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Multi-block analysis coupled to laser-induced breakdown spectroscopy for sorting geological materials from caves

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ABSTRACT

In this study, multi-block analysis was applied for the first time to LIBS spectra provided by a portable LIBS system (IVEA Solution, France) equipped with three compact Czerny-Turner spectrometers covering the spectral ranges 200–397 nm, 398–571 nm and 572–1000 nm. 41 geological samples taken from a laboratory-cave situated in the "Vézère valley", an area rich with prehistoric sites and decorated caves listed as a UNESCO world heritage in the south west of France, were analyzed. They were composed of limestone and clay considered as underlying supports and of two types of alterations referred as moonmilk and coralloid.

Common Components and Specific Weights Analysis (CCSWA) allowed sorting moonmilk and coralloid samples. The loadings revealed higher amounts of magnesium, silicon, aluminum and strontium in coralloids and the saliences emphasized that among the three spectrometers installed in the LIBS instrument used in this work; that covering the range 572–1000 nm was less contributive. This new approach for processing LIBS data not only provides good results for sorting geological materials but also clearly reveals which spectral range contains most of the information. This specific advantage of multi-block analysis could lead for some applications to simplify the design and to reduce the size of LIBS instruments.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has become a very popular analytical method in the last decade in view of some of its unique features such as applicability to any type of sample [1–5]. Today, LIBS is considered as an attractive and effective technique with the capability of detecting all chemical elements in a sample, of real-time response, and of close-contact or stand-off analysis of targets.

In LIBS analysis, every material with a different chemical composition has a unique LIBS signature indicative of the existence of characteristic elements that can be discerned from its broadband spectrum [6,7]. However, the interpretation of LIBS data is often complex due to the simultaneous presence of a big number of emission lines in the same spectrum. Different chemometric methods such as partial least squares discriminate analysis (PLS-DA) [8–10], soft independent modeling class analog (SIMCA) [11,12], K-nearest neighbor method (KNN) [13], support vector machines (SVM) [14], artificial neural networks (ANN) [15,16], independent components analysis (ICA) [17], partial least squares discriminate analysis (PLS) [18] and multiple linear Regression (MLR) [19] have been used in order to improve the accuracy of qualitative and quantitative LIBS analysis. In this paper, a multi-block method called Common Components and Specific Weights Analysis (CCSWA) was applied to the LIBS data to extract the relevant information. It allowed the identification of the atomic lines responsible of the efficient sorting of geological samples and also the determination of the most contributive spectral range to this sorting.

There are several multi-block methods, also called multi-tables methods, used for the simultaneous study of multiple sets of matrices with different variables describing the same samples [20–23]. These methods are especially useful to combine several series of data related to the same series of samples that have been recorded from different experimental techniques. One such multi-block technique is CCSWA [24]. This chemometric method has

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already been used for processing data from various analytical techniques such as gas chromatography/mass spectrometry (GC–MS) [25], liquid chromatography/mass spectrometry (LC–MS) [26], mid-infrared spectroscopy [27], proton nuclear magnetic resonance [28], front-face fluorescence spectroscopy [29], and sensory and preference analyses [30,31].

In the present study, CCSWA was used in an innovative way since it was applied to a series of three LIBS spectra provided by a portable system equipped with three separate spectrometers. Thus, three blocks were considered, each one corresponding to a given spectral window. The goal of the multi-block approach was first to sort some geological samples and secondly, to determine the most influential spectrometer in order to reduce the large number of variables in the obtained LIBS spectra.

The studied geological samples were taken from a laboratory-cave called "Leye cave" situated in the "Vézère valley" [32], an area rich with prehistoric sites and decorated caves listed as a UNESCO world heritage in the south west of France. These samples are representative of two types of white alteration, called moonmilk and coralloid, that threatens many prehistoric caves by hiding walls drawings and paintings as well as their underlying supports (limestone and clay).

The two types of alterations can be distinguished with the naked eye. In fact, coralloid samples present a popcorn like aspect while moonmilk ones correspond to a thin veil characterized by the presence of needle fiber calcite. In addition to the morphological dissimilarity, the sorting of these alterations by LIBS could emphasize the differences in their elemental composition. Moreover, unlike moonmilk samples that have been widely studied, works related to coralloids are very limited. Thus, LIBS having already demonstrated its potential for chemical analysis of minerals, rocks, soils, sediments, archeological samples and other natural materials [33–40] is expected to provide, through elemental finger-print, important information to understand the genesis and the development of these alterations observed on most of the caves walls.

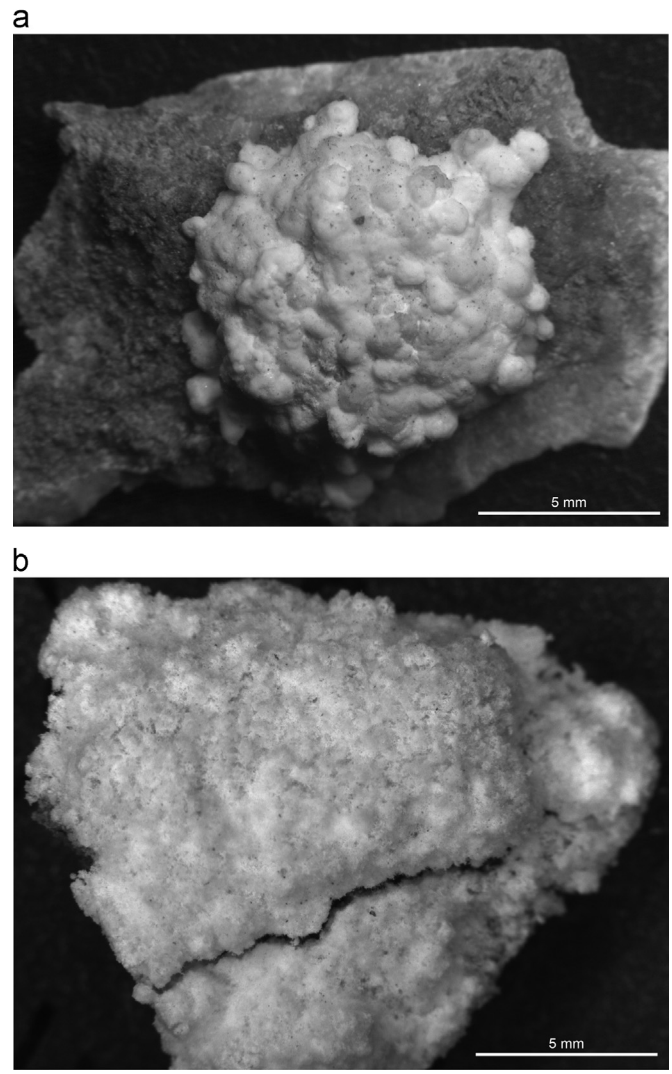

Fig. 1. The two types of alterations covering the caves walls: (a) coralloid, (b) moonmilk.

2. Materials and methods

2.1. Samples

A corpus of 41 geological samples was considered for this study. All the samples were taken from the laboratory-cave that has been selected [32] as representative of the prehistoric ornated caves of the same area called the "Vézére valley". The set of samples was composed of 17 samples of limestone and 15 samples of clay considered as the supports, and of 4 samples of moonmilk and 5 samples of coralloid corresponding to the two types of white alteration shown in Fig. 1. It should be noticed that both moonmilk and coralloid are mostly composed of calcium carbonate ($CaCO_3$). Thus, LIBS analysis is expected to focus on minor or trace elements in order to highlight the differences between these two types of materials.

2.2. LIBS measurements

The LIBS analyses were performed using a portable system (IVEA Solution, France) equipped with a Nd:YAG laser operating at a wavelength of 1064 nm and at a repetition rate of 1 Hz, and delivering 5 ns pulses with 43 mJ per pulse. Although these laser parameters are fixed, this portable LIBS system has been customized in order to allow off-contact LIBS analyses. Thus, the focusing distance of the laser beam was 8 cm and the laser beam diameter at the focus was 250 μm.

The plasma emission was collected via an optical fiber bundle that split it into three separate fibers in order to inject it into three separate compact Czerny-Turner spectrometers (Ocean Optics, USA). A single spectrum was provided by the software as the result of the concatenation of the three original spectra. The use of three spectrometers offers a broad spectral range for LIBS analysis, from 200 nm to 1000 nm.

The portable LIBS system exploited in the present study potentially allows direct on-site measurements. However, cave is characterized by a temperature around 10–12 °C and a high relative humidity close to 100% which could lead to noisy spectra with high risk of fluctuation. This is why; the results presented in this paper were obtained in more stable laboratory conditions in order to evaluate the potential of the LIBS method by focusing on the chemical properties of the materials and not on the physical parameters of the experiment.

For each of the 41 samples considered in this work, 10 laser shots at the same point were performed.

2.3. Multi-block analysis: CCSWA

Most of the samples analyzed in the present study are basically composed of calcium carbonate with minor additional elements. As a consequence, several atomic emission lines related to calcium (Ca) in the obtained LIBS spectra were saturated. These saturated