Man-Portable Laser-Induced Breakdown Spectroscopy System for *in Situ* Characterization of Karstic Formations

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This paper reports the development and field testing of a man-portable instrument based on laser-induced breakdown spectrometry (LIBS) for inspection and analysis of speleothems. The 50 mJ of a Q-switched Nd:YAG laser operating at 1064 nm was used to generate a plasma on the sample. Plasma emission was then guided using a fiber-optic cable to a 1/10 m spectrometer equipped with a charge-coupled device (CCD) array detector. Plasma light was automatically processed in order to obtain surface and in-depth information from the speleothems. A field campaign in the interior of Nerja Cave (a large karstic formation in the South of Spain) has been carried out, aimed at evaluating the analytical performance of the instrument when operating in an unfriendly environment. Identification analysis of the speleothems' alteration layers and depth profiles of Sr and Ca is carried out and reported.

Index Headings: **Laser-induced breakdown spectroscopy; LIBS; Man-portable LIBS; *In situ* analysis; Sr-to-Ca ratio; Karst; Alteration layer; Surface analysis; Nerja Cave.**

INTRODUCTION

During the last decade, field analytical instrumentation has become a valuable option when a fast, inexpensive, and *in situ* analytical method is demanded. Applications related to human safety, soil sampling, or quality assessment are prone to be faced with using field analytical instrumentation since these tasks require a near real-time response. This fact has resulted in a great number of works aimed at the design and construction of a large variety of field instrumentation based on gas chromatography,[1,2] mass spectrometry,[3,4] X-ray fluorescence,[5,6] immunoassay techniques,[7] or test kits,[8] among others. The topic has been reviewed elsewhere.[9–12] These reports emphasize the feasibility of using field instrumentation to gather useful information from chemical data and discuss the advantages and the limitations of each of these field chemical analyzers.

These days, laser-induced breakdown spectroscopy (LIBS) has become a truly field-deployable technique.[11–18] Technological advancements in lasers, detection systems, the field of fiber optics, and data processing capabilities permit the construction of LIB spectrometers with most of the desirable features required for a portable instrument: ruggedness, transportability, fast analysis, simplicity, and ease of use.[11,18,19] In general, no significant detriment in analytical capabilities occurs when downsizing. Additionally, LIBS offers valuable characteristics when compared to classical methods, including chemical analysis on a wide range of materials without sample preparation, access to chemical information in real time, and precision and accuracy levels compatible with many real-life analytical problems.

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In a previous report, a portable LIBS instrument[20] was described for analysis of crusts in karstic formations. While field tests demonstrated a satisfactory performance for alteration layer monitoring, the relatively large weight and size of the instrument impeded its use in narrow and tight cave galleries. The present paper describes an advanced man-portable LIBS analyzer for *in situ* chemical screening in areas of geochemical importance such as the Nerja Cave. The analytical capabilities of the instrument in terms of variability of Mg and Sr signal along the axial and radial growing direction of the speleothems and the depth resolution have been assessed and compared with the results obtained when operating under laboratory conditions. For this purpose, identification analysis of minor elemental constituents in different locations inside the Nerja Cave and in-depth determination of strontium-to-calcium signal ratio in speleothems and karstic formations have been carried out. The results presented in this work demonstrate how a man-portable LIBS system could be efficiently used for *in situ* inspections and in-depth characterization of cave formations.

EXPERIMENTAL SETUP

Instrumentation. The schematic diagram of the man-portable LIBS instrument is plotted in Fig. 1. As shown, the overall system consists of a hand-held probe, a main unit, and the laser power supply. The spectrometer and the computer components are enclosed in the main unit, which consists of a specially adapted backpack. Conversely, the laser head (CFR Model, Big Sky Laser, MO) and collection and focusing optics arrangements are housed in the hand-held probe. A fiber-optic cable guides the plasma emission from the probe to the spectrograph (HR2000 Model, Ocean Optics Incorporated, FL). The entire system is controlled wirelessly by means of a hand-held PDA device that permits data visualization as well as control of the spectrometer and the laser parameters. Each of these parts are interconnected by means of an umbilical cable housing the fiber-optic cable, trigger signal cable, I/O, and refrigeration lines among others. These blocks can be easily split, permitting effortless transportation of the instrument separately. Power for the LIBS analyzer is supplied by a portable generator that provides autonomy of several hours.

The hand-held probe encloses a compact laser head and the focusing and collection optics. Figure 1 also shows a detail of a cross-section of the laser head showing the location of the foremost hand-held probe components. The probe consists of two main blocks: the first of them forms the ablation chamber, designed to both hold the focusing and collection optics and to enclose the cavity where plasma is generated. These parts were machined in aluminum, which provides lightness and robustness to each part of the probe. The second block of the probe consists of a nylon structure that encloses the laser head and

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