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Handheld laser-induced breakdown spectroscopy instrument for the diagnosis of the conservation state of stone monuments

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***Abstract* – Laser-induced breakdown spectroscopy (LIBS) has been in use for decades, but only recently the technique has progressed so to allow the construction of efficient handheld, self-contained commercial instruments featuring a large range of capabilities. In particular, the development of portable instruments able to perform non-invasive spatially resolved in-situ analysis has provided an impressive impulse to the scientific investigation of cultural heritage materials. In this work, the design of an handheld LIBS instrument and the first test measurements performed on a sedimentary rock monument are presented. A full broadband emission spectrum was recorded from a single laser shot in few secondswhich provided information on the elements present.**

I. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) has been only relatively recently used successfully to perform the identification and accurate chemical analysis of geological materials [1-2]. Repeated laser pulses are also able to remove dust coatings and analyse weathering layers,thus allowing detailed investigation of rock varnish features and underlying pristine rock composition.

LIBSoffers several advantageswith respect to other analytical techniques such as Scanning Electron Microscopy, Secondary Ion Mass Spectroscopy, X-ray Photoelectron Spectroscopy and nuclear particle irradiation. These include simplicity, robustness of instrumentation, almost no sample preparation, and no restriction of the sample shape and size, and allows in-situ measurements under atmospheric conditions [3].

Within the last five years several commercial handheld LIBS instruments have become available, some of which feature capabilities that rival traditional bench-top instruments. These include resolution to 0.1 nm, spectral ranges from vacuum ultraviolet (UV) to near-infrared (NIR), argon purging, and rastering. The portability of handheld analyzers now enables LIBS field applications that were heretofore impossible [4].

This study illustrates how a portable, handheld LIBS analyser can be used for real-time chemical analysis under simulated field conditions for element and mineral identification.Further, different layers could be discriminated on a rock (carbonate minerals) subjected to weathering effects.

This, by impinging a few laser pulses on the same spot which allowed to obtain spectra withspecific chemical composition and track rapidly elements such as Al, C, Ca, Fe, K, Mg, Na and Si.

II. MATERIALS AND METHODS

The sample used in this work is a limestone fragment collected from a block of the masonry of Castello Svevo, Bari, Italy. The sample showed a surface degradation featuring a black crust layer.

A handheld LIBS instrument named NanoLIBS(Fig. 1)by B&WTek (Newark, DE, USA)was used to perform the measurements. This instrument consists of a miniature diode pumped, solid-state, short pulsed laser emitting at a wavelength of 1064 nm with a maximum output of 300 mW, a pulse duration of 500ps and a maximum pulse energy of 150 µJ. The laser operates at a high repetition rate between 1 and 5 kHz.

A compact spectrometer allows to record the spectra in the non-gated mode.The wavelength acquisition range of the spectrometer spans from 180 to 800 nm, i.e. from UV to visible, and its overall resolution is 0.1 nm for the entire spectral range. The whole setup is enveloped in a lightweight handheld body as shown in Fig. 1. The mass and dimensions of this instrument are approximately 1.8 kg and 26x10x30 cm, respectively. A liquid crystal display (LCD) touch screen control panel allows to control the spectrometer and the acquisition settings.For safety reasons, a sensor accompanies the analysis head for automatic control of the laser output.

When operating in the field,NanoLIBS is provided with a rechargeable Li-ion battery that allows more than 5

Fig. 1. NanoLIBS handheld instrument.

hours of operation. Although the analyser was primarily designed to operateas a handheld device using a Linux operating system with graphic user interface (GUI), it can also operate while connected to AC power.

LIBS measurements were carried out by placing the nose of the instrument against a sample and initiating the analysis via a trigger, i.e. a screen icon on the analyser. Data were stored in the analyser and accessed via GUIby downloading via Wi-Fi or Ethernet.

III. RESULTS AND DISCUSSION

Full broadband emission spectra of the superficial deterioration layer, i.e. the black crust, and the bulk underlying limestone wereobtained byaveraging a three-laser shots, which provided the ”chemical fingerprint” [5] of the sample(Fig. 2). The main elements,i.e., Al, C, Ca Fe, K, Mg, Li, Na, Si, Sr, present in the samples (Fig. 2, Table 1) were identified in a short time.

Although the immediate comparison of the two full spectra and their emission lines did not show at first glance any particular differences marked variations of the elemental composition could be observed whenthese specific spectral ranges, i.e. from 220 to 270 nm, from 270 to 310 nm and from 710 to 780 nm were considered(Fig. 3).Fig. 3shows a comparison between the LIBS spectra obtained for the black crust layer and the bulk underlying limestone at different spectral ranges.

The relative emission line intensities in the spectra of the sample confirm the presenceof Ca, C and Mg as the major constituents of the limestone and Si, Al and Feas the main contaminant elements in the black crust, whichare not present in the bulk limestone.

The presence of Al, Fe, Si in the black crust may be originated from atmospheric pollution and particulate deposition, whereas the presence of Na and K may be due to the marine aerosol that pervades the urban area in which the monument is located. The possible source for Sr could be the limestone itself, as Sr is known to concentrate in the hardest part of aragonite (polymorph $CaCO_3$) originated from marine organisms.

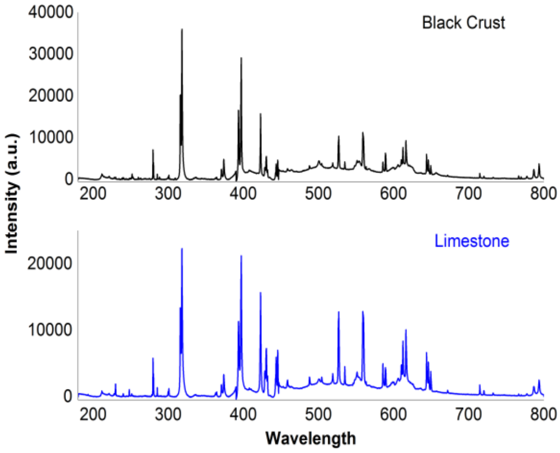

Fig. 2. Full broadband LIBS emission spectra of the superficial black crust (top) and underlying limestone (bottom).

Table 1. Main spectroscopic atomic emission lines of samples examined.

Element	Wavelength (nm)
Al I	308.21; 309.27
C I	193.09; 247.85
Ca I	300.09; 300.68; 428.30; 428.94; 429.90; 430.78; 431.87; 442.55; 534.95; 558.22; 558.89; 559.02; 559.47; 559.87; 560.16; 560.29; 585.74; 671.72; 720.22
Fe II	234.52; 234.81; 235.91; 259.93; 261.18; 274.91
K I	766.49; 769.89
Li I	670.77
Mg I and Mg II	280.98; 285.21 279.55; 280.27
Na I	588.99; 589.59
Si I	288.17
Sr I	460.73

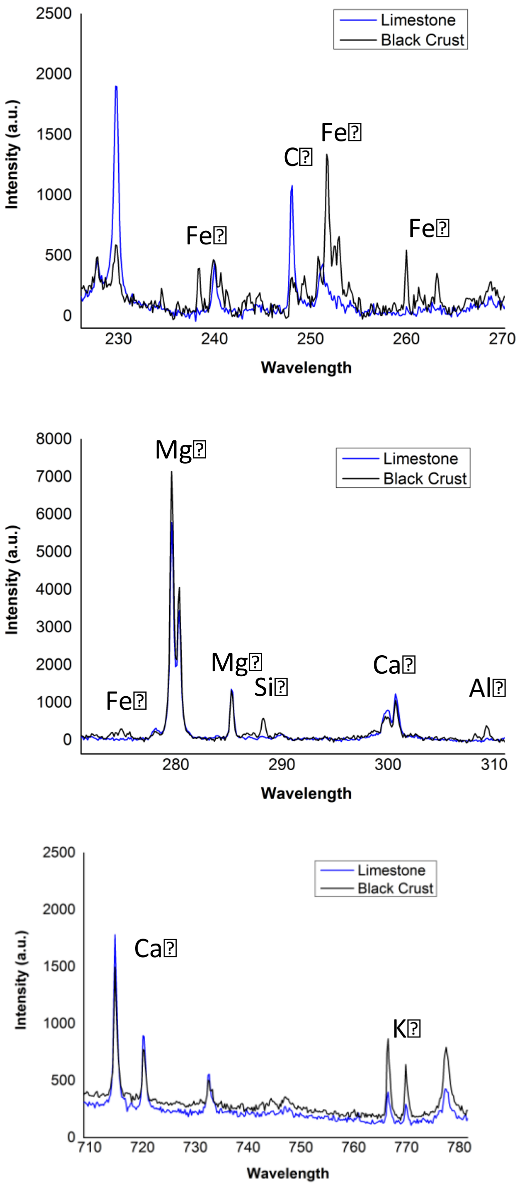

*Fig. 3. LIBS spectra of the black crust and limestoneat three specific spectral ranges,i.e. from*220 to 270 nm,from 270 to 310 nm, from 710 to 780 nm.

IV. CONCLUSIONS

Results of this preliminary study show that the NanoLIBShandheld, commercially available, portable instrument appears to be an effective tool for the rapid elemental analysis of weathered stone monuments, without requiringany sample preparation, and allowing itsuse in conjunction with multivariate statistical processing for geomaterial discrimination and provenance determination. In particular, the main elemental composition of two distinct layers, i.e. the superficial black crust and the underlying limestone rock, could be rapidly identified and discriminated with a high degree of confidence. The use of NanoLIBS handheld instrument in the cultural heritage field is thus particularly promising to perform analysis in-situ, including building monument outdoors, archaeological sites and mural and cave paintings. Further work is presently underway to optimise the technique in order to obtain quantitative analysis of a quality like similar to that ofother analytical techniques, e.g., electron probe microanalysis, and extend the approach to new areas of application.

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