Evaluation of the standard normal variate method for Laser-Induced Breakdown Spectroscopy data treatment applied to the discrimination of painting layers☆

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ABSTRACT

Nowadays, Laser-Induced Breakdown Spectroscopy (LIBS) is frequently used for in situ analyses to identify pigments from mural paintings. Nonetheless, in situ analyses require a robust instrumentation in order to face to hard experimental conditions. This may imply variation of fluencies and thus inducing variation of LIBS signal, which degrades spectra and then results. Usually, to overcome these experimental errors, LIBS signal is processed. Signal processing methods most commonly used are the baseline subtraction and the normalization by using a spectral line. However, the latter suggests that this chosen element is a constant component of the material, which may not be the case in paint layers organized in stratigraphic layers. For this reason, it is sometimes difficult to apply this normalization. In this study, another normalization will be carried out to throw off these signal variations. Standard normal variate (SNV) is a normalization designed for these conditions. It is sometimes implemented in Diffuse Reflectance Infrared Fourier Transform Spectroscopy and in Raman Spectroscopy but rarely in LIBS. The SNV transformation is not newly applied on LIBS data, but for the first time the effect of SNV on LIBS spectra was evaluated in details (energy of laser, shot by shot, quantification). The aim of this paper is the quick visualization of the different layers of a stratigraphic painting sample by simple data representations (3D or 2D) after SNV normalization.

In this investigation, we showed the potential power of SNV transformation to overcome undesired LIBS signal variations but also its limit of application. This method appears as a promising way to normalize LIBS data, which may be interesting for in-situ depth analyses.

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1. Introduction

Conservation science is the study of the composition and the alteration of work of art from cultural heritage. In this field, it is important to investigate these two last points for a better understanding of the life story of the artifact and its alteration processes. The knowledge of the material involves a quantitative or qualitative analysis, on surface or in depth of the sample. Moreover, cultural heritage is often composed of a multiplicity of materials, so several analytical methods are employed to meet these many expectations and especially techniques based on spectroscopy. However these techniques like SEM-EDS, XRD, Raman spectroscopy, FTIR, XRFS… [1–8] often require sampling. Therefore, in order to minimize such removing valuable cultural heritage matter, research for science conservation moves towards in situ

analysis. This solution is necessary when works of art are immovable, but also allows an analyzing strategy to reduce the sampling. Analyzing on field involves portable instrumentation and only few measurement systems can overcome this limitation like XRFS (X-Ray Fluorescence Spectroscopy) [9–11] and Raman spectroscopy [12–15] for a surface analysis. For in depth analysis, Terahertz imaging is an instrument which allows a stratigraphic view and could highlight for instance the sinopia [16–18] (drawing or underpainting for frescoes). However, it cannot provide sufficient resolution for a smaller scale as the stratigraphy of a paint layer and can't supply the chemical composition. Therefore Laser-Induced Breakdown Spectroscopy (LIBS) shows many advantages to fulfill this purpose by its multi-elemental analysis capability, portability on site, and stratigraphic investigation efficiency. Nowadays, this method is often used for identification of materials from cultural heritage [19–26]. It is based on laser–material interaction. A high power pulsed laser is focused on the surface of the material to be analyzed. A tiny amount of the material is vaporized and particles are consequently created, giving rise to a plasma plume. The resulting light is directly collected and corresponds to the emission of the

characteristic spectral lines of the elements. Nonetheless, in situ analyses may imply fluency variations and matrix effects thus inducing modification of LIBS signal, which deteriorates spectra and then results. Usually, to overcome these experimental errors, LIBS signal is processed. The most commonly used processing signals are the baseline subtraction and the normalization by using a spectral line [27–31]. However, the last treatment suggests that this chosen element is a constant component of the material, which may not be the case in paint layers organized in stratigraphic layers. For this reason, it is sometimes difficult to apply this normalization.

The new way was to use another normalization to throw off these signal variations. Standard normal variate (SNV) is a normalization sometimes employed in Diffuse Reflectance Infrared Fourier Transform Spectroscopy or in Near Infrared Spectroscopy [32–38] and in Raman Spectroscopy [39–41]. This transformation is a standard score calculation for each point of the signal. According to the literature [32,41], this normalization seems to be encouraging. However, it has been less often used on LIBS spectra. Only a few papers [42–44] have applied SNV on LIBS spectra, where it seems to reduce the standard deviation [42] and could be used as preprocessing step for chemometric methods as multivariate analysis [43,44]. So the effect of SNV transformation on LIBS data has not been presented before in details. In this way, the aim of this study was first to test the SNV transformation ability to correct undesired variation signal observed on LIBS spectra. However, normalizing induced a change in intensity of the spectra and could result in a loss of concentration information. In order to ensure that it is not the case, we experimented in the second part the SNV ability to make an elemental semi-quantitative analysis. Finally, SNV normalization was achieved on LIBS analysis on model sample as found in historic monument for a stratigraphic study. Indeed, this example would be representative of in situ LIBS analyses on mural paintings where there are both fluence variations and elemental evolution through the different layers. At last the limits of this normalization will be pointed out and especially the difficulty to understand the physical meaning of SNV transformation on LIBS spectra.

2. Experimental analysis

2.1. LIBS instrumentation

Two LIBS instrumental systems were used, the one was the laboratory system which was also portable and sometimes used for field applications, and the second was a portable and lightweight system really dedicated for in-situ analysis.

In the first hand, the laboratory setup for LIBS measurements is schematically shown in Fig. 1. A Minilite II Q-Switched Nd:YAG laser (Continuum, USA) was used as an excitation source operating at a fundamental wavelength of $\lambda = 1064$ nm, with an energy of 30 mJ/pulse. The spotsize was 500 μm.

The laser pulses have 5 ns duration, and were triggered by the operator shot by shot. The laser pulses were focused onto the sample, at normal incidence, using a 100 mm focal length lens to induce a plasma plume. The laser beam diameter at the focal point was about 500 μm.

The emission was collected at a 45° angle with respect to the incident beam. A second lens (100 mm focal length) was used to focus the signal on a 7-fiber optical bundle (core diameter: 600 μm). Three of the fibers were connected to the entrance slits (5 μm width) of three spectrometers using a HR2000 (Ocean Optics, USA) which enabled the coverage of the wavelength range between 200 and 940 nm (from 200 to 340 nm and 335 to 445 nm, two 1800/mm gratings with a resolution of 0.1 nm, and from 510 to 940 nm, a 600/mm grating with a resolution of 0.31 nm) ensuring multi-elemental analysis. One can notice that using only 3 on 7 fibers, the setup discarded light The emission spectrum was recorded with an internal 2048 CCD array detector (delay: 1 μs after the laser Q-Switch with a minimum integration
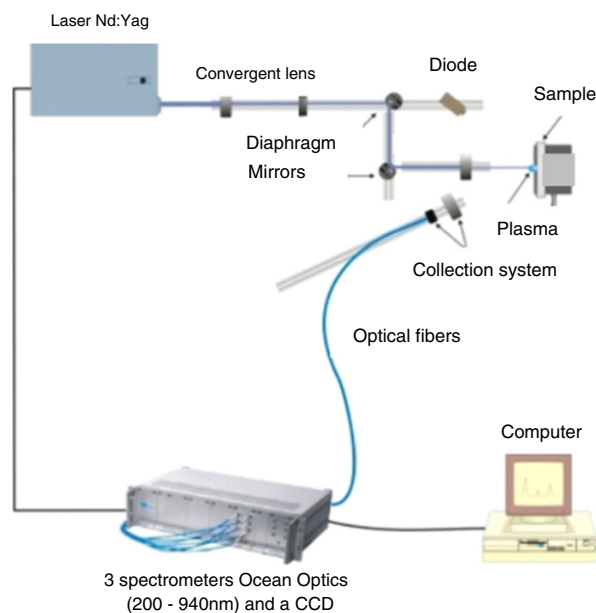

Fig. 1. Laboratory LIBS instrumentation.

time of 2.1 ms). All experiments were performed under ambient atmospheric conditions.

In the second hand the portable system is the EasyLIBS system (IVEA solution, FRANCE) which used a Nd:YAG laser operated at 1064 nm with an energy under 25 mJ/pulse and a frequency of 1 Hz. The spotsize was 250 μm. Three of the fibers were connected to the entrance slits (5 μm width) of three spectrometers using a HR2000+ (Ocean Optics, USA) which enabled the coverage of the wavelength range between 200 and 935 nm (from 200 to 341 nm, from 330 to 467 nm, from 485 to 935 nm). The emission spectrum was recorded with an internal 2048 CCD array detector and all experiments were performed under ambient atmospheric conditions.

2.2. Samples

As part of this study, several kinds of samples were analyzed. Firstly, calibration curves normalized by either a spectral line or by SNV were plotted in order to see the SNV ability to quantify the trace elements present in lead matrix based standards. Then model samples were stratigraphic paint and metal layers used to test SNV ability to highlight the elemental signal evolution in depth analysis.

– The lead standard used were seven SYLAB references: PR1, PR2, PR3, PR4, PR5, PR7, and PR8. The standards were based on about 99% of lead with different concentrations of trace elements as shown in Table 1. Five trace elements were used in this study: Ag, Bi, Cu, Sb and Sn [5].
  10 pre-shots and 30 shots were fired on each analysis area with a 10 Hz frequency and 5 analysis areas were designated per sample resulting in 150 spectra for each sample analyzed.

Table 1
Lead matrix based standards with different trace elements concentrations used for LIBS calibration curves.

Standard	PR1	PR2	PR3	PR4	PR5	PR7	PR8
[Ag] ppm	880	530	30	140	5	3000	5500
[Bi] ppm	800	177	390	140	28	5000	11,300
[Cu] ppm	60	390	570	150	7	2200	330
[Sb] ppm	50	530	900	120	1	8400	2500
[Sn] ppm	40	950	480	90	2	2100	5900