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Portable instrument and analytical method using laser-induced breakdown spectrometry for *in situ* characterization of speleothems in karstic caves

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A portable laser-induced plasma spectrometer has been developed and tested in the determination of thickness and semi-quantitative composition of alteration layers on the surface of speleothems. The portable instrument consists of a 50 mJ pulse $^{-1}$ Q-switched Nd:YAG laser operating at 1064 nm and a high resolution spectrometer equipped with a 2048-element linear silicon CCD array detector. Its weight and size allow *in situ* analysis in difficult environments or relatively inaccesible places such as caves, avoiding sample collection or extraction. The instrument was evaluated in the interior Nerja Cave (Spain) over soils, rocks and speleothems. The geochemical degradation of these materials has been studied by the portable instrument. Laser-induced plasma analysis reveals the remarkable presence of several elements in the surface of the speleothems, such as Fe, Si, Al or Mn which are absent in non-degraded regions of the speleothem. Composition depth profiles of these elements have been measured in order to evaluate alteration processes in the Nerja Cave.

Introduction

Conservation plays an essential role in areas of geological importance, environmental control being one of the most important tasks to be carried out in sceneries such as tourist caves with a high number of visitors. Several degradation processes may occur in these sceneries involving geochemical and biological processes noticeable as crusts or layers with different coloration and alteration degree. Additionally, human activities carried out inside of these geological formations may have acted as a catalyst in such degradation phenomena. This fact has been the object of a number of experimental studies and reports centered in determining the alteration source and its composition.[1–4]

Nerja Cave, located in the easternmost part of Málaga (Spain), was originated by the dissolution of dolomitic marbles (calcium and magnesium carbonates) dated from the Triassic age. It comprises one of the most important examples of karstic caves in the south of Europe with respect to the amplitude and spectacular nature of its halls with a large variety of speleothems formed by chemical precipitation of carbonates (stalactites, stalagmites, columns or calcitic layers). Their antiquity is estimated as 800 000 years with phases of growth ranging from the medium Pleistocene to today.[5] In addition, cave paintings have been identified along the cave.[6] However, despite being considered as a protected area, this geological formation is not free of the above-mentioned degradation processes. In this sense, since 1960 Nerja Cave is one of the most visited caves, being visited by approximately 500 000 people each year. Indeed, the presence of an alteration layer on speleothem surfaces has been noticed by simple visual inspection. This situation has provoked a particular interest in determining both composition and thickness of observed alteration layers. However, analytical chemistry has to face up to various drawbacks to study this type of situation: first, sampling limitation due to the importance and exclusivity of the samples is required. Thus, a relatively non-destructive and *in situ* analytical technique is required, avoiding collection and, therefore, speleothem damage when sample is collected. Secondly, *in-situ* measurements inside the cave require portable instrument with enough robustness and portability to work in a complex environment.

In comparison with the traditional laboratory techniques, laser-induced breakdown spectrometry (LIBS) offers the possibility of performing rapid and *in situ* measurements besides providing a quasi-non-destructive analysis. As well, LIBS has been successfully applied to a large variety of matrices with different objectives in many situations. Several reports have been published showing LIBS as an appealing technique capable of measuring the thickness of diverse multilayered materials such as metallic coatings[7–9] or solar cells.[10,11] Also, speleothems and geological samples have been studied by LIBS.[12,13] Many studies have been reported involving laser-based cleaning processes in buildings, cathedrals or artworks. LIBS has been reported as an useful technique for the monitoring, cleaning and removal of alteration layers or crusts.[14–16] On the other hand, many efforts have been devoted to demonstrate LIBS as a powerful field technique with the development of a number of portable LIBS instruments in recent years. Contaminated soils, paints or quality assessment have been the objective of these field analyzers.[17–20]

In the present work, LIBS is shown as a promising technique for the *in situ* analysis of crusts in speleothems, avoiding the need of transportation or sample collection. For this purpose an analytical method allowing determination of both semi-quantitative composition and thickness of the alteration layer of speleothems has been developed. The paper reports on the estimation of the ablation rate values and composition depth profiles, as well as the necessary modifications to an already existing portable LIBS instrument previously reported by our group.[17]

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