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Laser-Induced emission, fluorescence and Raman hybrid setup: a versatile instrument to analyze materials from cultural heritage

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Abstract
The aim of this research project was the development of a hybrid system in laboratory coupling together three analytical techniques, namely laser-induced breakdown spectroscopy (LIBS), laser-induced fluorescence (LIF) and Raman spectroscopy in a single instrument. The rationale for combining these three spectroscopies was to identify a material (molecular and elemental analysis) without any preliminary preparation, regardless of its organic or inorganic nature, on the surface and in depth, without any surrounding light interference thanks to time resolution. Such instrumentation would allow characterizing different materials from cultural heritage. A complete study on LIBS-LIF-Raman hybrid was carried out, from its conception to instrumental achievement, in order to elaborate a strategy of analysis according to the material and to be able to address conservation issues. From an instrumental point of view, condensing the three spectroscopies was achieved by using a single laser for excitation and two spectrometers (time-integrated and not time-integrated) for light collection. A parabolic mirror was used as collecting system, while three excitation sources directed through this optical system ensured the examination of a similar probe area. Two categories of materials were chosen to test the hybrid instrumentation on cultural heritage applications (copper corrosion products and wall paintings). Some examples are reported to illustrate the wealth of information provided by the hybrid, thus demonstrating its great potential to be used for cultural heritage issues. Finally, several considerations are outlined aimed at further improving the hybrid.

Keywords : Cultural heritage ; Raman spectroscopy ; LIBS ; LIF spectroscopy ; hybrid

1. Introduction

For a correct safeguarding of cultural heritage, it is essential to understand deterioration’s causes, to characterize the conservation state, and to have knowledge on the life story of the artwork. These cultural-historical questions cannot sometimes be solved by philological and stylistic methods alone. In such cases, the knowledge of its physic-chemical state could help to clarify these issues about the artwork. However, it is a challenge to analyze such materials since they are different (pigments, alloys, organic...), complex (mixed, not homogeneous, altered or weathered), and precious with irreplaceable historic value. As a consequence, the “perfect” analytical technique would be the one which provides as much as information as possible on the characterization of the sample while minimizing the damage in order to guide the more pertinent conservation/restoration decision. The information collected through the physic-chemical state of the material could be elemental, molecular composition, stratigraphic organisation, or quantitative analysis. A single analytical technique will usually provide only one of the information. It is thus common to use several spectroscopic methods in order to get a complete information on the material. However, some difficulties may arise because different analytical methods may require different analysis probe area, sampling and/or preparation of the sample. Moreover, the preparation and the sampling could be considered as “destructive” even if the analysis itself is not, this is why in situ analyses are sometimes more suitable. Therefore, in order to overcome these dilemmas, one could envision a portable hybrid system combining several spectroscopies. However, a remote instrument involves a compact system and so the use of the same excitation and collection optics for the combination of the different analytical techniques. Moreover, the surrounding light in *in situ* analyse should not interfere with the emitted light