

Recent Advances in Characterizing Asian Lacquer

Center for Conservation and Preservation, Yale University, July 15 – 19, 2013

SESSION OUTLINE

SESSION TITLE: THM-Py-GC/MS Analysis of Powdered Lacquer Samples

INSTRUCTOR: Michael Schilling

ABSTRACT

Pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide for thermally-assisted hydrolysis and methylation (THM-Py-GC/MS) is presently the best analytical technique for comprehensive characterization of organic materials in Asian lacquers. It is capable of identifying numerous organic materials, resolving mixtures, and offers excellent limits of detection for powdered samples roughly 100 micrograms in size. The daunting challenge of systematically sorting through the vast number of resulting chromatographic peaks in order to accurately locate marker compounds that are characteristic of lacquer raw materials can be greatly aided through the judicious use of GC/MS quantitative analysis software. A marker compound calibration table developed at the GCI, which is an essential element of the data processing, makes it possible to produce a peak area report of nearly 400 marker compounds present in lacquer samples. Used in conjunction with a custom Excel worksheet to semi-automatically analyze and interpret the peak area report, it is possible to identify a wide range of Anacard tree saps, drying oils, fats, carbohydrates, proteins, resins, resinous diluents, preservatives and other materials present in samples from individual lacquer layers.

OBJECTIVES

By the end of this session, participants should be able to:

- Understand the fundamentals of Py-GC/MS.
- Recognize the significance of marker compounds for the identification of complex organic materials.
- Assess the effects of thermally-assisted hydrolysis and methylation on Py-GC/MS marker compounds.
- Prepare and analyze powdered samples from individual lacquer layers by THM-Py-GC/MS analysis.
- Detect and measure marker compounds in THM-Py-GC/MS analysis results for lacquer samples using Agilent's Chemstation software with a custom calibration table.
- Identify artists' organic materials present in lacquer samples based on marker compound distributions in THM-Py-GC/MS analytical results through the use of a custom Excel worksheet.
- Prepare and report their complete analytical findings.



SESSION OUTLINE CONT'D.

CONTENT OUTLINE

- Basic principles of Py-GC/MS as a method for analyzing large organic molecules.
- Marker compounds in Py-GC/MS and their role in identifying organic materials.
- On-line chemical derivatization using tetramethylammonium hydroxide (TMAH) as a means of improving Py-GC/MS results.
- Analysis of foundation layer and decorative layer samples from a lacquered object using a Frontier microfurnace pyrolyzer and Agilent GC/MS with TMAH reagent.
- Application of Agilent Chemstation quantitative software for evaluating THM-Py-GC/MS test results for lacquer samples, verifying the marker compounds and tabulating them into a peak area report.
- Identification of artists' materials in the lacquer samples through interpretation of the peak area report using a custom Excel data evaluation worksheet.
- Compilation of Excel results into a presentation and poster.

METHODOLOGY

Monday: The lecture will begin with the basics of Py-GC/MS, focusing on the operation of the Frontier microfurnace pyrolyzer, the formation of small molecules from pyrolysis of organic materials, and eventual separation and identification of the molecules by GC/MS. Particular emphasis will be given to the concept that small molecules uniquely formed by a particular organic material, which are called **marker compounds**, can aid in the identification of unknown materials. The benefits of chemical derivation in THM-Py-GC/MS will be then reviewed, with a discussion of how pyrolysis products are changed by on-line reaction with TMAH. The lecture will conclude with a review of specific marker compounds for Anacard tree saps, based upon research from the GCI and other laboratories. Videos will highlight important topics that will be covered in the laboratory sessions.

Tuesday and Wednesday: These laboratory sessions, held in the Organic Materials Laboratory of GCI Science, will consist of THM-Py-GC/MS analysis of the powdered foundation and decorative layer samples that were prepared in the 'layer unpacking' session. While the groups wait for the analysis of their layer samples to finish, they will become familiar with the software and procedures for interpretation that will aid teams in interpreting data and preparing final reports. Training sessions will introduce participants to the Agilent GC/MS Chemstation data evaluation software, the quantitative analysis program and the GCI custom Excel worksheet that will be used during the data processing and interpretation sessions on Thursday.

Thursday: In this laboratory session, held at the Getty's Information Technology computer training laboratory, the groups will analyze the THM-Py-GC/MS analytical results from their foundation and decorative lacquer layers using the concepts developed during the previous laboratory sessions. Each group will analyze their two THM-Py-GC/MS chromatograms, detect and identify marker compounds using the Chemstation software, and prepare peak area reports. After copying the Chemstation reports into the custom Excel worksheet and verifying the marker compounds, the artists' materials present in the two samples will be identified on the basis of the Excel tables and graphs. The session







SESSION OUTLINE CONT'D.

will conclude with the groups preparing presentations of their results using the Power Point report template provided by the Getty, and then transferring the completed slides to a poster template for subsequent printing.

BIBLIOGRAPHY

 = Essential reading material

 = Available online

- Baumer, Ursula, Patrick Dietemann, and Johann Koller. 2009. Identification of resinous materials on 16th and 17th century reverse-glass objects by gas chromatography/mass spectrometry. *International Journal of Mass Spectrometry* (284): 131-141.
- Bonaduce, Ilaria, Catharina Blaensdorf, Patrick Dietemann, and Maria Perla Colombini. 2008. The binding media of the polychromy of Qin Shihuang's terracotta army. *Journal of Cultural Heritage* 9 (1): 103-108.
- Burmester, A. 1983. Far Eastern lacquers: classification by pyrolysis mass spectrometry. *Archaeometry* 25 (1): 45-58.
- Chiavari, G., and R. Mazzeo. 1999. Characterization of paint layers in Chinese archaeological relics by pyrolysis-GC-MS. *Chromatographia* 49 (5-6): 268-272.
-  Derrick, Michele R., C. Grzywacz, and F. Preusser. 1988. FTIR analysis of finishes on Oriental style 18th century European furniture. In *Urushi: Proceedings of the Urushi Study Group, June 10-27, 1985, Tokyo*, edited by N.S. Brommelle and P. Smith, 227-234. Los Angeles: The Getty Conservation Institute.
-  Frade, J.C., M.I. Ribeiro, J. Graca, and J. Rodrigues. 2009. Applying pyrolysis-gas chromatography/mass spectrometry to the identification of oriental lacquers: Study of two lacquered shields. *Analytical and Bioanalytical Chemistry*: 2167-2174.
- Garner, Sir Harry. 1963. Technical studies of Oriental lacquer. *Studies in Conservation* 8 (3): 84-98.
- He, Ling, Maiqian Nie, Giuseppe Chiavari, and Rocco Mazzeo. 2007. Analytical characterization of binding medium used in ancient Chinese artworks by pyrolysis-gas chromatography/mass spectrometry. *Microchemical Journal* 85 (2): 347-353.
-  Heginbotham, Arlen, Herant Khanjian, Rachel Rivenc, and Michael Schilling. 2008. A procedure for the efficient and simultaneous analysis of Asian and European lacquers in furniture of mixed origin. In *15th Triennial Conference, New Delhi, 22-26 September 2008: Preprints (ICOM Committee for Conservation)*, edited by Janet Bridgland, 608-16. New Delhi: Allied Publishers.
-  Heginbotham, Arlen, and Michael Schilling. 2011. New Evidence for the use of Southeast Asian raw materials in seventeenth-century Japanese export lacquer. In *East Asian Lacquer: Material*



SESSION OUTLINE CONT'D.

Culture, Science and Conservation, edited by Shayne Rivers, Rupert Faulkner and Boris Pretzel, 92-106. London: Archetype Publications.

Honda, T., N. Kitano, Y. Kamiya, R. Lu, and T. Miyakoshi. 2008. Identification of excavated black lacquer resin by pyrolysis-gas chromatography/mass spectrometry. *18th International Symposium for Analytical and Applied Pyrolysis* 23.

📖 Honda, T., R. Lu, N. Kitano, Y. Kamiya, and T. Miyakoshi. 2010. Applied analysis and identification of ancient lacquer based on pyrolysis-gas chromatography/mass spectrometry. *Journal of Applied Polymer Science* 118: 897-901.

Honda, T., R. Lu, R. Sakai, T. Ishimura, and T. Miyakoshi. 2008. Characterization and comparison of Asian lacquer saps. *Progress in Organic Coatings* 61: 68-75.

Honda, T., X. Ma, R. Lu, D. Kanamori, and T. Miyakoshi. 2011. Preparation and characterization of a new lacquer based on blending urushiol with thitsiol. *Journal of Applied Polymer Science* 121: 2734-2742.

Judet-Brugier, Nicole. 2000. From Asia to Europe: Asian lacquerware applied to French furniture. In *Ostasiatische und europäische Lacktechniken / East Asian and European lacquer techniques*, edited by Michael Kühnenthal, 47-50. Munich: Bayerisches Landesamt für Denkmalpflege.

Kamiya, Y., and T. Miyakoshi. 2000. The analysis of urushi by pyrolysis-gas chromatography and mass spectrometry. In *East Asian and European Lacquer Techniques: International Conference of the Bavarian State Department of Historical Monuments and the German National Committee of ICOMOS Together with the Tokyo National Research Institute of Cultural Properties, Munich, 11-13 March 1999*, edited by Michael Kühnenthal, 107-20. Munich: Bayerischen Landesamtes für Denkmalpflege.

📖 Koller, Johann, and Ursula Baumer. 1997. Baroque and Rococo transparent gloss lacquers: II. Scientific study of lacquer systems. In *Lacke des Barock und Rokoko / Baroque and Rococo lacquers*, edited by Katharina Walch and Johann Koller, 52-85. Munich: Bayerisches Landesamt für Denkmalpflege.

📖 Koller, Johann, Katharina Walch, and Ursula Baumer. 2000. French lacquered furniture of the 18th Century: Criard, Desforge and Dubois. A technical and scientific investigation on imitation lacquers. In *Japanische und europäische Lackarbeiten: Rezeption, Adaption, Restaurierung / Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, edited by Michael Kühnenthal, 537-60. Munich: Bayerisches Landesamt für Denkmalpflege.



📖 Kumanotani, J. . 1995. Urushi (oriental lacquer) - a natural aesthetic durable and future-promising coating. *Progress in Organic Coatings* 26: 163-195.

📖 Le Ho, A.S., M. Regert, O. Marescot, C. Duhamel, J. Langlois, T. Miyakoshi, C. Genty, and M. Sablier. 2012. Molecular criteria for discriminating museum Asian lacquerware from different vegetal origins by pyrolysis gas chromatography/mass spectrometry. *Analytica Chimica Acta*



SESSION OUTLINE CONT'D.

710: 9-16.

- Lu, R., Y. Kamiya, and T. Miyakoshi. 2006. Applied analysis of lacquer films based on pyrolysis-gas chromatography/mass spectrometry. *Talanta* 70: 370-376.
- Lu, R., Y. Kamiya, and T. Miyakoshi. 2007. Characterization of lipid components of *Melanorrhoea usitata* lacquer sap. *Talanta* 71: 1536-1540.
- Niimura, N., and T. Miyakoshi. 2000. Identification of oriental lacquer films using pyrolysis-gas chromatography/mass spectrometry. In *Japanische und europäische Lackarbeiten: Rezeption, Adaption, Restaurierung / Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, edited by Michael Kühnenthal, 123-34. Munich: Bayerischen Landesamtes für Denkmalpflege.
- Niimura, N., and T. Miyakoshi. 2003. Characterization of natural resin films and identification of ancient coating. *Journal of the Mass Spectrometry Society of Japan* 51 (4): 439-457.
-  Niimura, N., T. Miyakoshi, J. Onodera, and T. Higuchi. 1999. Identification of ancient lacquer film using two-stage pyrolysis-gas chromatography/mass spectrometry. *Archaeometry* 41 (1): 137-149.
- Okada, F. 2000. A study on the structure of the coating film of urushiware at the Linden Museum. In *Japanische und europäische Lackarbeiten: Rezeption, Adaption, Restaurierung / Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, edited by Michael Kühnenthal, 135-48. Munich: Bayerischen Landesamtes für Denkmalpflege.
- Piert-Borgers, B. 2000. East Asian lacquerwork on French furniture. In *Japanische und europäische Lackarbeiten: Rezeption, Adaption, Restaurierung / Japanese and European Lacquerware: Adoption, Adaptation, Conservation*, edited by Michael Kühnenthal, 479-516. Munich: Bayerisches Landesamt für Denkmalpflege.
- Pitthard, V., S. Wei, S. Miklin-Kniefacz, S. Stanek, M. Griesser, and M. Schreiner. 2010. Scientific investigations of antique lacquers from a 17th-century Japanese ornamental cabinet. *Archaeometry* 52 (6): 1044-1056.
-  Wan, Y., R. Lu, Y. Du, T. Honda, and T. Miyakoshi. 2007. Does Donglan Lacquer tree belong to *Rhus vernicifera* species? *International Journal of Biological Macromolecules* 41: 497-503.
- Wei, S., V. Pintus, V. Pitthard, M. Schreiner, and G. Song. 2011. Analytical characterization of lacquer objects excavated from a Chu tomb in China. *Journal of Archaeological Science* 38: 2667-2674.



SESSION OUTLINE CONT'D.

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