgitt, 'Comparative study of the effect of traditional pigments on artificially aged oil paint systems using complementary analytical techniques', in ICOM-CC 15<sup>th</sup> Triennial Conference New Delhi, Preprints Vol. II (2008) pp. 833-842

## Mixtures of egg and oil: Fat tempera or oil paint?

Patrick Dietemann, Wibke Neugebauer, Irene Fiedler, Ursula Baumer

Doerner Institut, Munich, Germany

Tempera paintings by Arnold Böcklin (1827-1901) were studied. Written sources were compared with results from technological study of the paintings (including visual examination and cross-section analysis) and binding media analyses by GCMS and ion exchange chromatography. This approach turned out to be very successful, although in unexpected and disturbing ways.

It is demonstrated that areas of paintings assumed from documentary and visual evidence to be made with egg tempera reveal a significantly lower egg-to-oil ratio than areas painted “in oil”. While confusing at first sight, this observation can be explained by the principles of colloid chemistry. It can be shown that “fat egg tempera” can chemically consist of 90% oil when dry. On the other hand, significant quantities of egg were used in many paintings presumed to be made only with a classic oil medium, as analyses of paintings (15<sup>th</sup> to 17<sup>th</sup> centuries) in our laboratory have shown [1, 2].

This raises the question whether it is possible to analytically distinguish between “fat egg tempera” and “oil paints containing egg”, because this distinction cannot be linked to the egg-to-oil ratio.

### References:

1. S. Dietz, H. Autzen, U. Baumer, P. Dietemann, I. Fiedler, C. Krekel, A. Schöne-man, A. Stange, ‘Studying the ‚Graue Passion‘ by Hans Holbein the Elder’, in Studying Old Master Paintings. Technology and Practice, The National Gallery Technical Bulletin 30 Anniversary Conference Postprints (2010) pp. 89-94
2. J. Koller, I. Fiedler, U. Baumer, ‘Vermeers Maltechnik – eine Mischtechnik. Untersuchung der Bindemittel auf dem Gemälde „Bei der Kupplerin“’, in Johannes Vermeer – Bei der Kupplerin, Staatliche Kunstsammlungen Dresden (2004) pp. 65-75

## **Characterization of free and total fatty acids in oil: Clyfford Still's painting materials**

Joy Mazurek

Getty Conservation Institute, Los Angeles, CA, USA

As part of the GCI's Modern Paints Project, samples from paintings by American Abstract Expressionist Clyfford Still (1904-1980) were analyzed by GCMS. The research generated data that may answer questions about Still's use of hand-ground pigments and his use of tube oil paints. He had access to Bellini tube oil paints, and they are known to contain linseed oil, castor oil, and Thixcin "R" (glycerol tris 12-hydroxystearate) in varying amounts. Markers for Thixcin "R" are hydroxystearic acid and castor oil contains ricinoleic acid. Both of these markers were found in several of Clyfford Still's paintings and imply that these were not hand-ground; however, it cannot be ruled out that Still added castor oil to his paint before mixing. Possible drying oils are identified, and information about the percent hydrolysis of the oils is discussed. Data are shown that highlight the difficulties in identifying oil based on palmitic/stearic (P/S) ratios when mixtures of oils and metal soaps are present.

## **Study of 15<sup>th</sup> and 16<sup>th</sup> century applied brocades of the Southern Netherlands**

Steven Saverwyns<sup>1</sup>, Delphine Steyaert<sup>2</sup>, Ingrid Geelen<sup>2</sup>, Jana Sanyova<sup>1</sup>,  
Cécile Glaude<sup>1</sup>, Wim Fremout<sup>1</sup>

1 Laboratories Department, Royal Institute for Cultural Heritage (KIK/IRPA),  
Brussels, Belgium

2 Conservation-Restoration Department, Royal Institute for Cultural Heritage  
(KIK/IRPA), Brussels, Belgium

In the 15<sup>th</sup> and 16<sup>th</sup> centuries fine textiles played an important role in the decoration of interiors. In the visual arts they were imitated as closely as possible by using creative illusionist painting and relief techniques. Applied brocades succeeded best in imitating textiles. Over the last few years a team of art historians at KIK/IRPA specialized in medieval polychromy techniques made an inventory of the applied brocades of the Southern Netherlands in the 15<sup>th</sup> and 16<sup>th</sup> centuries. Their visual and technical study of the applied brocades was complemented by laboratory studies focusing on the stratigraphy and the chemical composition of the constituents. Of the more than 80 works described, 40 were studied in the laboratory by means of around 200 microsamples. During this presentation a summary of the results is given, with an emphasis on the organic components (mainly waxes and oils, sporadically proteins) that were studied by means of GCMS and FTIR.

## **Quality assurance in archaeometry: A round robin test of a XVII century pharmaceutical formulation replica**

M.P.Colombini<sup>1</sup>, F. Modugno<sup>1</sup>, M.C. Gamberini<sup>2</sup>

1 Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

2 Dipartimento di Chimica e Chimica Farmaceutica, Università di Modena, Italy

The chemical analysis of archaeological and historical residues of ancient medical preparations has the potential to provide valuable information on ancient medical practices. Nevertheless, chemical analysis is affected by the complexity of the mixtures of organic and inorganic materials present in pharmaceutical/medical preparations as balms or ointments, by the transformations due to ageing, and by interferences of the various components of the matrix. Consequently, a multi-analytical approach and special caution in the interpretation of the results are necessary. In order to contribute to the improvement of analytical strategies for the characterization of complex residues and to reconstruct ancient medical practices, a replica of a XVII century pharmaceutical formulation was prepared in the laboratory following the procedure reported in an ancient text. A portion of the material was sent as a blind sample to 11 laboratories to be analyzed independently with various techniques, including spectroscopic, chromatographic and mass spectrometric methods. Herein, the main results of the round robin exercise are reported and discussed.

## **Novel efflorescence on museum objects in relation to off-gassing of polyester polyurethane foams**

Clara Granzotto<sup>1</sup>, Adriana Rizzo<sup>1</sup>, Masahiko Tsukada<sup>1</sup>, Daniel Hausdorf<sup>2</sup>

1 Department of Scientific Research, The Metropolitan Museum of Art, New York, USA

2 Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art, New York, NY, USA

Commercial polyester polyurethane foams retain in their bulk volatile components from their manufacture, including monomers, additives and catalysts, which are then released in the atmosphere. The tendency of polyurethane foams to 'off-gas' and their consequent stiffening over time are well known [1, 2]. Due to their remarkable cushioning properties, these foams are used extensively as padding in crates for transport of artworks, but in some cases they have been used as cushioning in storage in the past, without consideration of their archival properties. Volatile and semi-volatile amines have been identified in efflorescence, deposits and coatings on the surface of wooden and metal objects, and earthenware. These amines are of the same type as those used as catalysts in the manufacturing of flexible polyurethane foams. The study involved the use of GCMS techniques (TD-Py-GCMS, Py-GCMS, SPME-GCMS), applied to museum objects as well as references and replicas, to deepen the understanding of the extent and potential effects of off-gassing of polyurethane foams on selected materials.

### References:

1. T. van Oosten, 'Crystals and crazes: degradation in plastics due to microclimates' in *Plastics in Art. History, Technology, Preservation* (2002) pp. 80-89
2. P.B. Hatchfield, *Pollutants in the Museum Environment - Practical Strategies for Problem Solving in Design, Exhibition and Storage* (2002)



## **Organic off-gas analysis in the Oddy test vessel with SPME-GCMS**

Masahiko Tsukada, Clara Granzotto, Adriana Rizzo

Metropolitan Museum of Art, Department of Scientific Research, New York, USA

The “Oddy test” is a widely accepted screening method in museums for the evaluation of materials for their safe usage in display and storage of artworks. The sample material is enclosed in a test vessel with metal coupons under elevated temperature and humidity conditions, but not in contact, and the test evaluates the effect of off-gassing from the material on the metal coupons. Different test set-ups have been published [see for example 1, 2], but the nature and extent of off-gassing that affects the metal coupons is not well studied. In order to explore this aspect of the Oddy test, air from appropriately designed Oddy test vessels was analyzed with SPME-GCMS. In this presentation, some considerations about the test vessel and preliminary results will be discussed.

### References:

1. J.A. Bamberger, E.G. Howe, G. Wheeler, *Studies in Conservation* 44 (1999) 86-90
2. L. Robinet, D. Thickett, *Studies in Conservation* 48 (2003) 263-268

## **Peptide mass fingerprinting for protein identification in artificially aged egg films**

Katherine Phillips, Daniel P. Kirby

Straus Center for Conservation and Technical Studies, Harvard Art Museums,  
Cambridge, MA, USA

Many different proteins can be found in artworks, for example, in the binder in casein and egg tempera paints or in animal glue grounds. Peptide mass fingerprinting (PMF) using MALDI-TOF, a common method for protein identification in the biotechnology field, can readily be applied to artworks. In this presentation, we report the use of PMF in an art museum setting, in particular to develop a set of marker ions to identify egg proteins using pigmented and unpigmented egg-based films. Further, the films were aged with heat and light to approximate ageing of real artworks and verify that the markers remain intact. In addition to hen eggs, other avian species' eggs were studied for the first time in an effort to develop a technique to differentiate among the different species. Finally, applications to samples from artworks will be shown to illustrate the technique.

## **Towards a dedicated peptide LC-MS/MS library for conservation science**

Wim Fremout<sup>1,2</sup>, Maarten Dhaenens<sup>3</sup>, Steven Saverwyns<sup>1</sup>, Jana Sanyova<sup>1</sup>,  
Peter Vandenabeele<sup>4</sup>, Dieter Deforce<sup>3</sup>, Luc Moens<sup>2</sup>

1 Royal Institute for Cultural Heritage (KIK/IRPA), Brussels, Belgium

2 Ghent University, Department of Analytical Chemistry, Ghent, Belgium

3 Ghent University, Laboratory for Pharmaceutical Biotechnology, Ghent, Belgium

4 Ghent University, Department of Archaeology, Ghent, Belgium

The use of liquid chromatography tandem mass spectrometry (LC-MS/MS) on tryptic digests of cultural heritage objects presently attracts a lot of attention. It allows unambiguous identification of peptides and proteins, even in complex mixtures, and species-specific identification becomes feasible, while further reducing sample consumption. Determination of the peptides is commonly based on theoretical cleavage of known protein sequences and comparison of the expected peptide fragments with those found in the MS/MS spectra. Complex computer programs, such as Mascot, perform well identifying known proteins, but fail whenever protein sequences are unknown or incomplete. Also, when trying to distinguish the evolutionary well preserved collagens of different species, Mascot lacks the necessary specificity. By creating a dedicated library of MS/MS spectra of species-specific peptides using the familiar NIST MS Search tool, more accurate information on the proteins can be obtained. First results in cultural heritage studies are discussed.

## **Application of capillary electrophoresis mass spectrometry to the analysis and dating of museum biological specimens**

Mehdi Moini

Smithsonian Institution, Museum Conservation Institute, Suitland, MD, USA

Proteins are present in all living and dead organisms as well as in objects such as textiles, papers, and paints. Identification of the protein contents of these materials and their degradation products in combination with their age is often critical to the identification of the specimens, their authenticity, and their preservation. MALDI, HPLC, and CE in conjunction with mass spectrometry are among the fastest growing analytical techniques for the analysis of non-volatile and biological compounds. CE-MS can analyze complex mixtures with a wide range of molecular sizes, charges, masses, quantities, heterogeneities, and modifications. In addition to proteins and peptides, CE-MS can characterize small molecules such as amino acids and determine their D/L isomers. The technique potentially serves as an independent method for dating biological material. In this presentation, the advantages of CE-MS in the analysis and dating of museums' proteinaceous specimens will be discussed.

**Analytical challenge and conservation:  
The case of the early restoration of a medieval tapestry**

I. Degano<sup>1</sup>, M.P. Colombini<sup>2</sup>, M. Biesaga<sup>3</sup>, M. Trojanowicz<sup>3</sup>

1 ICCOM-CNR, Pisa, Italy

2 Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

3 Faculty of Chemistry, University of Warsaw, Warsaw, Poland

A 15<sup>th</sup> century tapestry, L'assalto finale a Gerusalemme (1480, Belgium), was studied as part of a conservation project with the Opificio delle Pietre Dure, Florence. Coloured areas were sampled in order to characterize the dye palette. With regard to black areas, very degraded and darker yarns could be distinguished from less degraded and slightly lighter ones. Conservators hypothesized that the darker yarn originated from an 18<sup>th</sup> century restoration. Samples belonging to the two classes of blacks were analyzed by an optimized LC-MS/MS analytical procedure to validate this hypothesis. The analytical results suggest that the original dye was based on gallo-tannins, which caused the yarn dyed by this technique to degrade quickly. A different yarn, dyed by superimposing colours, was used during restoration. The results demonstrate that LCMS was essential for detecting chromophores in the sample extracts at sub-ppm concentrations, thus allowing the identification of minor components of extremely complex dye mixtures.

## **Two analytical procedures for the GCMS analysis of saccharide binding media in paintings**

Ilaria Bonaduce<sup>1</sup>, Maria Perla Colombini<sup>1</sup>, Joy Mazurek<sup>2</sup>, Anna Lluveras Tenorio<sup>1</sup>

<sup>1</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

<sup>2</sup> Getty Conservation Institute, Los Angeles, CA, USA

Two different GCMS analytical procedures allowing the characterization of saccharide binders in works of art are described. The procedures have been separately developed at two laboratories: the Getty Conservation Institute (GCI) in Los Angeles, USA and the Department of Chemistry and Industrial Chemistry (DCCI) of the University of Pisa, Italy. The GCI procedure is based on the methoxylamine acetate derivatization method of neutral sugars (aldoses and ketoses) obtained from saccharide materials after hydrolysis. The DCCI procedure is based on the analysis of the mercaptal derivatives of the parent aldoses and uronic acids obtained after microwave-assisted hydrolysis. A comparison of each analytical step (hydrolysis to free monosaccharides, purification from inorganic and other organic materials, derivatization), and advantages and drawbacks are discussed. The analysis of reference materials and painting samples shows that both methods give comparable results, and highlight important considerations in data interpretation.

## **The source for the natural resin used by the Inka to decorate qero cups**

Richard Newman<sup>1</sup>, Emily Kaplan<sup>2</sup>, Charlotte Taylor<sup>3</sup>

1 Museum of Fine Arts, Boston, MA, USA

2 National Museum of the American Indian, Cultural Resources Center, Suitland, MD, USA

3 Missouri Botanical Garden, St. Louis, MO, USA

Late in the pre-colonial period, the Inka began to utilize an unusual resin to decorate wood qero cups, although the resin appears to have been known for some time prior to this. The resin, which is hard and insoluble, can be made rubbery by boiling in water or chewing, and is thought to have come from *Elaeagia pastoense*, first identified in southern Colombia by Mora in 1977. Pigments were kneaded into the rubbery material, which was then stretched and cut into small pieces for inlaying into low relief compartments on the qeros. Our earlier work showed that the resin on the qeros closely resembles the material from the plant studied by Mora [1]. However, the same or closely related plants that supply similar resin have been found from Panama to Peru. In order to determine the relationship of the resin found on qero cups to the specific plant identified by Mora and other related plants, twenty samples of *Elaeagia* from two botanical collections were analyzed, as well as a sample collected by Mora in his original study. Analyses were carried out by GCMS, following methylation using m-(trifluoromethyl)phenyltrimethylammonium hydroxide (TMTFTH); and by pyrolysis GCMS, using simultaneous methylation with tetramethyl ammonium hydroxide.

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1. R. Newman, M. Derrick, 'Painted Qero Cups from the Inka and Colonial Periods in Peru: An Analytical Study of Pigments and Media', in *Material Issues in Art and Archaeology VI* (2002) pp. 291-302

## **GCMS investigation of natural resins from a 300 year old material collection (Vigani Cabinet, Cambridge)**

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The project aimed to provide a body of chemical reference data for future investigations of resinous materials, but also elucidation of historical nomenclature and ageing processes were part of the investigation. The Materia Medica Cabinet, compiled by John Francis Vigani 1703/1704, has been at Queens' College in Cambridge for the last 300 years. From this collection natural resins were investigated together with reference materials from modern collections and botanical sources. The analytical method used was GCMS following a special extraction scheme with and without derivatization with trimethylsulfoniumhydroxide (TMSH). This technique provides detailed molecular compositions of complex mixtures and makes it possible to establish data profiles of materials. The analytical results obtained from the historical samples were compared to the data profiles of reference and botanical samples, and marker molecules of samples from Cupressaceae, Pistacia and Pinaceae were identified.



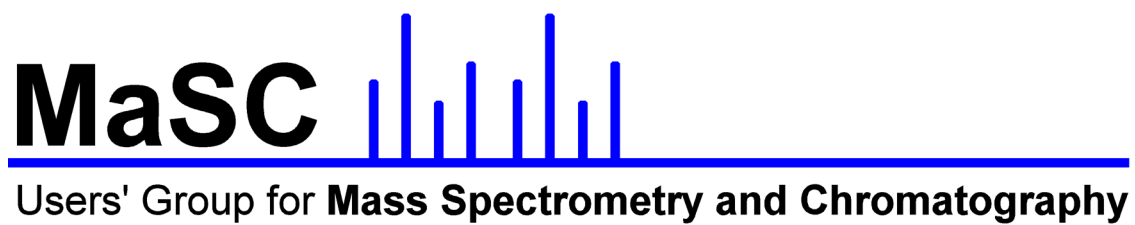
## **Development of a pyrolysis-GCMS procedure for characterizing Asian and European furniture lacquers**

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The J. Paul Getty Museum's collection includes nine pieces of French furniture dating to the mid-eighteenth century that incorporate panels of Asian and European lacquer as part of their surface decoration. As part of a systematic study associated with preparing catalogues of the French furniture collections, the materials and methods of both Asian and European lacquers were studied in some detail, in the hope that temporal, geographic or workshop trends might begin to emerge that would aid in the overall interpretation of these objects. Careful layer-by-layer sampling allowed the analytical program to shed light not only on the presence of these raw materials, but also the ways in which they were selected and used. This paper focuses specifically on the results of organic analysis using TMAH-Py-GCMS.



## Poster Abstracts

## **MALDI-TOF mass spectral identification of plant and animal dyes in historical artefacts**

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The high sensitivity and the simplicity of sample preparation characteristic of MALDI-TOF mass spectrometry are attractive for the study of museum samples. We have used this method to identify the lichen dye vulpinic acid in wool from a Northwest Coast First Peoples ceremonial blanket and an insect dye, probably a laccaic acid, in printing ink from an early 20<sup>th</sup> century Japanese block print. We compared mass spectra from the artefacts with spectra from authentic samples of lichen (“wolf moss”) and insect lac. In these latter spectra, we detected additional ions (such as  $\beta$ -glucans in the lichen sample) that, apart from the dye species, might provide useful insight in some work.

## **GCMS study of the curing of alkyd paints under artificial ageing**

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The chemical transformations occurring in alkyd paint layers during curing and the first stages of ageing processes were investigated at the molecular level by GCMS and FTIR. The aim of the research was to achieve a complete characterization of the paints, to study autoxidation during curing and ageing, and to investigate the effect of the pigment. Two kinds of alkyd paints were studied: Griffin (Winsor & Newton) and Ferrario, containing both inert (carbon black) and iron-based pigments. The paints were used to prepare reference films that were naturally and artificially aged in a climatic chamber. FTIR was used to investigate the changes in the functional groups during ageing. The results highlight the differences in the formulations of the two kinds of alkyd products, and model the main reactions occurring during the curing of the alkyd paint films.

## **GCMS and Py(HMDS)-GCMS characterization of modern and archaeological figs (*Ficus carica*)**

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The hydrolysable and soluble constituents, and the polymerized macromolecules of an archaeological fig (*Ficus carica*) recovered in Zaragoza (Spain), as well as modern dried figs, were analyzed by GCMS after alkaline hydrolysis, solvent extraction and trimethylsilylation, and analytical pyrolysis using hexamethyldisilazane for the in-situ derivatization followed by Py-GCMS. The morphology of the fig specimens was examined by SEM. The major aim was to study the diagenetic alteration undergone by the fig tissues in a peculiar archaeological environment: the fig was in a vessel and covered by a layer of a mixture of orpiment and gypsum. Comparison between the GCMS results from the modern and archaeological figs reveals that degradative reactions took place leading to the disappearance/depletion of reactive and labile compounds. Py-GCMS data provide evidence of a significant degradation of the saccharide and lipid components of the fig tissue leaving a residue enriched in polyphenols and polyesters.

## **The Short Life of Tannins – an innovative approach to the study of ageing processes in tannin dyed textiles**

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We present an innovative project on the study of tannin-based dyes (VAT, “The Short Life of Tannins”) recently funded by the Regione Toscana, Italy (FAS grants). The project involves the Department of Chemistry and Industrial Chemistry (Pisa), the ICCOM-CNR (Pisa) and the Opificio delle Pietre Dure (Florence). The project’s goals are to model ageing processes undergone by textile fibres dyed with iron galls and to identify suitable conservation protocols. Textile reference specimens, also artificially aged, will be analyzed by spectrophotometric, colorimetric and chromatographic and mass spectrometric techniques. HPLC-MS/MS and GCMS will be exploited not only to characterize the raw materials (lipids, proteins, dyes, phenols, etc.), but also to study the degradation products in order to elucidate the ageing processes. Molecular modelling strategies will be applied to study the physical properties of the compounds involved in the textile-dye system. The preliminary results achieved by GCMS analysis of raw materials are presented.

## **The COPAC project: Preventive conservation of contemporary art**

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The COPAC project is a two-year project funded by Regione Toscana actively involving important research institutions and museums (Museo Pecci of Prato, Palazzo Fabroni and Biblioteca of Pistoia). In collaboration with the participating museums, a selection of works of art including paintings by Kiefer, Parmiggiani and Melani will be subject to a detailed diagnostic campaign to:

- evaluate their conservation state;
- identify risk factors for their preservation;
- indicate suitable conditions to be adopted for their preventive conservation

COPAC aims at transferring to contemporary art museums and galleries in Tuscany an interactive system of data processing and diagnostic methodologies based on the chemical, physical and structural research developed during the course of the project.

## **The MEMORI project: Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets – Innovative Research for Market Transfer**

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The main aim of the MEMORI project (EU FP7 Supported Collaborative Project: 265132) is to provide the conservation market with innovative, non-destructive early warning technology for easy assessment of environmental impact on indoor cultural heritage, including a preventive strategy to secure the conservation of movable cultural assets in protective enclosures. Three major objectives are:

1. To perform assessment of degradation risks to a range of types of organic heritage objects due to indoor pollutants. Particularly, the project will investigate the effect of acetic and formic acids on the degradation of natural and synthetic resins, and will be aimed at understanding the best conservation conditions to be used for paintings and to choose appropriate mitigation methods to suppress aggressive pollutants in museum environments.

2. To facilitate integrated in situ measurements and evaluation of indoor environments for cultural heritage by development and marketing of new analytical instruments.

3. To optimize methods to mitigate degrading indoor pollutants.



## **Direct analysis of waxes, resins and lipids by DART/TOF mass spectrometry**

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Many different ambient surface desorption/ionization methods have appeared in recent years in mass spectrometry, such as DART (Direct Analysis in Real Time), introduced by JEOL in 2005 [1], DESI (Desorption Electrospray Ionization) [2] and PADI (Plasma Assisted Desorption/Ionization) [3]. In these processes, the compounds can be ionized under atmospheric pressure, directly in solid state without preparation. The reactive species of DART ionization are produced by an electrical discharge in a helium flow. Placed directly in this stream of metastable helium He(23S) and charged water cluster, the sample is ionized in the open air in front of the analyzer orifice. This technique could provide an alternative method for organic material analysis in cultural heritage as described in a recent publication [4]. A range of resins, waxes and lipids has been analyzed both by GCMS and DART/TOF MS in order to evaluate the potential of this new method to identify some natural substances in the field of cultural heritage.

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3. L.V. Ratcliffe, F.J.M. Rutten, D.A. Barrett, T. Whitmore, D. Seymour, C. Greenwood, Y. Aranda-Gonzalvo, S. Robinson, M. McCoustra, *Analytical Chemistry* 79 (2007) 6094 - 6101
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## **Identification of indigo and its degradation products on silk textile fragments using GCMS**

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The use of m-(trifluoromethyl)phenyltrimethylammonium hydroxide (TMTFTH) extraction and derivatization, followed by GCMS, has proven to be a simple and fast technique for the analysis of indigo dye on textiles. Not only does the procedure allow for the identification of the main dye component, indigotin, but it also provides information on the degradation of indigo on textiles. This presentation discusses key compounds formed through the reactions of TMTFTH with indigotin and the main degradation products of indigo with reference to a study performed on two Indian textiles from the Sultanate period (13<sup>th</sup>-15<sup>th</sup> centuries) in the collection of the Fine Arts Museums of San Francisco. This analysis method is also currently being used by the Canadian Conservation Institute to extract and identify other natural and synthetic dyes on textiles. Examples of the chromatograms obtained from these extractions will be presented and discussed.

## **Characterization of celluloid objects from Czech museum collections**

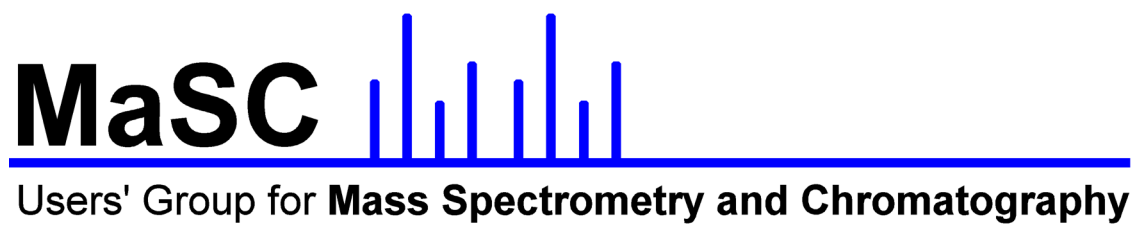
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Celluloid is a plastic material based on cellulose nitrate and camphor, and its production started in the second half of the 19<sup>th</sup> century. Initially, its primary uses were for utilitarian objects. In this study, we examined some objects made with celluloid, such as combs and glasses, which are presently stored in the collections of two Czech museums (the Museum of Decorative Arts in Prague and the East Czech Museum in Pardubice). Almost all these objects are in poor condition, showing large internal cracks. The main aim of the present work was the identification of the chemical components and the evaluation of the state of conservation of the objects analyzed. For this purpose the chemical, elemental and morphologic analyses were carried out by Py-GCMS, FTIR and SEM-EDS. The analytical results and potential conservation methods will be discussed.



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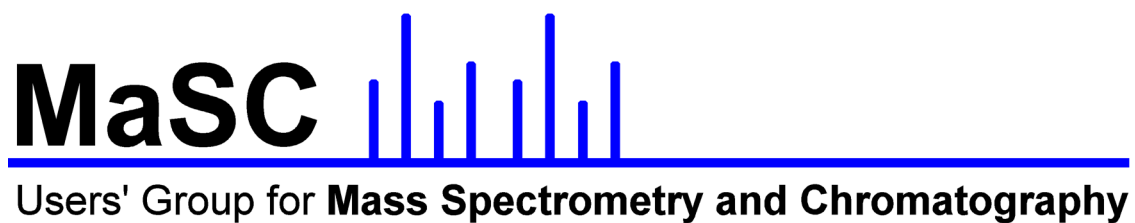
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Users' Group for **Mass Spectrometry and Chromatography**

## **Guide to Cambridge & Boston**

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There are over one hundred dining establishments located in the Square.  
Further suggestions can be found at: [www.harvardsquare.com/restaurants.aspx](http://www.harvardsquare.com/restaurants.aspx)

### **AMERICAN (TRADITIONAL)**

#### **Au Bon Pain, 1350 Mass. Avenue**

Baked goods, sandwiches, soups, and more

#### **Boloco, 71 Mt. Auburn Street**

Salads, smoothies, and wraps

#### **Broadway Marketplace, 468 Broadway (one block from the Sackler)**

Deli sandwiches, soups, salad bar, muffins, and pastries

Take-out with a few tables available

#### **Charlie's Kitchen, 10 Eliot Street**

Famous double cheeseburger with a wide assortment of draught and bottled beers

#### **Clover, 7 Holyoke Street**

Local, organic, vegetarian and vegan sandwiches, soups, and more

#### **Darwin's Ltd., 1629 Cambridge Street**

A unique deli and cafe, serving up "Best of Boston" gourmet sandwiches, take-out dinners, local bakery breads and goodies, deliciously rich coffee, and a great selection of loose teas.

#### **Grafton Street Pub & Grill, 1230 Massachusetts Avenue**

Contemporary American cuisine for lunch and dinner seven days a week. The bar boasts an extensive selection of beer, wine and liquor, and features several signature cocktails.

#### **The Garage, entrances at 36 J.F.K., 81 Mt. Auburn, and 35 Dunster Streets**

The Garage consists of restaurants and retail shops, including:

Crazy Dough's – Pizza, subs and Italian specialties

Chutney's – Indian fast food

Felipe's Taqueria – Burritos, tacos, and authentic Mexican food

Le's - Vietnamese food. Excelling in pho (noodle soup)

#### **The Greenhouse, Harvard University, Science Center, first floor**

Good for cafeteria food: pizza, chicken sandwiches, salad bar, and assorted baked goods

#### **Grendel's Restaurant & Bar, 89 Winthrop Street**

Established in March 1971, Grendel's features a cozy Harvard Square atmosphere serving casual gourmet dishes and international specialties.

#### **Harvest, 44 Brattle Street (on the walkway)**

Food & Wine Magazine's Best New Chef, Chef Mary Dumont of Harvest presents contemporary New England cuisine focused on the regions freshest ingredients.

#### **John Harvard's Brew House, 33 Dunster Street**

American food, including chicken pot pie, grilled tuna steak salad, and home-made meatloaf, while watching the brewers make today's fresh beer.

**Mr. & Mrs. Bartley's Burger Cottage, 1246 Massachusetts Avenue**

Bartley's Burger Cottage is a Cambridge tradition. It's a hole-in-the-wall, crowded, student atmosphere with a huge variety of hamburgers, including veggie burgers.

**Russell House Tavern, 14 JFK Street**

Serving seasonally-inspired, classic dishes from New England and beyond. Hand-crafted cocktails and a distinctive collection of American wines and craft beers.

**ASIAN**

**Café Sushi, 1105 Massachusetts Avenue**

Fresh sashimi, maki sushi, Japanese meat dishes, gyoza dumplings, and more

**Spice Thai Cuisine, 24 Holyoke Street**

**Shabu Ya, 57 JFK Street**

Shabu-shabu, Korean, and sushi

**Wagamama, 57 JFK Street**

International noodle restaurant, wagamama is open daily for lunch and dinner. Enjoy the restaurant's Asian inspired menu including a delicious selection of noodle and rice dishes, salads, fresh juices, wines, sake and asian beers.

**CAFÉS & SWEETS**

**Burdick's Chocolates, 52D Brattle Street**

Offers a full array of chocolates and pastries, coffee, and tea

**Dado Tea House, 50 Church Street**

Tea, coffee, pastries, healthy organic entrees, and sandwiches

**Finale Desserterie & Bakery, 30 Dunster Street**

Sandwiches, soups, salads, and pastries

**Peet's Coffee and Tea, 100 Mount Auburn Street**

Fresh whole-bean coffees, premium hand-selected tea, and pastries

**Starbucks, 31 Church Street, 36 JFK Street, 468 Broadway**

**INDIAN**

**Café of India, 52A Brattle Street**

Watch as Tandoori chefs prepare your sizzling & steaming delicacies and fresh breads in the glass enclosed Tandoori kitchen.

**Tamarind Bay, 75 Winthrop Street**

Menu draws on various regions of the sub-continent

**Tanjore, 18 Eliot Street**

Regional Indian cooking, buffet available for lunch

## **ITALIAN/PIZZA**

### **Cambridge 1, 27 Church Street**

Unique salads, ultra-thin crust gourmet pizza. Beer and wine available.

### **Oggi Gourmet, 1350 Massachusetts Avenue - Holyoke Center Arcade**

Pizza, salad, and sandwiches

### **Pinocchio's, 74 Winthrop Street (Intersection of JFK and Winthrop)**

Excels in Sicilian pizza slices, as well as sandwiches. Open late.

### **Rialto, The Charles Hotel, One Bennett Street**

James Beard award-winning chef/owner Jody Adams celebrates regional Italian cuisine interpreted with New England ingredients. Award-winning wine list includes a range of organic and biodynamic wines as well as a unique selection of champagnes and sparkling wines.

### **The Upper Crust, 49B Brattle Street**

Menu includes classic combos to more unique and daring pairings - all atop an award-winning thin crust pizza.

### **Veggie Planet, 47 Palmer Street**

Vegetarian and vegan-friendly, pizzas, salads, soups. Daily specials.

## **MEXICAN/SPANISH**

### **Border Café, 32 Church Street**

Mexican, Cajun and Tex-Mex food; full bar

### **Café Pamplona, 12 Bow Street**

Authentic Spanish cuisine

### **Chipotle Mexican Grill, One Brattle Street**

Burritos, tacos, and salads

### **Qdoba Mexican Grill, 1280 Massachusetts Avenue**

Burritos, tacos, quesadillas, salads and soups

## **PUBS & CLUBS**

### **Middle East, 472/480 Massachusetts Avenue**

A Middle Eastern restaurant with two music clubs, upstairs and downstairs. Local and national rock bands. Food served until midnight. Cover varies.

### **Noir, The Charles Hotel, One Bennett Street**

A warm, sophisticated bar serving classic cocktails, signature drinks, and a menu suited for a late afternoon or late night snack.

### **Plough & Stars, 912 Massachusetts Avenue**

A neighborhood pub with a long, narrow bar, a friendly atmosphere, and a large selection of beer. Live music nightly.

### **Regattabar, The Charles Hotel, One Bennett Street**

Widely acknowledged as Boston's best jazz club with critical acclaim from the New York Times, Rolling Stone, Boston Globe and Boston Herald.

### **Shay's Pub & Wine Bar, 58 JFK Street, Cambridge**

A low-key Harvard Square watering hole for fans of beers and wine.

### **Tory Row, 3 Brattle Street, Cambridge**

Euro-American menu and wide selection of beer and wine

## **PLACES OF INTEREST**

To augment this listing pick up a copy of The Boston Phoenix or Boston's Weekly Dig in one of the many newspaper boxes around Harvard Square.

## **GALLERIES**

There are many commercial galleries on Newbury Street in Boston and in Boston's South End.

## **MUSEUMS**

### **deCordova Sculpture Park and Museum, 51 Sandy Pond Road, Lincoln, MA**

Tuesday–Sunday, 10 am - 5 pm

deCordova's 35-acre campus offers visitors a unique opportunity to experience contemporary art in the Museum galleries and outdoors in the Sculpture Park.

### **Harvard Museum of Natural History, The Glass Flowers Collection**

**26 Oxford Street, Cambridge, MA**

Open daily, 9 am - 5 pm

This unique collection of over 3,000 models was created by glass artisans Leopold Blaschka and his son, Rudolph.

### **The Institute of Contemporary Art, 100 Northern Avenue, Boston, MA**

Tuesday and Wednesday, 10 am - 5 pm, Thursday and Friday, 10 am - 9 pm,

Saturday and Sunday, 10 am - 5 pm

Located in a breathtaking waterfront building, the ICA is Boston's destination for new art and ideas.

### **Isabella Stewart Gardner Museum, 280 The Fenway, Boston, MA**

Tuesday-Sunday, 11 am - 5 pm

An art collection of world importance, including works that rank among the most significant of their type—from ancient Rome, Medieval Europe, Renaissance Italy, Asia, the Islamic world, 19<sup>th</sup> century France, and America.

### **MIT List Visual Arts Center, 20 Ames Street, Bldg. E15, Atrium level Cambridge, MA**

Tuesday-Wednesday 12 - 6 pm, Thursday 12 - 8 pm, Friday-Sunday 12 - 6 pm

Exploring challenging, intellectual, inquisitive contemporary art making in all media.

### **MIT Museum, 265 Massachusetts Avenue, Bldg. N51, Cambridge, MA**

Open daily, 10 am - 5 pm

Exhibitions and interactive programs with an emphasis on robotics, holography, and current MIT research.

### **Museum of Fine Arts, Boston, 465 Huntington Avenue, Boston, MA**

Monday and Tuesday 10 am–4:45 pm, Wednesday – Friday 10 am–9:45 pm,

Saturday and Sunday 10 am–4:45 pm

Fifty-three new galleries are now open in a new wing devoted to the Art of the Americas, from the Pre-Columbian era through the third quarter of the twentieth century.

### **Peabody Museum of Archaeology and Ethnology, Harvard University, 11 Divinity Avenue, Cambridge, MA**

Open daily, 9 am - 5 pm





