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## The characterization of canvas painting by the Serbian artist Milo Milunović using X-ray fluorescence, micro-Raman and FTIR spectroscopy

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## HIGHLIGHTS

- *In situ* EDXRF, micro-Raman and FTIR spectroscopy were employed.
- Palette of painting “The Inspiration of the poet” by Milunović has been determined.
- Obtained results allowed evaluation of the painter’s technique.
- Milo Milunović worked on the clay ground imitating Nicols Poussin’s technique.

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## ABSTRACT

A canvas painting by Milo Milunović “The Inspiration of the poet” was studied by energy dispersive X-Ray fluorescence (EDXRF), micro-Raman and Fourier transform infrared (FTIR) spectroscopy in order to identify materials used by the artist and his painting technique. Study is performed combining *in situ* non-destructive method with the preparation and study of cross-section samples and raw fragments of the samples. Milo Milunović, an eminent painter from Balkan region, made a copy of the Nicolas Poussin’s original painting in Louvre in 1926/27. Obtained results revealed following pigments on the investigated canvas painting: vermilion, minium, cobalt blue, ultramarine, lead white, zinc white, cadmium yellow, chrome-based green pigment and several earth pigments – red and yellow ochre, green earth and umber. Ground layer was made of lead white mixed with calcium carbonate.

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## 1. Introduction

Canvas paintings are among the most heterogeneous works of art and their characterization is a demanding analytical task (Orvola et al., 2014). Traditionally, characterization of canvas painting has been mainly carried out by art-historians and restorers by naked eye and by microscopic analysis. Information obtained in this way, combined with consistent evidence of the art materials obtained by physico-chemical techniques can help conservators and restorers to select the most appropriate procedures for the purposes of restoration.

The scientists always have to balance the possible risks of damage against the benefits that are gained from the investigation of

the art-work. Hence, the risk of damage/information ratio should be considered and optimized carefully for each investigation (Dredge et al., 2003; Ortega-Avilés et al., 2005). Significant progress in this area is made by continuous advances in non-invasive experimental techniques (Adriaens, 2005; Miliani et al., 2010; Alföld and Broekaert, 2013). In the cases where samples are available, amounts of obtained material are usually in micro or sub-micro range containing different analytes. These complex mixtures most often include organic and inorganic compounds, thus use of different analytical techniques is required for a complete characterization of the investigated samples (Doménech-Carbó et al., 2001).

In this work we present multianalytical study of canvas painting “The inspiration of the poet” made by Milo Milunović (1897–1967), a distinguished painter from Balkan region. He studied art in Florence under the apprenticeship of Antonio Augusto Giacometti (1912–1914), and later in Paris (1919–22; 1926–32). During

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his stay in Paris, he developed friendships with many artists such as Chaim Soutine, Massimo Campigli, Antoine Bourdelle (who bought several Milunović's paintings, which are now in the Bourdelle Museum in Paris – two paintings are included in the permanent exhibition).

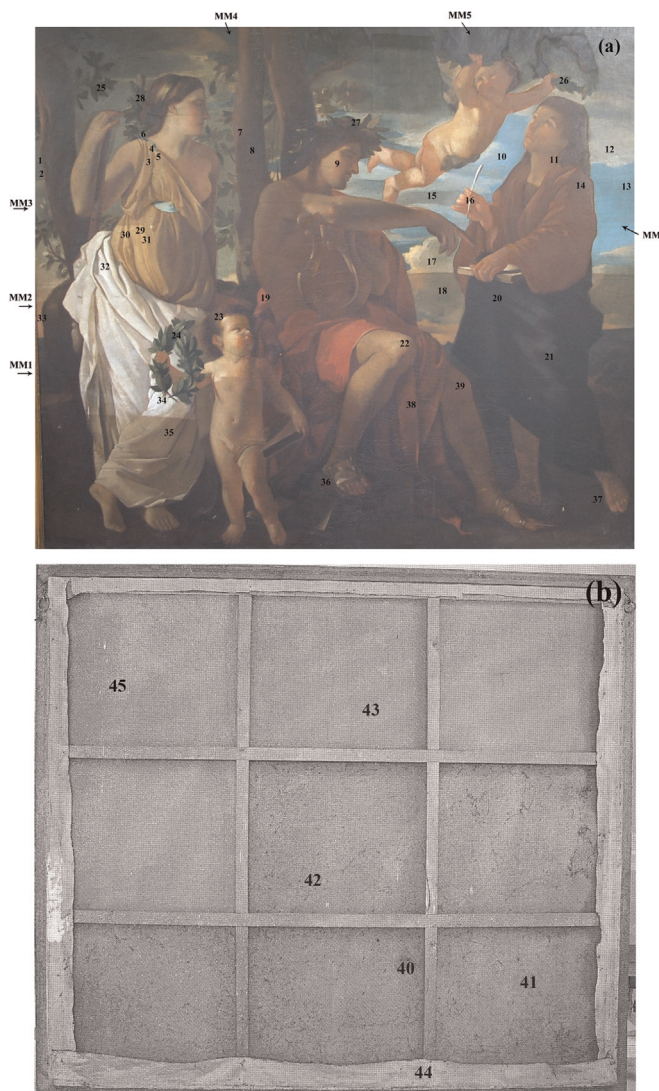
With two colleagues, Milo Milunović founded the Academy of Fine Arts in Belgrade, Serbia in 1937, where he worked as a professor. He was also cofounder of School of Fine Arts in Cetinje, Montenegro in 1947. Milo Milunović's artistic importance and regional influence is manifested through domestic and international exhibitions: 45 independent (e.g. Paris, Cardot Gallery, 1928–29, 1932) and over 320 group (e.g. Salon des Tuileries, 1927 and Galerie Bernheim Jeune, 1931) exhibitions. His creative work is described in monographies, prefaces of catalogs, books and encyclopedias (Trifunović, 1973; Čelić-Simeonović and Milunović, 1997; Jovanović, 2001). Almost consistently following the beliefs of Cezanne, who was his great inspiration, that "The Louvre is a book from which we learn to read" and that "One should do Poussin all over from Nature" Milunović copied the Nicolas Poussin's painting "The inspiration of the poet" in the Louvre in 1926/27.

"The Inspiration of the poet" painted by Milunović is 2.18 m × 1.80 m large. The painting was firstly in the possession of Milunović's brother at Cetinje, Montenegro till 1931, when it was sent to Belgrade to his friend Kosta Hakman. The painting was sold to the French Club in Belgrade in 1935 where it stayed till the beginning of the World War II. It is not known where the painting was till 1967 when it was displayed again in the hall of the Craftsman Workhouse building in Belgrade. Since 1990 it has been permanently exhibited in the hall of the Faculty of Fine Arts in Belgrade. This painting was brought to the Faculty of Applied Arts in Belgrade for restoration, which provided a unique opportunity for a scientific investigation.

This is the first scientific study of Milo Milunović's artwork and it was performed combining *in situ* non-destructive energy dispersive X-Ray fluorescence (EDXRF) spectroscopy, which has been proven to be efficient in the study of canvas painting materials (Rosì et al., 2009; Campos et al., 2014; Van de Voorde et al., 2014), with the preparation and study of cross-section samples as well as raw fragments of the samples. In-house developed portable EDXRF spectrometer was used for investigation of well-preserved regions of the painting, while paint chips taken from the edges of the damaged regions were investigated by optical microscopy, micro-Raman and FTIR spectroscopy. The aim of this study was to gather information about materials (pigments and ground layer) and painting technique used by the artist, combining data obtained by different analytical techniques.

## 2. Experimental

Portable in-house developed EDXRF spectrometer was used for the non-invasive and non-destructive analysis of the painting. The excitation X-ray tube (Oxford, Rh anode, max voltage 50 kV, max current 1 mA, air cooled) is mounted on a motorized platform which allows easy movement along all three axes. The construction allows precise movement of 1 mm in each direction. The detection of the characteristic X-rays was made by compact X-ray spectrometer (X123, Amptek Inc.) with Si-PIN detector (6 mm<sup>2</sup>/500 μm, Be window 12.5 μm thickness and 1.5 in. detector extension) which is mounted on the excitation X-ray protection box together with two laser pointers which enable alignment of the measuring system at the desired point to be analyzed. The energy resolution of used detector was 160 eV at 5.89 keV. The excitation X-ray beam has been collimated passing through especially designed collimator mounted at the end of the tube. The



**Fig. 1.** Photographs of Milo Milunović's canvas painting "The Inspiration of the poet": (a) front side-EDXRF spectra were collected at the points labeled 1–39, samples were taken from the areas labeled MM–6; (b) backside-EDXRF spectra were collected at the points labeled 40–45. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

measurements were performed without additional filtering of the excitation beam. Measuring system is mounted on the cantilever which enables portability, sufficient stability, easy movement and handling, even during analysis of large scale paintings like the one analyzed in this study. Geometry of the experimental setup for all measurements was the same: distance between surface of the painting and the end point of the collimator was 16 mm, distance between analyzed surface and detector window was 21 mm and angle between detector and X-ray tube axes was 45°. The X-ray tube voltage was altered to give excitation of 40 keV. In this experimental setup, with detection path in the air, only elements heavier than Si can be detected. For all the measurements filament current was set at 300 μA and acquisition time was 40 s since only qualitative analysis was performed. For the spectra acquisition and processing ADMCA software was used (Amptek Inc.). Total of 45 points (see Fig. 1) were analyzed. Analyzed points were selected to represent particular colors on the surface layer of the painting. Few points on the backside of the painting were also analyzed for the characterization of preparation layer.

Investigated canvas painting was well-preserved. Hence it was

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