

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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COSCH Case Study that has employed this technology: Germolles

Definition

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a high-energy laser pulse as the excitation source. The laser focuses on the sample, which atomizes, excites, and ionizes the material inducing the creation of plasma. The light emitted by the plasma is analysed through a spectrometer. The emission lines are characteristic of each type of atom present in the plasma that enable an elemental identification to be made. In principle, LIBS can analyse any type of matter regardless of its physical state, be it solid, liquid, or gas.

Description

Although LIBS is better known for its industrial applications, this analytical technique can be successfully used for cultural heritage characterization. Many publications have been devoted to the identification of pigments and stones, or archaeological metal characterization (Anglos and Detalle 2014). The conservation of wall paintings is a significant part of our activities at the Laboratoire de Recherche des Monuments Historiques (LRMH) laboratory, which is part of the French Ministry of Culture and Communication. The research has two main directions: the study and identification of materials, including the development of new investigation techniques, and the diagnosis for conservation and restoration.

Dealing with this kind of heritage, we often face very heterogeneous and large surfaces (up to several hundred square metres). Their study requires a corresponding number of samples to be removed from the wall and then analysed in laboratory via “traditional” techniques such as optical microscopy and scanning electron microscopy, coupled with energy dispersive spectroscopy, infrared spectroscopy, or X-ray diffraction. Therefore, the acquisition of knowledge about the

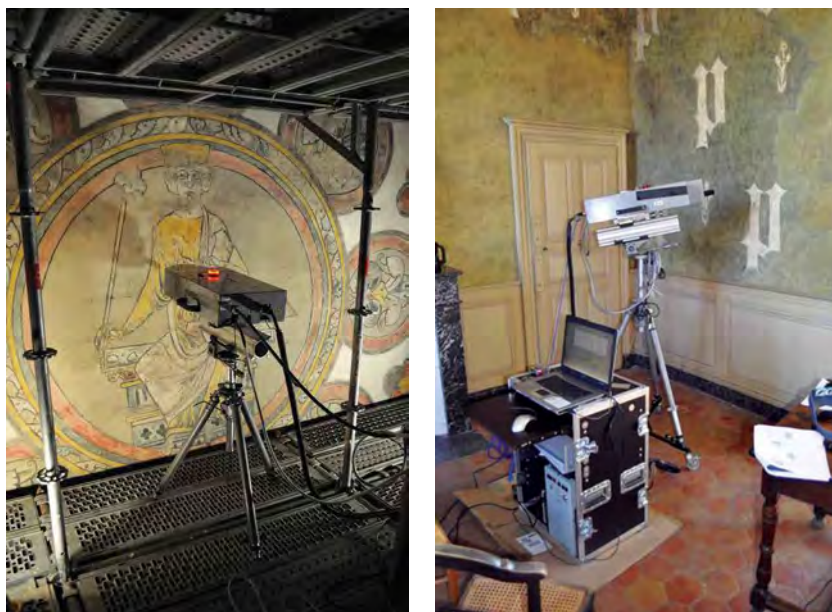


Figure 17.1. LIBS in operation at Chartres Cathedral (left) and Château de Germolles in Burgundy (right). © LRMH, 2011 and 2015.

materials is hampered by lengthy analytical processes in the laboratory. In order to reduce the need for sampling by the selection of relevant areas, and to obtain topographical information about the distribution of materials on the surface, and also to improve the direct understanding of materials, the LRMH has developed over the past ten years a portable instrument for laser-induced breakdown spectroscopy (LIBS) for elemental investigations. In fact most of the materials found in wall paintings are metal oxides or salts, so LIBS appears to be a suitable technique for the identification of both pigments and the products of degradation. Indeed LIBS is characterized by high sensitivity and selectivity and can be performed *in situ*.

The LIBS approach offers new possibilities as it requires neither removal nor preparation of samples and can supply a conservator's particular requests with quick answers, relevant enough to make decisions on condition and treatment. Furthermore, as only a small amount of the sample is consumed in the process of atomization (less than 100 pg depending on the laser energy), this technique is micro-destructive. It is therefore possible to have in-depth access to layers, while other analytical techniques are restricted to the surface. Hence LIBS can reveal stratigraphic information about the multi-layered structures of wall paintings, for example.

LIBS Principle and Portable Setup

LIBS relies on the analysis of a plasma induced by focusing a pulsed laser beam on the surface of a sample. The characteristic light emitted by the excited elements contained in the sample when they settle back to equilibrium is collected via optical fibres and sent to spectrometers. Spectral analysis enables elemental identification and quantification. The portable instrumentation is composed of a 1064 nm Nd-YAG laser, with a 5 ns pulsing time and a maximum energy of 50 mJ/pulse; with a detection system located behind a lens of focal length 100 mm and based on a seven-fibre optical bundle connected to three integrated spectrometers, which cover the range 200–940 nm. The emission spectrum is recorded with an internal 2048 CCD line array detector. The optical fibres are coupled with alignment lights to control the focal spot, placed at a distance of 130 mm from the convergent lens. The laser is controlled by the spectrometer software and pulses are triggered manually, in single shots or in series. The enclosure of the lenses in a rigid case, mounted on a camera tripod with wheels, makes on-site use possible. Figure 17.1 shows the portable system developed by the LRMH in use at two different sites: first on scaffolding in Chartres Cathedral to characterize the thirteenth-century wall painting discovered in 2010; and second during a study of the painting of the Château de Germolles in Burgundy.

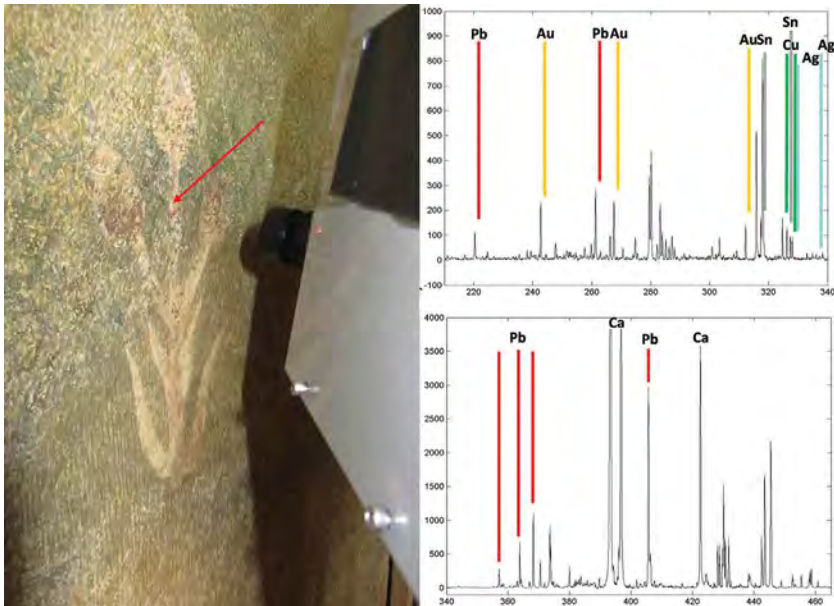


Figure 17.2. Château de Germolles, wardrobe of the Countess of Nevers, north wall, measurement localization and LIBS spectra of the third measurement. © LRMH, 2015.

The LIBS system has been applied *in situ* for many studies of mural paintings and polychromy. For example at the cathedrals of Paris, Strasbourg, Poitiers, Chartres, the papal palace of Avignon (Saint Martial Chapel), and more recently in the Château de Germolles.

The great advantage of the technique is its capability to penetrate inside the material and hence to determine the stratigraphy. Figure 17.2 shows the identification of the painting technique. This measurement is located at the transition of different layers. The top layer is made of gold (Au), then a tin (Sn) foil layer, while copper (Cu) and lead (Pb) were identified on the green background layers. LIBS confirmed these results on many other thistle motifs. The results also indicated that the gold is alloyed with silver.

In conclusion, LIBS as an analytical technique is now well established for *in situ* characterization of material. It is a very good addition to more “classical” analytical techniques such as X-ray fluorescence or diffraction. Its advantages have been demonstrated and its ability to be coupled with other laser techniques, such as Raman spectroscopy and laser fluorescence, will ensure its key role in the future of cultural heritage study.

Reference

Anglos, D., Detalle, V. 2014. “Cultural Heritage Applications of LIBS.” In Musazzi, S., Perini, U., eds. *Laser-induced Breakdown Spectroscopy: Theory and Applications*, 531–54. Heidelberg: Springer. doi:10.1007/978-3-642-45085-3_20.