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Depth-Resolved Analysis of Historical Painting Model Samples by Means of Laser-Induced Breakdown Spectroscopy and Handheld X-Ray Fluorescence

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Abstract

Paintings represent composed materials arranged in successive layers. Development of a suitable method for a depth-profiling analysis is essential for acquiring the information on the stratigraphy as well as on the chemical composition of individual layers, revealing the pigments which had been used. In this study, a depth-resolved analysis of multi-layered model samples of historical easel paintings was performed by means of laser-induced breakdown spectroscopy (LIBS) in combination with non-invasive X-ray fluorescence (XRF). The LIBS analysis was carried out using modified laser ablation system, UP-266 MACRO, equipped with a Czerny-Turner spectrometer. The XRF analysis was performed by handheld spectrometer, Delta Premium. In LIBS experiments, a set of six spots was examined with 5, 10, 15, 20, 25 and 30 pulses respectively, for each of the studied paint samples. Digital and 3D optical microscopy was employed to measure individual layer thickness and to obtain the information on average ablation rates of each sample. The chemical composition of the model samples with each layer partly uncovered was known, and this enabled to directly compare the results obtained by LIBS depth profiling with a fast analysis carried out with the handheld XRF spectrometer. The LIBS depth profiling proved to be a suitable method to distinguish layers of a different material composition and estimate their thickness. The combined use of LIBS and XRF analyses offered essential complementary information on the elemental composition of analysed multi-layered samples.

Keywords

LIBS; XRF; depth profiling; paintings; ablation rate

1. Introduction

The scientific examination of the works of art is a very delicate process which aims to answer, among others, the question about their origin, age, paint technique and used materials. Painted artworks are often multi-layered systems composed of original layers and possibly also later overpaints and/or corrosion layers. Therefore, they require both surface and sub-surface analyses. A wide range of modern optical and analytical techniques offering imaging (e.g. X-ray radiography or infrared reflectography, optical coherence tomography) is used, together with the elemental or molecular composition determination (e.g. optical spectroscopies), atomic and molecular structure and sub-surface defects examination (e. g. X-ray diffraction) and many other techniques. In recent years laser-based methods have significantly contributed to the preservation of cultural heritage [1, 2].
As the works of art are usually of a high value, *in situ* methods (either non-invasive or micro-invasive) are highly preferred to prevent an extensive sampling. However, a cautious use of complementary laboratory non-destructive or micro-destructive techniques performed on samples can provide more detailed and thorough information. Analyses of sample cross sections, such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) [3] are widely used to obtain stratigraphy and elemental composition of the layers. Laser ablation-based techniques, such as laser-induced breakdown spectroscopy (LIBS) or laser ablation inductively coupled plasma mass