LACONA XII

PARIS, 10TH-14TH SEPTEMBER 2018

CONFERENCE ON LASERS IN THE CONSERVATION OF ARTWORKS

LRMH
Laboratoire de Recherche des Monuments Historiques

Fondation des Sciences du Patrimoine

Centre de Recherche et de Restauration des Musées de France

BOOK OF ABSTRACTS

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Fondation des Sciences du Patrimoine

Centre de recherche et de restauration des musées de France

Laboratoire de recherche des monuments historiques

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SHIFTED EXCITATION RAMAN DIFFERENCE SPECTROSCOPY FOR THE STUDY PIGMENTS IN THE BINDING MEDIA MATRIX. STUDY OF ORTHODOX ICON OF ST. MARK

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Keywords : Raman, SERDS.

One of the important stages preceding the process of restoration is the choice of its strategy. This choice is based on the current state of the object, the technique of the author and the materials. The Raman spectroscopy is among the powerful methods that allow us to characterize accurately the material. Its main advantage is the ability to identify the substance, its phase, the ability to monitor the changing process under certain conditions. Difficulties arise with the investigations associated with the weak intensity signals, and with negative influence of luminescence. One of the approaches is using Shifted Excitation Raman Difference Spectroscopy (SERDS) techniques to combat interfering luminescence. Using a 785 nm laser decreases the possibility of luminescence and still allow us to conjugate spectrometer with other research techniques, using UV-visible-NIR sensitive detector devices. At the moment SERDS technique is relatively rarely used in the art objects study, now it needs the studies of the application possibilities. In this work, within the framework of the restoration of the St. Mar[illegible] the application of the technique is tested and the results c[illegible]c fluorescence removal SERDS [1] realized on the Senterra s[illegible] (Bruker) are demonstrated. To assess technical capabilitie[illegible] pigments found in organic binders layers were chosen. Thi[illegible] us to study the author's [illegible] corresponding pigments. For such study was chosen the icon of Saint Mark the Evangelist from the Holy Doors of the XVII century Russian orthodox iconostasis from the rural church. The icon was made on an unusual carved and gilded wooden base. The elliptic painted surface framed with baroque style carving made on the same piece of wood. Samples for the study of pigments were selected in the process of restoration. In the study of the icon by the SERDS method it was possible to identify that white lead ($2PbCO_3 \cdot Pb(OH)_2$) was used as the white background, cinnabar (α-HgS), iron compounds based on hematite (α- -Fe_2O_3) were used as red-orange pigments, Parisian (Prussian) Blue ($C_{18}Fe_7N_{18}$) was used in blue shades. A signal from red lead was also identified, but its origin may be associated with later records. The set of identified pigments and bonds in them allowed to distinguish a number of bands in the range from 200 to 2200 cm^{-1}, corresponding to such stable functional groups as CO_3^{2-}, CN^- and the most intensive phonons modes in the cinnabar, hematite, in order to test their identifiability at different signal to noise ratio and correctness of processing by the method [1] in connection with the spectral and technical characteristics of the detection system of the Raman spectrometer. The authors also compare the spectra obtained using the SERDS method with standard spectra in which the luminescence is baseline subtracted and the possible discrepancies and their prerequisites are analyzed.

[1] US Patent 6,281,971

The measurements were performed at Research Park at Center for Optical and Laser Materials Research of Saint Petersburg State University.

POSSIBILITY OF LASER APPLICATION FOR BRONZE DISEASE TREATMENT

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Keywords : SEM EDS, raman spectroscopy, copper chloride, patina, malachite, atacamite, 1064 nm, Nd:Yag, bronse desease, bronze, copper.

This work evaluates the possibility of using laser cleaning for certain stages of restoration of metal artifacts. For the study, a 17th century coin and a bronze mirror (3rd century BC) were chosen. As a source of laser radiation, a pulsed Nd: YAG laser with a wavelength of 1064 nm was used. Laser cleaning was carried out in an aqueous medium and under normal atmosphere conditions. The composition and microtopography of the surface were investigated before and after laser cleaning by Scanning Electron Microscopy (SEM) (Merlin, Carl Zeiss) and Energy Dispersive X-ray Spectroscopy (EDS) (Inca X-act, Oxford instruments), FTIR spectroscopy (Nicolet 8700 Thermo Fisher Scientific) and Raman spectroscopy (Senterra, Bruker) with excitation wavelength λex = 785 nm (1 mW) and 532 nm (0.2 mW). The formation of various mineral composition layers on archaeological findings made of bronze and other copper alloys has occurred. Their formation takes place during a long stay in the soil, and then, when extracted in the process of archaeological excavations, their composition undergoes natural modifications in the modern atmosphere. The group of basic copper carbonates (malachite, azurite) formed in the soil and relatively stable in the atmosphere make up the so-called noble patina. These layers are

important as evidence of authenticity, and are often carefully preserved in the process of restoration. Minerals belonging to the Cu-Cl group (nantokite, clinoatacamite, atacamite) are not so stable in a humid atmosphere and are involved in active corrosion processes leading to the destruction of objects. The remaining contamination minerals during different stages of surface cleaning are placed under the control of Raman spectroscopy instead of the widely used LIBS technique in such cases. It allowed us to discriminate materials on compound level instead of pure elemental composition. Another reason for combination of such techniques lies in its possible combination in portable devices in future. The perspectives, advantages and disadvantages of such an approach will be discussed. This class of minerals attributed with so-called "bronze disease" are usually removed from the surface during the restoration treatments. Our approach is to selectively remove minerals responsible for active corrosion, while preserving noble patina minerals on the surface of the object. And to answer the question: "Could be the laser application innovative approach against traditional methods for bronze disease treatments?", the work was carried out using the equipment of the Interdisciplinary Resource Center in the direction of Nanotechnology and the center Optical and laser methods of substance research of the Science Park of St. Petersburg State University.

13TH CENTURY FRENCH LEGENDARIUM : OPTICAL AND LASER STUDY

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Keywords : 13th century, French Legendarium, spectroscopy.

The presented work aim at investigating the Legendarium - a 13th century manuscript, which is now preserved in the Russian Academy of Sciences Library (Saint Petersburg, Russia). The document was wetted because of an unknown incident before the 1930s, and, therefore, the parchment codex, decorated with miniatures, turned into a rigid lump, and the sheets had stuck together. The prolonged stay in the high humidity conditions had caused almost total destruction of codex state, which came to an extremely damaged form. It led to the swelling of parchment because of unlimited moisture absorption, so the manuscript was easily exposed to microorganisms. In 1959, the Legendarium was passed for restoration to the Laboratory of conservation and restoration of documents as an unknown monument of the medieval French literature. For a long time the Legendarium was in a list of manuscripts irreversibly ruined as a result of improper storage. Some sheets in the beginning of manuscript survived well enough to give a view about the beauty of its original design (general color of text and ornament, refinement of miniatures, golden edging glow, finely written out decorations). The ideas about scientific value and art advantages of medieval manuscript have caused interest in revealing all or, at least, the largest number of existing sheets. Therefore, the decision about manuscri...

made [1]. The works on highly difficult case of parchment codex exfoliation, which had laid in the form of monolith for several decades, were successfully finished in 1960. Each sheet of parchment was kept in special conditions for several decades and periodically was placed under the press. In the present time, the manuscript consists of 214 separated sheets, encapsulated into special conservation envelopes. It was established that some of the sheets are missing and, probably, the manuscript had 225-230 sheets initially. An optical-photographic study to find satisfactory methods for text reveal and separation of complex ornaments and drawings overlaying are among research tasks now. The method of visible luminescence photoexcitation under 300-400 nm excitation gives the best results for these investigations. A special detailed study by optical methods will be undertaken with precipitations from the Legendarium's sheets. The number and composition of precipitations allow us to estimate the degree of manuscript's preservation and expedience of folios' storage in encapsulated form. Research by vibrational spectroscopy (Raman, FTIR) methods permits to conclude about the parchment's composition and the inks and pigments that were used for the manuscript. A Raman spectrometer equipped with a confocal microscope was chosen (SENTERRA, Bruker). The Raman spectra were measured with a 785 nm and 532 nm laser excitation (1 mW power). The spectrometer is built on the basis of the optical microscope (BX-51, Olympus). Infrared measurements were carried out on Nicolet 8700 spectrometer (ThermoFisherScientific) using ATR accessory.

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THE FIRST NON-INVASIVE STUDY OF THE RARE POLYCHROMIC BELT BUCKLES OF ANCIENT NOMADS BY VIBRATIONAL SPECTROSCOPY

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Keywords : polychromic belt buckles, ancient nomads, raman, archaeology, incrustation, minerals.

Raman and IR spectroscopy provide the important advantage of measuring directly on the surface without sampling. This is especially significant when studying valuable objects and when surface damaged are impossible, for example, when studying materials of jewelry, of historical and cultural heritage objects. This work presents a study of ancient belt buckles decorated with polychrome inlay. These rare nomads jewelry were found in South Siberia, on the bank of the Yenisei River, during archaeological excavations by the Tuva Archaeological Expedition of the IHMC RAS in 2017. Such findings are very rare for archaeologists. Artifacts are related to the Xiongnu culture. The buckles are made of black material and decorated with light blue and red incrustations and engravings. Various opinions were expressed about the manufacturing materials. It was supposed that the base material could be slate of dark color, coal or jet. The basis of the buckle was investigated by both FTIR and Raman spectroscopy. In the Raman spectra, the characteristic peaks of carbon materials D and G were observed. Investigation by the FTIR spectroscopy made it possible to determine such additional compounds as kaolinite (Al2O3·2SiO2·2H2O), dolomite (CaMg(CO3)2) and quartz (SiO2), in addition to the signal from some organic component, which is currently being investigated. On the surface of the buckle

there were natural formations with characteristic peaks of lepidocrocite (γ-FeOOH) and possibly goethite (γ-FeOOH). Another aspect of the buckles study was the identification of mineral composition of preserved geometrically arranged incrustation. It was possible to identify, using the Raman spectroscopy, the presence of turquoise as a blue-green incrustation. Minerals of the silicate group were also found from Raman spectra that had a dominant signal from quartz. These minerals by color could be divided into a murky orange and a transparent red. In the case of orange incrustations, the presence of inclusions with a structure close to hematite (γ -Fe2O3) and goethite was proved by Raman spectroscopy. In the case of red minerals, hematite inclusions were also found, which suggest that both minerals are cornelian. The difference in the red Raman spectra of the red region from the orange was the presence in the red region of an additional stable low-intensity peak at about 500 cm-1, which admittedly refers to the moganite that is the polymorphic monoclinic modification of SiO2 [1]. Materials were determined as a result of the research. Visually similar materials turned out to be different minerals. Jewelry materials has sacred significance in ancient times. The use of turquoise in one case is replaced by a visually similar in color muscovite mineral in the other. This again emphasizes the question: what was sacred in the culture of ancient nomads : particular material or special color ?

The measurements were performed at Research Park at Center for Optical and Laser Materials Research of the Saint Petersburg State University.

References :

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INDIVIDUAL DESTRUCTION OF IRON CORROSION COMPONENTS BY THE LASER. NEW APPROACH TO LASER CLEANING OF METALLIC HERITAGE OBJECTS

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Keywords : XRD, SEM, absorption, corrosion, iron oxides, laser cleaning.

Laser cleaning of archaeologically corroded iron is used in restoration and sometimes leads to a darkening of the surface due to the oxidation process. The 1064 nm Nd:YAG laser is widely used in the industry. At present work, the spectral dependence of the absorption coefficient of radiation by typical iron corrosion components (FeOOH, Fe2O3, and others) and selection of laser is held. The laser's wavelength determination in maximum (or the nearest to maximum) of absorbance would allow, in our opinion, use of less energy as to avoid overheating and darkening of the surface. Water soaking of the surface and its impact in the absorption coefficient are also taken into account in this work. X-ray diffraction and scanning electron microscopy have been used to investigate structural and compound changes in irradiated samples.

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