LASERS APPLIED TO THE STAND-OFF ANALYSIS OF MATERIALS

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Since its inception, the laser has occupied a privileged position in the development of science. Its characteristics have become the laser in an indisputable element, responsible for the development of analytical techniques such as laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy, being, perhaps, one of the main advantages of these analytical techniques the possibility of their applications as stand-off sensing analytical techniques.

LIBS

Laser-induced breakdown spectroscopy uses the light of a pulsed laser proper focused on a very small area to generate plasma of the material on which the beam impinges. After the event in a series of physicochemical processes, emissions from excited species found in the plasma can be detected and analyzed by atomic emission spectroscopy. The information provided by the technique is a spectrum based on the emissions, mainly atomic, of all the elements which compose the material.

The proper processing of the signals provides qualitative information, which makes it an ideal technique for the characterization and identification of solid samples. The relationship between signal intensity and concentration of the element responsible that signal raises up, allows the use of the technique for quantitative analysis by using a calibration method with the appropriate standards.

LIBS sensor showed in Figure 1 employs a Nd:YAG laser emitting in the fundamental state (1064 nm) thus providing to the sample an irradiance value higher than 1 Gw/cm^2.
The laser pulse is focused on the target using a Cassegrain telescope (open-truss class) which, at the same time, permits to collect the light emitted from the plasma and focused it on the tip of an optical fiber. This optical element guides the light up to a spectrometer where it is dispersed by using a diffraction grating. Next, light dispersed in their wavelengths is detected by using an intensified CCD (charge-coupled device) camera.

Figure 1. Photograph of the LIBS sensor for stand-off analysis of materials.

RAMAN

Not only as a consequence of the advent of lasers but also with the subsequent arrival of more sensitive detectors, Raman spectroscopy has found a wider scope.

The Raman effect, described in detail in the Figure 2, occurs when a beam of monochromatic light interacts with the electron cloud of the bonds of a molecule causing a deformation of this cited cloud with respect to the vibrational coordinate (the shift in the molecular polarizability or the appearance of new frequencies with a certain offset from the frequency corresponding to the incident radiation -Rayleigh frequency-).

The system used for the analysis of materials based on Raman spectroscopy is depicted in the Figure 3. This sensor exhibits a biaxial and static configuration based on a Nd:YAG laser source emitting at the second (532 nm) harmonic.

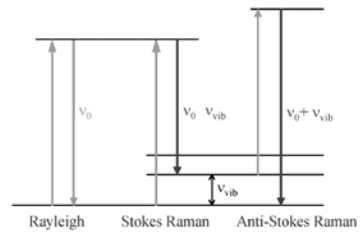

Figure 2. Description of the Raman effect.

The scattered radiation is collected by using a Cassegrain telescope which permits to focus the light onto the tip of an optical fiber to conduct it up to a spectrometer. By using a diffraction grating scattered radiation is first dispersed and then detected with an intensified CCD camera.

Raman spectroscopy provides highly specific vibrational information (molecular and structural) from all those different chemical bonds which are present in the molecule.

Thus, this analytical technique generates a particular molecular fingerprint of the molecule which can be identified. The spectral region of the fingerprint cited above spans from 500 cm^{-1} up to 2000 cm^{-1}.

Figure 3. Photograph of the Raman sensor (also configurable for LIBS) used for the analysis of materials at a distance and view of the experimental corridor (50 meters total length).

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RAMAN-LIBS

The fact that Raman spectroscopy (molecular data) and of laser-induced plasma spectroscopy (atomic data) share almost the same instrumentation has attracted, in recent years, a great interest in the combination and / or fusion of both techniques in a single sensor in order to obtain either sequentially (after defining an appropriate hierarchy of action) or simultaneously, qualitatively different but, at the same time, obviously complementary information from the same target.

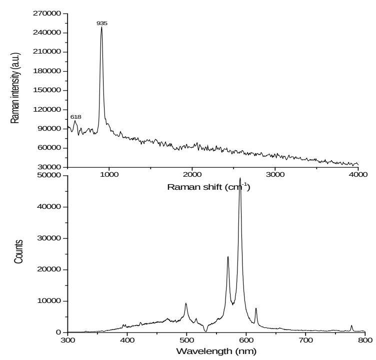

Figure 4. Raman spectrum (top) and LIBS spectrum (bottom) of sodium chlorate ($NaClO_3$) simultaneously obtained at a distance of 20 m.

Advantages

The possibility of analyzing samples that do not require any prior preparation, as well as their applicability for analysis at a distance, are a pair of relevant advantages which make LIBS and Raman techniques the unique two analytical methodologies capable of providing information about targets exhibiting a limited accessibility for the operator or those that may endanger the physical integrity of the analyst.

Objectives

Are priorities of this research line:

- The development and the adjustment of analytical methods and strategies for the detection, using laser techniques, of residues of explosives in order to identify the existence of potential threats at real time.
- Research, development and optimization of chemometric algorithms and strategies to satisfactorily resolve the information derived from such cited analysis.

Applications

Among the large number of fields of application of these techniques, we can highlight:

Analysis of cultural heritage

- This application is intended not only for the qualitative and / or quantitative detection of the elements that may compose the piece in question (thus generating a compositional fingerprint), but mainly also to conservation and restoration tasks. Laser cleaning is a promising technique of conservation that can be used for the removal of surface layers of architectural and historic buildings.

Analysis of energetic materials

- One of the most demanding applications today is linked to the research and the development of new solutions for security and defense areas, in particular, those related to the recognition (detection and discrimination) of explosive residues at a distance.