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Near-crater discoloration of white lead in wall paintings during laser induced breakdown spectroscopy analysis ☆

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Abstract

During Laser-Induced Breakdown Spectroscopy (LIBS) analysis of white lead pigment (basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$), used in wall paintings of historical interest, a yellow–brown discoloration has been observed around the crater. This phenomenon faded after a few days exposure under ambient atmosphere. It was established that the mechanism of this discoloration consists in lead oxides (PbO) formation. It was verified by further experiments under argon atmosphere that recombination of lead with oxygen in the plasma plume produces the oxides, which settle around the crater and induce this discoloration. The impact of discoloration on the artwork's aesthetic aspect and the role of atmosphere on discoloration attenuation are discussed. The mechanism is studied on three other pigments (malachite, Prussian blue and ultramarine blue) and threshold for discoloration occurrence is estimated.

Keywords: LIBS; Wall paintings; Discoloration; Pigments; Basic lead carbonate

1. Introduction

From several years, a growing demand and need for cultural heritage promotion has been noticed and a particular interest is given to restoration of historical sites, artworks and monuments. Precise knowledge regarding the artwork history, the conditions of its achievement and the artistic techniques used is necessary, preliminarily to restoration works. Obtaining on-site information about the artwork or degradation products nature can represent a significant time saving, especially for monumental artworks and wall paintings, which cannot be transported to laboratory. Currently, the most common process for wall paintings studies consists in sampling small fragments in different areas of the artwork, to get a large overview of the work-of-art complexity. These samples are sent to laboratory, where they are analyzed by several techniques (optical and electronic microscopy, IR or Raman spectroscopy, X-ray fluorescence (XRF), X-ray diffraction (XRD), Inductively coupled plasma associated with atomic emission spectroscopy or mass spectroscopy (ICP-AES and ICP-MS), secondary ion mass spectroscopy (SIMS), particle-induced X-ray emission (PIXE), chromatographies and chemical tests) [1]. Analytical means used depend on the information and accuracy needed to characterize the sample. Since sampling on the object is necessary, all these laboratory techniques are invasive.

In this context, the LIBS method seems to perfectly meet requirements for in situ analyses. The sharply focused laser beam induces matter vaporization, allowing sampling and atomization of small amounts of analyte. Emission lines from atoms in the resulting laser plasma enable an instantaneous identification of the sample atomic composition. In situ LIBS measurements, with portable or on-line instrumentation, have already been performed in metallurgy, environment or nuclear industry [2–5]. Regarding in situ analysis of cultural heritage, techniques widely used are Raman spectroscopy and XRF [6–9]. LIBS has often been

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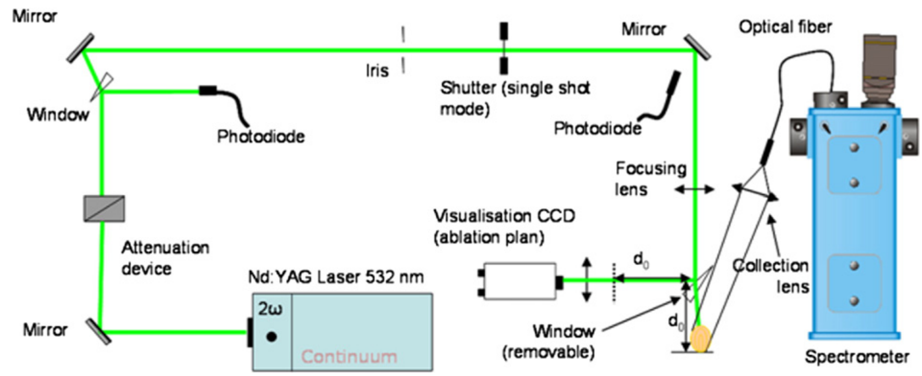

Fig. 1. Schematic diagram of the LIBS experimental set-up; λ:532 nm, pulse: 5 ns, fluence: 0.4–9 J cm^{-2}, beam profile: top hat, interaction size: 265 μm.

applied in laboratory analysis with transportable artworks or samples [10–14], but very few on-site LIBS analysis of historical monuments have been reported yet [15].

In this particular field, the main constraint is to ensure maximal artwork preservation, by limiting the sampling surface. By nature, LIBS is a locally invasive method, which effects can be controlled regarding the crater formation. Micrometric craters can be achieved with LIBS, by using a microscope objective to focus the laser beam onto the sample surface [16]. This configuration requires a quite complex optical system and is not perfectly suitable for in situ analysis, since it demands accurate positioning (millimetric working distance). For in situ paint analysis, a sampling zone of about 50 μm (laser spot diameter on the paint) is required for a limited alteration of the artwork (laser crater is invisible to the naked eye), and is obtained with a simple lens system. In addition to laser crater formation, for high fluence and sufficient number of laser pulses, discolorations can occur around the crater. This phenomenon must be avoided since it degrades the artwork's aesthetics by increasing the sample area affected by the analysis beyond the crater size.

The goal of this work is to study the nature and origin of discoloration occurring on paintings during LIBS analysis with nanosecond laser pulses. Studies have been performed on a model white lead ($2PbCO_3 \cdot Pb(OH)_2$) painting where discoloration was observed, with the second harmonic of a Nd:YAG laser, under ambient and argon atmospheres. The causes of discoloration (beam spatial profile, plasma heating, plume deposit) were investigated. X-ray Photoelectron Spectroscopy (XPS) measurements were performed for identification of the discoloration product nature. Results were verified and extended to three other pigments: malachite (green, $CuCO_3 \cdot Cu(OH)_2$), Prussian blue ($Fe_4[Fe(CN)_6]_3$) and ultramarine blue ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$). Fluence threshold for discoloration appearance on white lead is also estimated.

2. Experimental

2.1. LIBS set-up

Experimental set-up is presented on Fig. 1. LIBS analyses were performed with a Q-switch Nd:YAG Surelite laser (Continuum, USA) operating at the wavelength of 532 nm, with a 20 Hz repetition rate and a 5 ns pulse duration (FWMH). An attenuator controls the delivered energy, measured with a Fieldmate powermeter (Coherent, USA). A shutter enables to select a defined number of laser pulses for paint ablation. A 1.53 mm-diameter diaphragm is imaged on the sample by a lens of 150 mm focal length. With convenient positioning of the sample in the image plane of the diaphragm, the energy distribution was homogeneous on the surface, with straight and clear beam edge (top hat spatial profile). The laser spot diameter was 265 μm, for all laser fluences applied in the experiments (from 0.4 to 9 J cm^{-2}). A removable semi-transparent plate enables to image the incident beam on a CCD camera to control the spatial profile in the ablation plane.

The plasma emission was imaged by a lens (focal length : 50 mm, 25.4 mm diameter, ×0.25 magnification) at the entrance of an optical fiber, with a 5° angle with respect to the normal incident laser beam. The optical fiber was connected to the entrance slit of an Echelle spectrometer ESA 3000 (LLA, Germany) equipped by an ICCD camera. This detection system allowed verifying that experiments were carried out in realistic LIBS conditions, with detectable plasma emission enabling species identification. Fig. 2 shows a LIBS spectrum acquired on a white lead sample prepared in glue binder, for 6 J cm^{-2} fluence, 3 accumulations (delay after laser shot: 700 ns, accumulation time : 4.5 μs). Lead emission lines at 357.273, 363.957, 367.149, 368.346, 373.393, 401.963, 405.781, 406.214 or 416.803 nm are clearly visible on the spectrum.

Several configurations of LIBS analysis were tested to verify hypotheses regarding the discoloration mechanism: different beam profiles, high and low ablation fluences, different number of shots, with or without an air jet on the sample surface.

2.2. Samples

Samples used in this work were prepared by a mural paintings restorer. It consisted in a concrete plate, covered with a mortar made of sand and lime. The pictorial layer (20–25 μm thick) contained pigments mixed with rabbit skin glue as binding medium. The main pigment used was white lead, known for its discoloration properties under direct laser exposure. Malachite, Prussian blue and ultramarine blue pigments were also tested to verify the discoloration presence. To study the influence of the binding medium on the discoloration, another white lead sample