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RAMAN REVIEWED: A SHORT HISTORY OF THE TECHNIQUE IN ART AND ARTIFACT STUDIES

Gregory Dale Smith

Indianapolis Museum of Art, Indianapolis, US

Abstract:

The widespread adoption of Raman microspectroscopy by cultural heritage scientists has dramatically changed our ability to study artwork non-destructively. What arose as a curious light scattering phenomenon in the days of Nobel Laureate C. V. Raman is now a workhorse technique in museum, industrial, and academic laboratories. This transition largely occurred in the past decade and can be attributed to the development of small, intense laser sources; sensitive Peltier-cooled detectors; and inexpensive computing power. Furthermore, the miniaturization of all of these components is allowing Raman spectroscopy to leave the lab to explore artwork in situ in exotic and sometimes rugged locations. This talk will trace the major developments in the history of Raman spectroscopy for cultural heritage and discuss the hurdles that have been overcome and those yet to be surmounted.

Greg's Essential Bibliography

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Biography

Greg Smith is the Otto N. Frenzel III Senior Conservation Scientist at the Indianapolis Museum of Art (IMA). He holds a Ph.D. in physical/analytical chemistry from Duke University and completed postdoctoral research at the National Gallery of Art, Washington, DC; the National Synchrotron Light Source, Brookhaven National Laboratory, Long Island, NY; and University College London, UK. Prior to his arrival at the IMA, Greg served as the Andrew W. Mellon Assistant Professor of Conservation Science at

Buffalo State College, one of only three graduate programs for comprehensive art conservation training in the United States. Greg's research interests include studying condition issues affecting modern polymers used in art, pigment degradation processes, preservation environments, and development and testing of innovative conservation treatments. He also has undertaken archaeological fieldwork in Galilee, Israel, serving as field chemist and supervisor on two excavations. Greg's academic and professional career is distinguished and he has been honored with a Marshall Sherfield Postdoctoral Scholarship for study in Britain, National Science Foundation Research Fellowships, and a Barry M. Goldwater Science Scholarship.

BASIC PRINCIPLES OF RAMAN SPECTROSCOPY

Jennifer Mass

Winterthur Museum, Garden and Library, DE, US

Abstract

Raman spectroscopy is a vibrational spectroscopy technique that probes a molecule's vibrational energy levels indirectly using laser light scattering. The lasers used for excitation include wavelengths in the ultraviolet, visible, and near infrared (NIR) regions. Typically, the molecule starts out in the vibrational ground state; the laser light then excites the molecule into a virtual electronic state, from which it relaxes back down into a vibrationally excited state. Thus for the molecule's different vibrational modes, Raman spectroscopy indirectly measures the energy level gap between the molecule's ground state and its first excited state. This is in contrast to infrared (IR) spectroscopy, which involves direct excitation of vibrational modes in a molecule through the absorption of mid-IR radiation. The achievement of the virtual electronic state required for a Raman spectrum is dependent on the polarizability of the molecule (the ability of the electron cloud to distort, which is improved when higher atomic number atoms with large electron clouds, such as lead and mercury are present), whereas for IR bands a permanent dipole moment is required.

Raman's indirect mechanism confers some advantages to Raman spectroscopy over IR spectroscopy for the molecular "fingerprinting" of artists' materials, their degradation products, and their conservation and restoration materials. These advantages include the ability to observe characteristic bands that lie outside of the mid-IR region, narrower bands, and a smaller number of bands, reducing the challenges with band overlaps and the identification of mixtures commonly encountered with IR spectroscopy. However, for IR, the availability, number, and quality of references available through the IRUG Spectral Database have greatly facilitated our interpretation of IR spectra of artists' materials. For Raman, the current lack of reference spectra makes definitive interpretation of artists' materials, particularly degraded ones, challenging. In addition, the data collection component of IR spectroscopy is relatively straightforward, while in Raman spectroscopy the user must often make numerous choices including laser wavelength, laser power, and photobleaching time before fluorescence is minimized and an acceptable spectrum is obtained.

As a result of these factors, Raman spectroscopy is best employed in art conservation as a complementary technique for IR rather than as a replacement for it. For example, Raman spectroscopy excels at the identification of metal oxide and sulfide pigments, such as vermilion and red lead that are not active in the mid-IR and so cannot be observed using IR spectroscopy. However, IR excels at the classification of organic binding media such as waxes, resins, gums, and proteins, as well as, polyoxoanion-based pigments and metal corrosion products, for example, brochantite and atacamite. While polyoxoanion pigments, like calcite and aragonite, sometimes are distinguishable by Raman

spectroscopy, the minor bands that may provide a definitive identification (as opposed to the major carbonate stretching band) often are buried in the high fluorescence background commonly encountered in the Raman spectra of oil paints.

In general, Raman spectroscopy is extremely useful for the identification of inorganic pigments, synthetic organic pigments, polymers, metal corrosion products, glass opacifying agents and degradation products, and certain natural organic dyes, such as indigo. An FT Raman spectrometer (vs. dispersive) with NIR excitation is required to study organic binding media and in general multiple laser wavelengths are required to identify the full range of materials encountered in objects of art. In summary, in the past ten years Raman spectroscopy (especially μ Raman spectroscopy) has become an essential tool for the study of cultural heritage materials, joining FTIR and XRD as a critical phase identification technique for the rapid and specific identification of a wide range of inorganic and organic compounds. In fact, due to the high cost of diffractometers with area detectors required for the analysis of microsamples, Raman has replaced XRD in many museum laboratories as the preferred method of phase identification.

Jennifer's Essential Bibliography

1. Brosseau, Christa L., Francesca Casadio, and Richard P. Van Duyne. "Revealing the Invisible: Using Surface-enhanced Raman Spectroscopy to Identify Minute Remnants of Color in Winslow Homer's Colorless Skies." *Journal of Raman Spectroscopy* 42.6 (2011): 1305-310.
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Biography

Jennifer received her Ph.D. in Inorganic Chemistry from Cornell University and afterward was awarded an Andrew W. Mellon fellowship at the Sherman Fairchild Center for Objects Conservation at the Metropolitan Museum of Art. She currently holds the positions of Director and Senior Scientist of the Winterthur Museum Scientific Research and Analysis Laboratory and is a faculty member in the Winterthur/University of Delaware M.S. Program in Art Conservation. Jennifer has conducted research on the degradation mechanisms of artists' materials and helped to develop a confocal x-ray fluorescence microscope for depth profiling of paintings. For her XRF research, she received awards from the Italian Society for Nondestructive Testing and the American Materials Research Society. Jennifer has published numerous research articles in the art conservation, physics, and materials science literature and recently co-edited a volume on handheld XRF applications in art and archaeology (due October 2012). Jennifer recently co-organized two symposia on the synchrotron-based methodologies for the study of cultural heritage. Her current research interests include XRF methodologies for historic silver alloys, overglaze enamel technologies in porcelain and earthenware, and pigment alterations in the works of the early modern painters.

OVERVIEW OF RAMAN INSTRUMENTATION

Thomas J Tague Jr.

Bruker Optics, Inc., Billerica, MA, US

Abstract

Raman instrumentation has evolved considerably over the last 20 years. This evolution has been dependent on technical innovations in many areas of related technology (1). Initially, Raman spectroscopy was a costly niche technique relegated to research or national laboratories. Excitation lasers were very large, required water cooling, were unreliable, and performed only adequately. Today's diode lasers are robust and very reliable (2). High quality gratings were available, but required substantial effort to position and were typically fixed, limiting spectral resolution options. Detectors were single element and very fragile as well as being limited in sensitivity and response (3). The calibration of Raman systems was very painful, as laser sources tended to shift over time (4). These systems were very costly to build and maintain and user-friendly software was non-existent. Today's Raman systems are very easy to use and achieve outstanding performance. The components of state-of-the-art Raman instruments will be discussed with the expected improvements in data collection. Lastly, a review of the safety requirements for the use of Raman systems will be discussed (5).

Tom's Essential Bibliography

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Biography

Thomas Tague is the Applications Manager for Bruker Optics and has managed the microscopy related business for Bruker Optics for the last ten years. Tom is a member of the Visiting Committee of the Metropolitan Museum of Art and the Advisory Board of EOS Photonics. Tom received his Ph.D. in

Chemistry from the University of Utah in 1992 and his B.S. from the University of Texas at San Antonio (also in Chemistry) in 1988. He is a member of the American Chemical Society, Society for Applied Spectroscopy, and the Microscopy Society of America. Tom has more than 40 peer-reviewed publications and 5 US Patents (one provisional).

RAMAN ANALYSIS OF MINERALS & PIGMENTS

Richard Newman

Museum of Fine Arts, Boston, US

Abstract

This presentation compares infrared and Raman spectroscopy as techniques for identification of inorganic materials, with a particular focus on compounds containing polyatomic ions (carbonate, sulfate, phosphate, chromate, arsenate, etc.). Common spectral features that are characteristic of compounds containing a specific anion are reviewed, along with standard nomenclature for vibrational bands. Vibrational spectroscopy of silicates is also discussed, including an overview of glassy silicates.

Richard's Essential Bibliography

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7. Mysen, B. O., D. Virgo, and C. M. Scarfe. "Relations Between the Anionic Structure and Viscosity of Silicate Melts- a Raman Spectroscopic Study." *American Mineralogist* 65 (1980): 690-710.

Biography

Richard Newman is head of scientific research at the Museum of Fine Arts, Boston, where he has been a research scientist since 1986. He currently teaches a biannual seminar in 'Materials and Methods of Works of Art' at Wellesley College and is an annual lecturer in a team-taught introductory course on archaeological science at MIT. Although he is particularly fond of rocks and minerals, he has carried out research on a wide range of cultural artifacts and materials, including most recently an unusual rubbery resin used by the Inka.

RAMAN ANALYSIS OF MUSEUM OBJECTS: ADVANTAGES, LIMITATIONS, & PRACTICAL TIPS

Lucia Burgio

Victoria and Albert Museum, London, UK

Abstract

This presentation will discuss advantages and limitations of Raman microscopy with specific reference to the analysis of various types of museum objects and their pigments. Attention will be paid to all practical aspects of Raman experiments, such as the choice of experimental setup, excitation wavelength, routine procedures, and experimental conditions. Practical examples taken from past Victoria and Albert Museum analyses will be given, including the analysis of manuscripts, portrait miniatures, corrosion products, prints, painted sculptures and decorated furniture. Problems that can be encountered during any routine analysis (such as fluorescence, interference and vibrations) also will be discussed in detail. Finally, a series of practical tips and suggestions will be given.

Lucia's Essential Bibliography

Reviews

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Online Databases

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2. University of Parma database of minerals: <http://www.fis.unipr.it/phevix/ramandb.php>
3. University College of London spectroscopic library:
<http://www.chem.ucl.ac.uk/resources/raman/index.html>

Pigments

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Biography

Lucia Burgio is the Senior Object Analysis Scientist at the Victoria and Albert Museum, providing analysis and identification of: materials and techniques, methods of construction, manufacture, history, and possible dating of museum objects. Her research interests include the analysis of pigments, oriental lacquer and other artists' materials and the application of scientific techniques to art and cultural heritage issues. She graduated in Chemistry from the University of Palermo, Italy, in 1996, completed a Ph.D. in chemistry at University College London in 2000 with a thesis on the analysis of pigments on art objects using Raman microscopy and other techniques. After a few months working at ENEA (New Technologies, Energy and Environment Agency) in Italy, she joined the Science Section in the Conservation Department at the V&A in 2000. She has been an Honorary Research Fellow at UCL since 2001.

RAMAN ANALYSIS OF GEMS

Danilo Bersani

University of Parma, Dept. of Physics and Earth Sciences "Macedonio Melloni", Parma, IT

Abstract

Gems, gemstones and related materials are widely encountered in cultural heritage and conservation studies. Raman spectroscopy, being non-destructive and requiring short measurement times, low amount of material and no sample preparation, is valuable for routine investigation in the study of gemstone inclusions and treatments and for the characterization of mounted gems.

In this paper, a review on the use of laboratory Raman and micro-Raman spectrometers and of portable Raman systems in the gemological field is given, focusing on gem identification and on the evaluation of their composition, provenance and genesis. Many examples are shown of the use of Raman spectroscopy as a tool for the identification of imitations, synthetic gems and enhancement treatments in natural gemstones.

Particular attention is devoted to the possible mistakes that can occur during a Raman measurement and the consequent identification and to the effects that can make difficult the comparison between the spectrum of an unknown gem and a reference one. In addition, a case study on the composition of garnets is shown.

Danilo's Essential Bibliography

1. Bersani, Danilo, and Pier Paolo Lottici. "Applications of Raman Spectroscopy to Gemology." *Analytical and Bioanalytical Chemistry* 397.7 (2010): 2631-646.
2. Kiefert L., Chalain J. P., Haberli S. "Case Study: Diamonds, Gemstones and Pearls: From the Past to the Present." *Raman Spectroscopy in Archaeology and Art History*. Ed. Howell Edwards and John M. Chalmers. Cambridge: Royal Society of Chemistry, 2005. 379-402.
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5. Shigley, James E. "A Review of Current Challenges for the Identification of Gemstones." *Geologija* 50 (2008): 227-36.

Biography

Danilo Bersani received his undergraduate degree in physics in 1992 and his PhD in physics in 1997. He is currently Researcher at the Physics Department of the University of Parma. His research fields include: minerals, cultural heritage, nanocrystalline oxides, and sol-gel derived materials. Danilo's instrumental expertise is in Raman and micro-Raman spectroscopy. At the University of Parma, he teaches courses in physics and laboratory, spectroscopic and nuclear techniques for cultural heritage, and physics techniques in forensic sciences. He also is the President of the Master in Forensic Sciences of the University of Parma. Danilo was the chair and organizer of the 6th International Congress on the Application of Raman Spectroscopy in Art and Archaeology (RAA 2011 – Parma) in 2011. He was also the Guest Editor of the related special issue of Journal of Raman Spectroscopy. Danilo has authored over 120 scientific publications in international journals and delivered more than 220 presentations at national and international conferences.

ANALYSIS OF GLASS ARTEFACTS - APPLICABILITY OF XRF, SEM/EDX, FTIR, AND RAMAN

Manfred Schreiner, Dubravka Jembrih-Simbuenger

Institute of Science and Technology in Art, Academy of Fine Arts, Vienna, AT

Abstract

The analysis of glass artefacts requires non-destructive and in many cases non-invasive techniques, as sampling is rather difficult or even impossible for such artworks. The advantage of X-ray fluorescence analysis (XRF) in comparison to other analytical techniques is its applicability in air and that it can be performed without any changes or alterations before, during or after the investigation of an object. Furthermore, miniaturization in the field of electronics has yielded x-ray tubes, as well as x-ray detectors, of a few kilograms and below. Therefore, devices can be easily transported to an archaeological site or into museums, libraries and galleries for analytical investigations.

Unfortunately, only elements with an atomic number higher than 16 (sulphur) can be detected by XRF in air, which means that sodium, aluminium or silicon – the main constituents of glasses – can hardly be determined. For this reason and where sampling is possible – e.g. for archaeological glass fragments – scanning electron microscopy in combination with energy dispersive x-ray microanalysis (SEM/EDX) is a complementary method for the determination of the material composition of glass. Fourier transform infrared spectroscopy (FTIR) and Raman spectrometry can be carried out in air too and in a non-destructive way. These analytical methods deliver information concerning the chemical bonding in the silicate structure and studies focusing on the structure of the silicate glasses can be performed.

In this presentation the scientific investigation of glass artefacts will be discussed. There are two main topics a scientist working in the field of cultural heritage is confronted with:

- Determination of glass composition to address questions of where, when or by whom an object was made (e.g. to investigate authenticity), or which procedure was applied for manufacturing (e.g. glass with an iridescent layer).
- Understanding glass degradation. As glass seems to be a generally stable material, degradation processes (e.g. of medieval stained glass, but also objects in showcases in a museum) have been underestimated in the past. However, corrosion processes can occur in acidic, neutral and alkaline environmental conditions yielding a leached layer on the glass surface or even to crystalline corrosion products (weathering crusts) that reduce the transparency of an object.

Case studies and examples will be presented to illustrate the applicability of these analytical methods, especially Raman spectrometry, and the complementary nature of the analytical tools is discussed.

Manfred and Dubravka's Essential Bibliography

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7. Schreiner, M. "Corrosion of Historic Glass and Enamels." *Comprehensive Analytical Chemistry* 42 (2004): 713-754.

Biography

Manfred Schreiner studied chemistry at the Vienna University of Technology, where he received an engineering degree. After his Ph.D. in materials science, he was as a postdoctoral fellow at UCSD (University of California, San Diego, CA). In 2000 he became full professor and head of the Institute of Science and Technology in Art of the Academy of Fine Arts in Vienna, Austria. His main research interests are degradation (corrosion) of materials in historic and contemporary art, nondestructive (noninvasive) material analysis, and documentation of objects of art and archaeology using visible, infrared, UV, and X-ray radiations.

Dubravka Jembrih-Simbuerger has an engineering degree in chemistry and a Ph.D. thesis in the field of electron probe techniques and ion beam analysis for identification and classification of historical glass (Institute of Analytical Chemistry, Vienna University of Technology and the Institute of Chemistry, Academy of Fine Arts in Vienna), and since 2002 has been a staff Scientist at the Institute of Science and Technology in Art, Academy of Fine Arts in Vienna, with main research areas in the material analysis of objects of art and archaeology (glass, historical inks, traditional and modern painting materials) using non-destructive analytical techniques.

INTRODUCTION TO THE IRUG RAMAN SPECTRAL DATABASE & WEBSITE SOFTWARE

Beth Price, Philadelphia Museum of Art, US; Gabriel Richards, Enderotech Inc., US; Charles Davis, The Dow Chemical Company, US; Boris Pretzel, Victoria and Albert Museum, UK; Suzanne Lomax, National Gallery of Art, US; Andrew Lins, Philadelphia Museum of Art, US; Marcello Picollo, Institute of Applied Physics "Nello Carrara", CNR, IT

Abstract

With the increasing use of Raman spectroscopy for the study of cultural heritage, there is a pressing need for a readily-accessible database of high-quality Raman reference data that are relevant to the museum community (1). To help address this need, the Infrared and Raman Users Group (IRUG) and Philadelphia Museum of Art (PMA) have partnered to create a web-based Raman spectral database, supported by an Institute of Museum and Library Services (IMLS) National Leadership Grant for Advancing Digital Resources. The Raman database is being built with MySQL® and other open source technologies on a re-structured IRUG website (www.irug.org). The database is the second to be undertaken by IRUG, which previously developed and distributed several infrared compilations online, including the recent Edition 2007, containing over 2,100 IR spectra (2). This paper provides an introduction to the IMLS funded project; the IRUG protocol for collection and review of spectra; the customized, platform-independent JCAMP-DX (ASCII) file format used for spectra; and beta versions of the Raman spectral database and associated software.

The newly re-structured IRUG website includes an interface for submission, peer-review, editing, formatting, and distribution of spectra. Other key features are a searchable version of the Raman spectral database, a searchable Raman bibliography with a library of open source papers, and a chemical structures index and glossary. The web interface will allow users to upload spectra into a personal account after conversion from the "native" (proprietary instrument) format to a "raw" JCAMP-DX (ASCII) format (3). The system software will merge the uploaded "raw" JCAMP-DX files with supporting descriptive information provided by submitters via an online submission form. The merged files then will be forwarded for peer-review. During this multistep online review process each spectrum will be examined and evaluated by a minimum of two scientist reviewers using standardized criteria. Submitters who have achieved "contributor" status by contributing 10 or more accepted spectra to the IRUG database will be able to download digitized spectra, from the entire collection, from the website.

The IRUG Raman spectral database project is a broad collaborative effort across many institutions. It is unique in that the interactive software architecture enables all aspects of the data exchange to transact via a website. The project is ongoing and its ultimate success will rely on the contribution of spectra by individuals in the international museum and academic communities. Thus far over 1000 Raman spectra have been pledged. The Raman database is expected to benefit generations of scientists, conservators, and students, as well as the public interested in preservation of our cultural heritage. Individuals

wanting to participate should contact their IRUG Regional Chair: Beth Price (bprice@philamuseum.org), Americas; Boris Pretzel (boris.pretzel@vam.ac.uk), Europe and Africa; Marcello Picollo (m.picollo@ifac.cnr.it), Asia, Australia and Oceania; or the IRUG Raman Committee Chair, Suzanne Lomax, (s-lomax@nga.gov).

1. See Smith, G., R. Clark, Raman Microscopy in Archeological Science, *Journal of Archaeological Science* 31(2004): 1137-1160; and Smith, G., R. Clark, Raman Microscopy in Art History and Conservation Science, *Reviews in Conservation* 2 (2001): 92-106.
2. Price, B. and B. Pretzel, Eds., *Infrared and Raman Users Group Spectral Database, Edition 2007*, Infrared and Raman Users Group: Philadelphia (2009).
3. Most Raman instrument software packages (and almost all FTIR software packages) have "export" or "conversion" to create "raw" JCAMP-DX spectral files.

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Biographies:

Beth Price is a senior scientist in the Scientific Research Laboratory at the Philadelphia Museum of Art, Philadelphia, PA. Her recent research includes work on the introduction of western pigments in Himalayan polychromy and thangkas, the drawing media used by self-taught American artist James Castle, and the photographic collage materials of Marcel Duchamp's *Étant donnés*. Beth serves as the Americas Chair of IRUG and as an IRUG Board of Directors member. Prior to joining the Museum in 1990, she worked as a Research Chemist at FMC Corporation in Princeton. Beth obtained degrees in chemistry, art history, and liberal studies from Rutgers University and the State University of New York.

Gabriel Richards is President and CEO of Ender Technology Corporation (EnderTech), Torrance, CA. Gabe received his BA with an emphasis in Philosophy from the University of California, Irvine. He began building websites for his first business, Pennywise PC Consulting, during high school (around 1995). While in college he worked as a computer resource specialist, maintaining the website and databases for the UC Irvine Campus-wide Honors Program. It was there that Gabe learned to combine database technology with web technology to create database-driven websites and the seed for EnderTech was planted. Today, 12 years after its founding, EnderTech has grown into a team of 16 software developers happily serving dozens of active clients with their complex web and software development needs.

Charles Davis has spent his career in IT Database Administration as a technical manager. He is currently employed by The Dow Chemical Company as a Service Support Manager. Charles has been associated with Infrared and Raman Users Group (IRUG) since 2006, working closely with Beth Price, Boris Pretzel, and Suzanne Lomax to sustain the current IRUG web site. He also participated in the complete re-design and re-write for the new IRUG web site. Charles helped locate and coordinate with IT industry experts to develop the site and worked very closely with the IRUG team to improve the data quality of all JCAMP-DX files. Charles is happy to have had a role in helping to preserve the world's cultural heritage via IRUG and is proud to be associated with such a fine organization. He has a Bachelor's degree in Business Administration from The College of New Jersey, with IT Consultancy and Management courses at Villanova University. He has been Database Administration Manager with The Dow Chemical Company (formerly, Rohm and Haas Company) for 17 years. Prior to that, he worked at Macmillan Publishing for 13 years and was a programmer at The Central Penn Bank in Philadelphia. Charles enjoys cooking and woodworking.

Boris Pretzel is the Head Scientist at the Victoria and Albert Museum. He joined the Museum as the Materials Scientist in the Conservation Department's Science Section in 1989, taking over all charge of the section in 2010. His responsibilities include a broad range of strategic heritage science issues relating to the storage, display and preservation of artifacts. His research interests include the interaction of artifacts with environments, lighting, colour perception and measurement, and materials analysis. Boris serves as the IRUG Chair for Europe and Africa, is a member of the Journal of Cultural Heritage editorial board, and the Coordinator of the ICOM-CC Preventive Conservation Working Group. Prior to joining the

V&A, Boris worked as a Patent Examiner in the European Patent Office in The Hague and Berlin, and, before this, spent a year as a research fellow with the Polymer Group at the University of Bristol.

Suzanne Quillen Lomax received her Ph.D. in organic chemistry from the University of Maryland. After postdoctoral research at Northwestern University, she joined the Scientific Research Department of the National Gallery of Art as an organic chemist. Her current research focuses on the identification of synthetic organic pigments by techniques including Raman spectroscopy and laser desorption ionization mass spectrometry. Suzanne has served as a member of the IRUG Board of Directors since 1998 and is a spectral reviewer for that organization, as well as the Chair of the IRUG Raman committee.

Andrew Lins is Chairman of the Conservation Department, Philadelphia Museum of Art. He has supported IRUG's development and mission since its inception.

Marcello Picollo graduated in geology from the University of Florence in 1988. He is a researcher at the Institute of Applied Physics "Nello Carrara" (previously known as Institute for Research on Electromagnetic Waves, IROE) of the National Research Council of Italy (IFAC-CNR), Florence. He has been working on spectroscopic investigations of works of art since 1991. His main focus is pigment characterization using non-invasive spectroscopic, imaging and X-ray techniques. In January 2009 he became the coordinator of the IFAC Applied Spectroscopy Group on the research line Integrated spectroscopic techniques for the non-invasive diagnosis, conservation and access to the objects of art. At IFAC, he is the coordinator for three Scientific Collaborations: one between the University of the Balearic Islands, ICVBC-CNR, and IFAC-CNR, the second between the National Institute of Information and Communications Technology (NICT), Tokyo, and IFAC-CNR, and the last between the Scuola Universitaria Professionale della Svizzera italiana (SUPSI), Dipartimento Ambiente Costruzioni e Design, Istituto materiali e costruzioni (DACD-IMC), Lugano, and IFAC-CNR. He is also the IRUG Chair for Asia, Australia and Oceania as well as the Coordinator of the Colour Thematic Area (Area Tematica del Colore) Group of the Italian Archaeometric Association (AIAr).

SYNTHETIC ORGANIC PIGMENTS: STRUCTURES & PROPERTIES

Suzanne Quillen Lomax

National Gallery of Art, Washington, DC

Abstract

Synthetic organic pigments are laboratory-made pigments used in many fields, one of which is artists' materials. Other relevant uses include the coloration of textiles and plastics, and in printing inks and automotive paints. The first synthetic organic pigments were manufactured in the mid to late 1800s and new pigments continue to be introduced. The majority of these pigments are red, yellow and orange. Many of these pigments contain the azo linkage (N=N). The diazotization reaction was discovered in 1858 and, by varying the primary aromatic amine and the coupling component, different classes of pigments can be synthesized. Early azo-based pigment classes include the β -naphthols, BONA, Naphthol AS, Hansa (monoarylide) yellows and diarylide yellows. Non-azo based pigment classes have been generally introduced later, and include the phthalocyanines, quinacridones, perylenes, perinones, and DPP pigments. This talk will focus on the different classes of synthetic organic pigments, discussing their structures, properties and uses.

Suzanne's Essential Bibliography

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Biography

Suzanne Quillen Lomax received her Ph.D. in organic chemistry from the University of Maryland. After postdoctoral research at Northwestern University, she joined the Scientific Research Department of the National Gallery of Art as an organic chemist. Her current research focuses on the identification of synthetic organic pigments by techniques including Raman spectroscopy and laser desorption ionization mass spectrometry. She has been a member of the IRUG Board of Directors since 1998 and is a spectral reviewer for that organization as well as the chair of the Raman committee.

RAMAN ANALYSIS OF 19TH & 20TH CENTURY SYNTHETIC ORGANIC COLORANTS

Nadim C. Scherrer

Bern University of the Arts, Bern, CH

Abstract

The identification of synthetic organic pigments by Raman spectroscopy is a powerful means to deliver solid arguments in chronological discussions on works of art. The possibility to distinguish between polymorphs, to analyze different sample types, and to perform analysis in-situ at high spatial resolution, makes Raman a valuable addition to the conventional armory of PLM, SEM, FTIR, HPLC or GC-MS techniques. With the inverse signal intensity of the pigment/binder components in many paint samples, when compared to FTIR, Raman delivers excellent performance on many classes of synthetic organic pigments without sample preparation or sample loss. Identification of pigments in paint samples with the help of an electronic reference database is considerably more reliable than with the often complex FTIR spectra. Raman, however, misses out on other important information such as type of binder and presence or absence of degradation products that accumulate with age, such as soaps. Thus, it is a great advantage if information from more than one technique is available.

This lecture will address several practical aspects of Raman analysis for the identification of synthetic organic pigments in painted artworks.

Nadim's Essential Bibliography

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Biography

Nadim Scherrer graduated with a B.Sc. Hons. in geomorphology from the University of New England in Armidale, NSW, Australia, in 1996 and received a Ph.D. in Earth Sciences, Mineralogy, from the University of Bern, Switzerland, in 2001. He worked as a scientific collaborator at the Bern University of the Arts (BUA), where he has been lecturing within the department of conservation and restoration since 2002. He has participated in several funded research projects. In 2006, he entered a collaboration contract with the art technological laboratory of the Swiss Institute for Art Research (SIK-ISEA), Zurich, to exploit the synergies between the art technological laboratories at SIK-ISEA and BUA. Since 2008 he is laboratory manager of the art technological laboratory at BUA as part of the Bern University of Applied Sciences. The main focus of the SIK-ISEA and BUA collaboration is conservation science research on paintings, mainly by Swiss artists such as Ferdinand Hodler and Cuno Amiet, as well as analytical service work regarding chronological questions on paintings or painted objects. Nadim entered the field of Raman spectroscopy in 2007 with a research project on synthetic organic pigments in artists' paints of the 19th and 20th centuries and has gained experience with the technique ever since, applied in service, research and teaching.

SURFACE-ENHANCED RAMAN SCATTERING (SERS) OF NATURAL & SYNTHETIC COLORANTS

Marco Leona

Metropolitan Museum of Art, New York, US

Abstract

Surface-enhanced (resonance) Raman scattering (SE(R)RS) – the giant enhancement of Raman scattering experienced by molecules adsorbed on the surface of atomically rough metallic surfaces – has found increasing application in museums for the identification of organic colorants. The non-destructive or microanalytical identification of these materials, which have been used as textile dyes or pigments in artistic and decorative objects for millennia, is extremely problematic due to their very low concentration and generally high fluorescence. The high sensitivity of SE(R)RS to organic dyes, its minimal sample size requirements (fragments as small as 25 micrometers in diameter have been successfully analyzed), and the relative ease and speed at which the analysis can be carried out (30 minutes from sampling to positive identification) make possible a range of investigations that are precluded to traditional techniques (Polarized Light Microscopy, FTIR, HPLC). At the Metropolitan Museum of Art, SE(R)RS has been used to investigate well over one hundred objects, ranging in dates from 2000 BC to the present. Among the results so far obtained, we have documented the earliest use of a madder lake pigment, the earliest known use of lac dye in European art, and several examples of kermes and cochineal glazes, and madder, cochineal, methyl violet, and eosine lakes, from Ancient Egypt to the Impressionists and to Contemporary Art.

The exploitation of surface-enhanced Raman scattering in chemical analysis has generally been hampered by the perceived complexity of the technique and the misconceived notion that the results lack reproducibility. Historical trends in surface-enhanced Raman research, dominated by the controversy over the nature of surface-enhancement and by the development of a large variety of plasmonic substrates – each claiming vast superiority over all others – have undoubtedly contributed to such confusion. It can be shown however that silver colloids generally outclass complex plasmonic substrates in terms of sensitivity and that spectrally reproducible results are always obtained when analyzing the same analyte under comparable conditions (wavelength, pH, etc.). Furthermore, a simple understanding of the samples to be analyzed, of the chemical properties of each target molecule, and of their interactions with the colloidal substrate is sufficient to optimize each SE(R)RS experiment.

In our work we have developed a microanalytical protocol featuring the use of resonant excitation, a monodisperse silver colloid produced by microwave supported reduction of silver sulphate with glucose and sodium citrate, and a lossless non-extractive hydrolysis sample treatment. We demonstrate that the colloid we synthesized has well defined properties, can be easily and reproducibly prepared, and is stable over a period of months. We also show that the non-extractive hydrolysis process we use increases considerably the sensitivity of the method over other approaches discussed in the literature.

Finally, we show that SE(R)RS spectra can be successfully searched and matched against custom made SERRS spectral libraries.

In addition to the standard microanalytical protocol, two alternative approaches to SERRS analysis have also been developed and will be discussed: solid-phase dye microextraction (a non-destructive sampling approach), and colloid microdots piezoelectric delivery (the deposition of microscopic amounts of colloid, for in situ analysis of objects). These methods hold great potential for the non-destructive application of SE(R)RS to the analysis of both works of art and samples of forensic interest.

Marco's Essential Bibliography

Books

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Biography

Marco Leona is the Scientist in Charge at The Metropolitan Museum of Art (MMA), Department of Scientific Research. Marco holds a M.Sc. in Chemistry (1991) and a Ph.D. in Crystallography and Mineralogy from the University of Pavia, Italy. Prior to joining the MMA, Marco was a research scientist at the Freer Gallery of Art in Washington DC, and the Los Angeles County Museum of Art LACMA. At the MMA, Marco supervises a team of ten scientists conducting research on artist's materials and techniques and on art conservation. He also teaches an Instrumental Analysis (primarily molecular spectroscopy) graduate class at the Conservation Center of New York University's Institute of Fine Art. Marco chaired the Andrew W. Mellon Foundation and the US National Science Foundation sponsored workshop on the Chemistry and Materials Research at the Interface between Science and Art. As a result of the workshop, the NSF launched its first initiative to support scientific research on art and art conservation. Marco's contributions to the field include the development of new techniques for the non-invasive analysis of works of art by reflectance spectroscopy; the study of Tibetan painting techniques and materials; Infrared and Raman spectroscopy studies of the pigments indigo and Maya blue; Surface Enhanced Raman spectroscopy analysis of natural dyes; and various other topics. Dr. Leona's work on surface-enhanced Raman scattering has been published in the Proceedings of the National Academy of Science, Accounts of Chemical Research, and Journal of Raman Spectroscopy. His broader reach articles have appeared in Nature Chemistry, Nature Materials, Chemistry World, and online on Science News, ABC News, the Discovery Channel, and other outlets.

SYNTHETIC POLYMERS: SPECTRAL INTERPRETATION

Bruce Chase

University of Delaware, Newark, DE, US

Abstract

The use of vibrational spectroscopy to study polymers can be challenging, due to the differences between small molecule crystalline solids and polymeric materials that can simultaneously have crystalline and non crystalline regions. The subtle variations in the spectra arising from chain conformations, temperature, pressure, and other effects can sometimes confuse the interpretation of the spectral intensities. In this presentation, the influence of primary and secondary molecular structure on the vibrational spectroscopy of polymers will be discussed.

Bruce's Essential Bibliography

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Biography

Bruce Chase received his B.A. from Williams College in 1970 and his Ph.D. in physical chemistry from Princeton University in 1975, where he worked with Professor Donald S. McClure on studies of charge transfer excitation of transition metal ions in alkali fluorides. He then joined E. I. DuPont de Nemours as a research chemist in the Spectroscopy Division of the Central Research Department. He retired from DuPont in 2009 as a DuPont Fellow and Chair of the DuPont Fellows Forum. He is now a Research Professor in the Department of Materials Science and Engineering at the University of Delaware (UDel) and the Chief Technical Officer of Pair Technologies, LLC.

Bruce's primary area of research is in vibrational spectroscopy, FT-IR and Raman techniques, and applications to industrial analytical problems. In collaboration with Dr. Tomas Hirschfeld, he developed an FT-Raman spectrometer that demonstrated the utility of near IR excitation. Recent efforts include the development and utilization of polarized Raman scattering for the determination of orientation in fibers. Parallel work has involved developing multichannel detection instrumentation for the near IR. In collaboration with Professor John Rabolt (UDel) he has developed an approach to IR spectroscopy based on focal plane area detectors.

Among the awards that Bruce has received are the Williams-Wright award (1989), EAS New York Section Gold Medal award (1990), Delaware Valley ACS Section Award (1991), SSP Award from Spectroscopy Society of Pittsburgh (1994), Bunsen-Kirchhoff Prize from the German Chemical Society (1994 co-winner), Bomem-Michelson Award (1998), ACS Analytical Division Award in Spectrochemical Analysis (1999), Anachem Award (2002), EAS Award for Analytical Chemistry (2005), and the Hasler Award (2007).

THE IDENTIFICATION OF PLASTICS IN MODERN AND CONTEMPORARY ART OBJECTS USING FIBRE OPTICS RAMAN SPECTROSCOPY

Suzan de Groot, Thea B. van Oosten, Baudien te Nijenhuis
Cultural Heritage Agency of the Netherlands, Amsterdam, NL

Abstract

Artists nowadays are using new plastics, all of which were developed for household use or for automotive or other industries. These artists often adopt highly innovative fabrication processes to create bright and pristine-looking objects. The nature of these surfaces indicates that sampling for analysis is not possible; therefore technical examination of these artworks requires non-invasive methods. Fiber optics Raman spectroscopy, being a non-destructive method, was explored for the analysis and identification of these pristine-looking objects.

For the proper approach to the conservation of plastic objects, identification of the materials is fundamental and suitable analytical techniques and well defined reference materials are required. Therefore the SamCo box of the POPART project was brought to life. SamCo is a Sample Collection of plastics containing 96 plastics references (standards and objects). The standards, which are resins from various manufacturers, were derived from a commercially available ResinKit™. The objects, which are processed plastics, were found in flea markets and shops.

SamCo already proved to be a useful resource for the identification of plastics using FTIR and Py-GCMS in the POPART project. To research the applicability of Raman spectroscopy during the POPART project, also the whole SamCo collection has been analyzed using the Raman microscope. This has resulted in a Raman database containing 96 plastics reference spectra. Using the fibre optic probe Raman spectrometer, a second SamCo Raman reference database was compiled. Using the the fibre optic probe Raman spectrometer and this database, modern art objects have been analysed non-destructively and the composition of various plastics in those objects identified.

Suzan's Essential Bibliography

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Biography

Suzan de Groot studied analytical chemistry at the Hogeschool Amsterdam and graduated in 1996. She has been employed by the Cultural Heritage Agency of the Netherlands (RCE), Movable Heritage Department since 1996. She is currently engaged in Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy analyses of organic materials, especially plastics in objects of cultural heritage and modern materials in modern and contemporary art objects. She also is involved in testing physical and mechanical properties of various types of materials and carrying out artificial ageing experiments.

RAMAN ANALYSIS OF PAINTINGS, PHOTOGRAPHS, & WORKS OF ART ON PAPER

Silvia Centeno

Metropolitan Museum of Art, New York, US

Abstract

In this lecture, the advantages and limitations of Raman spectroscopy to analyze photographs, works on paper and paintings will be discussed. Within the photographic media, the focus will be on the identification of pigment-based processes, of coatings and image deterioration in daguerreotypes, and of polymeric materials in negatives (1-2). These particular examples will highlight the sensitivity of Raman, such as for identifying contaminants on daguerreotype images, but also will show that additional techniques need to be used in many cases, such as FTIR and XRF, for the full identification of the materials in pigment-based photographs. The chemistry of logwood, iron gall, sepia, and lithographic inks on paper will be discussed and, based on this, what kind of information is accessible non-invasively by Raman, and what questions on the chemistry and the conservation of these materials require the use of complementary techniques, such as FTIR and XRD (3-5). Although the binding medium in traditional oil paintings is generally below the detection limit of Raman under the experimental conditions typically used in museum laboratories, results of practical case studies will be shown in which information about the pigment-binder interactions can be obtained. Finally, the characterization of a deterioration process in oil paintings will be presented that highlights the advantages of the molecular specificity and the spatial resolution of the Raman technique (6-7).

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Biography

Silvia Centeno is currently a Research Scientist in the Department of Scientific Research at the Metropolitan Museum of Art in New York. Silvia received her Ph.D. and M.S. degrees in Chemistry from the University of La Plata, Argentina, and after a postdoctoral position in the same university she was awarded an L. W. Frohlich Fellowship in the Objects Conservation Department at the Metropolitan Museum to study unusual gilding techniques in Precolumbian metalwork. In 2001, she was appointed Associate Research Scientist in the Paintings and Paper Conservation Departments in the Museum and in 2004 she joined the newly created Department of Scientific Research, where her main responsibilities include the investigation of paintings, works of art on paper, and photographs. Silvia currently oversees team projects on the deterioration of traditional oil paintings and on the elucidation of 19th century

photographic processes. She has published and lectured on a number of topics ranging from medieval illuminated manuscripts and old master paintings to 19th century drawings, early lithographic inks, photographic materials, and modern paints.

RAMAN ANALYSIS WITH PORTABLE INSTRUMENTS

Costanza Miliani

CNR-ISTM, Institute of Molecular Science and Technologies, Perugia, IT

Abstract

Raman spectroscopy is a powerful technique for functional group analysis and molecular speciation of organic and inorganic chemical compounds, which has found numerous applications in the study of Cultural Heritage materials. Recently, the availability of miniaturized optical components has made it possible to perform non-invasive and in-situ Raman scattering measurements from unique objects that cannot be moved from their current locations, without any sampling or contact with their surface. Benefits and limitations of Raman analysis with portable instruments will be discussed, considering both the available literature and experience gained from the activity of the European mobile laboratory MOLAB.

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Biography

Costanza Miliani obtained a PhD in Chemistry at Perugia University in 1998 (Dissertation title: spectroscopic characterization of material of interest for cultural heritage). She was later a post-doc in the Photochemistry group at the Chemistry Department in Perugia, and visiting researcher at the PMI of

Princeton. Her current position is researcher at the CNR Institute for Molecular Science and Technologies (ISTM-CNR), where she has been since 2002. She has published more than 75 papers in ISI Journals concerning spectroscopic methods for analysis and physicochemical properties of cultural heritage materials. Her current research interests are the development and application of non-invasive methods for the identification and mapping of dyes, pigments, binders and their degradation products. She is responsible for MOLAB Transnational Access within the activity of the European Project Eu-ARTECH (6FP) and CHARISMA (7FP). Costanza, is member of the Scientific Advisory Committee of IPANEMA, Ancient Materials Research Platform, at SOLEIL Synchrotron, France, and a member of the board of SMAArt (Scientific Methodologies applied to Archaeology and Art), Perugia, Italy.

PICK YOUR WAVELENGTH: DISPERSIVE & FT RAMAN APPROACHES TO THE ANALYSIS OF ART MATERIALS

Francesca Casadio

Art Institute of Chicago, Chicago, US

Abstract

The availability of multiple excitation wavelengths in benchtop spectrometers from the ultraviolet to the near infrared, the latter coupled with Fourier Transform systems, allows extreme versatility when tackling the Raman analysis of Museum objects. Such objects are complex, hierarchical materials, often comprising mixtures of organic and inorganic compounds. This talk will describe experimental approaches for the identification of organic coatings, binding media and organic colorants, comparing 785 nm excitation in a dispersive system with 1064nm excitation with an FT-Raman. With the option of open-architecture microscope set-ups, both techniques can be adapted for in-situ, non-invasive examination of large-format artifacts.

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Biography

Francesca Casadio joined the Art Institute of Chicago in 2003 as its first A.W. Mellon Senior Conservation Scientist to establish and direct the conservation science laboratory. Dr. Casadio has also established and co-directs a research and education collaborative program in conservation science with Northwestern University. She received her Ph.D. and M.S. degrees in Chemistry from the University of Milan, Italy. In 2006 she was awarded the L'Oréal Art and Science of Color Silver Prize for her collaborative research with Professor Richard P. Van Duyne of Northwestern University. Her current research interests focus on new applications of FTIR and Raman microspectroscopies (especially Surface Enhanced Raman Spectroscopy), the investigation of artists' materials and techniques, and applications of synchrotron radiation techniques to studies of museum objects. She is the author of over 70 articles, book chapters and other publications, of which 50 are peer reviewed.