IRUG

IRUG – 8

The Eighth Biennial Conference of the Infrared and Raman Users Group

March 26 – 29, 2008
Academy of Fine Arts
Vienna, Austria

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Book of Abstracts

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www.irug8-2008.at

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Academy of Fine Arts
Schillerplatz 3
1010 Vienna, Austria

Book of Abstracts

(edited by Manfred Schreiner, Rita Wiesinger, Christoph Kleber)

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Dear IRUG-8 Conference Participants,

Scientific research on our cultural heritage, both for the study of its material aspects and for designing and controlling conservation and preservation strategies, faces a diversity of challenges due to the complexity and intrinsic value of the materials and objects. Furthermore, environmental conditions all over the world have inflicted increasing damage or at least deterioration of surfaces meant to be created for eternity. By conventional techniques we are able to ameliorate most of these dangers, but new approaches of high technology must be explored to preserve the heritage of human civilization as well as single objects of former generations.

Photonics, the science of generating, controlling, and detecting photons, especially in the visible and infrared region has offered possibilities to answer questions a scientist working in the field of cultural heritage is confronted with from art historians, archaeologists or conservators. Vibrational spectroscopy techniques have become more and more common in research as well as museum laboratories and micro-FTIR and Raman spectroscopy have enabled us to analyze the broad variety of unknown findings as artist's and archaeological materials. In consonance with the rapid development of laser technology, together with synchrotron-based methods, and optical systems, new solutions are available for the study, conservation, and preservation of our cultural heritage for the next generations.

However, there is still much work to be done in our field for IRUG, the Infrared and Raman Users´ Group. The concept of building up a database with the materials' spectra in the mid-IR has been highly appreciated. New but also experienced scientists are using this tool in their daily work. The biennial meetings of IRUG serve as a valuable opportunity to meet with colleagues and share their experiences, but also to discuss new developments and possibilities in the field of vibrational spectroscopy for the (non-destructive) examination of materials in art and archaeology.

In this context, it is a great honor and pleasure for the members of the Academy of Fine Arts in Vienna, the Federal Office for Care and Protection of Monuments in Austria, and the University of Vienna to host the Eighth International Conference of the Infrared and Raman Users Group. The Academy of Fine Arts has been for more than 3 centuries a place, where theory and practice of art and a creative exchange of ideas occurred. The program of IRUG-8 should reflect this fact with presentations dealing not only with the identification of materials using IR or Raman spectroscopy, but also with the stability and degradation of modern materials used in contemporary arts as well as describing and explaining corrosion phenomena on traditional objects. Additionally, progress in vibrational spectroscopy – theoretical as well as instrumental developments – will be presented accompanied by an exhibition of commercial products and instruments.

On behalf of the organizing committee, I am delighted to welcome all IRUG-members and guests at IRUG-8. As IRUG continues to grow – there are more than 85 contributions at this meeting – this underlines the significant contribution of IR and Raman spectroscopy in the analysis of art and archaeological material. For that reason, we look forward to disseminating this valuable body of information that we are creating together.

Finally, I want to express my sincere thanks to all members of the Organizing Committee for their unmatched enthusiasm and dedication to make IRUG-8 a success. Further, there should be mentioned the invaluable support by the Board of IRUG and the Scientific Committee and last but not least the companies exhibiting their instruments and sponsoring our conference.

Prof. Dr. Manfred Schreiner
Head of the Institute of Science and Technology in Art
Academy of Fine Arts Vienna

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16:00 – 18:00 Pre-registration, Academy of Fine Arts Vienna, Schillerplatz 3

Wednesday, March 26, 2008

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Manfred Schreiner: Chairman of IRUG8-2008
Beth Price: Board Member of IRUG
Stephan Schmidt-Wulffen: Rector of the Academy of Fine Arts in Vienna
Peter Seitz: Federal Ministry for Science and Research

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Friday, March 28, 2008

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Academy of Fine Arts, Schillerplatz 3

19:00 Presentation of the New Media Lab - Research Lab for Film & Television
Semperdepot, Lehargasse 6-8, Mehrzwecksaal, 2nd floor

Reception of the Rector of the Academy of Fine Arts
Semperdepot, Lehargasse 6-8, Mehrzwecksaal, 2nd floor

Saturday, March 29, 2008

10:00 Excursions to Museums in Vienna

Upper Belvedere (Oberes Belvedere) – Prinz Eugen-Str. 27

The Upper Belvedere houses the impressive collection of Austrian art dating from the Middle Ages to the present day. At the heart of the displays of "art around 1900" is the world's largest Gustav Klimt collection. The glittering highlights are Klimt's golden pictures "The Kiss" and "Judith", and masterpieces by Schiele and Kokoschka. Prominent works by the French Impressionists and the outstanding collection of Viennese Biedermeier paintings are further attractions at the Upper Belvedere.

Kunsthistorisches Museum, Treasury (Schatzkammer) - Schweizerhof, Hofburg

The objects kept in the Secular Treasury are of the highest order and reflect more than a thousand years of European history. Particularly deserving of mention are the insignia and jewels of the Holy Roman Empire, including the imperial crown. They represent the most important collection of medieval royal objects still in existence today. The vestments and other treasures of the Order of the Golden Fleece, with 17th century additions, entered the treasury in the late 18th century. The gems, jewellery and heirlooms from many different centuries are of great historical, as well as monetary, value. The Ecclesiastical Treasury holds the liturgical plate, vestments, reliquaries and altar fittings used and collected by the imperial court for its chapels and religious services.

Kunsthistorisches Museum, Collection of Greek and Roman Antiquities – Maria Theresien-Platz

The Collection originating from the former estate of the Habsburgs is among the most important of its kind in the world. The exhibits cover a period of history extending from Cypriot Bronze Age pottery from the 3rd millennium B.C. to Slavic finds from around the turn of the first millennium A.D. Above all, the collection is internationally renowned as the home of the unique cameos and archeological treasures dating from the Great Migration an the Early Middle Ages.

Museum of Modern Art (Museum Moderner Kunst - MUMOK) – Museumsquartier, Museumsplatz 1

The aim of MUMOK is to preserve, enlarge, analyze, and make available to the public the collection of artworks from the 20th and 21st centuries, compiled since the opening of the Museum of 20th Century Art, by applying state-of-the-art scientific and museological methods. The Museum serves as collection site, archive, research institution, and exhibition venue.

With its emphasis on Pop Art and Photorealism, taken from the Austrian Ludwig Foundation, Fluxus and Nouveau Réalisme, taken from the Hahn Collection, and Viennese Actionism, MUMOK offers a unique blend of art focusing on society and reality as well as of performative art of the 20th century.

12:00 End of the Conference

ORAL PRESENTATIONS

IR and Raman Spectroscopy: From the Laboratory to On-site Applications

Brunetto G. Brunetti, Costanza Miliani

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IR and Raman spectroscopy find large applications in laboratory research. However, four years of experience of MOLAB have demonstrated their possible wide application on different typology of objects also for on-site studies, i.e. directly in a museum or in a conservation laboratory or even in a restoration site.

MOLAB consists of a network of Italian infrastructures (University of Perugia, CNR-ICVBC/INOA, and OPD) providing a coherent access, under a unified management structure, to a set of mobile equipment for *in-situ* non-invasive chemical and morphological analyses on artwork materials. The service is offered to European scientists and conservators/restorers through Eu-ARTECH (Access, Research and Technology for the European Cultural Heritage), an I3 initiative within the 6th Framework Program of the EU (http://www.eu-artech.org). The MOLAB facility includes compact and versatile equipment for: mid-FTIR, near-FTIR, micro-Raman, and Vis-NIR, as well as IR-colour scanner reflectography, XRF, UV-Vis fluorescence, fluorescence imaging, laser micro-profilometry, NMR relaxometry, AFM, video-microscopy, micro-drilling, and thermography.

The application of mobile facilities allows an easier approach to the study of real artworks, due to the non-invasivity and the non-necessity of movement of the object under study. The possibility of extensive studies on numerous artworks offers the opportunity to extend to real cases the knowledge achieved through laboratory studies on material properties and, *viceversa*, allow scientists to find new problems to be put under the focus of laboratory research.

Case studies will be presented on examination of stones, paintings and Italian Renaissance majolica.

References:

C. Miliani, F. Rosi, I. Borgia, B.G. Brunetti, A. Sgamellotti: Fiber-optic Fourier transform mid-infrared reflectance spectroscopy: a suitable technique for *in-situ* studies of mural paintings. *Appl. Spectr.* 61 (2007) 239.

C. Miliani, F. Rosi, A. Burnstock, B.G. Brunetti, A. Sgamellotti: Non-invasive *in-situ* investigations versus micro-sampling: a comparative study on a Renoirs painting. *Appl. Phys.* A 89 (2007) 849.

S. Higgott, E. Sani, L. Cosentino, B.G. Brunetti, C. Miliani, L. Cartechini, F. Presciutti, A. Sgamellotti: Italian Renaissance majolica at the Wallace Collection: an *in-situ* study of materials by non-invasive techniques. *Faenza* (2008) in the press.

A Comparative Study of Vibrational Imaging Techniques Analyzing Paint Cross Sections of Modern Art

Jens Stenger[1,2], Katherine Eremin[1], Narayan Khandekar[1], Martin Vogel[3],
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The identification of materials in paint cross-sections provides important information about the technique and condition of a painting or other work of art. In particular, microscopic chemical imaging can be a powerful tool for understanding the material nature of works of art. While scanning electron microscopy provides detailed information about inorganic materials, binders and organic pigments cannot be identified by this method. Imaging techniques using vibrational spectroscopy overcome this shortcoming.

In this paper we survey different infrared and Raman imaging techniques. Fourier Transform Infrared (FTIR) imaging using a Focal Plane Array (FPA) detector is compared to FTIR mapping with an Attenuated Internal Reflection (ATR) objective. While the FTIR approach often suffers from overlapping bands, the complementary vibrational spectroscopy tool, Raman imaging frequently has other trade-offs. In conventional Raman spectroscopy the Stokes signal overlaps with the fluorescence typical for organic binders and pigments. We discuss the effectiveness of a fluorescence subtraction technique using two Raman spectra of the same sample with slightly different excitation wavelengths. Conventional Raman is compared to images acquired using Coherent Anti-Stokes Raman Scattering (CARS) microscopy. The CARS process has the advantage that the anti-Stokes signal is blue shifted with respect to the one-photon fluorescence. This eliminates the overlap problems encountered with conventional Raman techniques. However, for organic pigments, this comes at the cost of two-photon fluorescence.

Our comparative vibrational imaging study focuses on cross sections of twentieth-century paintings by Mark Rothko. Rothko is well known for his use of an unusual combination of traditional and modern materials and thus provides an ideal starting point for this investigation. He frequently used a variety of binding media such as rabbit skin glue, oil, and alkyd paint within one painting. We discuss the significant additional challenges encountered in identifying the binding media when modern organic pigments are present.

Investigation of the Dark Spots in 19th Century Watercolor Painting by Combination of Micro-FTIR, Micro-Raman, and Micro-XRD Techniques

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The article is devoted to investigation of darkening spots in 19th century watercolor painting by Sadovnikov V. S. (1800-1879) from the State Hermitage Museum collection. The micro-FTIR method is a technique useful for preliminary express revealing of the presence of both inorganic and organic materials. Research has been carried out in an attempt to find the reasons of discoloration of painting materials. We have found the presence of lead white by means of micro-FTIR spectroscopy. The artist used lead white as ground and extender. Further analysis has focused on the identification of the products of the pigment alteration by the combination of micro-Raman and micro-XRD techniques for this reason.

The examination by using these highly sensitive micro-analytical techniques yielded the artist' painting materials: lead white, Prussian blue, lead chromate and protein as binding medium. Additionally, the sulfur-containing degradation products such as lead sulfide, lead oxide sulfate, and lead dioxide could be determined.

The analysis of data obtained and mounted materials allowed to understand the reasons of alteration of the painting layers and recommend conditions for their storage and exhibition.

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R.J. Gettens, H. Kühn, W.T. Chase: Lead white in artists´ pigments: A handbook of their history and characteristics. Vol.2, ed. A. Roy, Oxford University Press, Oxford (1993) 67-82.

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FTIR and Raman Microscopy Study of Paints Used by Sam Francis

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Sam Francis (1923-94) was one of the most influential painters in the 20th Century. After his death, 63 pre-mixed containers of paints were found in his studio in Santa Monica, California. From discussions with Dan Citron - his studio assistant for many years – it is known that Francis used both commercially available paints as well as custom-made formulations prepared by Citron that often included unusual pigments rarely used in artist's paints. As part of a study into Francis's painting materials, these paints were analysed to determine both binder and pigments. Although a number of techniques were assessed, a combination of FTIR (using ATR) and Raman microscopy (785 nm) enabled the vast majority of pigments (both inorganic and organic) and binders to be identified.

FTIR appeared better suited to the detection of the binder (primarily acrylic emulsion) which typically gave very strong and distinctive peaks, but sometimes it also gave clear peaks from some organic pigments. However, in many cases FTIR failed to identify any pigment component at all, and for these paints Raman microscopy was far more successful. Raman microscopy gave fairly weak and broad peaks for the binder, but in most cases gave very distinctive peaks for all pigments, both organic and inorganic. The inorganic pigments identified included natural and synthetic pigments such as hematite, goethite, magnetite, cobalt violet, cobalt titanate, ultramarine, amorphous material such as graphite but also barytes and calcite fillers. 16 different organic pigments were also detected, including examples from the azo, phthalocyanine, quinacridone, disazo, diarylide, dioxazine, indanthrone and perinone families. In cases where the organic pigments were also visible in FTIR, it was concluded that they were simply present in much higher quantities.

One major difficulty encountered with Raman microscopy was that a good reference database of modern organic and inorganic pigments does not yet exist, unlike FTIR where the IRUG database now contains hundreds of such spectra. Consequently, a wide range of reference spectra of over 100 synthetic organic pigments was also collected to assist with the interpretation of data from the Francis paint samples.

Micro-Raman and FTIR Study of Effects of Diagenesis and Consolidation Treatments on Archaeological Bone Material

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Prehistoric remains are generally composed of bone, flint, stones, and later ceramics or wood. Bone and alike materials, including ivory and antler, are particularly important because they record a wealth of information on the past through changes in their morphology, structure as well as in their chemical and isotopic composition. Such materials are generally highly structured and essentially consist of collagen molecules and hydroxyapatite crystals on a nanoscale. A crucial step to preserve these samples lies in their consolidation either in the field or in the laboratory before use for scientific or exhibition purposes. The treatment generally involves impregnation with a polymer which has to provide strength to the structure. Although absolutely necessary, one of the major drawbacks of the method is that the consolidation agent can modify the appearance, the chemical composition and the micro- and nanostructure of the bone material. It can also cause additional severe alteration processes linked with the degradation of the strengthening polymer. As a result, to our knowledge, there is no established conservation protocol available today which fully respects the degree of preservation required in the archaeological and museum conservation context.

The conservation method chosen depends on the state of preservation of the bone material. Thus, an analytical strategy adapted to the complexity of this nanocomposite biomaterial was developed to characterize the state of preservation of the of archaeological bone materials at different scales [1, 2]. In particular, information on the modification of the collagen at macro-, micro-, and nanoscale was obtained by means of differential scanning calorimetry; FTIR and Raman micro-spectroscopy coupled with transmission electron microscopy (TEM) on thin sections, respectively.

FTIR and Raman micro-spectroscopy are the techniques of choice in this analytical methodology because they enable simultaneous analyses of the organic and mineral fractions and they do not necessarily require destruction of the analysed material. In addition, they provide spatially resolved information on the modification of the chemical composition and of the structure of the mineralized collagen preserved in the bone section or of the consolidation product eventually applied on the consolidant.

This study was conducted on archaeological bone material from the Neolithic site of Chalain (France) and on non-consolidated and consolidated Palaeolithic reindeer antler from Dordogne (France) [3]. Deconvolution of the amide I band in the vibrational spectra in particular shows modifications in the collagen conformation induced by diagenetic processes and/or consolidation treatment of the studied bone and antler samples.

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Investigation of Organic Materials Based on Synchrotron Infrared Radiation

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Fourier transform infrared (FTIR) spectroscopy is a well established method for the identification of organic materials in conservation science. FTIR spectroscopy can easily reveal the general category of an organic medium. Usually small samples of paint layers or varnishes are taken from art objects and measured in transmission mode. Transmission measurement is the most established method in this specific field of IR spectroscopy. Very small amounts of the sample under investigation can be measured today by use of diamond anvil cells. Non-destructive methods are under development to study the surfaces of art objects. There are contact techniques such as attenuated total reflection FTIR spectroscopy (ATR-FTIR), and non-contact techniques like fiber-optic IR spectroscopy or synchrotron based FTIR spectroscopy (SR-FTIR).

Many objects encountered in the cultural heritage context contain multiple thin layers. The surface techniques mentioned above can naturally not be used to reveal information concerning the layers beneath the surface. In order to study all of the layers the approach is either to separate the layers and look at these individually, or to examine in cross-sections with a technique of suitably high spatial resolution to allow the individual layers to be distinguished. However, the mechanically separation of different layers is often a difficult, or even an impossible task due to the smallness and complexity of the samples.

The results presented here indicate that SR-FTIR micro-spectroscopy is a suitable method to analyze organic layers in cross sections with a spatial resolution close to the diffraction limit. This is exemplarily shown on different samples. The technique can easily be transferred to more complex structures. Meaningful IR spectra of samples taken from original art objects can be gained from small analytical areas within a reasonable acquisition time - not possible with standard IR microscopes using a Globar source. Due to the high brightness of the infrared synchrotron radiation the signal to noise ratio of such spectra is comparable to that of spectra measured with conventional transmission techniques on larger samples. Another advantage of SR-FTIR is the possibility to analyze all layers of a cross sections directly, with high spatial resolution, avoiding a complicated procedure of sample preparation. Once a cross section is produced the method is non-destructive, i.e. the cross sections can be stored and used for further research. SR-FTIR micro-spectroscopy might not be a standard method in the field of archaeometry and conservation science due to the limited availability of storage ring facilities. However, it will be of benefit for a series of multilayered samples, where conventional techniques do not provide the specificity and spatial resolution necessary.

Combination of Synchrotron Based Imaging Techniques for the Study of Ancient Paintings

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FTIR spectroscopy has already demonstrated its relevance for the chemical analysis of paintings. Indeed, it is an ideal technique for the study of hybrid materials as it is sensitive to both organic and mineral matters.

The combination of a microscope to FTIR spectroscopy was a decisive step for the study of paintings as it was then possible to see and to choose the location of the spectrum acquisition. The analysis was no longer obtained as an average over the whole sample; instead molecular images were accessible. In addition to offer "geographical" information, the imaging can be very useful for the better understanding of spectra. Indeed, by searching correlation between the maps of various absorption bands, it is possible to correlate these vibrational features. This way, the contribution of the different compounds can be better resolved from the mixture thanks to this "geographical" correlation.

An even more decisive step was achieved thanks to synchrotron sources which provide a much brighter source compared to thermal sources. With such equipment, the beam size can be easily lowered below 10 x 10 μm^2 without significant loss of flux. This point is essential for the discriminative analysis of each layer of the painting.

This technique was recently used in combination with micro X-ray fluorescence and micro X-ray diffraction at the ESRF, on painting fragments from Bamiyan. This synergic approach offers a powerful tool for the extensive identification of both pigments and binders, even in very complex stratigraphy.

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Studies on Degraded Ancient Silk Fibers by FTIR Microscopy Equipped with Synchrotron Radiation Light Source

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The analysis of excavated organic materials such as textile fibers, lacquers, and ambers are generally one of the difficult problems in conservation science. Firstly, these materials are usually degraded from long-term burial. Additionally, the amount of material allowed for sampling is usually extremely small.

In studies on ancient silk fibers, we found that the FTIR microscopy using the synchrotron radiation is suitable for our purpose. In Japan, Japan Synchrotron Radiation Research Institute has the facility called SPring-8 (Electron energy: 8 GeV). The results obtained by using FTIR microscopy with synchrotron radiation are presented.

Silk fibers less than 1 mg were laid between two flat diamond plates and pressed to produce a thin-layer. In the transmission mode spectra were measured from 4000 cm^{-1} to 400 cm^{-1} wavenumber applying the diamond cell.

The most notable change in the spectrum of degraded silk was the decrease in intensity of amide I and II peaks and consequently the superpositioning of these two peaks as one broad peak. Furthermore, a new strong peak around 1000 cm^{-1} was observed. The intensity of this peak seems to dependent on the extent of degradation of silk fibers.

Since synchrotron radiation is polarized, the spectrum curve is influenced by the orientation of the silk fiber on the diamond cell. We generally chose the longitudinal direction of the single fiber samples as it is the direction of the most intense beam line output. It was found that the polarized spectrum shows the degradation of secondary structures of silk fibroin molecules.

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Estimating Condition of Plastic Art Works Using Degradation Indexes

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Plastics in modern and contemporary art works degrade and conservators are confronted with the limited durability of these materials: crumbling, disintegrating, deformation, cracking, delaminating, discolouration, and chalking. For setting priorities in the conservation/restoration of plastics, the condition and rate of decay of an object should be known. Two decades of conservation research into the degradation of plastics has shown that those two parameters depend on composition, production method, added anti-ageing components, service life of the objects and conditions surrounding the objects.

Poly(ether)urethane flexible foams, PP and PE artworks degrade relatively fast and main cause of degradation is photo-oxidation due to light, oxygen, heat, often accelerated by pigments. Outdoor unsaturated polyester resin art work surfaces not covered by a protection layer will suffer from environmental influences and degrade due to exposure to light, heat, oxygen and moisture. Rubber objects degrade mainly due to the influence of oxygen and ozone, and loss of elasticity and total brittleness is the result.

By measuring increase of photo-oxidised components or decrease of specific double bonds using FTIR, kinetics of plastics can be determined and condition of objects can be established. Tests were carried out on polyester, polypropylene, polyethylene, flexible PUR ether foam and rubber objects. Infrared spectra were recorded after artificial light- and heat ageing. Degradation index was determined; for PP and PE as the increase of the carbonyl index (C=O), for polyether urethane flexible foams and unsaturated polyester as increase of the hydroxyl index (C-OH) and for rubber as the decrease of the vinylidene index (C=H-, cis deformation).

Differences in degradation index were measured at the outer surface and inside materials, which has to do with the permeation of oxygen into a material. Only after the surface has become crumbly deeper layers will start to oxidise. It clarifies, however not unknown at all, that degradation is taking place on the outer surface of objects.

The usefulness of protecting surfaces from ageing or in worst case scenario from outdoor weathering is undoubtful. However in some cases direct action is needed and in others some delay in treatment is appropriate, depending on the condition of (the surface) of an object.

For already degraded objects, determining their condition by measuring the degradation index using FTIR is useful. However, as FTIR it is a rather insensitive technique an early warning system such as chemiluminescence analyses can provide valuable information for new acquired objects.

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An FTIR-based Exploration of the Effects of Wet Cleaning Artists' Acrylic Emulsion Paints

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Understanding the potential changes to acrylic emulsion paint films during wet surface cleaning treatments has been identified as a priority for conservators of modern painted surfaces. Such changes take place on paint surfaces as well as bulk films from the extraction/removal of soluble components. To explore these phenomena, acrylic paint films made from contemporary paint formulations as well as works of art were examined using a range of FTIR techniques: transmission microscopy, attenuated total reflectance (ATR) and *in-situ* non-invasive reflectance FTIR (available through the transnational access MOLAB). With all three FTIR techniques, the major materials identified on the surface of acrylic emulsion paint films - and in aqueous bulk film extracts - were polyethoxylate-type surfactants. These surfactants, which include the Triton-X series, are used in the base emulsions as stabilisers and are added to paints as pigment dispersants.

FTIR studies revealed that surfactants were extracted from bulk films within thirty seconds; even from films with no FTIR-detectable surface surfactant. The identification of all of the components present in 24-hour aqueous extracts was hampered by the proprietary nature of many of the constituents. Some minor inorganic constituents were also identified in short (1-2 minute) aqueous extracts taken directly from paint surfaces.

Combined results from the FTIR techniques used on paintings suggest a possible association between the presence of surface surfactant and paints containing synthetic organic and some iron-based pigments. However, varying degrees of surfactant were also detected on several contemporary paint formulations containing titanium white, azo yellow (PY3), phthalocyanine green (PG7) and burnt umber, perhaps suggesting some brand dependency. When exuded onto paint surfaces, surfactants have been shown to be at least partially removed by aqueous swabbing regardless of pigment type and age of the paint film and are not affected by aliphatic solvents. ATR analysis of model samples and *in-situ* non-invasive reflectance FTIR of the surface of acrylic paintings dating between 1962 and 1973 also confirmed the reduction of surfactant with aqueous cleaning. Continued ATR monitoring of model samples after aqueous cleaning has shown that surfactant continues to migrate to the surface.

The Examination Drawings by Georges Seurat Using Fourier Transform Infrared Micro-spectroscopy (Micro-FTIR)

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Drawings by Georges Seurat in the collection of The Museum of Modern Art were examined for a recent exhibition. Fourier Transform Infrared Micro-spectroscopy (micro-FTIR) has found a shellac fixative on all of the drawings examined. It is apparent that Seurat applied this resin because it appears localized to areas corresponding to the early passages and not always over the final stages of the drawing. Evidence suggests that the fixative was either applied to regions where he felt his drawing medium, Conte Crayon, would disrupt lower layers of the composition or that his hand would smudge a particular area. In addition, it cannot be discounted that Seurat may have been manipulating the subtle shift in appearance between fixed and unfixed passages. Typically, the layers of shellac are extremely thin and based on color suggestive of decolorized shellac. This is a distinct contrast from his contemporary, Odilon Redon, who consciously used unrefined shellac to impart an instant 'Old Master' look in his drawings and paintings. In addition, the use of an ultraviolet (UV) illumination attachment on the FTIR microscope was the first step toward a more concise understanding of the composition of Conte crayon, Seurat's drawing medium of choice. Under UV no autofluorescence indicative or organic binder was observed in any of the samples of Conte Crayon examined. Subsequently, samples of reference Conte crayon were analyzed by gas chromatography mass spectrometry (GC-MS) and found <u>not</u> to contain wax in any concentration as anecdotal information has suggested. Rather, the qualities that give rise to its 'wax-like' handling properties come from the graphite and clay in the pencil. These findings correspond well with Conte's original patent from 1795.

Raman Spectroscopy: New Light in Archaeometry

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Raman spectroscopy is an analytical technique, which is increasingly more frequent used for the non-destructive investigation of artistic and archaeological objects. Instrumental improvements have allowed adapting the methodology depending on the specific requirements for the non-invasive investigation of precious historical objects of art. Several advantageous properties, including its non-destructive character and the ability to obtain spectra of inorganic as well as of organic compounds make the technique well-suited for these investigations. Moreover, mobile Raman spectroscopy allows us to investigate objects *in-situ*, in a virtually non-destructive way.

When performing archaeometrical research, one always has to balance the results obtained from the examination against possible damage to the artifact. Performing direct and non-invasive investigations can be a valuable alternative instead of sampling the object of art. In this presentation, several examples will be given of the direct analysis of art objects, by using mobile Raman spectroscopy.

In recent research papers on Raman spectroscopy in archaeometry, different trends can be observed, like combined-method approaches and the analysis of biological materials. This presentation will discuss on the general approach when using Raman spectroscopy in this field, and will give several examples of the application of Raman spectroscopy for art analysis as well as for the investigation of archaeological fragments.

Raman Mapping on Large Objects Using a Novel Scanning Method

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Raman imaging is of a great importance for the analysis of works of art, as it provides a non-destructive way of adding chemical information to standard optical images. Traditionally, Raman imaging is performed using a motorised XY stage moving the sample in a step-by-step manner in two spatial directions under a Raman microscope.

One limitation of such an approach or scheme is that it cannot be implemented with artifacts that are too large to be placed under a microscope. Other schemes include the use of fiber-coupled Raman probes, but these have other limitations in terms of optical throughput and flexibility (multiple laser excitation, mapping capability etc).

A novel scanning mechanism, which allows in-situ Raman imaging on large artefacts using a horizontal exit is presented in this paper. Two advantages of this scheme are that it maintains full confocality and is compatible with multiple laser excitations. Additionally, it also does not suffer from the poor coupling efficiency of fibre-coupled probes, as the in-situ measurement is performed in direct coupling.

Some examples of Raman images obtained by using this scheme are also presented by the authors.

Investigation into the Painting Material of the Late-15th Century Manuscript Illuminator Jean Bourdichon

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Jean Bourdichon (1457-1521) was one of the major French illuminators of his time, and was the official court painter to four successive French kings: Louis XI, Charles VIII, Louis XII and Francois I. One of his most important works is the *Hours of Louis XII,* painted in 1498-99. However, by the early 17th century the individual leaves of the *Hours of Louis XII* had been separated and dispersed. In 2006, an exhibition organized by the J. Paul Getty Museum and the Victoria and Albert Museum reunited fifteen of the sixteen surviving miniatures, and provided the impetus for a study into Bourdichon's painting materials and techniques [1].

For the study presented here, three different manuscripts spanning nearly the entire length of Bourdichon's career were examined: the *Katherine Hours* (ca. 1480, J. Paul Getty Museum), the *Hours of Louis XII* (1498-99, J. Paul Getty Museum) and the *Book of Hours for Rome Use* (1515, Pierpont Morgan Library, New York). The pigments in several illustrated folios from each manuscript were examined using the non-invasive techniques of X-ray fluorescence and Raman spectroscopies. The results revealed that Bourdichon rarely used pure pigment, but rather created complex mixtures using a palette consisting of at least twelve different pigments and colorants to create a wide range of hues. Perhaps the most surprising finding was the discovery of the use of bismuth black, a pigment not normally found in manuscript illumination, in the background, shadow areas, and architectural elements of the compositions. Interestingly, the use of this somewhat unusual pigment may have been an innovation of Bourdichon's, as bismuth black has not been found in any works by his mentor Jean Fouquet that have been examined to date. Bismuth black has been identified in Italian panel paintings dating to the early 16th century [2], but its identification in Bourdichon's *Katherine Hours* dating to ca. 1480 may represent the earliest documented use of this material as a painting pigment [3].

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Identification of Phthalocyanine Pigments in Paintings by Means of Raman Micro-spectrometry and Express *"In-situ"* Method

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A collection of 70 phthalocyanine pigments containing different metal ions and surrounding ligands has been analyzed at 2 cm^{-1} resolution using Nicolet Almega XR Raman microspectrometer. Peak assignments were done and characteristic frequencies were selected for unambiguous identification of phthalocyanine pigments in paintings. A searchable database was formed.

Detection of phthalocyanine pigments by Raman spectroscopy proved to be the most effective way to reveal fake works referable to Russian Vanguard painters of 1900-1920 years.

For quick analysis of painting without probes extraction we suggest using a handheld analyzer of bank notes and securities. We used the model A-14M manufactured in Russia by Vildis (http://www.vildis.ru English version is available). This instrument was designed to detect protective "green inks" by their absorption in near IR. Instrument issues sound warning when the optical sensor is close to parts containing phthalocyanine pigments.

Raman and Surface Enhanced Raman Spectra of Early Synthetic Dyes

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Over the past few years, Surface-enhanced Raman spectroscopy (SERS) has attracted the attention of researchers in the conservation science field. This technique has been successfully applied to the study of a number of natural dyes (e.g. alizarin [1], carminic acid [2], berberine [3], quercetin [4] and laccaic acid [5]). The study of these materials by normal Raman spectroscopy can be difficult due to the low Raman cross-section of the dyes and the high fluorescence emitted from them. These drawbacks can be overcome by using SERS spectroscopy. This is due to the huge enhancements of the Raman emission produced, together with the quenching of the overlapping fluorescence. On the other hand, extremely low concentrations can be detected, allowing detection of very small quantities of the sample.

In this work, we present the Raman and SERS analysis of various early synthetic dyes including xanthenes, triarylmethenes, azines, oxazines and azo dyes. The normal Raman and SERS spectra were registered using a dispersive system with 633 and 785 nm laser wavelengths. Normal Raman spectra with a Fourier transform system at 1064 nm were also obtained.

This study shows that both Raman and SERS spectroscopies provide excellent spectra for all the synthetic dyes examined. Certain conditions, such as response to various laser wavelengths and fluorescence of the sample, came into play in normal Raman, but were easily overcome with SERS.

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Raman and Surface Enhanced Raman Spectra of Natural and Synthetic Flavonoids

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The Raman and Surface Enhanced Raman spectra (SERS) of synthetic (3-OH, 5-OH, 7-OH, and 3', 4'-di-OH) and natural flavones have been obtained. Flavones and flavonols found in plants are yellow compounds and are the main components of a number of natural dyes used in textile dyeing since antiquity. Fustic, young fustic, quercitron, Persian berries, weld, dyer's broom and sawwort, which are important yellow dyes, all contain flavonoids such as quercetin, luteolin, fisetin, rhamnetin, genistein and morin. Extracted from plants, they are easily hydrolyzed from the glycosides to their parent flavonoid and can be applied to textiles as mordant dyes.

The normal Raman spectra are taken with an FT-Raman system in the powder form. The SERS spectra are obtained on both Ag colloid and in some cases Ag electrode substrates. Due to large enhancements of the Raman signal, SERS enables detection of very small quantities, but provides simultaneous suppression of fluorescence background. Assignments of the spectrally observed normal modes are aided by density functional theory (DFT). Excellent fits are obtained for the observed spectra with little or no scaling. The most intense lines of the normal Raman spectra are those in the C=O stretching region (near 1600 $\mathrm{cm^{-1}}$). These lines are relatively weakened by proximity to the surface, while other lines at lower wavenumber, due to in-plane ring stretches, tend to be strongly enhanced by the surface. We compare the spectra and determine discriminants, which will enable detection and identification of species in small quantities and in mixtures.

Vibrational Spectroscopy as an Analytical Tool in the Identification and Characterization of Flavonoid Molecules: *In-situ* Detection of Weld Dye in Textile Fibre

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The identification of dyes used in works of art is essential for dating, restoring and conserving artwork and for studying art history in general. Raman and Infrared vibrational spectroscopies are well-accepted techniques for the molecular characterization of a large number of materials presents in artworks. The complementary use of both techniques, currently also available at the microscopic level and with portable instruments, allows the detection of pigments, binders and substrates, even with *in-situ* diagnosis. Moreover, by means of SERS, the inherent limitations of Raman spectroscopy are readily overcome thanks to the use of nanostructured metal surfaces to enhance the signal and to quench the fluorescence at the same time. The intensity of the normally weak Raman scattering is increased by factors as large as 10^8 for compounds adsorbed onto a SERS substrate, allowing for trace-level detection [1].

One of the most recent application of SERS of our group is the detection and characterization of natural dyes employed as pigments in artworks. In general, the vast majority of organic coloring materials belong to the chemical classes of flavonoids (yellow), anthraquinones (red), and indigoids (blue). These dyes were largely used for textiles [2]. Detection of coloring agents in old textiles is difficult due, not only to the poor light fastness of some of molecular markers and to the complexity of the degradation processes, which are not yet completely unveiled, but also to their trace amounts and different substances used for dyeing purposes. We have already demonstrated the suitability of SERS for the detection and characterization of the anthraquinone red pigment alizarin [3] and carminic acid [4]. For flavonoids the situation was/is obviously more challenging as only limited Raman and SERS studies applied to flavonoids have been published so far [5-7].

In this work a detailed vibrational characterization was accomplished for a group of flavonoids with related structure which varies depending on the presence of double bond and/or carbonyl group as well as on the number and position of substituted hydroxy groups. The first SERS *in-situ* experiments on reference samples – silk and wool fibres coloured by the weld dye and treated by different types of mordant – are discussed. The presence of flavonoids, particularly of Lut, was detected without the necessity for dye extraction.

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Fluorescence Suppression in Resonance Raman Spectroscopy of Organic Dyes by Subtracted Shifted Raman Spectroscopy

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The identification of natural dyes on works of art is very important for historical and conservation purposes. Dye analyses can give information on the dating and origin of the object and provides a better understanding of its original colour and appearance and highlights any particular degradation risk suggesting the most appropriate method of restoration. In this work a resonance Raman study of dyes belonging to different classes (namely, quinochalcones, anthraquinones, phenoxazones, homoisoflavonoids) is reported. The use of a Nd:YAG green laser with emission at 532 nm enhances the Raman scattering of the red chromophores with low spectral interferences from the surrounding matrix (for example the substrate where the colorant is applied). The strong fluorescence which generally characterizes the resonance Raman spectra was eliminated by using subtracted shifted Raman spectroscopy (SSRS). A systematic study on reference organic dyes was firstly carried out to evaluate the suitability of the method and to estimate also limitations and strengths of the spectrum reconstruction process. Secondly, the same methodology was successfully applied for the non invasive identification of madder on an ancient dyed silk textile (*manutergium*). This object was recently found in Ascoli Piceno (Italy) and it is supposed to belong to the Syrian artistic textile production of the VIII-IX Century A.D. Finally, taking advantage of the simple experimental requirements of SSRS, subtracted shift Raman spectroscopy has been efficiently carried out for the study of the above mentioned reference dyes using a portable micro-Raman fiber optic instrument.

Ambient Phase Effects on Infrared Spectra of Thin Layers

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Infrared spectra of thin solid films are strongly influenced by the adjacent media, namely the supporting substrate on one side and the ambient phase on the other side. These influences include a variety of superimposed effects such as electrical field enhancements, selectivities for different dipole moment orientations, optical distortions as well as chemical interactions at the film/ambient interface, which sometimes result in highly complex absorption profiles and very different spectra for the same film in contact with different ambient media. It will be shown here that these effects can be modeled and predicted by spectral simulations, providing the key to a successful interpretation of experimental spectra and a deeper understanding of how the sensitivity and selectivity of infrared absorption is often dictated by the surrounding media. As an extension of these efforts, a novel sample configuration will be presented where a thin film is sandwiched between two solid materials. It is shown both by theoretical calculations and experimental results that this setup yields sensitivity enhancements up to two orders of magnitude compared to conventional transmission or reflection measurements and provides currently by far the most sensitive infrared technique for thin films of nanometer thicknesses. Moreover, it allows previously inaccessible sample regions such as buried solid-solid interfaces to be probed with monolayer sensitivity and reactions and processes taking place at such interfaces to be monitored spectroscopically. This will be demonstrated with some experimental examples of organic monolayers embedded between two bulk solid phases.

Analysis of Metal Surfaces by *In-situ* Infrared Reflection Absorption Spectroscopy (IRRAS) Measurements*)

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The exact knowledge of the reactions occurring in the metal-atmosphere interface during a degradation process of metallic materials is of great importance for the understanding of the mechanism of such processes. Therefore, methods like in-situ Infrared Reflection Absorption Spectroscopy (IRRAS) measurements should be applied which enable a time resolved tracking of these reactions on a molecular level. Besides other surface sensitive methods such as Tapping Mode Atomic Force Microscopy (TM-AFM), Quartz Crystal micro-Balance (QCM), and Time of Flight Secondary Ion Mass spectrometry (TOF-SIMS) in-situ IRRAS measurements allow the identification of the formed reaction products as well as the determination of the steric orientation of the surface bonded reaction products. These investigations take place under an angle of incidence of the IR light on the sample surface of 78° off normal. Therefore, a special cell was constructed which enables the investigation of non transparent surfaces under atmospheric conditions with or without addition of acidifying gases [1].

On copper – when weathered in humidity – the growth of an oxide layer could be followed in situ as well as the growth of copper sulfite when exposed to a SO_2 containing atmosphere indicated by the occurrence of bands at 645 cm^{-1} and 1055 cm^{-1}, respectively [2]. Furthermore, the amount of the reversible bounded physisorbed water layer on the sample surface could be monitored at 3400 cm^{-1}. On the investigated iron samples the existence of $FeSO_4.xH_2O$ could be proven when weathered to humidity and SO_2 and NO_2. On silver the influence of UV light for the formation of basic silver carbonate $AgOHAg_2CO_3$ on the surface at 1450 cm^{-1} was followed in dependence of the CO_2 content of the ambient atmosphere [3, 4].

The results obtained from the investigations of copper, iron and silver clearly showed the applicability of the constructed experimental IRRAS set-up for the investigation of metals during the early stages of degradation and is therefore a valuable tool in this field of research.

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*) This research project is supported by the Austrian Science Fund, Project No. P-17430/N11

Investigation of Multilayer Samples by μ-FTIR Spectroscopy in Reflection Mode

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The objective of this work was to evaluate the capabilities of a method for the study of binders in stratigraphic cuts originating from art works. In this connection, infra-red spectroscopy was chosen for its sensitivity to organic components and considering the size of the layers to be analyzed (20 to 50 μm thickness), the use of a microscope was essential. While preserving intact the samples (which can then be analyzed by other means), the technique is able to identify and possibly quantify a binder in the layers, and this, in presence of a strongly absorbing pigment. Ultimately, the purpose was to evaluate the detection limit of a binder into a given pigment.

With this intention, multi-layer samples of known proportions of pigment/binder mixtures were first prepared, while following a procedure similar to that of ancient artists. The samples were set into a PMMA resin, then polished and each layer was analyzed. The studied reference binders were egg white, egg yolk and linseed oil whereas the pigments were Prussian blue and azurite. In order to investigate the interference between components spectra, the mixtures were made with one, two or three of the binders within one given pigment.

Problems encountered during analysis will be presented: the size of the layers, contamination by the resin upon polishing, non-homogeneity of the samples and the subsequent lack of reproducibility, possible strong overlap of the components spectra. For instance, the reproducibility of spectra recorded on several zones within the same layer was estimated and an average 30% variation of the absorbance ratios of the principal binder bands versus those of the pigment was measured.

In spite of the observed large fluctuations and provided that the overlap is taken care of by software, the characteristic bands intensities evolve close to linearly with the binder content. Consequently, the study of the multi-layer samples of variable proportions pigment/binder indicates that the studied binders are detectable down to a proportion of approximately 1:1 (expressed in weight) into Prussian blue as well as in azurite.

Finally, the method was applied to practical cases, i.e. historical samples. Among other conclusions, it was possible to show that the blue layer of one of the sample, made up mainly of azurite, revealed the presence of a protein binder where the proportion of azurite compared to the binder was estimated to be less than 2.5.

The Characterization of Artists' Alkyd Paints on Different Supports Using Mid-IR Fibre Optic Reflectance Spectroscopy

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Mid-IR fibre optic reflectance spectroscopy (FORS), a non-invasive and flexible spectroscopic technique, has been drawing attention in the conservation field for about 10 years now, because of it's ideality for on-site and *in-situ* analysis of art objects. However, the spectra obtained by this technique are complicated and can be difficult to interpret. Due to the surface roughness, geometry and refractive indices, the reflected energy is usually very low resulting in low intensity and noisy spectra. Spectra are also complicated by the shifting of the peaks to higher wavelengths, compared to transmission IR, and distortion of the peaks, such as *reststrahlen* bands. An understanding of the reflected energy is required for the employment of the correct spectral corrections, such as the Kubelka-Munk and Kramers-Kronig for diffuse and specular reflections, respectively.

The mid-IR FORS results presented in this study are a part of a larger characterization and stability study of artists' alkyd paints; studied was it's applicabilty in the identification of alkyd binders and paint fillers and to compare the binder absorptions of the same paints on different supports. Mid-IR FORS spectra of titanium white and alizarin crimson films from three different artists' alkyd paint brands cast on four different supports were collected with a fibre optic probe, containing a bundle of chalcogenide glass fibres, placed 90° to the sample surface. The four substrates were: aluminium, ideal for reflectance spectroscopy, canvas pre-prepared with an acrylic ground layer, canvas prepared with a rabbit skin glue – gesso di Bologna ground layer and an un-prepared linen canvas. The spectra collected on the aluminium substrate appeared as IR transmission spectra, because of beam reflection off the substrate and back through the sample. The spectra collected for the alkyds painted on other substrates were more difficult to interpret, requiring the employment of the two corrections described above. In general, the carbonyl peak of the alkyd was the most intense and characteristic peak in the spectra. Other characteristic alkyd binder peaks were identified; however, in many of the samples noise distorted their maxima, especially those in the finger-print region. The filler materials could be identified in all the spectra. The intensity of alkyd binder and paint filler peaks differed between substrates. On the prepared canvases, alkyd peaks were easier to identify and the spectra were less noisy. On the raw linen canvas, it was more difficult to observe and distinguish the peaks, more so in the finger-print region. Overall, many of the peaks corresponding to the alkyd binder and paint fillers were successfully identified using mid-IR FORS; however, without a FORS spectral library, previous knowledge of the paint compositions was helpful when interpreting the spectra.

Surface Finishing and Materials: Fiber-optic Reflectance Spectroscopy (FORS) Problems in Cultural Heritage Diagnostic

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The controlled reduction of invasive sampling, both destructive and micro-destructive, in the diagnostic step of restoration is one of the main targets of a modern approach to conservation. This approach necessarily leads to developing techniques able to investigate materials and surfaces without altering the integrity of art works. The coupling of mid-IR spectroscopy and fiber-optic technology (chalcogenide and halide fibers) has allowed to introduce a powerful tool, totally non-invasive and extremely useful, for diagnostic of materials in Cultural Heritage field.

This contribution aims studies and critical evaluates the problems, such as optical distortions and the treatments of experimental data, occurring when a surface is investigated with this technique, so that a comparison with classic absorbance/transmittance reference spectra can be done. IR reflectance spectra are affected by important modifications in shapes, frequencies and intensity of absorption. These features arise with opaque surfaces where specular and diffuse reflectance phenomena are in competition and give complex interactions strictly related to the concentration of absorbing species, to refraction indexes and to surface roughness.

In this work, IR-FORS spectra coming from different materials (marble, calcarenite, methacrylic resin and polyethylene) with different superficial finishing (polished, roughed and treated with Paraloid B72 in the case of stone materials) are studied in order to evaluate the influences of the nature, opacity and superficial finishing of the samples on peak shifts and intensities.

The investigation is developed through the following steps:

- establish the optimal measurement conditions (working distance and incidence angle) for each substrate
- record and compare spectra of materials with different finishes
- apply the correction algorithms (Kubelka-Munk and/or Kramers-Kronig) when spectral distortions due to diffuse and specular reflectance component are present
- compare the spectra with those obtained with traditional ATR technique.

The objective is to highlight the reliability of diagnostic setup and verify the extendibility of the IR-FORS technique to different substrates even when analyzed *in-situ* where surface conditions (roughness, pollutants, treatments, etc.) cannot be controlled.

Non-destructive Characterization of Image Deterioration Processes in Daguerreotypes

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The daguerreotype process was the first commercially successful method for making photographs. It was announced in 1839 and practiced extensively from the 1840's to the early 1860's. The daguerreotype image consists of mercury-silver or mercury-silver-gold amalgam particles over a silver-coated copper substrate. Average particle size and density vary in highlight and shadow areas, with average diameters between 0.1 and 50 microns and smaller particles in the highlight areas. The daguerreotype image has been characterized by several authors, however the exact composition and other properties of the constituent nanosized particles are still a matter of debate [1-3].

Dramatic condition changes were noted in a group of 19th century daguerreotypes during a ten month-long exhibition featuring masterworks of the prominent Boston-based studio of Southworth & Hawes [4]. The changes took the form of a hazy, extended white surface layer and of white spots that partially obscured the images. Daguerreotypes are highly sensitive, inherently vulnerable objects. Often times, only non-invasive techniques may be applied to study these objects to preserve the integrity of the extremely delicate image structure. Raman microscopy, FTIR in the reflection mode, and SEM-EDS were used *in situ* on a group of eight plates from the studio with the aim to characterize the deterioration observed. Raman proved to be a sensitive technique to non-invasively identify the compounds on the plates due to the fact their Ag surfaces behave as SERS (surface-enhanced Raman scattering) substrates. A band at ca. 242 cm^{-1} assigned to the Ag-Cl stretching mode was observed in the areas where a white surface layer or white spots are present. In some of the areas probed, substituted aromatic compounds were also detected. The presence of Ag-Cl bonds on daguerreotype surfaces has profound implications for their exhibition and preservation due to the photosensitivity of silver chloride in the ultraviolet-visible range, which can generate metallic silver that would re-deposit on the surfaces. The possible sources of the compounds detected on the surfaces of the plates will be discussed.

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SURVENIR: A New Non-destructive Tool for Analysis of Historical Paper Based on IR Spectroscopy and Chemometry

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The diagnostic tools and methods currently used to determine paper properties of interest to the conservator are often destructive or time demanding. Possibilities for use of spectrometric techniques for direct analysis are limited due to complexity of the degraded paper material. On the other hand, the development of chemometric techniques enables us to extract chemical information from complex spectra of samples of known composition and successfully model the desired properties from spectra of unknown samples. For this purpose, we use partial least squares and examples of developed methods, include determination of ash content, lignin content, pH, mechanical properties (tensile strength and tensile strength after folding), degree of polymerisation etc., on the basis of NIR spectra.

Additionally, we have built a new dedicated NIR spectrometer for the purpose of condition assessment of paper-based objects in libraries and archives. The instrument is portable and lightweight. Considering that no sample preparation and no chemicals are needed, the instrument can easily be used outside laboratories, in library and archival environments.

Since the described approach is non-destructive, it can be used for analysis of even the most valuable paper objects. In addition, the analysis of an individual object can be performed in a matter of seconds, thus enabling us to survey whole collections effectively. For this purpose, we built software, which enables the end-user to survey whole collections or assess the condition of an individual artefact.

The Use of Near Infrared Spectroscopy as a Diagnostic Tool for Historic Silk Artifacts

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As a prestigious and expensive textile, silk is found in many historic artifacts of cultural importance. However, as silk ages it becomes increasingly fragile and thus prone to damage through handling, display or even conservation treatment (Fig. 1). These problems are exacerbated by some of the processing methods traditionally applied to such materials. Therefore, in order to minimise damage to these objects, it is vital to have a good understanding of the physical state of the silk component, and a technique that would provide this information simply and non-invasively would be of great value.

To this end, our current work has focused on the application of near infrared spectroscopy, in combination with chemometric analysis, to the assessment of tensile stresses within silk. NIR spectra were recorded from silk samples tensioned in a mechanical tester (Fig. 2), and these then were used to develop a strong predictive model. We have shown that this method can be used to accurately assess the physical condition of simple silk objects. Although the analysis is rendered more difficult by the complex construction of some artifacts, it can still be used to highlight areas at particular risk of mechanical damage.

As NIR spectroscopy may readily be used with a fiber optic probe, these analyses can be performed *in-situ*, rapidly and in a non-invasive manner. This allows assessment to be carried out in collections and displays without requiring samples to be taken, limiting the disturbance to artifacts. In addition, the technique can also highlight the presence of additives (such as weighting agents) which may be implicated in degradation and may complicate conservation procedures. Therefore, the combination of fiber optic probe NIR technique with chemometric analysis provides a valuable tool to gain a practical understanding of the nature and condition of silk artifacts, and a means of informing conservation, display and storage strategies.

Fig. 1: Degraded Silk

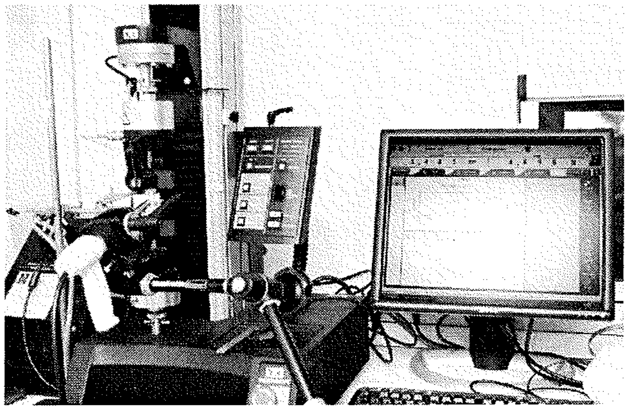

Fig. 2: Experimental Set-Up

PAS-FTIR: A Method Proposed for the Quality Control of Conservation of Organic Resin

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Fourier transform infrared spectroscopy technique is well established in the analysis and characterisation of cultural heritage samples as it is widely diffused and the results are immediately and quickly read. The Photo-Acoustic Spectroscopy (PAS-FTIR) analysis gives the same information as a traditional FTIR technique, as the authors have shown in previous works, but the PAS-FTIR doesn't modify the samples, in fact there isn't any sample treatment or preparation. This feature has been used for the characterisation of different kinds of materials like ancient paints, varnishes, woods, mortars, glass modification and other materials used in art objects.

In this work, using PAS-FTIR it was possible to prepare samples on specific supports and use the same, after different treatment such as natural and artificial ageing, being sure to analyse always the same point like the first analysis. The different ageing has been done to verify the kinds of support, using standard materials as natural and synthetic resins. The aim was to point out a standard support that can be used to follow the ageing processes of natural and synthetic materials used in cultural heritage without interference problems coming from the natural material. This method could be used like a standard method for quality control of the material used in cultural heritage field and with a rapid and cheaper analytical method like FTIR.

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Damage Assessment of Archival Parchment by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

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A recent study of archival parchment with Attenuated Total Reflection / Fourier Transform IR (ATR/FT-IR) spectroscopy has shown that it is possible to assess the level of damage to the collagen polymer in parchment. The work was part of the EC project 'Improved Damage Assessment of Parchment' (IDAP, EVK4-CT-2001-00061) [1]. Samples were obtained from the School of Conservation and the Royal Library ,Copenhagen, Denmark, the National Archives of Scotland, and the Archivio di Stato, Florence, Italy. The ranking of damage by ATR-FTIR was compared with results obtained from other techniques, Dynamic Mechanical Analysis (DMA), Thermogravimetric Analysis (TGA), ^{13}C Solid-State Nuclear Magnetic Resonance (^{13}C SS-NMR), Microthermal Analysis (μ-TA) and Atomic Force Microscopy (AFM) [1,2]. It was also compared to the currently accepted method for determining damage based on values of shrinkage temperature measured using the micro hot table method (MHT) [1]. The damage marker identified from the FTIR spectra was based on alterations in the Amide 1 peak and was quantified by the absorbance ratio at wavenumber positions 1660:1630. Previous studies showed that an increase in this ratio is indicative of changes in the collagen helical structure [3]. Samples which had been thermally denatured gave an additional marker; a shift in the position of the amide II absorbance band from 1545 to 1530 cm^{-1}. Moreover, collagen oxidation was detected in samples exposed to controlled levels of inorganic pollutants by the evolution of the 1350-1290 cm^{-1} band. The latter has been associated with methionine sulfone and confirmed by LC- and GC/MS [4]. The presence of lipids was identified by a band in the region of 1730 cm^{-1} and confirmed by ^{13}C SS-NMR [5]. In some cases, sulphate (1620 cm^{-1}) and carbonate (1450-1400 cm^{-1}) bands complicated the analytical procedure because of overlapping with the amide bands I and II respectively. For this reason most of the analyses by ATR-FTIR were performed on the grain side. Differences in damage were observed in samples from different archives, and from within the same archive for samples where there were differences in lipid and inorganic content, and whether they had been previously used as manuscripts or bookbindings. This correlated to some extent with data from other techniques [1]. The database that has been obtained in IDAP makes it possible to validate the approach using ATR-FTIR. Further work is in progress with samples in the context of the Piedmont region research project "Old Parchment, Evaluation, Restoration and Analysis" (OPERA).

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Limits on Determination Performed by Using Micro-FTIR and SEM in Artworks Materials Characterization

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Different materials applied, by the artist, with creative skill and imagination composes artworks. Under an analytic point of view, these artworks are layers or group of materials structured to produce an object.

The establishment of the material composition could permits to know the artist's painting procedure, the materials used and, finally, to design preventive and palliative conservation treatments. Otherwise, there are two important aspects to consider in the material characterization of artworks, one related to the works of art and the other related to the analytical techniques.

As far as artworks are concerned, it is important to bear in mind that materials have been applied with free judgment and on an arbitrary creation so they are macro and microscopically heterogeneous. On the other hand, and related to the analytical techniques used, it is important on the artwork's material characterization to maintain the integrity on the message because of the aesthetic, historical and economical value of the artworks.

Results obtained from artworks material characterization sometimes omits information about the analytical conditions, as well as the limitations of the analytical techniques that are totally linked to the results (detection limit). Therefore, sometimes it is wrongly assumed that artworks are only composed by the elements and molecules detected. For this reason, the objective of this study consists on establish the detection limit and limitations of the most common used and complementary techniques applied to the study of artworks (micro-Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy).

As a first step, the study has been done on these two analytical techniques (micro-FTIR and SEM) and focused on oil easel paintings, one of the most common artistic disciplines. The study has been done on easel painting mocks made with the binary mixture of three different blues (Prussian blue, phtalocyanine and ultramarine) on different proportions between 1-50%.

Results will be discussed depending on the presence or the absence of the signal studied and the intensity relation between the characteristic elements or frequency signals of each pigment.

From Beckmann to Baselitz: Towards an Improved Micro-identification of Organic Pigments in Masterworks of 20th Century Art

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Since the late 19th / early 20th century artists have experienced a gradual yet tremendous change in the composition of their painting materials: the introduction of new binding media such as acrylic resins and hundreds of new pigments. Synthetic organic pigments, such as mono and diazo, chinacridone or phthalocyanine compounds, now play a major role as colourants of excellent lightfastness in artists` paints. Their analytical determination in paintings has gained steady importance with respect to attribution and studio practice of certain artists, as well as dating and authentication.

However, it is a challenging task to identify fully all organic and inorganic colourants and fillers in a minute sample (some µg to 100 µg) that has been taken from a painting under a microscope. Synthetic organic pigments vary greatly in their chemical structure and properties such as colouring strength, solubility or thermal stability. Therefore, a new procedure for a case-by-case-modified application of complementary analytical techniques was developed that is now routinely used for painting analyses at the Bavarian State Painting Collections. This approach combines preliminary micro-chemical tests undertaken directly in the depository or gallery with microanalyses in the laboratory by thin layer chromatography (TLC), high performance liquid chromatography (HPLC), pyrolysis gas chromatography – mass spectrometry (PyGC/MS) and/or Raman microscopy, as well as scanning electron microscopy with energy dispersive analysis (SEM/EDX) for inorganic pigments.

In this paper, special emphasis is placed on the capabilities and limitations of Raman microscopy.
Raman microscopy – previously more routinely applied to inorganic pigments or natural organic lakes in art and archaeology – performed surprisingly well in our tests. It is an extremely powerful and fast method with high sensitivity, low matrix disturbance and high differentiation power for modern organic pigments. In forensic science Raman microscopy is already an established method for the identification of organic pigments in lacquer particles. In contrast to IR spectroscopy, the binding medium usually does not significantly contribute to Raman radiation very well, so it does not contribute peaks to the spectrum. However, special attention has to be drawn to sample preparation – here experiences from forensic science using aluminium foil as a sample carrier of good heat conductivity helped to reduce the thermal background. Different laser wavelengths are inevitable to overcome well-known fluorescence, but for most of the paint samples analyzed Raman microscopy gave positive results for almost all organic pigments regardless of their chemical class and even in mixtures.

Examples for the successful identification of organic pigments in masterworks of German modern art, e.g. Max Beckmann, Georg Baselitz or Gerhard Richter, will be presented.

Investigation of Prehistoric Body Pigments and Pigments from Excavations by Means of Micro-Raman Spectrometry*)

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Identification of pigments by means of micro-Raman spectrometry (MRS) has already been established and a number of artworks, from ancient cave paintings through till modern inks have been investigated. The goal of this investigation was to determine and to compare the composition of pigments from stratigraphic excavations and pigments covering human bones, found in Northpatagonia, Neuquén and Rio Negro provinces, Argentina [1]. The discovery - bones of a newborn child, dated from 6-7 thousand years BC - are coated with spots of yellow-red-brown pigments. Along with the bone spots, 20 samples of pigments collected from excavations in archaeological sites located in Northpatagonia were also analyzed.

Yellow and red ochres (which consist of iron oxide + clay + silica) were often detected as a composition of rock-painting and in archeological dig of ceremony burials. Nevertheless we did not detect iron oxide bands for bone pigments. The spectra of bone spots consist of several bands in the region 500-600 cm^{-1} and 1300-1600 cm^{-1}. Some of these bands (at 520, 550 and 1460-1490 cm^{-1}) might correspond to calcium carbonate, whewellite and weddellite. The spectra of blue and black bone pigments show wide bands (D and G) of amorphous carbon. Only a few red and red-brown pigments investigated by MRS provided spectra corresponding to hematite. Unfortunately, the Raman scattering of many pigments was compromised by huge fluorescence, which can be caused by the presence of clay in rock pigments.

MRS measurements were complemented by SEM/EDX which gives elemental compositions. The results revealed the bone pigment contained Ca, P, C, O, S, Mg, Mn, Fe, Al, Si, K, Na, which can form the following yellow-red-brown pigments: $CaC_2O_4{\cdot}2H_2O$, $KFe_3(SO_4)_2{\cdot}(OH)_6$, $MnPO_4$, $Ca_3(PO_4)_2{\cdot}CaCO_3{\cdot}$ $Ca(OH,F)_2$ and alumosilicates. The orange-red-brown pigments can be divided in two groups – with or without P and S in their composition. Each rock pigment consists of Ca, Co, C, O, S, Mg, Mn, Fe, Si, K, Na. The same elements are the main components of Fe_2O_3, $K_3[Co(NO_2)_6]{\cdot}3H_2O$, $KFe_3(SO_4)_2{\cdot}(OH)_6$, Fe_3O_4 and phosphates.

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*) This research was partially supported by the Universidad de Buenos Aires under the UBACYT I809 and by the IAEA contract ARG13864.

In-situ Raman Microscopic Identification of Organic Red Colorants

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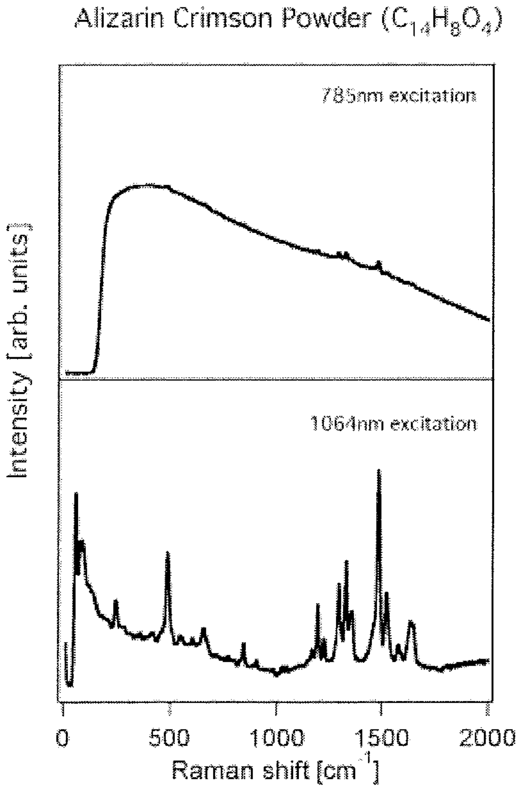
Raman spectroscopy has emerged as a widely-applicable, non-invasive spectroscopic method for the identification of artistic colorants [1]. Although it has demonstrated great utility in the identification of inorganic and modern synthetic organic pigments, Raman spectroscopy is less broadly applicable to the identification of traditional organic red colorants derived from plant or animal sources. When excited using visible radiation, these pigments fluoresce strongly, obscuring vibrational information that would allow unambiguous identification. Recent attempts to characterize red organic colorants via Raman spectroscopy have focused on surface enhancement techniques to overcome this obstacle [2-5], but these methods require the removal and processing of colorant samples. Unfortunately, removing even minute samples is impractical for many works of art, in particular for illuminated manuscripts. Therefore, there remains a need to develop an *in-situ* methodology for the identification of organic red colorants. This is the focus of the presented work.

Raman spectra of red colorants were obtained *in-situ* using a Renishaw InVia dispersive Raman microscope equipped with a 1064 nm laser source and InGaAs array detector. By employing near-IR excitation, the fluorescence of organic colorants is significantly reduced compared to visible wavelengths. Typical collection times of 100 s or less are used, and all spectra are collected in a single acquisition. Spectra presented include alizarin crimson, carmine naccarat, lac dye, cochineal lake, brazilwood, dragon's blood, sandalwood, logwood, safflower and madder lakes. Analyses of dry pigments versus those applied in binding media demonstrate the capabilities of Raman microscopy to characterize organic red pigments using this excitation wavelength.



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Characterization of Some Orange and Yellow Organic and Fluorescent Pigments by Raman Spectroscopy

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Raman spectroscopy is now one of the most widely vibrational analytical techniques for the investigation of paint samples [1] and notably for the organic pigments. Both the spatial resolution in the order of 1 µm and the versatility of the laser wavelength, in the case of dispersive Raman, make Raman a method of first choice in conservation science laboratories.

While pyrolysis gas chromatography mass spectrometry (Py-GC-MS) has been well developed for modern materials analysis and especially for synthetic organic pigments [2, 3], it is a micro-destructive technique. The prospect of using Raman spectroscopy as a non-destructive alternative is promising. It would provide enough information for the characterization of the colouring matters either on raw samples, on cross-sections or in-situ. One of the advantages of Raman spectroscopy over Fourier transform infrared spectroscopy is that it allows the detection of the characteristic vibrations of certain chemical groups that are weak in the IR, such as some functional groups present in azo pigments, the biggest family of organic pigments found in artist paints [4].

The large variety of organic pigments make it important to classify them according to their chemical structure [5]. The purposes of this work are: first, to complement the existing database on both yellow and orange pigments [6], mainly found in artist paints, and second, to introduce the analysis of some fluorescent pigments. The latter have an obvious aesthetic interest, as they are widely developed in the industry for paints, plastics, and textiles) [7] and their ageing behaviour is of interest from the conservation point of view.

A short list of organic pigments has been drawn according to their use in painting (artwork and industrial paints), complemented by some inorganic pigments, also found in artworks and some pigments which are mainly found in the automotive paints.

Analyses were performed with dispersive micro-Raman spectroscopy. The prospect of interference by fluorescence led to the preferential use of a diode laser at 785 nm.

The results have shown that Raman spectroscopy allows the characterization of the various chemical groups of organic pigments. In the case of fluorescent pigments, the differentiation is more difficult since the formulations of such pigments/dyes are quite complex. Further research on this topic must be undertaken both for the knowledge of the photostability of these materials and for the improvement of the characterization via vibrational analytical techniques [8].

Some of the conclusions drawn from this study were used for the identification of two fluorescent paint samples which have been taken from a late XXth century Ben artwork.

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Darkening of Impressionist Grounds: Studying Ground Layers Using FTIR Microscopy

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The ground plays an essential aesthetic role in many Impressionist paintings. It is not only a preparation layer for the paint layers, but may also be key part of the composition. Impressionists were concerned with the colour and the absorbency of their grounds. While the absorbency might influence the surface matteness, the colour of the ground would influence the balance of the composition. Discolouration of the ground may occur on ageing due to past conservation treatments such as relining or varnishing or accumulation of dirt and this has had an effect on the colour balance and perception of the picture.

As part of a larger project studying grounds from paintings by Paul Cézanne, Camille Pissarro and Lucien Pissarro from the Courtauld Institute of Art, analyses using FTIR microscopy using the diamond compression cell of samples was carried out. The FTIR spectra recorded of different regions of a ground sample on the diamond cell in some cases showed very diverse spectra indicating some degree of heterogeneity of the sample. A ground could show several fractions with different combinations of components such as: protein – lead white – chalk – gypsum; protein – lead white; drying oil – lead white; protein – chalk – starch. These results would suggest multi layered ground systems, the use of emulsion type binders, remnants of relining treatments, the mixing with sizing layers or a combination. Cross sections of the ground did not always confirm these results.

To further investigate the origin of these components and the feasibility of the FTIR microscopy approach for adequate detection of the grounds, historically accurate reconstructions of model grounds on sized canvasses, prepared by Leslie Carlyle and colleagues as part of the HART project were analysed using FTIR microscopy. Differential Thermal Mass Spectrometry (DTMS), Gas Chromatography (GCMS), and Scanning Electron Microscopy combined with Energy-dispersive X-ray Microanalysis (SEM-EDX) confirmed and completed the FTIR results.

Towards the Establishment of a Raman Database of Early European Porcelain Productions

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Raman studies on porcelain artefacts were first published in 2001 thanks to the collaboration between the LADIR and the National Ceramics Museum and Manufacture of Sèvres. More studied followed, published by several groups, on the possibility to distinguish porcelains issued from different French and English manufactures. A few essays have also been made of the use of a portable spectrometer for the *in-situ* characterization of extremely precious artefacts (16th century dishes from the Medicis' production and porcelains and stonewares dating to the early years of the Meissen manufacture). These studies have well demonstrated how the Raman spectra of a porcelain fragment or whole object can be obtained in a completely non-invasive way to determine body and glaze composition, making it possible to determine the type of porcelain, its manufacturing technology and often its provenance. Being such a technologically advanced material, porcelain has had since its beginning very specific recipes, whose secrets were also carefully guarded and therefore represent a real "factory mark" from the point of view of manufacturing technology. There have in fact been cases in which a comparison between an (unmarked) porcelain artefact and a marked piece have been made, providing analytical support for an attribution to the same factory. Many early European productions of porcelain have so far been characterized by Raman spectroscopy, and data have been published in a number of articles. There seems now to be a great need for the systematization of such a large corpus of spectroscopic data, in order to identify "reference" Raman signatures for each manufacture and possibly to standardize the experimental procedure for Raman analysis on ancient porcelains. Up to now a similar need has been fulfilled mainly for the Raman spectra of single minerals, pigments and binders, which have been the object not only of many publications, but also of some systematization and implementation over the internet. A database for the identification of porcelain manufactures will require a slightly different approach, because only the combination of Raman signatures for both paste and glaze will be able to characterize a single production. Moreover, more than one spectrum may be needed in order to fully characterize each paste, this material being not quite homogeneous. Thus not a single spectrum, but rather a series of spectra will constitute each "entry" of the database. This work presents the first steps which have been made towards the establishment of the database and of an experimental protocol for the Raman analysis of porcelain.

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Spectroscopy Studies of Medieval Serbian Ceramics from Ras and Novo Brdo

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In order to determine provenance of pottery fragments, archaeologists classify samples according to their physical characteristics, decoration and aesthetic style. This is important for identification of historical and geographical context in which objects can be placed. However, more objective multidisciplinary approach, based on undoubted results, is necessary to complete this study.

Although early medieval Serbian ceramic is well described by the archaeologists and historians, knowledge of the Balkan ceramic production is still limited. Archaeometric study of ceramics provenance, technology of preparation and used pigments as well as influence of neighboring countries and specific characteristics of different workshops has never been performed so far.

In this work we present results of systematic investigation of pottery shards from two archaeological sites: Ras and Novo Brdo. The term Ras, has an outstanding importance for the history of medieval Serbia and Old Ras was the first capital of the medieval Serbian state of Raska. Founded between the 9th and 10th centuries, and deserted in the 13th, Ras sat in the middle of the growing empire, on the crossroads between the Adriatic see and the state of Zeta, with Bosnia in the west and Byzantine in the south.

On the other hand Novo Brdo was a large and rich mining and trading center of Serbia in the 14th and 15th centuries. A large number of ceramic samples found during the systematic excavation of these two sites allow good choice of samples for both destructive and nondestructive analysis. The primary aim of our work was to attest the local production of ceramics but also to analyze obtained results in the framework of economic and cultural exchanges in the Byzantine period between Balkan's countries.

Twenty archaeological pottery samples from Ras and twenty seven archaeological pottery samples from Novo Brdo were investigated. In this study we focused on non-destructive analysis of glaze and pigments by a multianalytical approach combining X-ray fluorescence (XRF), FTIR and micro-Raman spectroscopy. Data of FTIR spectroscopy have been used for chemometric, PCA and cluster analysis.

Obtained results confirm that ceramic from Ras is imported, and those from Novo Brdo has domestic origin.

Carbon Dioxide Encapsulated into the Sodalite β-Cage of Natural Ultramarine Blue

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In 1999 a study of the GCI reports about a small and sharp absorption band at 2340 cm^{-1} in samples of ultramarine blue from several Italian paintings of the XV and XVI centuries [1]. Derrick and co-worker noted that the absorption band at 2340 cm^{-1} occurred only in natural ultramarine from Afghanistan and tentatively assigned it to the sulfur species S_6^+. Despite the interest of this finding, the small band at 2340 cm^{-1} has not been further considered by other authors dealing with vibrational properties of lapis lazuli [2,3]. In this paper we present a spectroscopic investigation of natural ultramarine pigments aimed to furthering our understanding on the origin of this absorption band at 2340 cm^{-1}. Non-invasive reflectance mid-FTIR measurements have been carried out on more than 15 ultramarine minerals belonging to the historical mineral collection of the Museum of Natural History, University of Florence, revealing that the absorption at 2340 cm^{-1} is present in all the samples from Afghanistan and generally with minor intensity also in sample from Siberia. The band 2340 shows a satellite peak at 2275 cm^{-1} with a relative intensity of about 2%. The value of d shift (65 cm^{-1}) and the relative intensity of the two bands allow them to be correlated to the presence of CO_2 that is responsible of the absorption at 2340 as $^{12}CO_2$ and at 2275 as $^{13}CO_2$ [4]. The value and shape of v_3 asym. of CO_2 stretching suggest that the molecule is weakly adsorbed on the silicate framework [4]. The thermal behavior of powdered natural ultramarine from Afghanistan, has been studied by FTIR, XRD, UV-vis and Raman from 300°C to 850 °C. Data show that CO_2 and the S_3^- chromophore behave in the same way during the heating experiment, being released only at $T > 650°C$ when the sodalite b-cage starts to be distorted as effect of the temperature.

All these data demonstrate that CO_2, as the S_3^- chromophore, is encapsulated within the sodalite β-cage of natural ultramarine blue, originating the sharp signal at 2340 cm^{-1} visible by non-invasive mid-FTIR on blue areas of several Renaissance paintings [5].

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Late Neolithic Painted Ceramics from Szombathely-oladi Plató (Western Hungary): An FT-Raman Spectroscopic and FTIR Microscopic Study

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The excavations in 2006-2007 in Szombathely-Oladi plató, Western Hungary revealed a late Neolithic, early Lengyel Culture settlement excavated by Gábor Ilon (Savaria Museum, Szombathely, County Vas). The early period of the Lengyel culture is characterized by polychrome painted pottery (red, yellow and white), as we can see in the already excavated settlements of Sé-Malomi dűlő and Gór-Kápolnadomb [1]. Large amounts of painted pottery and fragments of pigments were found on the site: most of them are pits belonging to the settlement, but some are special features, probably associated with cult activities.

The identification of pigments on archaeological materials is fundamental for understanding an object's history, to verify its authentication and to solve certain restoration and conservation problems. Our investigation strategy was based on the techniques of infrared and Raman spectroscopy to study the mineral (and possibly organic) content of the samples, backed up by other techniques, like scanning electron microscopy (SEM). Raman spectroscopy (FT-Raman and μ-Raman), together with FTIR microscopy are extremely effective in the study of archaeological materials due to their non-destructive, non-invasive properties, allowing *in situ* measurements of samples like decorated pottery fragments.

We also investigated raw materials of pigments, found at the excavation site, which were supposed to be similar to those applied on the ceramics. Beside yellow and red ochre raw pigments, a piece of purified hematite was identified. On ceramic fragments, however, the red decoration's coloring component was found to be mercury sulfide (HgS), mixed (diluted) with kaolinite. IR, Raman and EDX elemental analyses support this observation. The use of cinnabar (HgS) for decoration of ceramics is quite unusual in this archaeological period. (To our knowledge, cinnabar was used first in the antiquity of Hungary, in the Roman times.) *In-situ* μ-FTIR mapping (in reflection mode) indicate a homogeneous presence of kaolinite, suggesting a deliberate mixing or diluting of the cinnabar.

μ-FTIR imaging of cross-sections of orange-red paint layer (3 μm microtomed slides, embedded in epoxy resin) are dominated by clay sediments bands. The orange paint layer does not contain any kaolinite (no bands of outer and inner hydroxyl groups – 3699, 3669, 3655 and 3623 cm^{-1}, respectively – are present.
The white painted parts consist of pure calcite.

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Raman Spectroscopy of Museum Polymers: Challenges in Identification and Sorting of Mixtures

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Identification of polymers and polymer composites in the museum context is an ongoing need that can be approached using Raman spectroscopy. The technology is advancing in two directions with the development of highly resolved laboratory instruments and miniaturized versions that have been made portable at the cost of some resolution. These advances have expanded the range of applications for polymer analysis, from rough sorting of plastics during surveys to more careful studies of degradation processes. Challenges of the technique include obtaining usable spectra, and interpreting spectral data for composite samples. There are merits and trade-offs in choice of excitation wavelength, approach to data analysis, and portability when characterizing polymers and deconstructing polymer composites.

Polymers exist in museums in many forms. Organic artifacts in ethnography and natural history collections and many 19th-21st century artifacts include natural and synthetic polymers. Conservation treatments, exhibits, and collections storage areas use plastic vitrines, containers, and supports, as well as paints, coatings, and adhesives. "Plastics" are often composites of a polymer plus additives that modify its working properties, appearance, and performance. Understanding the composition of polymers and polymer composites has ramifications for the ways in which artifacts are classified historically, stored, repaired, and, in the case of some synthetic plastic artifacts, whether they are acquired by a museum at all. Yet whereas the need to characterize polymers is clear, the process of doing so is not. Polymer testing in industry employs diverse analytical techniques including GC-MS and DSC, both of which are destructive. Sampling limitations for museum objects make these techniques less appealing. FTIR spectroscopy often requires sampling or direct contact with an artifact. On the other hand, Raman spectroscopy is non-contact, potentially non-invasive, and potentially non-destructive. Molecular information can be obtained for a wide range of organic polymers and the organic and inorganic additives that one would expect to find therein.

Obtaining Raman spectra and interpreting data can be challenging. Fluorescence and the susceptibility of some materials to burn, melt, or otherwise be altered by the excitation laser can make it difficult to generate usable spectra. These problems can be mitigated to some degree by selection of an appropriate excitation wavelength. However, choice of wavelength is related to and must be balanced against the risk to an artifact, and detection limits. Once usable spectra are in hand, the challenge becomes spectral interpretation. Polymer composites can confound computerized database searches and lead to incorrect identifications. Understanding the effect of component interaction on spectra and methods for deconstructing spectra of mixtures, both computer-aided and manual, can improve interpretations greatly.

The ongoing trend in photonics toward miniaturization is resulting in semi-portable instruments that can be moved on a cart or handheld. It seems that portable Raman spectroscopy will open up great possibilities for molecular characterization of materials that cannot be sampled, are located away from the laboratory, or are to be surveyed in large numbers. MCI's experiences with Ahura Scientific's FirstDefender handheld Raman spectrometer will be compared to those with the Nicolet Almega XR Dispersive Raman Spectometer and NXR FT-Raman Spectrometer, on both reference materials and objects in Smithsonian collections.

Investigation on Palette and Techniques of Some High Middle-age Codes: Materials in the VI-IX Centuries by Raman Microscopy

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Before 1000 AD in some important centres of the old Roman Empire manuscripts were elaborated and differentiated works as regards to style, materials, and type. Not only religious texts, but also scientific and literature texts were executed. One of the most important was the so-called "Neapolitan Dioskurides" (ex Vindobonensis graecus 1) a code of Italian production of the end from the V or the VI century, probably from Ravenna. The text treated the "Materia Medica" and is a Herbarium.

In order to understand the changes in illumination materials occurring from the VI to the IX cent. an old series of manuscripts from the Abbey of Nonantola in Northern Italy, dating from startdate to enddate, and now preserved in the National Library in Rome, were analysed by using a portable Raman microscope, since no sampling was allowed.

Some observations are made about the conservation state of the code in general, the execution technique and the materials used in writing, illuminations and letters.

In the oldest manuscript (intended to be the Neapolitan Dioskurides) always metallogallic ink was used, as in all the more recent codices from Nonantola (VI – IX cent.). In comparison, the analysis of a series of atramentaria from Pompeii and Herculaneum (I cent.) showed only the presence of carbon ink, though its formation was a chemical reaction already known at Pliny's times.

Vergant, an intimate mixture of orpiment and indigo, is observed on the oldest manuscript, whereas it is absent in the more recent ones, but orpiment and indigo are present separately. Different rules are used for rendering special hues necessary for the illuminations. Minium and vermillion and their mixtures in different proportions are present in the Nonantola manuscripts. A violet was rendered by red and blue indigo, probably a fluorescent lake in the Greek codex, white is white lead, and brown and black are obtained by iron oxides and not by carbon.

Assessing Indoor Lead Corrosion Using Raman Spectroscopy During Electrochemical Reduction

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Even though kept in cultural institutions, artefacts can undergo to accelerated deterioration due to high concentration of pollutants in enclosed spaces. Potentially harmful conditions have been evaluated by electrochemical reduction of corrosion products formed on metallic coupons which have been exposed in selected places. In the case of silver coupons, this technique allowed chemical identification of the tarnish layer (sulphides and chlorides), as well as determination of the amount in which they were present [1]. Extension of this approach to lead raises some difficulty as identification of the reduction peaks is more complex. In this work we combined electrochemical reduction of corrosion products with *in-situ* Raman spectroscopy [2] to unambiguously correlate the reduction peaks with the compounds present on the surface of coupons previously exposed in different French institutions. Raman analysis, prior to electrochemical reduction in a sodium sesquicarbonate solution, revealed that the corrosion layer contains lead oxides, hydroxycarbonates and carbonates. Potential dependent *in-situ* Raman analysis allows unambiguous identification of reduction peaks associates with disappearance of massicot, and then progressive dissolution of hydrocerussite. A passive layer of pure cerussite remains at more negative potential.

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POSTER PRESENTATIONS

Far and Mid-IR Micro-spectroscopy with Synchrotron Radiation in the Study of Ancient Paintings

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The usefulness of FTIR technique with synchrotron radiation in the characterization of materials in ancient paintings has already been demonstrated in a number of studies. SR allows focusing on areas of only a few microns, as a consequence of the high brightness and high collimation of the beam resulting in spectra with very good signal-noise ratio.

SR-FTIR micro-spectroscopy allows us to isolate and identify materials from very small samples, with a complex and heterogeneous mixture of substances that were applied in submillimetric layers. However the commercially available FTIR microscopes are fitted with mid-IR detectors. There are a lot of pigments such as oxides, sulphides, etc. that doesn't show bands over 700cm^{-1}, but they do show them in the far infrared region. Others as a consequence of their overlapping with bands make their identification difficult. When the far-infrared technique is used interferences from binding media are decreased. The use of SR-FTIR microspectroscopy with a bolometer detector allows far-infrared to be reached and thus expand the possibilities of this technique in the study of ancient paintings. The high intensity and high brilliance of synchrotron radiation in the far infrared is necessary for the measurements.

In this study several examples of identification of pigments in the XV and XVI century paintings are shown.

SR-FTIR microspectroscopy spectra of minium pigment from XVI century paintings.

Spectroscopic Studies of Lead Coupons Exposed in the Proximity of Historical Organ Pipes

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The overall aim of the SENSORGAN project 'Sensor system for detection of harmful environments for pipe organs' (contract. no 022695) is to develop dosimeters based on piezoelectric quartz crystals for characterization of microclimates within organ pipes [1]. To assist in this process lead coupons were used since the previous COLLAPSE project had demonstrated that they could provide information on corrosivity levels in the vicinity of pipes in organs [2, 3]. Corrosion products were analysed by ion chromatography and X-ray diffraction [3]. In the SENSORGAN project non-invasive spectroscopic techniques were also used. Polished metal (pure lead and Pb-2%Sn alloy) were placed in the palletbox of the organ in St. Botolph without Aldgate, London. A parallel study was conducted in the laboratory where the coupons were exposed to humid acidic environments generated in closed glass vessels. Characterization of the site exposed lead coupons was performed by ATR/FTIR (attenuated total reflection infrared spectroscopy), Raman spectroscopy, ion chromatography, and X-ray diffraction. The pure lead coupons exposed for 4 months showed formate, carbonate, and acetate bands. The location of the formate band was previously determined from exposure of lead coupons to formic acid vapour. Results after 16 months' exposure at St.Botolph showed a stronger formate band together with carbonate and acetate bands. Analysis by ion chromatography showed that acetates, formates, and trace amounts of chlorides and sulphates had accumulated on the pure lead sample surface. Raman spectroscopy also showed the presence of carbonates, acetates and formates. Moreover, the group of bands in Raman in the 1300-1600 cm^{-1} region was the same as those found in samples exposed to a mixture of acetic and formic acids and which were not present in coupons exposed only to acetic or formic acids. X-ray diffraction indicated that no crystalline lead formate was detected in contrast to the COLLAPSE project where the main corrosion product was lead formate hydroxide. This may indicate that the environment in St.Botolph's consists of high levels of acetic acid and only low levels of formic acid. ATR-FT/IR data of lead coupons exposed in the laboratory vessels containing only oak or only pine blocks for 2 months showed in both relatively strong carboxylate (1640-1390 cm^{-1}) and acetate (650-610 cm^{-1}) bands, and relatively weak carbonate bands (680 cm^{-1}). After six months' exposure in the oak containing vessel there is a strong absorbance band indicating formation of lead formates (760 cm^{-1}). Exposure of lead for the same period next to pine blocks showed that lead formates formed on shorter exposures, even after 2 months, compared to oak-exposed coupons. This work is still in progress, also within the framework of the PROPAINT project (Improved protection of paintings during exhibition, storage and transit, contract no.044254) project where lead coupons are exposed in microclimate frames containing paintings.

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The Use of FTIR in the Study of Romanian Amber (ROMANIT)

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The existence of a Romanian variety of amber is only known within a narrow group of specialists interested in mineralogy. However, Muzeul Chihlimbarului (The Amber Museum) in Colti, Buzau county, Romania was established in 1973 and exhibits raw and processed amber collected from the area (in Colti amber is present in soil, in unveiled surface and depth layers).

Recently, a consortium of specialists with multidisciplinary background was developed in order to study the Romanian amber (romanit, rümanit) and establish any existing particularieties which may distinguish it among other varieties. The results obtained will be used in the study of amber jeweleries from Romanian museum collections.

The poster presents the infrared spectra (FTIR/Transmission) obtained on romanit, compared with those collected for succinite (Baltic amber) and the amber spectra on the IRUG website. Romanit presents in the infrared spectra all the bands mentioned in literature as typical for amber [1,2,3]. As expected, they miss the „Baltic shoulder" (1250-1160 cm^{-1}) while a maximum at 1241 cm^{-1} is always present. The exoclyclic bands at 3076, 1644, 887 cm^{-1} are not present in romanit. However, these bands are mentined in [1] as being typical for amber, exist in all the „succinite" analysed samples but not in all samples described as „amber" on the IRUG website.

The studies prove once the usefulness of FTIR in the characterisation of natural resins and confirms the IRUG database as an important tool for all those interested in an analytical approach of materials in objects of archaeological, historic and artistic value.

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Design and Application of a New Cell for *In-situ* IRRAS Measurements of the Metal Atmosphere Interface

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Carbon dioxide is one of the major pollutants in the atmosphere and plays an important role in the atmospheric corrosion and degradation of silver. As UV-light and the formation of ozone may also have an impact on this degradation, a new experimental set-up consisting of a cell for studying reactions occurring in the metal/ atmosphere interface by applying in-situ InfraRed Reflection Absorption Spectroscopy (IRRAS) is presented. This cell consists of a gas mixing unit for the generation of moist air with or without the corrosive gas, a window for UV-light radiation and an optical system coupled with a FTIR spectrometer. This new set-up was tested by using a specimen of polycrystalline silver, where the formation and the growth rate of Ag_2CO_3 and Ag(OH) on the polished surface could be observed in synthetic air containing up to 90 %RH and different levels of CO_2 gas [1].

In order to proof the experimental results obtained a computer simulation program was used for calculating the peak position of silver carbonate. The simulations are based on a 2x2 transfer matrix formalism where the sample is modeled as a stack of parallel layers with perfectly smooth interface boundaries. The transfer matrix formalism calculates the electric field amplitudes at the phase boundaries between the layers. The relationship between the reflected and the incident amplitude yields the reflection coefficient r of the layer stack that might be converted to the power reflectance R. Since only longitudinal modes are IR-active, the simulations were carried out for p-polarized light [2].

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Identification of Synthetic Organic Pigments in Paintings of the Early 20th Century by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence Analysis (XRF) and Optical Microscopy

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Synthetic organic pigments and their identification in works of art have been subjects of increasing interest in the fields of art history, science in conservation and conservation-restoration during the last decades as nowadays up to 70% of the colour ranges of almost every contemporary artists' paint brand contain those modern organic colorants. Such materials were already used for early 20th century paintings, but there are only few evidences on works of art published so far. As part of a PhD project paint material investigations were carried out on two paintings (dated 1923 and 1925) of the period of Viennese Kineticism by My/Marianne Ullmann (1904-1994) by courtesy of Wien Museum, Vienna [1]. Based on the combination of energy dispersive x-ray fluorescence analysis (XRF) and Fourier transform infrared spectroscopy (FTIR) as well as microscopy, red and yellow synthetic organic pigments of the early 20th century could be detected and identified in both paintings. The poster presentation provides a perspective on the usage of synthetic organic pigments in artists´ paints in the 1920ies accordingly to the results of the investigation and addresses the issues of the yellow mono azo pigments (Hansagelb, e.g. PY1, PY3) and the red ß-naphthol pigments (e.g. Toluidinred, PR3) relating to "vermilionettes".

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The Case of the Sweating Nude Analysis of Surface Exudates on a Painting by Kees Van Dongen

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In support of its conservation treatment, the Worcester Art Museum conducted technical analysis of *Reclining Nude*, c. 1925, oil on canvas, by the Dutch-born Fauve artist Kees Van Dongen (1877-1968). The painting, which was a 2004 gift to the Museum, exemplifies the artist's work as a member of the 1920s Parisian beau monde.

Visual examination of *Reclining Nude* suggested Van Dongen employed unorthodox materials and techniques to achieve variations of color depth and surface sheen. Although largely unvarnished, the artist chose passages of the painting for selective varnishing to achieve subtle adjustments to saturation and gloss. Examinations of five other works by Van Dongen in the collection of the Stedelijk Museum, Amsterdam indicate the artist used this approach on several occassions. FTIR analyses of varnish samples taken from the Stedelijk's *Anna de Brancovan, Countess de Noailles* and the Worcester painting produced comparable results indicating the use of a natural resin varnish, most likely mastic.

Microscopic examinations of the paint surface of *Reclining Nude* also revealed an eruption of resin-like beads from within unvarnished areas of the paint. This exudate is limited to areas thought to be artist-applied retouches done years later. Technical analyses, including visible and UV light microscopy in combination with attenuated total reflectance (ATR) FTIR spectroscopy, revealed that the resin-like beads are heterogeneous in composition. They include polysaccharide material that may be a combination of gum arabic and honey, two common components in watercolor formulations. The presence of gum arabic was supported by findings using the immunological method of analysis known as ELISA (enzyme linked immunosorbent assay). These findings, along with empirical evidence gathered from other conservators familiar with Van Dongen's work, suggest that the artist was prone to reworking passages of his earlier paintings. In the case of *Reclining Nude*, it was hypothesized that, in order to achieve a harmonious surface sheen with surrounding aged and unvarnished paint, Van Dongen experimented with additives to his oil paint when retouching older passages.

The identification of water-soluble components erupting from the painting's surface may indicate that the artist attempted to modify his oil paint with gouache or watercolor, which ultimately resulted in phase separation and subsequent beading up of water-soluble components from within the oil paint. Although the exact cause of the formation of the exudates remains open for debate, the identification of water-soluble materials within an otherwise non water-soluble paint surface proved critical in formulating an appropriate cleaning approach and now serves as a cautionary note to other conservators faced with the challenge of cleaning the variable surfaces of paintings by Van Dongen.

Classification of Synthetic Organic Pigments by Multivariate Data Analysis of FTIR Spectra

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Synthetic organic pigments are nowadays known as the largest group of colorants used in contemporary artists´ paints. Thus, investigation of those pigments in works of art has become increasingly important. For the identification of the pure pigments FTIR-spectroscopy has been established as a powerful analytical technique, as FTIR-spectra of those modern organic materials are characterized by very sharp and characteristic multitude of absorptions in the fingerprint region. Due to this fact, usually the identification of synthetic organic pigments by FTIR-spectroscopy is processed by comparing the spectrum of an unknown sample with the spectra present in a database, which has to be as complete as possible. Spectra of unknown samples are difficult to identify if they don't match one of the libraries spectra. In that case even class assignment can be performed only by expert analysis.

In the paper presented, methods of multivariate statistical analysis are applied to data sets of FTIR spectra of synthetic organic pigments in order to predict the class of such unknown samples. Partial Least Square Discriminant Analysis (PLS-DA) was performed to compute regression models for prediction of class membership [1]. Pigment classes were defined according to the usual classification system of organic colorants based on their chemical constitution [2]. Classification results of unknown paint samples will be presented and compared with results obtained by expert analysis.

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The Investigation of 17-19th Century Colored Prints: Distinguishing Coloring Campaigns

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In preparation for a 2008 exhibition entitled "The Marvel of Peru", a group of nine colored prints containing Peruvian themes was examined. The prints, dating from the early 17th to early 19th centuries, consist of maps as well as illustrations depicting the peoples of Peru, or Europeans dressed in Peruvian fashion. Although the dating of the prints themselves was secure, whether or not the coloration was contemporary with the print was the subject of this investigation.

The prints were examined using two complementary non-invasive and non-destructive analytical techniques: X-ray fluorescence (XRF) spectroscopy (Bruker Tracer III handheld spectrometer with Rh anode and Ti/Al filtering) and Raman microscopy (Renishaw InVia spectrometer equipped with 514, 633, 785 and 1064 nm excitation sources).

Only four of the prints were found to contain pigments that would have been available at the time of printing. Pigments available since antiquity such as vermilion, red lead, azurite and indigo were found in one of the prints. The other three prints, dating from 1693 to 1815, were found to contain gamboge, a pigment introduced into Europe in the mid-17th century, and therefore would have been available at the time the prints were produced. However, the availability of pigments alone is insufficient evidence to conclude that the coloration is original to the print.

The five remaining prints all were found to contain nineteenth and twentieth century pigments which must have been added subsequent to the printing, including: cerulean blue, phthalo blue (PB15), chrome yellow, Hansa yellow (PY3), acid green 1, acid yellow 23 and Perylene vermilion. Although it is possible that only certain areas of the prints were colored later, in most cases, the modern pigments were found together with traditional pigments throughout the print, suggesting the colors were applied in a single campaign, most likely sometime in the 20th century.

This group of prints is part of the Gutierrez collection, an assemblage of ~1400 lithographs, prints and clippings gathered by Pr. Gutierrez and his wife before entering the collection of the Getty Research Institute in 1984. Because many of these pieces were not considered works of art, it is likely that they were colored by dealers in an attempt to increase interest (or value). The use of Raman microscopy to detect modern pigments on prints and its role in determining the sequence of color application will be discussed. Further investigations are planned to try and understand the recent coloring history of the prints, in order to ascertain any relationships between the modern coloration campaigns.

Infrared Spectroscopic Analysis of Natural Dyestuffs by Using Polyacrylonitrile Nanofiber Assembly as a Receptor

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The ultra-thin layer made of nanofiber assemblies has large surface area to volume ratio and unique porous structure. We tried to use this new material as a receptor of organic dyestuffs for the highly sensitive infrared spectroscopic analysis. Polyacrylonitrile (PAN) nanofiber assemblies (Fig.1) was fabricated by electrospinning procedure. This receptor was highly transparent in the whole waveumber range. As a preliminary test of this material, the dilute solution of crystal violet (CV) was used. A small amount of solution was added drowse on the surface of nanofiber assemblies. After gentle drying of whole system, infrared measurement was performed. By measuring the peak intensity of CV at 1363 cm^{-1}, the linear relationship between absorbance and concentration of CV was confirmed (Fig.2). We are now applying this procedure for natural dyestuffs such as berberine. These nanofiber assemblies are also found to be useful as a receptor for the visible absorption or fluorescence analysis of natural dyestuffs.

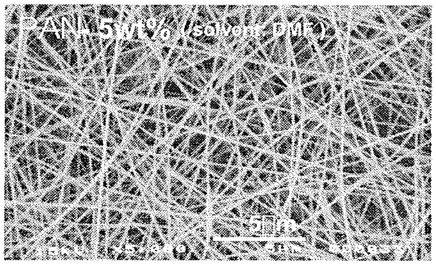

Fig.1: SEM micrograph of PAN.

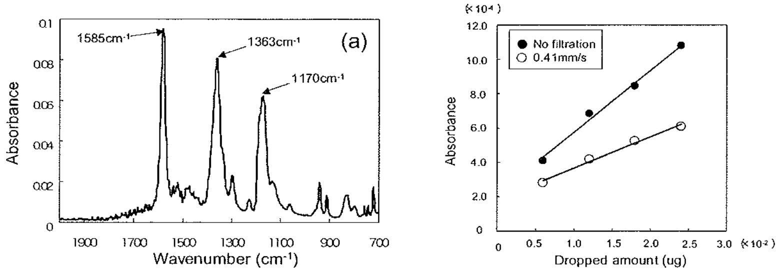

Fig.2: IR spectra of (a) CV and relationship between absorbance and dropped amount. Measurement point is 1363 cm^{-1} of CV.

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The *LAUDARIO OF SANT'AGNESE*: A Preliminary Investigation of 14th Century Florentine Manuscript Illumination

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Pacino di Bonaguida, a painter and manuscript illuminator active in Florence in the early fourteenth century, was a prolific artist thought to have produced the majority of commissioned illuminations in Florence at that time. He was also an accomplished panel painter, producing altarpieces and other devotional works. An upcoming exhibition organized by the J. Paul Getty Museum will explore the work of Pacino, and will include a technical component examining the artist's methods and materials.

This paper will discuss the analysis of three leaves in the Getty's collection from Pacino's most important manuscript commission, the *Laudario of Sant'Agnese*. The pigments in two *Laudario* leaves attributed to Pacino (*The Ascension* and *The Martyrdom of St. Lawrence*) and one leaf attributed to one of his collaborators (*The Pentecost*) have been studied using the non-invasive techniques of X-ray fluorescence (XRF) and Raman spectroscopy. Results from this work may provide insight into Pacino's materials, techniques, and workshop practices. This preliminary investigation constitutes the first stage of a larger study of Pacino's works, which will explore the materials and techniques used in the creation of illuminated manuscripts in relation to those in panel paintings.

The Use of FTIR and XRF in a Parchment Musical Score Investigation

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The poster presents the results obtained in a case study developed within PERGAMO (Multidisciplinary approach aimed to establish the historical and cultural parchment documents degradation mechanisms), a project funded by the Romanian Ministry of Research, Education and Youth and coordonated by ICPI, in which INCCR is partner.

A 17th century parchment musical score belonging to a private collection was investigated by two non-invasive methods: FTIR/ATR (Attenuated Total Reflectance Infrared Spectroscopy) and XRF (X-Ray Fluorescence). Scientific investigation included the evaluation of parchment degradation level (results were corelated with shrinkage temperature) and the identification of added materials (pigments and ink).

The studies prove once more the usefulness of non-invasive investigation methods and development of common research projects between research units and institutions dedicated to cultural heritage.

Investigation by Vibrational Spectroscopies of Felt-tip Pen Inks for Art Design

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Felt tipped markers or pens are used frequently as fine arts materials. They are based largely on dyes dissolved in a solvent and have a poor or at least suspect reputation for colorfastness. Destructive techniques have been employed in forensic sciences for ink identification or dating in questioned documents. Some attention has been paid on staining problems on paper or surfaces due to the usage of felt-tipped pens in archiving or museum practice, but little work has been done on the conservation problem due to the discoloration of felt-tipped pen inks on paper-drawings of artistic and historical interest as the collections of famous graphic designers conserved at CSAC-Center, University of Parma.

Micro-FTIR, micro-Raman and spectral reflectance measurements are important tools to investigate these materials. Seven different colors of several different felt tip pen brands have been analyzed during an accelerated ageing process through exposition to UV radiation.

SERS (Surface Enhanced Raman Scattering) measurements using colloidal Ag solutions give significant results in spite of strong fluorescence especially on red, orange and yellow colored inks. All colors show FTIR and SERS spectral variations during ageing, with different characteristics and rates according to the brand, whereas the colorimetric data give significant variations only for the absorbance of light blue and green colors.

The attribution of a felt tip pen to a specific brand may be done through multivariate chemometric analysis. The Discriminant Analysis on the FTIR spectroscopic data allows the attribution of all colored felt tip pens. Further discrimination is possible also on the basis of the UV irradiation time.

Identification of Excavated Historic Silks by FTIR Microscopy

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Though the silk fragments have been rather popular objects found at various archaeological sites in Japan, the scientific analysis of natural fibers is not so easy task by using various instruments. We have been continuing the research on degraded state of historic silks by using FTIR microscopy. As a result of numerous analyses, we are able to summarize the general features of silk degradation during long-term preservation in archaeological sites.

The most distinguished change in IR spectrum of silk fibers is the decrease in peak intensity of amide I and amide II. At the same time, the heavily degraded silk fibers show the superposing of both peaks and hence they finally form one broad peak. The decrease in peak intensity of amide III is also observed. Besides, the two strong peaks at 1400 cm^{-1} and 1090 cm^{-1} are generally observed in the case of heavily degraded silk. Both peaks seem due to the degraded molecules of lower molecular weight.

To analyze the peak deformation in degraded silk fibers in secondary molecular structure level, we used the secondary differentiation of original spectrum curve. The lowest position of each component corresponds to the position of the component peak.

According to the progress in degradation of silk fibers, the transition of component peak-position was generally observed.

We will show the results of analysis for degraded silk fibers found from the stone tumulus of 3rd century AD and 6th century AD in Japan.

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Micro-Raman Pigment Analysis of Wall Paintings from Churches in the Skopje Fortress, Republic of Macedonia

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In the year 2007, an extensive excavation has been carried out on several sectors in the Skopje Fortress (Skopsko Kale), Republic of Macedonia. The site is known to be inhabited since Neolithic times. In several layers, 1500 different archaeological objects, mostly dating from the Middle Ages, were excavated. Remains of sacral and profane buildings were also unearthed, among them at least one church. According to archaeological finds, it originated from the middle or the second half of the 14th century, with evidences of reconstructions dateable to the 16th century, and more recent ones, from the 19th century. Fragments of wall fresco painting were uncovered in its direct vicinity or at some distance, as well as at a second site close by, suggesting the probable existence of another church dated between the end of 11th and mid 13th century.

Samples of wall painting fragments from both sacral sites from Skopje Fortress were collected and the pigments were analyzed by a micro-Raman spectrometer, LabRAM 300 (Jobin-Yvon Horiba), with 633 nm He-Ne laser line. Most of the pigments are natural, mineral based, with a limited palette, while a larger variety was found in the over layer decorations dated from the 16th and 19th century. The identification of pigments was made by comparing their Raman spectra to the reference database of pigments [1]. Red pigments were identified as vermilion, red earth and litharge, blue pigments as lapis lazuli, black as carbon black and white as chalk. Among the two different yellow colors of the wall paintings, only the second layer yellow pigment was identified as Indian yellow. This could support the tentative dating of the decoration of the second layer of wall paintings: it could have been made not earlier than beginning of the 16th century when Indian yellow was introduced as a pigment [1]. Further evidence for this suggestion is the recorded Raman spectrum of the green pigment, identified as smalt, also being in use from the beginning of 16th century [1].

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An Evaluation of Firing Temperature of Byzantine Pottery from Serbia

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Byzantine ceramics, imported from various imperial centers for the manufacture of pottery were discovered in archaeological excavations of fortified towns, fortresses and monasteries on the territory of Serbia. The lack of analysis on Byzantine material still limits strongly the attribution of local production to their respective source.

The aim of this contribution is to improve the knowledge of production technology of pottery by the evaluation of firing temperatures. The samples investigated were ceramic shards (mainly shards of bowls, plates and pitchers), found during excavations (from 1990. to 1995) in early medieval sites in central Serbia. The firing temperatures were estimated on the basis of mineralogical composition of the pottery but also by thermal simulations of its production [1]. The mineralogical composition of 30 selected powdered samples was determined by FTIR analysis and X-ray diffraction (XRD). It was found that all the investigated samples contain quartz, muscovite, and orthoclase and that the majority contain feldspars (Na, K) and calcite. Hematite was detected in several samples. In addition, the absence of high-temperature Ca-silicates is a clear indication of relatively low firing temperature. Thus, identified mineral composition indicates temperature of firing in the range of 700-800 °C. One group of samples contains anorthite and gehlenite, indicating a higher firing temperature of about 900 °C.

In order to check the determined firing temperatures, thermal simulations of a clay raw material from locations close to the excavation sites of analyzed pottery, was heated in electrical kiln to temperatures between 600 -1000 °C for 6 hours in air. FTIR spectra of clay raw materials before and after heating were analyzed after deconvolution processing of characteristic Si-O bands. The location and the width of Si-O stretching band at 1030 cm^{-1} and of Si-O deformation band at 471 cm^{-1} show changes dependent on the heating temperatures [1]. The stretching band was broadened and progressively shifted from 1030 cm^{-1} in the unheated raw material to higher frequencies up to about 1080 cm^{-1} with increasing temperature of heating. The changes in IR spectra are the consequence of the progressive destruction of the clay minerals in the fired clay material, formation of an amorphous phase and recrystallization of new minerals at elevated temperatures. By comparing the location of stretching Si-O band in heated clay raw material and in analyzed samples the firing temperature of pottery was evaluated. The obtained results were analyzed statistically and the existence of two groups of pottery fired at different temperatures was confirmed. These data can be applied to the determination of the provenance of analyzed pottery.

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In-situ Raman Spectroscopic Characterization of Polymers Used in Past Conservation Treatments

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The evaluation of conservation materials can be aided by an assessment of the current condition of previously restored artifacts. An important aspect of this is the long-term behavior of polymers used as adhesives, coatings and gap-fillers. The natural ageing of polymers from past treatments is a valuable guide to the suitability of different products for future use.

This Poster will focus on one conservation application; the repair of broken and fragmentary glass objects with adhesives and gap-fillers. In the past, many different polymers have been used, with mixed long-term success due to variations in the photo- and thermal-degradation of the different products used. Polymer degradation is usually accompanied by yellowing which disfigures the glass artifacts. Repaired vessel glass and stained glass frequently require re-restoration because of polymer yellowing but in some cases objects are still in good condition several decades after restoration.

In order to predict the stability of polymers to degradation, the examination of the current state of past conservation treatments is therefore very instructive. However, records documenting the polymers used are often incomplete or totally absent and, up to now, the non-destructive identification of polymers on objects *in-situ* has not been possible.

This Poster will report the successful characterization of polymers from past glass conservation treatments by means of Raman spectroscopy with a fiber-optic probe. It has been demonstrated for the first time that this methodology is well suited to the examination of polymers used as adhesives and gap-fillers for conservation of glass artifacts. Polymer identification is straightforward for gap-fillers and for adhesives we have also successfully distinguished different polymer classes, even in a glass/adhesive/glass bond less than 100 microns in width. In addition, Raman spectroscopy has the potential to probe chemical changes as a result of polymer photo-degradation. We have utilized the fiber-optic probe of the Perkin Elmer Raman Station 400F to undertake depth profiling, thereby revealing that photo-degradation of epoxy resins used in conservation is most pronounced at the polymer surface.

This Poster will illustrate these developments in relation to Flemish stained glass panels as part of the CONSTGLASS Project, designed to investigate conservation treatments for Europe's stained glass heritage, supported by the European Commission.

Integrated Analytical Techniques for the Characterization of Painting Materials in South American Polychromy

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South American polychrome sculptures produced during the so-called Colonial period (XVII-XVIII cent.) are part of what has been identified as the process of evangelization conducted under the Spanish domain. These images installed in churches, convents or small chapels, show the diverse iconographic discourses that were necessary to develop that process: virgins, saints, Christs etc. manufactured in workshops by Spanish, indigenous and creoles people, who used diverse materials – wood, stone etc. – to carve and paint them. The identification of pigments, dyes, resins, clays and gold by chemical analysis is relevant, as results can be compared with manuscripts and prints (inventories, list of merchandise, manuals, treatises) where the materials are described or mentioned by their uses and meanings in that region [1-3].

In this study, we have worked on a group of 6 sculptures and a ciborium that were produced in the Jesuit Missions of Paraguay during the XVIII century. We used several analytical techniques to identify the pigments and plaster layers. First, cross-sections of the samples were examined by optical microscopy and SEM-EDX. Then, application of transmitted FTIR spectroscopy to selected samples confirmed the presence of gypsum ($Ca_2SO_4.2H_2O$) as the plaster in all sculptures except in one of them where chalk ($CaCO_3$) was identified. This is an indication of the application of technologies transmitted by German and Austrian masters in this region. Green earth, identified by a band around 1014 cm^{-1} and its characteristic elemental composition obtained by SEM-EDX was the green pigment most used in the manufacture of these sculptures. Copper resinate was identified in two sculptures by a combination of FTIR, SEM-EDX and gas chromatography together with its characteristic color as observed in the cross-sections of both samples. Other pigments identified in the sculptures were Prussian blue, vermilion, hematite, and lead white.

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Application of Mixture Analysis to Museum Artifacts Using a Handheld Raman Spectrometer

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Ahura Scientific, in collaboration with the Smithsonian Institution Museum Conservation Institute, has used a portable, handheld, ruggedized Raman spectrometer with embedded analysis software to identify neat polymers and polymer mixtures in museum artifacts. The system uses a 785 nm wavelength laser and spectral fingerprinting to identify neat chemicals by matching them with an onboard library of over 6000 materials. The strength of this library is compounded by onboard mixture analysis capabilities which can combine up to five items through a formal optimization (i.e. the algorithm is not subtraction based). This allows the instrument to account for up to 9.65E16 possible mixtures of materials. Tactical use of the instrument, details of the analysis and decision making process employed by the software will bè discussed in the context of successful analysis of polymers and polymer mixtures in artifacts.

Imaging FTIR Spectroscopic Investigations in the Wood: Paint Interface of Aged Polychrome Art Objects

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Until now most infrared spectroscopic investigations of painted objects focussed on the study of pigments or binding media. Only few works involved the study of the wooden carrier art works are painted on. In this work the heavily damaged medieval altar from the St. Bartholomaeus Church in Recknitz (Northern Germany) was studied. The focus has been laid on the IR spectroscopic investigation of its wood and ground layer.

Cross sections of 10 µm thickness were made to study the wood / ground zone in transmission mode. The appropriate embedding medium for the support of the samples during microtoming was investigated. FTIR imaging with high spatial resolution was carried out using a FPA detector consisting of 64 x 64 single detectors. In combination with an IR microscope an area of 267 x 267 µm could be measured at once.

FTIR imaging was found to be a useful technique to investigate the wood – ground interface. The achieved spectra were evaluated using univariate und multivariate data analysis. By univariate analysis the whole spectra of a small area or the intensity of a representative wavenumber on the whole area were displayed. The multivariate methods cluster analysis and principal component analysis supplemented the evaluation, showing clearly the separation of the main components of this part of the studied altar (wood, animal glue, chalk) as well as localized changes in the IR spectra of the wooden carrier.

Reactivity of Rust Layers on Iron Artifacts Investigated by Raman Spectroscopy and Cavity Ultramicroelectrode

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Oxidative corrosion of buried iron objects needs a reductive counterpart to take place. In classical atmospheric process, reduction of oxygen is the necessary source of electrons but it is thought that in deep geological burial situation, without access of surface oxygen, corrosion will be stopped by lack of reductive mechanism unless previously formed iron oxides can provide the cathodic reaction.

This mechanism has been evidenced by [1] in atmospheric corrosion of iron. In order to verify this hypothesis we have tested the reactivity of iron oxyhydroxides goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) which are known to be typical compounds of rust layer on iron and compare their behaviour with a true patina from an artifact of Bois l'Abbé, Gallo-Roman site in France.

As these materials are insulating by nature and in small disposable amounts when using true archaeological samples we have combined Raman spectroscopy as an analytical tool and a cavity microelectrode [2], which allows working on some μm^3 of powdered samples, to expose the iron compounds to controlled reductive conditions.

It has been proved that reduction of lepidocrocite takes place during hydrogen evolution and gives magnetite (Fe_3O_4) as reduction product. Reduction of goethite is much more difficult and leads to dissolution leaving a few amount of magnetite inside the cavity.

Reduction of the true rust layer, mixture of goethite and magnetite, is easier but is also taking place with hydrogen evolution which prevents the possibility of the combination iron oxidation/iron oxide reduction at least with these stable compounds.

Nevertheless the use of Raman spectroscopy coupled with this microelectrode is of great interest to study patinas behaviour especially with limited quantity of available material.

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The Use of Calcium Fluoride Windows as a Substrate for an Aging Study of Waterborne Acrylic Emulsion Paints by Transmission FTIR Spectroscopy

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FTIR is theoretically an excellent tool for following the chemical changes to acrylic emulsion painting materials induced by accelerated ageing. However, an appropriate sampling method is required to ensure that the subtle changes can be properly observed. For example, if FTIR measurements are made in transmission mode using a diamond cell, this method does not ensure a reproducible film thickness in the compression of samples, and this leads to variations in the spectra that mask the actual chemical changes occurring. Reflective modes of IR measurement, in particular ATR, have received much attention recently in the study of these materials and can be used to follow surface changes, but these tend to be dominated by the exudation of surfactant, and the bulk changes to the acrylic polymer are not seen.

One of the best ways to follow these chemical changes would be to cast acrylic paints onto IR transparent windows that remain the sample substrate throughout the aging study. This way, the sample film thickness remains constant and a more quantitative comparison of chemical changes with age can be achieved. One of the more common substrates used for this type of study in other materials is potassium bromide windows. However, for water-borne acrylic latexes, its high water sensitivity prevents its use, and so a different window material is needed.

We report here the use of calcium fluoride windows (rounds: 13 x 2 mm) in a photooxidative ageing study of acrylic emulsion paints and unpigmented media. Calcium fluoride renders an infrared transparent (70,000 - 1110 cm^{-1}) window material which is water insoluble, hard and cleanable. The photooxidative stability of several acrylic emulsion paints and their unpigmented binding media applied to calcium fluoride windows as thin films was investigated under artificial solar irradiation for several months. The primary signal of advancing oxidation during the irradiation was a progressive broadening of the carbonyl-stretching bands near 1700 cm^{-1}, as well as changes in the O-H stretching region.

Characterization of the Ceramic Artifacts from Republic of Macedonia: Infrared and Raman Analysis of Late Roman/Early Byzantine Finds

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In this work, a total of 30 ceramic samples from two archeological sites in the Skopje region (Markovi Kuli and Skupi), dating from 6th century AD, were analyzed using infrared and Raman spectroscopy. Basic molecular and mineralogical composition as well as the firing temperature of the ceramics were assessed.

The artifacts were classified in three groups: (a) tubes – found built-in the inside walls of the big cistern in Markovi Kuli, (b) ceramic vessels – coarse ceramics for daily use, with simple decorations, from Markovi Kuli, and Skupi, and (c) tableware and water jars – luxury funerary pottery, with good brightness, excavated in the Western Necropolis – Skupi.

The infrared spectra in the 4000-400 cm^{-1} region are very similar for the ceramics studied. As expected, one of the most prominent bands in the spectra of all analyzed objects is the stretching Si–O mode from silicates. The position of this band is influenced by the firing temperature of the ceramics and consequently appears at different frequencies in the spectra [1]. It was concluded that most of the analyzed ceramic samples have been fired at temperature between 700 and 800 °C. The only exception is the water-jar samples, which were found to have firing temperatures between 800 and 900 °C.

A considerable quantity of carbonates was found in the structure of the tubes, confirmed by the appearance of the band in the infrared spectra due to the antisymetric stretching CO_3 vibration. The spectra of the samples also showed that potters used calcareous raw material for preparing the tubes and the tableware. On the other hand, non-calcareous or slightly calcareous material was used for manufacturing the tableware and water jars from the Western Necropolis-Skupi.

The Raman spectra, recorded in the 1800-100 cm^{-1} region, indicated the minerals present in the ceramics body consisting mainly from alumino silicates, muscovite, quartz, carbonates and hematite [2].

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FTIR Microscopy and μ-XRF Analysis of Watercolor Buttons Used by the Austrian Painter Rudolf von Alt

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Rudolf von Alt (1812 – 1905) was a prominent Austrian landscape and architecture painter and genial describer of Viennese ambiances. Always at work and looking for new solutions he changed along his long professional period his way of painting. At the beginning he applied the technique of water coloring with high transparency and crystalline clearness; his late works are characterized by broad and blotched color applications. The group around Gustav Klimt prized his late technique and it is not surprising that Rudolf von Alt was nominated in old age as Honorary President of the Viennese Secessionists, which was the edge of the avant-garde.

In the collection of the Albertina in Vienna there are some 260 paintings of Rudolf von Alt and there is also a collection of his paint materials given to his relatives. In a co-operation some of the objects as well as all materials (paint buttons) could be analyzed by non-destructive X-ray Fluorescence analysis (XRF) using a self-built instrument with a micro-beam of about 120 μm in diameter [1]. In some cases, a small amount of painting materials could be gained from the water color buttons (in total 34 samples) and analyzed by FTIR microscopy using the diamond cell. The combination of FTIR and μ-XRF enabled the identification of both, inorganic constituents (pigments, substrates) and organic components (pigments, dyes, binding media): Arabic gum was found in all buttons as binder and protecting colloid, gypsum (calcium sulfate) in five buttons and blanc fix (barium sulfate) in two cases as substrate for dyes. For all water color buttons, except two, the pigments could be identified being zinc white, blanc fix, ultramarine, Prussian blue, indigo, hookers green, chrome yellow, Indian yellow, Kassel earth, ochre, cinnabar, madder lake, carmine and cadmium red. These results are in accordance with outcomes obtained only by μ-XRF at the objects of Rudolf von Alt in the Albertina [2]. These data provide a basis for further investigations on watercolor paintings of Rudolf von Alt in the Printing Collection of the Academy of Fine Arts in Vienna and other artists of the late 19th century.

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The Vibrational and Electronic Spectroscopic Characterization of Early Synthetic Dyes

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Triarylmethane dyes form a very important class of commercial colorants, representing one of the largest dye groups [1] with hundreds of hues spanning greens, blues and violets. They are among the first of the synthetic dyes to have been developed and today find applications in a wide and varied range of fields [2]. As such, they have newly attracted the attention of many scientists [3]. Interestingly the characteristic low photostability [5] of these dyes has been examined relative to the mechanisms of dye degradation as a means to assure appropriate conservation intervention. Nevertheless there remains a lack of published conventional analytical investigations regarding their characterization, thus qualifying the proposed study as one of great value, especially when considering the widespread use of synthetic dyes in modern and contemporary art [4].

In the present study a combination of non- destructive spectroscopic techniques, namely micro-Raman, reflectance mid-infrared and UV-vis fluorescence, have been employed to characterize 10 common triarylmethane dyes. These, including Diamond Greens, Victoria Blues and Crystal Violet, all exhibit stable quinoid structures which belong to a wide unpublished reference spectral database of more than 60 powdered synthetic dyes from 12 classes with relevance to the cultural and historical fields. Preliminary results indicate clearly definable fluorescence peaks and vibrational spectral features that derive from their structures as well as their interaction with the physical environment or substrate, of particular relevance for an eventual identification on veritable objects.

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Case Study: Frescoes and Stucco from Roman Wall Paintings in the Villa Adriana (Tivoli)

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The Villa Adriana is a Roman building dating to 117-138 A.C. The Emperor Adriano had personally followed the works of the Villa which is characterised by numerous buildings of different use: pavilions, gardens and nymphaeums [1].

Samples of both frescoes and *stucco* have been analyzed by Fourier Transform Infrared Spectroscopy using a FTIR Nicolet 380 with the accessory ATR (Smart Orbit) of Thermo Electron, in order to identify the chemical composition of the pigment or the plaster. They come from Palazzo Imperiale (emperor building), Nymphaeum, Hospitalia, Terrazza di Tempe (terrace), Accademia (academy), Palestra (gymnasium) and Pecile (big colonnade which bounded a garden with a big pool in the centre); in total 137 samples of pigments from wall paintings and *stucco.* Samples have been analysed as powder obtained by the first pigmented layer, in addition to scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analyses. All pigments are made of inorganic compounds, both earth pigments and alumino silicate minerals have been recognized, according also to the reference old texts (*De Architectura- Vitruvio* and *Naturalis Historia – Pliny the Elder*) [2].

Interesting information have been obtained in particular for the valuable pigments such as Egyptian blue [3], well isolated from the *intonachino* and recognized by the characteristic absorption peaks of the silicates at 1160, 1050 and 1008 cm^{-1}. The use of valuable pigments seems to reflect the hierarchical differentiation of the buildings, which allows to discriminate the rooms reserved to the emperor and to his followers.

Concerning pigmented *stucco*, they have been used in ceilings and vaults, in order to follow the buildings shape. They probably chose this technique because *stucco* is evocative in giving space illusion and substitutive in forging different valuable and refined materials. They are composed by a layer of gypsum, well separable from the last pigmented layer, on the contrary of wall painting where the pigments is adsorbed in the *intonachino* layer. The stained layers of *stucco* have been identified as ochre for red pigments [4] and Egyptian blue for light-blue pigments.

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Application of Raman Microscopy to the Analysis of China Pieces Recovered from the English Warship HMS *Swift* Sunk Near the Coast of Patagonia in 1770*

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On 13th March 1770 a British Royal Navy warship sank off the remote and barren coast of Patagonia, in the southwestern Atlantic. Discovered 200 years later, it has become a priceless source of archeological, historical and cultural treasures [1]. Of the more intriguing items found in the wreck are "oriental-style ceramics", which include white-blue porcelain. They comprise mainly tea bowls and plates, bearing common features of Chinese (oriental) decoration, made exclusively with a blue, underglaze paint. A piece of this white-blue china (ca. 7 x 6 cm^2) was investigated by means of Raman microscopy. The spectra showed the presence of kaolin; however the signal was strongly disturbed by fluorescence. Locally, fine grains of quartz were detectable. The glazing layer was not susceptible to a laser excitation, providing only strong fluorescent radiation. Investigation of the blue pigment was quite challenging, because there appeared to be two different blue paints applied during its manufacturing. One of them was "cobalt blue", recognized by its strong Raman shift at 509 cm^{-1}. This pigment was located on the surface of a mineral layer and under the glazing, which caused a bluish shade of the whole glassy covering. The other one, bright blue, was dispersed throughout the interface between the glazing and the core. It occurred as tiny blue spots of ca 10 µm diameter. Its Raman spectrum is very complex, with numerous shifts, of which the stronger are: 590, 680, 748, 1341, 1389, 1452, 1525 cm^{-1}. The ambiguous shape of the Raman spectrum probably reflects that this pigment contains more than one component. The Raman microscopy was also complemented by X-ray based techniques – XRF and SEM/EDX. The bulk elemental composition, determined by XRF, showed the main components as SiO_2 and Al_2O_3, minor components: K_2O, CaO, MnO, Fe_2O_3, Co_3O_4 and trace elements: Ti, Cl, Ni, Rb, Sr, Ba, Ce, Zn, Cu, Zr. SEM/EDX results revealed a distribution of major elements down to 500 µm below the china surface.

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**This research was partially supported by the Universidad de Buenos Aires under the UBACYT I809 and by the IAEA contract ARG13864.*

The Optimization of NIR Methodology to Differentiate and Monitor the Condition of Polyamide Material

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Successful characterization of artifacts enables informed collections management, facilitating key decision making concerning conservation treatments, storage, handling strategies and display. The aim of our work is to develop rapid, non-invasive methods, which can report on the identity and condition of textile materials *in-situ*, particularly for the benefit of keepers of contemporary collections.

We have already shown that near infrared reflectance spectroscopy (NIR) using a fiber optic probe is well suited to the on-site interrogation of organic artifacts [1]. As the major polymer classes have unique NIR signatures, spectral matching to a reference database has generally proved sufficient for the categorisation of modern textiles in the museum.

However, a more robust multivariate approach (principal component analysis) may be required for the differentiation of polymer sub-classes. We have demonstrated this successfully for the variety of polyamides, which are found as original fabrics and accessories, for example, zips and as conservation netting. The experimental work has utilized a Perkin Elmer Spectrum One Fourier-transform near infrared spectrometer, with an Axiom fibre optic probe. Spectral processing has been carried out using Thermo Galactic Grams AI version 7 and employing Camo Unscrambler for the multivariate modeling.

The deterioration of polyamides, especially after daylight UV exposure, is of some concern. Routine condition monitoring should highlight accessioned artifacts that would be at risk from interventive conservation treatments. The further potential of NIR for characterizing polyamide deterioration will also be described; multivariate analysis is again essential.

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An Unusual White Pigment in La Verna Sanctuary Frescoes: An Analysis with Micro-Raman, FTIR, XRD, and UV-Vis-NIR FORS

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The fresco cycle in the *Corridoio delle Stimmate* at the La Verna Sanctuary (Arezzo) was painted by Baccio Maria Bacci (Florence, 1888 – 1974) in two phases: in the 1930s and the 1950s-60s. In the second phase he depicted some new scenes and restored others from the first phase, which were heavily damaged during World War II.

A recent discovery of a box containing his pictorial materials in the attic of La Verna Sanctuary gave an opportunity to study the original materials used by the artist in the 1950s-60s. Among several powdered pigments only one white powder was found. It was initially analyzed by means of UV-Vis-NIR reflectance spectroscopy and X-ray diffraction.

The obtained data showed that its main constituents were zinc white (ZnO) and lithopone ($ZnS{\cdot}BaSO_4$). Surprisingly, when this powdered pigment was analyzed by using FTIR and micro-Raman spectroscopic techniques the result did not include zinc white. Instead, titanium white anatase (TiO_2) was one of the main components in the composition of the white pigment. This was especially evident in the micro-Raman spectra while FTIR spectra revealed anomalous absorption bands that could not be linked to any white pigments.

The present communication discusses the micro-Raman, FTIR, XRD, and UV-Vis-NIR FORS results more in detail providing an explanation for the contradictory data.

Far Infrared Spectroscopy Methods in the Field of Cultural Heritage

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Far Infrared (FIR) Spectroscopy is a complementary method of identification to Mid Infrared (MIR) spectroscopy especially concerning inorganic compounds such as painting materials and corrosion products. Furthermore FIR spectroscopy is an alternative to Raman spectroscopic technique. The FIR spectral region is below 400 cm^{-1} and is generally known as the finger print region for inorganic components.

In these experiments we have investigated the FIR region (600-50 cm^{-1}) of many standard pigments and corrosion products used for the characterisation and conservation of cultural heritage objects. Two different approaches are evaluated and discussed.

The first approach is the Polyethylene (PE) method [1]. Here 0.5-1.5 mg of sample is embedded in 70 mg of PE and the spectrum is recorded in the normal path way (transmission) of the FTIR spectrometer inside the sample chamber. PE is quite an inactive material in the FIR region and gives rise to only two small bands in the FIR spectrum.

The second approach requires the insertion of the ATR-diamond Smart Orbit™ accessory, which allows recording of FIR ATR spectra directly on sample. The ATR-diamond Smart Orbit™ can collect the spectra directly on a small fragment, i.e. wood sample with pigment, as well as on powder.

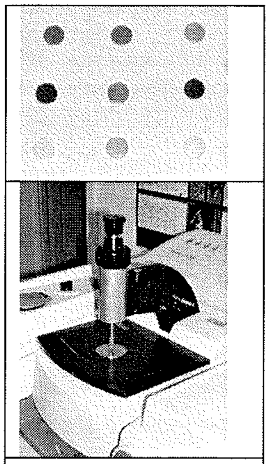

Fig. 1: Standard pigments embedded in PE pellets (Top image).
The ATR-diamond Smart Orbit(TM) accessory inserted in the spectrometer (Bottom image).

Approximately 100 standard compounds have been recorded in order to build a FIR-database library using the two different approaches described above. Some examples are presented and the results are discussed. An application on a real case study is also presented.

Instrument adjustments:

The spectrometer is from the beginning born as a normal FTIR spectrometer with a KBr beamsplitter in the MIR region. For recording spectra in the FIR region the beamsplitter is replaced with a solid-substrate™ beamsplitter and a DTGS Polyethylene detector is added to the spectrometer. Dry air from a Gas Purging Generator was used to remove any interfering spectral bands generated from ambient moisture.

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The Purple Background of Picasso's *The Red Armchair* (1931): Identification of Cobalt Violet Pigments by the "Triangulation" of Raman Spectra with FTIR, Raman, and XRD Reference Data

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Pablo Picasso's painting *The Red Armchair* (1931) depicts a blond female figure, Marie-Thérèse Walter, wearing a fur stole and sitting in a red- and maroon-striped armchair. The background contains four purple areas in addition to a yellow and mustard section. The softened impasto appearance of certain passages, including areas of the purple background, led to the ongoing investigation of the hypothesis that Picasso mixed artists' tube oil colors with a fluid, white non-artists' paint. This poster deals with the issue of identifying the colorants in the purple areas of the painting in order to evaluate whether they are characteristic of tube paints or non-artists' paints.

Microscopic samples were prepared as cross-sections and examined using reflected light microscopy and scanning electron microscopy - energy dispersive x-ray spectroscopy (SEM-EDX). The light purple paint layer consists of pinkish- and bluish-violet angular particles in a zinc oxide white matrix. SEM-EDX analysis of the violet particles suggests that both cobalt arsenate and cobalt phosphate compounds are present. As both occur in anhydrous and hydrated forms, crystallographic or vibrational spectroscopic methods are needed to definitively identify the colorants. Raman micro-spectroscopy is useful for such cases as it supplements visual and elemental data with molecular-level information for particles at the surface of the cross-section. Infrared and Raman spectra obtained for cobalt violet pigments in the collection of The Art Institute of Chicago were compared with published infrared (Corbeil et al. 2002, Frost et al. 2004) and Raman (Martens et al. 2003) spectra in order to establish a reference Raman dataset. Pinkish-violet particles are anhydrous cobalt arsenate while spectra of bluish-violet particles suggest the presence of both anhydrous cobalt phosphate and cobalt phosphate octahydrate. While the latter two were detected in an early 20th century tube of Lefranc *Violet de cobalt*, neither cobalt arsenates nor phosphates have been detected in French non-artists' paints (Gautier et al. 2008).

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Evaluation of Infrared and Raman Microscopy for Component Identification in Complex Pigment Mixtures

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151 cross-sections, from 23 oil paintings by Henrique Pousão — a Portuguese 19th century painter — belonging to the collection of Museu Nacional Soares dos Reis, Porto, Portugal were analysed by infrared and Raman microscopy. There are very few sources of information about this painter. A study such as this was essential in order to provide key information relating to a better knowledge of the painter, to future conservation interventions and even to the identification of possible Pousão paintings. About forty compounds present as pigments, extenders, impurities, trace components and products of reactions between pigments were identified, allowing some insight into Pousão's technique. Nevertheless, when analysing complex samples such as Pousão's, which are composed of several layers of various depths each consisting of a complex pigment mixture, difficulties arise that can compromise the results. Some of these difficulties are addressed as they were overcome by making use of the complementarity of the two vibrational techniques and/or because further techniques (X-ray diffraction and SEM/EDX) could be used to confirm the suppositions.

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FTIR Spectroscopy and SEM-EDX Analysis for Material Characterisation of Three Iconostasis Veils from Putna Monastery, Romania

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The Collection of Medieval Textiles from Putna Monastery has a well-known importance for Post-Byzantine Art History. Among these beautiful pieces of treasure are three handmade iconostasis veils dating from the end of the XV century.

The purpose of the present study was to establish the type and nature of materials used for threads and fabrics as well as to characterise their physical condition. The morphological structures were analysed using Scanning electron microscopy (SEM). The Energy Dispersive X-Ray (EDX) Spectroscopy provided the elemental composition for metal threads. Fourier transform infrared (FTIR) Spectroscopy was applied for degraded textile materials. Bands within the FTIR spectrum of silk are related with accompanying changes in the naturally aged textile materials and correlated with visual aspects.

The combined use of various analytical techniques on these materials made it possible to assess both the state of preservation and to understand the behaviour of these materials during the natural aging processes.

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FTIR and Micro-Raman Surface Characterization of Three Polychrome-decorated Western Han Bronze *Ming-Ch'i* (Spirit Vessels): a *Hu*, a *Bianhu*, and a *Fanghu*

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The subject of this investigation is the polychrome decoration and corrosion products found on three Western Han Dynasty (206 BC-AD24) painted bronze *ming-ch'i* vessels: a *hu*, a *bianhu*, and a *fanghu*. The *hu* is decorated with immortals riding mythological beast-driven chariots in a landscape, the *bianhu* is decorated with a seated immortal playing the *qin* and an immortal riding a lion, and the *fanghu* is decorated with dragons on two sides and birds (possibly phoenixes) on two sides. The vessels each have two loop handles; the *hu* and the *fanghu* handles are decorated with *t'ao-t'ieh* masks while the *bianhu* has plain loops. Overall the bronzes possess a polychrome surface decoration that includes white, red, pale green, black, orange, and brown pigments. The vessel surfaces also display evidence of white, red, blue, and green corrosion as well as brown accretions. The *bianhu* and the *fanghu* vessels display pseudomorphs of a finely woven textile in their corrosion layers. The vessel shapes and painted decorations are consistent with Western Han tomb furnishings. Aspects of the vessels' iconography are unusual, including the immortal playing the *qin* and the representation of landscapes including mountains and trees. Related images have been identified in wall paintings from an Eastern Han tomb and in painted bronze *ming-ch'i* vessels at the Museum of Fine Arts, Boston. The vessels' exceptional state of preservation prompted an examination of their polychromy and corrosion products. The composition of the pigments, corrosion products, and paint binders were determined using x-ray fluorescence (XRF), dispersive micro-Raman spectroscopy (Raman), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy energy-dispersive x-ray microanalysis (SEM-EDS), and gas chromatography-mass spectrometry (GC-MS).

Cinnabar was identified as the red pigment on the bronzes, along with red lead and cerussite minor phases. The latter may represent corrosion of the ternary Cu-Pb-Sn bronze substrate. Compounds identified in the whites included calcium and lead carbonates as well as calcium hydroxylapatite (bone white). The light green pigment was a mixture of bone white and malachite (with lead carbonate on the *hu).* The brown was found to be a mixture of cinnabar, bone white, lamp black, cerussite, and a clay mineral. The orange on the *hu* was comprised of red lead, cinnabar, lead carbonate, and bone white. Corrosion products identified on the bronzes included malachite, azurite, atacamite, paratacamite, lead carbonates, and cuprite. The corrosion stratigraphy and composition are consistent with a Han Dynasty attribution, as are the pigments with the exception of bone white, which has been previously observed in the Qin palette but not on a Han bronze. The origin of phosphate-based pigments in East Asian art is unclear, and further research into these materials is needed.

Raman and FTIR-spectroscopic Characterization of Sodium Lead Hydroxide Carbonate $NaPb_2(OH)(CO_3)_2$ - a Rarely Used White Pigment

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This study focuses on the investigation of sodium lead hydroxide carbonate [$NaPb_2(OH)(CO_3)_2$], a white pigment used instead of lead white. Raman and FTIR analysis was carried out to identify the title compound. The identification was confirmed by X-ray powder diffraction and scanning electron microscopy with EDX. These data were applied for an examination of a polychrome on an iron lattice of a tabernacle in the church St. Martin in Oberwesel (Rheinland) in Germany.

We assume that the formation of sodium lead hydroxide carbonate is related to the production of lead white. Since the 19th century in addition to lead white, other lead containing pigments occur in paints, like Pattison´s white, a lead oxide sulfate with a composition of $PbO*2PbSO_4$ to $PbO*3PbSO_4$ [1]. For this study reference materials were synthesized following historic recipes given in the literature [2].
The Raman- and FTIR-spectroscopic analysis was performed using the reference materials and sample from the art object compared to lead white. In the spectra characteristic differences were found in the signals assigned to the OH-group and the carbonate ions [3].

The Raman- and FTIR-spectroscopic examination of the compound obtained from both the art object and the reference materials provides analytical information for the identification of this white pigment. In addition to the analytical data, the properties of this sodium lead hydroxide carbonate pigment were described using this example of the St. Martin polychrome art work and the resulting application form and compared to lead white.

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Acknowledgement

The authors express their thanks to Professor Elisabeth Jägers, Doris Oltrogge and Andreas Rauschel, University of Applied Sciences, Cologne, Germany, for the fruitful discussions and Professor Ulrich Panne, Federal Institute for Materials Research and Testing (BAM), Berlin, Germany, and Reinhold Elenz, Landesamt für Denkmalpflege Rheinland-Pfalz, Germany, for the kind support.

Spectroscopic Characterization of Modern Cobalt-Titanate Green Pigments

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The American painter, sculptor and printmaker Jasper Johns (b.1930) is known to be deeply involved in the process of creating his pieces, and has been reported to mix his own colors. On the occasion of a recent exhibition at the Art Institute of Chicago and the publication of the catalogue *Jasper Johns: Gray*, the painting *Near the Lagoon*, 2002-3 (AIC, #2004.16) was carefully examined and its materials analyzed. The work is a remarkable piece due to its construction using added pieces of canvas, and its overall covering with strokes of gray encaustic. A close examination has revealed that before the gray was applied, the picture was initially painted with predominantly primary colors - red, yellow, and blue. Also present and applied above the different shades of gray encaustic are drips of the primaries, various grays and an intense green [1]. Of particular interest was the green paint, which was found to contain a complex mixture of pigments with beeswax, mainly cobalt-titanate green and carbon black, with additions of viridian, ultramarine blue, and small amounts of pale yellow (likely cadmium), iron oxide yellow, titanium white, and iron oxide red.

While most of these pigments are well characterized in the conservation science literature, the occurrence of cobalt-titanate greens in contemporary artists' palettes is not very well documented and thus has been further studied. This work provides a thorough spectroscopic characterization of this modern green pigment, presenting for the first time its Infrared and Raman spectra along with XRD and XRF data. Results obtained on John's *Near the Lagoon* green pigment are compared with samples of other commercial cobalt green reference pigments from various manufacturers.

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Water Colour Identification Based on Machine Vision Analysis

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In this paper we present a novel image-based approach for characterizing and classifying blue and green pigments as used in paintings based on their optical properties. Our aim is to develop a non-destructive method that can characterize and classify watercolours through a statistical approach which recognizes both the probabilistic nature of the optical watercolour information and the form in which we should express the results. Furthermore, this study also combines historical information and the statistical computation of the watercolour optical behaviour.

Our method is non invasive, does not involve sampling and can be applied in-situ. It is based on the optical properties of pigments as well as the correlation of pigment variations. Such variations are studied using co-occurrence matrices that capture the behaviour of the pigments during the painting process. Furthermore, the optical response of watercolour pigments can be represented using a mixture of Gaussian functions, and can be classified using a Bayesian decision rule.

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FTIR Spectroscopy and Micro-Raman Spectroscopy of Wallpaper of the Castle of Prangins/Switzerland

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The castle of Prangins is part of the group "Die Schweizerischen Landesmuseen" (Swiss National Museums) and houses a very special collection of wallpapers (second part of the 18th century up to the beginning of the 20th century). In 2009, the museum plans an exhibition of these wallpapers.

In preparation of the exhibition, some problems have to be solved. One is the fixation of the wallpapers of Prangins on cardboards during an older conservation. Unfortunately, the cardboards have warped after storage over decades. Another problem is that often two different parts of the wallpapers have been fixed to one cardboard, one on each side so it would be impossible to exhibit both papers. The cardboards are 50 by 50 cm or 50 by 70 cm.

In order to solve these problems, a small project has been started. The aim of this project was to find a method to detach the wallpapers from the old cardboards without destroying them. First, the glues had to be identified which were used for fixing the wallpapers on the cardboards. This was done by Fourier transform infrared spectroscopy (FTIR). To decide how to solubilise the glue without damaging the paper or the pigment layers the identification of the pigments and binders was necessary, too. For this question, FTIR was used as well as micro Raman spectroscopy. After this, different procedures for the removal have been tested. Both a hot steam and a cold steam method have been tested, and a wet method as well as an enzymatic method.

Two different glues have been identified (acrylic resin Plextol®, wheat starch) by FTIR. The pigments have been identified by micro-Raman spectroscopy as calcium carbonate and barite (white), lapis lazuli and Prussian blue (blue), chromium and mars yellow, and mixtures of these colours with carbon black (plant black).

All four methods were tested on wallpaper samples from up to 10 cm. The hot steam and the cold steam method saved the binder and the pigment layers but because of the long dissolution time the paper suffered from cracks. The wet method (dissolution by water) damaged the pigment layers. The enzymatic method was done with an Albertina Compress from Klug Conservation. This worked out to be the best method for dissolution of the glues without destroying the pigments and/or the paper. As a result, probably this method will be applied on the wallpapers of Prangins.

Observation of Cyclododecane on a Canvas Painting as a Temporary Consolidant

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The present investigation focuses on the physical behaviour and working properties of cyclododecane (CDD) when using as a temporary consolidant for oil paintings on canvas. Molten CDD was applied to a painting with brush. Sublimation of CDD was monitored by Raman spectroscopy and evaluated by scanning electron microscopy (SEM). The analysis evaluates the extent of sublimation of CDD from the painting and report on the presence/absence of residues. This practical analysis and a case study were used to evaluate the appropriateness and usefulness of CDD for temporary applications on paintings.

The investigation describes the rate of sublimation and reports on the presence/absence of residues of CDD on oil painting. Neither chemical nor surface damage is observed on the canvas after treatment with molten cyclododecane and subsequent natural sublimation of cyclododecane. The sublimation of CDD was completed in 11 days without leaving residues detectable with Raman spectroscopy and SEM.

It should be noted that sublimation rates depend on the size of the area applied with CDD, temperature and the thickness of the CDD layer.

Non-destructive and Micro-analytical Investigation Techniques (FTIR and RAMAN) of Sealboxes from "Augusta Raurica" (Switzerland)

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Augusta Raurica is a vestige of a Roman town near Basle in Switzerland, which was built in 44 BC. Between 150 and 200 AC, the town was spreading on nearly 106 hectares. 20 000 inhabitants were living on the southern edge of the river Rhine. A lot of bronze seal boxes were found during excavations. Such boxes were used to close writing tablets, coin purses etc. and then sealed by pouring wax over a cord. In addition to analyses of the alloys it was very important to know if it is possible to find remains of the wax and characterise it after being buried for almost 2000 years. An interdisciplinary project was started bringing the archaeologists of Augusta Raurica and the scientists of the Laboratory for Conservation Research of the collection centre of the "Schweizerischen Landesmuseen" to a collaboration.

FTIR Spectroscopy

To investigate the content of the seal boxes small samples were taken from seven seals. The contents are mixtures from inorganic and organic material. First, the content was investigated without extraction by using a diamond press cell. Five of the content materials could be determined to be bees wax. The others have been extracted with methylene chloride and then the extract has been investigated. These seal content of these boxes could also be identified as bee wax.

Raman Spectroscopy

Moreover, it was possible to investigate the content of the seal boxes by Raman micro-spectroscopy and in this way to determine the pigment which was used to colour the wax. These measurements were non-destructive which means the investigation was carried out on the seal boxes themselves. We used the laser 532 nm and identified peaks with 146.0 cm^{-1} and 341.3 cm^{-1} which indicated PbO.

Laser Assisting Cleaning of Soiling from Cellulose Supports

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The aim of our paper is the evaluation of the behavior to laser irradiation of organic compounds (carboxy methyl cellulose, fish glue, Arabic gum) used both for the sizing of the paper and in the recipes for the metal-gall inks. Basically, these compounds are quite sensitive to physical and chemical factors Their degradation products may interact with the cellulose support, damaging it. Such damage would be indicated by modifications in the pH functional groups.

Previous work proved a different behavior for unglued cellulose (new cotton paper) compared to that of glued paper (19th century cotton paper). This behavior may be caused by the presence of sizing agent in the glued sample. The organic compounds mentioned above are water soluble and also soluble in other solvents. FTIR spectroscopy, HPLC, SEM will establish the modifications that take place under the influence of laser irradiation. By examining the modifications occurring in our reference samples we will be able to elucidate the reaction mechanisms and also how these are affected by the parameters of the irradiation source.

The work was carried out part as an access to a research project (ULF-FORTH 001091 supported by ULF-FORTH, in the framework of a MARIE CURIE PREDOCTORAL FELLOWSHIP, from 2005, May-September.

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Investigation of Pigments Used in Roman Wall Paintings in the Vesuvian Area

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Some powder pigments found in bowls from the Pompeii archaeological site and some wall painting fragments from Vesuvian area (conserved in Naples Archaeological National Museum) were investigated by microscopic Raman and FTIR spectroscopy, XRD and SEM-EDX.

Brown, red and yellow pigments are common ochres based on goethite and hematite (the well known "austere pigments" by Pliny). Egyptian blue is responsible for the blue color. The Raman spectra, in addition to quartz, display occasionally tridymite and cristobalite features indicating firing temperatures in the 1000 - 1100 °C range. Cerussite was found in a powder sample, suggesting its use to lighten the color. Pink pigments were prepared both with purely inorganic materials, by mixing hematite, Egyptian blue and quartz (violet hue) or adding to an aluminium-silica matrix organic dyes of difficult identification by FTIR. In this last case microprobe analysis provides evidence for arsenic and phosphor, but arsenic sulfides were not found from XRD or micro-Raman investigations.

The white color in the wall paintings was obtained mainly by calcite or aragonite and by calcium sulfate in different hydrated forms. In one bowl the white powder is composed mainly of the unusual pigment huntite ($CaMg_3(CO_3)_4$) [1, 2]. Celadonite is found in the green samples from the wall paintings, together with Egyptian blue and basic lead carbonate, while the heterogeneous green pigment in a bowl shows malachite mixed with goethite, Egyptian blue, hematite, carbon, cerussite and quartz. An arsenate compound may be expected by Raman spectra: the presence of arsenic and zinc is indeed suggested by SEM-EDX analysis.

The origin of arsenic and zinc compounds in some pigments is discussed.

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Thermography Applied to Cultural Heritage and Museum Objects

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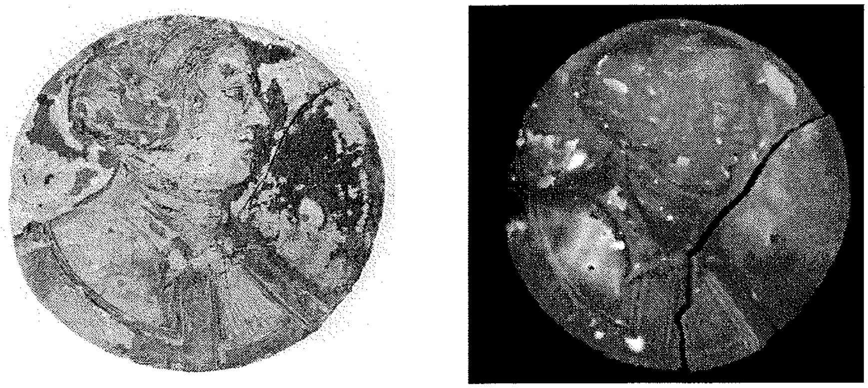
Objects of cultural heritage can have hidden features which are interesting for art historians and restorers. Tool marks, inscriptions, various signs, and other sources of information for art historians are often covered or became invisible in the course of time. Restorers on the other hand need to know how an object looks beyond the seemingly intact surface. If defects are present, their position and extension are of special interest. Furthermore, restorers need techniques to evaluate and document the restoration process. Thus, non-destructive techniques are often necessary to study cultural heritage objects.

In general, a feature of interest is associated with a difference in one or more physical quantities. A large number of non-destructive techniques has already been developed and applied to the study of artwork, focussing on quantities such as density, composition, mechanical stiffness etc. However, up to now little use has been made of differences in thermal properties such as heat capacity and thermal conductivity. These can be made visible by means of active infrared thermography which is well known in the area of non-destructive testing in engineering. Unlike x-ray technology or other techniques using ionizing radiation, infrared thermography does not need any safety measures. For this reason, outdoor use of this technique is possible, and it is even suitable for the imaging of very large objects such as whole buildings.

The figure below shows as an example a part of a terracotta frieze from Lüneburg in Northern Germany (left: photography, right: infrared image). The weathering caused the glaze to detach from the support in some places. These areas appear bright in the infrared image since the air gap between glaze and support has a different thermal conductivity than the good material.

In this paper, the principles of infrared thermography and its practical implementation will be explained. A number of examples from cultural heritage will be shown, and the perspectives and limitations of infrared testing of artwork will be discussed.



Constantinos' Post-Byzantine Mural Paintings at the Doamnei Church, Bucharest, Romania: Characterization of the Altered Red Lead Paint Layer

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The degradation of the red pigments in post-Byzantine mural paintings at the Doamnei Church has been studied using in-situ investigations with portable XRF and laboratory spectroscopic techniques, namely micro-Raman, micro-FTIR and SEM-EDS. The original red paint layer contains cinnabar, minium and red ochre as indicated by XRF investigations. The whitish thin layer that covers mainly the lead-based orange color of the garments has been investigated through micro-samples (Fig. 1). The results obtained for frescoes from the 17th century Doamnei church are compared with those from other Romanian wall paintings containing red lead pigment dating from the 16th and 18th centuries.

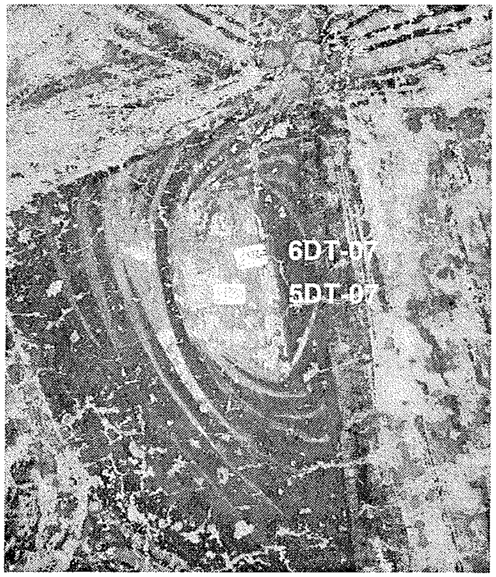

Fig. 1: Detail with the altered minium area from the porch of the Doamnei church, Southern half, South-West pendentive. Two samples have been taken from this area: one from the superficial white layer (5DT-07) and the other from the whitish discoloration of the red lead pigment (6DT-07).

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Laser Techniques in Atomic and Molecular Analysis of Artworks Materials

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Identification and characterization of materials used in artworks can provide important information for dating, authentication, and conservation treatment of these objects and studying art history in general. This paper aims to review laser techniques possibilities to atomic and molecular analyses of artworks materials.

The Laser spectral analyzer (LSA) is specially designed for the surface analysis and it includes a Q-switched Nd:YAG laser (1064 nm), optical and mechanical units, a microscope, a video camera, a PC-controlled moving sample table and a record system based on a CCD arrays. The laser provides both single- and double-pulse modes. The optical unit allows focusing the laser beam on the sample surface on a spot of a diameter from 60 to 800 μm. The laser action zone is imaged at the PC monitor and it can be positioned with 0.01 mm accuracy. The LSA allows to realize layer-by-layer laser induced breakdown spectroscopy (LIBS) of artworks materials *in situ*. As low as 0.001% elements content can be measured with a relative error of 3-7%.

Laser ablation can also be used practically as efficient technique for preparation of art pigments samples for their further atomic and molecular analyses with inductively coupled plasma optical emission spectroscopy (ICP-OES) and surface-enhanced Raman scattering (SERS).

The idea of technique is following: solid samples are transformed to colloidal analyte solutions of nanosized (10-15 nm) particles via laser radiation that have been focused on target surface placed in deionized water. Laser operation regime was chosen based on our earlier observations to obtain maximum solution uniformity and stability against sedimentation.

Using of this technique of sample preparation allows to minimize the amount of consumed sample from the objects with artistic or archaeological value while maximizing the amount of information extracted from the samples.

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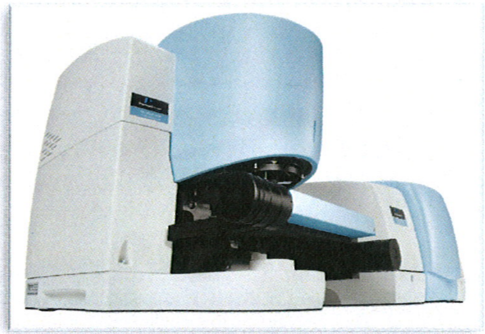


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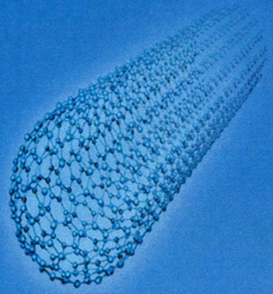

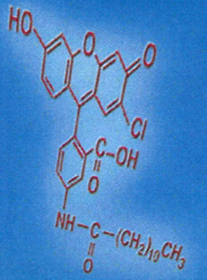
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