

# LASER SPECTROCHEMICAL MICROANALYSIS OF ARCHAEOLOGICAL FINDINGS AND PIGMENTS FROM CANVAS PAINTINGS

Victor Burakov<sup>1</sup>, Elena Dovnar-Zapolskaya<sup>2</sup>,  
Vasilii Kiris<sup>1</sup>, Alena Klyachkovskaya<sup>1,3</sup>, Sergei Raikov<sup>1</sup>

<sup>1</sup>Institute of Physics, 68 Nezavisimosti Ave., 220072 Minsk, Belarus

Tel: 375 17 284 00 30, [raikov@imaph.bas-net.by](mailto:raikov@imaph.bas-net.by)

<sup>2</sup>Institute of Arts, Ethnography and Folklore, 1/2 Surganov Str., 220072 Minsk, Belarus

<sup>3</sup>National Art Museum of Republic of Belarus; 20 Lenin Str., 220030 Minsk, Belarus

## ABSTRACT

*Detailed structural characterization and identification of key chemical constituents can uncover important information on historical and artistic significance of artworks and archaeological findings. The most difficult task during the process of painting investigation is the identification of pigments and bindings included in structure of the ground and paint layers. In the last decades, significant achievements in analytical science and instrumentation have led to a steadily increasing use of state-of-the-art analytical techniques in this field. Such powerful technique as X-ray material and structure analysis has some restrictions. In this context, laser-induced breakdown spectroscopy (LIBS), a rapid elemental analysis technique, which is applicable in situ and is nearly nondestructive, offers a potential alternative to X-ray fluorescence, which sometimes is not really non-destructive. The LIBS instrumentation used in our work is quite standard and relies on the use of multichannel detection for recording the time-, spatially, and spectrally resolved emission, produced by focusing a single laser pulse on a surface of the sample under study. Material consumption in our LIBS experiment is minimal (estimated volume is around  $10^{-8}$  cm<sup>3</sup> for a typical crater 5–10 μm deep and 50–100 μm wide), and any damage to the sample's surface is practically invisible to the naked eye. The funds of the main Belarussian museums contain a large number of non-identified and non-attributed archaeological and art objects of European value including items found in the territory of Belarus or imported into it. As typical archaeological objects with composite matrix, fragments of bracelets (presumably with a glass basis) have been chosen. The LIBS technique has been also applied for the layer-by-layer pigment material microanalysis of non-attributed paintings as well as of problematic sections of well known paintings of famous artists.*

## INTRODUCTION

Methods originating from the Natural Sciences are more widely used to examine archaeological findings and works of art. Comprehensive technological examination of products covering each structural element includes general examination by luminescent methods in ultra-violet and infrared beams and by X-ray imaging. The materials that were used in the creation of the painting are rather diverse and defined by the time of creation of the painting, the tradition of the respective art school, and also by the artist's individual preferences. The accumulation of all this information on the materials used in the respective different times and by different artists and the creation of database are the basic conditions for successful research. The most difficult task during the process of examining a painting is the identification of pigments and binders included in the structure of the ground and paint layers. Detailed structural characterization and identification of key chemical constituents can uncover important information on the historical and artistic significance of artworks. Their authenticity can be questioned if the pigments or binders used are not in agreement with the work's chronological placement.

Over the last decades, significant achievements in analytical science and instrumentation have led to the steadily increasing use of state-of-the-art analytical techniques in this field. Pigment identification is performed by means of methods such as microchemical analysis, petrography and various physical techniques, primary scanning electron microscopy/energy dispersive X-ray spectroscopy, X-ray fluorescence, different kinds of spectrochemical analysis (surface-

enhanced Raman spectroscopy, IR-Fourier-spectroscopy for bindings, and inductively-coupled optical emission or mass spectroscopy for pigments). Powerful techniques such as X-ray material and structure analysis have some restrictions. SEM coupled to X-ray microanalysis provides excellent compositional mapping, but special sample preparation is required, and again the analysis requires vacuum conditions. The lateral spatial resolution of XRF is rather poor, while the depth of analysis is limited to a very thin surface layer. In addition, the use of ionizing radiation is an important concern. ICP OES or MS allows identifying the chemical structure of a sample very precisely, but it requires plenty of sample. Besides, layer-by-layer analysis using this method is impossible or very complicated. Moreover, when valuable objects such as paintings are to be analyzed, the preservation of the integrity and aesthetic value of the object becomes a major concern. In this context, laser-induced breakdown spectroscopy (LIBS), a rapid elemental analysis technique, which is applicable *in situ* and is almost non-destructive, offers a potential alternative to other optical spectroscopic, mass spectrometric, or X-ray techniques. For the analysis of precious and archaeological samples, LIBS can compete with X-ray fluorescence, which sometimes is not really non-destructive.

## **EXPERIMENTAL**

The LIBS instrumentation employed in our work is at present quite standard and maximally suitable for a routine practice and relies on the use of multichannel detection for recording the space-, time-, and spectrally resolved emission produced by focusing a laser pulse in atmospheric air at normal pressure on the surface of a sample under analysis.

The fundamental (1.06  $\mu\text{m}$ ) or the second harmonic (0.53  $\mu\text{m}$ ) of a nanosecond Q-switched Nd:YAG laser with a pulse duration of 6-8 ns (depending on wavelength and energy) and 10-Hz pulse repetition rate is employed in our LIBS measurements. The laser used is an improved version with variable reflectivity mirrors (VRM). This model provides high stability of the emitted radiation. The VRM resonator gives excellent harmonic conversion efficiency due to an increased spatial uniformity of the output beam, a low divergence and a short pulse duration. The laser beam, with an aperture of  $\leq 6$  mm and a beam divergence of  $\leq 0.8$  mrad, is focused on the sample surface by a 50 mm focal length plano-convex quartz lens. The system enables both single- and multipulse measurements. A sample is fixed at a  $X$ ,  $Y$ ,  $Z$  translation holder, which enables precise adjustment of the ablation plume with respect to the optical axis of the detection system. The laser pulse energy can be varied from 10 to 270 mJ with an energy stability of  $\pm 3\%$ . The spot diameter on the sample is 50–100  $\mu\text{m}$  (depending on the focusing conditions). The maximum laser irradiance on the target surface was up to  $10^{12}$   $\text{W}/\text{cm}^2$ . The light emitted from the vertically expanding plasma plume is collected by a plano-convex quartz lens with a 63 mm focal length and imaged (1:1) onto the horizontal entrance slit of a compact spectrograph. This lens is mounted on a  $X$ ,  $Y$  translation stage that allows the collection of the light from different regions of the plasma along the direction of plume expansion with a precision better than 0.5 mm, so that the temporal evolution of the ablated plume may be observed without the necessity to utilize for this purpose an ICCD detector. A simple and relatively cheap CCD detector is more convenient for a routine spectrochemical practice and reduces the total price of the LIBS systems. In our experiments, to reduce the background caused by continuum radiation, a suitable delay from the laser pulse (depending on the material) is chosen to optimize the spectra obtained. The continuum background decays rapidly and the atomic emission lines become spectrally narrower. The delay time also ensures that LTE is achieved. This delay corresponds to the plasma observation region shifted from the target surface. It is easy to optimize in each case this delay as well as the laser energy so that a reasonable discrimination of the background in the on-line observations of

plasma spectra is achieved. The spectrograph is equipped with suitable diffraction gratings for high and medium spectral resolution measurements within a narrow or wide spectral range, respectively. A maximum spectral resolution of about 1 pm could be realized with the help of the echelle grating with double dispersion. The spectrum is recorded with the help of the optical multichannel analyzer with a linear CCD detector. Usually, a spectral window of about 120 nm (within 200-1060 nm range) for the multielement LIBS measurements is recorded in a single experiment. The individual spectra obtained from each laser pulse may be recorded or summed up and stored as a single spectrum using the software.

## **RESULTS AND DISCUSSION**

LIBS may be very close to the nondestructive mode because of the minimum possible ablated mass. This is very important in many applications, particularly when one deals with unique museum exhibits and archaeological jeweler samples. In general, the calibration-free procedure can be applied even using a single or just a few laser shots. In addition, the technique has the capability of providing depth-profiling, calibration-free information, provided that the laser used has a flat-top beam profile. Material removal in our typical single pulse experiment is minimal (estimated volume is around  $10^{-8}$  cm<sup>3</sup> for a typical crater of 5–10 μm depth and 50-100 μm diameter). On the other hand, the use of a few tens shots is preferable in order to improve the accuracy of the measurements by increasing the mass of ablated material. Clearly, the number of shots depends strongly on the requirements of the analysis. For example, in the case of bronze samples, usually up to 50 shots are used in our calibration-free measurements, while in the case of archeological gold and glass targets, two-three shots are typically used to minimize material consumption.

As typical archaeological objects with composite matrix, fragments of bracelets (presumably with a glass basis) from the National Museum of the History and Culture of Belarus have been chosen. These samples have been found in the compact places at excavations of the Minsk and Polotsk Fortresses. Polotsk is the oldest known town in the territory of Belarus. The time period of the archaeological layers, in which the given fragments of bracelets were found, is dated to the 11-13th centuries. The chemical compositions of the glass matrices and of the components responsible for specific coloring of the samples were determined by taking into account the recorded emission spectra. These findings were compared with the data obtained by several researchers mainly with the help of conventional chemical analyses performed on similar glass samples found in different regions of the world. In this specific case, we had no possibility to compare LIBS results with the results obtained by LA-ICP-OES because the later technique needs much larger volume of ablated material, which is unacceptable for the museum samples. The high probability of a local origin of bracelets has been confirmed, despite of the not found in Belarus appropriate workshops of that or earlier time. At present chemical composition is examining of a bronze archaeological findings (Velbar Culture, III century) from the Brest (Belarus) region. Similar technological examination of gold museum exhibits of different origin is carrying out.

As an example of canvas painting examination a laser ablation microanalysis method has been used for the analysis of pigment material from the well-known painting “Landscape of a Pool with an Obelisk and Ruins of an Aqueduct” painted at the beginning of 1790s by the famous French artist Hubert Robert. This painting from the National Art Museum of Republic of Belarus consists of two separate and stuck together sections (canvases): 134x87 cm (bottom section) and 58x87 cm (top section). The authenticity of the top section was questioned after some art examinations. Thus, the painting required thorough investigation of the pigments from both sections in order to identify their authenticity.

As a result of the analysis of the spectra obtained in a wide range it is possible to ascertain, that superficial layers of both (the artist's and alternative) series of analyzed microfragments (with colors identical to the eye) essentially differ in element composition. The conclusion made proves to be true upon analysis of the results of the layer-by-layer determination of the elements in the painting material. During identification of the chemical compositions of each layer from both sections of the painting, it was found that the ground of the top section contains elements such as Pb, Ca, Na, Mg, Si, and C, whereas in the bottom section we also detected Al and Fe. This means that the bottom section contains red ochre and lead white in the ground. On the other hand, the ground of the top section consists only of lead white ( $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ ). Accordingly, in addition to the microchemical examination of the painting, it has been established that the ground in the bottom section of the painting is mainly red, and the ground in the top section of the painting is mainly white and has been applied in two layers. In the bottom section, we detected Al, Fe, Pb, Si, Ca, and Na among the elements of the paint layers. Elements including Pb, Na, Si, and Ca were also detected in the glaze. This can be explained with the use of Prussian blue ( $\text{Fe}_4[\text{Fe(CN)}_6]_3 \cdot n\text{H}_2\text{O}$ ) as a main blue pigment, and red ochre which contains  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  and kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). For brightening the artist used lead white. In the glaze layer we detected lead white and chalk, whereas the concentration of other paint pigments was comparatively low for identification or perhaps the artist preferred to use organic pigments for the glaze. In the paint layers of the top section we found Pb, Co, Cd, Ba, Al, Na, Si, and Ca. These results were also unexpected for us. Thus, the unknown artist used synthetic ultramarine as the main blue pigment in this section of the painting which began to be applied after 1827. The presence of Co in these fragments implies the use of cobalt blue pigment ( $\text{CoO} \cdot \text{Al}_2\text{O}_3$ , 1802-1804). The presence of Cd points to the fact that the artist of the top section of the painting used cadmium red ( $\text{CdS}_x\text{Se}_{(1-x)}$ , 1910) and/or cadmium yellow ( $\text{CdS}$ , 1817) to paint the clouds. Besides, synthetic barium yellow ( $\text{BaCrO}_4$ , early 19th century) was also used. All these facts clearly show that the top section of this painting appeared after Robert's death, while the original section seems to have been lost for unknown reasons. Additionally a similar examination of pigments from the well-known painting "Garden of Borghese Villa in Rome" from the National Art Museum of Republic of Belarus was carried out to check the compositions of pigments used by Robert. The results confirmed the above conclusion about the expected doubtless authenticity of the bottom section of the painting "Landscape of a Pool with an Obelisk and Ruins of an Aqueduct" and about the preliminary unexpected unknown origin of the top section.

At present similar technological examinations of very interesting and problem paintings of Zygmunt Sidorowicz, Marc Chagall, Wassily Kandinsky, Albert Marquet and other famous artists are carrying out.

## CONCLUSION

The LIBS instrumentation and analytical procedures have been developed and successfully tested which allow determining chemical composition of any unique solid-state sample in almost nondestructive mode, in real time, *in situ*. The main disadvantage of the equipment used is that all our experiments with the archaeological findings and paintings can only be performed at present in the laboratory. Several improvements can be considered on the standard experimental system described above mainly by using of a compact laser of a modern design and a modern echelle grating monochromator of a compact design to carry out necessary measurements directly in a museum or painting gallery. Such specialized LIBSpectrometer will be realized in the Institute of Physics (Belarus) in the nearest future.

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