

LIBS development and Applications for Nuclear Material Analysis

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Abstract – Laser Induced Breakdown Spectroscopy (LIBS) is a powerful technique for determining the elemental composition of materials based on measuring line emission from excited ions and neutral atoms in a transient laser-produced plasma. Nearly all the elements, even the light ones, can be simultaneously analysed at atmospheric pressure and without any preparation, or with limited sample preparation [1, 2]. Able to perform fast and remote analyses, it looks quite well suited to analyzing nuclear materials. The presentation will first deal with the general aspects and characteristics of the technique. Examples of representative applications developed by CEA for the nuclear industry will be presented. Emphasis will be made on remote analyses and on microanalyses LIBS capabilities. As remote analysis is concerned, analytical results on samples isolated into glove boxes or hot cells will be discussed. Other results obtained with a specific LIBS system designed for onsite measurements during decommissioning of nuclear installations will also be presented. As microanalysis is concerned, the microprobe LIBS instrument developed by CEA will be described and results of high resolution chemical mappings of simulated MOX nuclear fuel will be presented.

INTRODUCTION

The basic principle of the LIBS technique consists in focusing the beam of a pulsed laser onto the surface of the material to be analyzed in order to create a plasma (Figure 1). Excited ions and atoms emit characteristic optical radiation as they revert to lower energy states. Detection and spectral analysis of this optical radiation using a sensitive spectrograph can be used to yield information on the elemental composition of the material (Figure 2). The analysis is fast since usual LIBS systems enable to perform few tens of measurements per second. Furthermore, progresses on laser technology should considerably increase these values, and systems working at few kHz are now described in the literature.

As an all-optical technique, LIBS is quite well suited to in-situ remote analysis [3]. This characteristic is particularly interesting when one deals either with toxic or radioactive materials confined inside a gloves box or into hot cells. Moreover, focusing the laser beam onto a small area allows to perform microanalysis at atmospheric pressure, with limited sample preparation. Measurements can be performed at atmospheric pressure, under vacuum or under pressures of few tens of atmospheres. Indeed, developments at CEA are underway in order to be able to analyze high pressure – high

temperature aqueous liquids or solids immersed in this medium.



Figure 1: Schematic of LIBS plasma generation

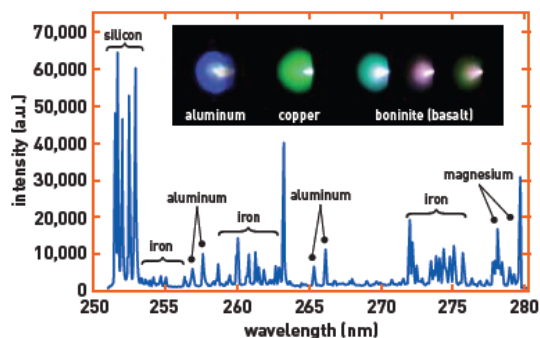


Figure 2: LIBS plasmas and optical emission spectra, leading to chemical element identification.

Any type of material can be analyzed : metallic or dielectric solid, liquid, aerosol, or gases, without any need of preparation. Most of the chemical elements, even the light ones as hydrogen can be analyzed with detection limits of few ppms (parties per million) [4].

Usually, quantitative analysis becomes possible as soon as a calibration curve is performed using reference samples (Figure 3).

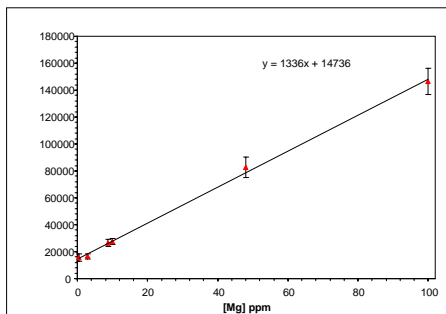


Figure 3 : calibration curve : Mg 285,2 nm in Al matrix, measured with 'OFILIB' system

Under the hypothesis of local thermal equilibrium conditions and considering an optically thin plasma whose atomic composition is representative of the sample composition, the measured line signal intensity I_λ of a given element corresponding to the transition between two energy levels E_j and E_i can be expressed as

$$I_\lambda(t) = k_\lambda N(t) A_{ij} \frac{g_i e^{-E_i/k_B T(t)}}{U_{T(t)}}$$

where k_λ is an experimental factor which depends on the experimental apparatus and on the measurement conditions, N the number of specific emitting atoms in the plasma, A_{ij} the transition probability for the given line, g_i the i level degeneracy, λ the wavelength of the transition, k_B the Boltzmann constant, T the plasma temperature and $U_{T(t)}$ the partition function at the plasma temperature [5]. **Source du renvoi introuvable.**

Matrix effects can occur, leading to a variation of the total number of emitting atoms and a variation of the plasma temperature. To overcome such effects, normalization procedure can be performed, by using different methods like internal standardization by a reference line

[6], or a calibration free method based on modelling of the plasma emission [7].

Developments carried out in our lab, are concerned with various types of applications, ranging from microanalysis and chemical mapping to remote stand off analyses, in the field of materials investigation in a hostile environment. Dedicated LIBS instruments are commercialized by IVEA [8], a start-up licensed by CEA and AREVA (Figure 4).



Figure 4: Transportable LIBS system

DESCRIPTION OF THE ACTUAL WORK

LIBS Microanalysis

Using a microscope objective, the laser beam can be focused onto a few micrometers square area. Combined with synchronized motorized stages, the system is able to perform automatic spot by spot analysis at ambient pressure. The spot size can be adjusted from 3 to 10 microns, depending on the required lateral resolution [9].

Compared with usual techniques of microanalysis, like Electron Microprobe Analysis, the main advantages of LIBS lie on its ability to perform fast multi elemental analysis at atmospheric pressure, without any vacuum chamber, with very limited sample preparation. Moreover, the sensitivity of detection of elements does not depend on the acquisition repetition rate, and both speed of measurement and simplicity of use make LIBS particularly attractive for such applications, as measuring the homogeneity of non-metallic materials (nuclear fuel, for instance), or measuring diffusion profiles in clays and cements intended for nuclear waste disposal.

Interest of the technique has been demonstrated for the analysis of simulated Ce-U Mox pellets.

Quantitative surface analysis is possible after calibration, and, as shown on Figure 5, the results are in excellent agreement with Electronic Microprobe, the reference technique for quantitative microanalysis.

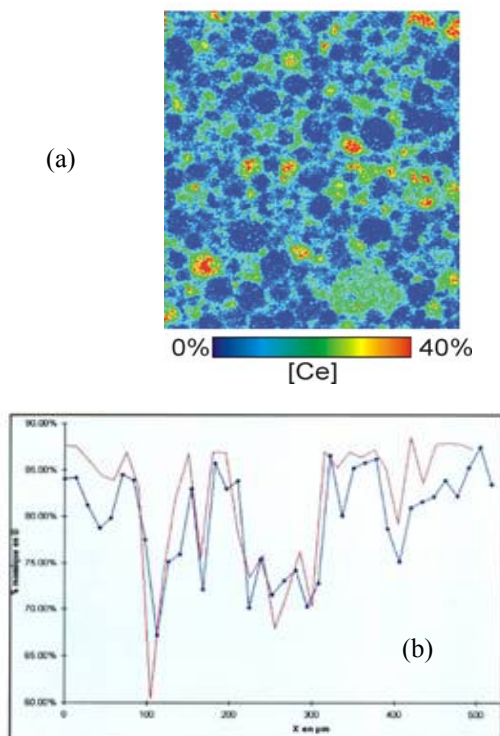


Figure 5: (a) distribution of Ce in a simulated MOX fuel pellet and (b) comparison of Uranium profiles obtained with LIBS and Electronic Microprobe

Another application of the LIBS microprobe under study in our lab is the diffusion of chemical elements, which is assumed to be the main transport mechanism governing radionuclides migration through a porous soil formation. Most of the results on the transport parameters in those media are usually obtained using through diffusion techniques on samples at a centimetric scale assuming homogeneous soil properties.

Using LIBS microprobe, looking at a cross section of the sample, it is possible to measure the local concentration of chemical species from the sample surface to the core. As presented on Figure 6 for Eu, the diffusion profile obtained can be well fitted with an erfc function (continuous line) using parameters like the effective diffusion coefficient, the retardation

factor and an overall medium porosity determined by through diffusion techniques. Moreover, the LIBS experimental profile shows peaks above the mean erfc profile which correspond to high local concentrations of both Eu and alumino-silicates phases illustrating local heterogeneity of the sample and preferential retention sites.

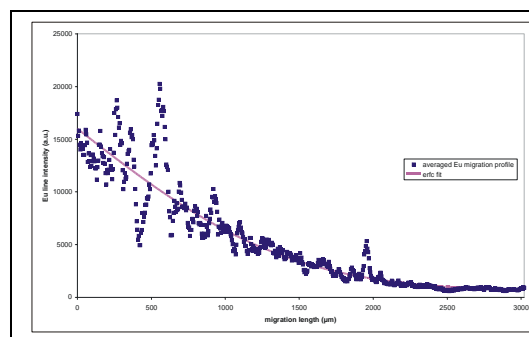


Figure 6: Eu diffusion profile measured by LIBS microprobe and erfc fit.

Another very important advantage of using LIBS instead of classical methods is the very small diffusion length required (mm typically), leading to a strong reduction of the duration of diffusion experiments (about one week instead of several months).

Remote Analysis

In-situ remote analysis is concerned, in particular, with materials hard to handling, whether because they present a potential hazard, or because measurement of these materials is meaningful only if they remain in their physical-chemical environment. The applications addressed by current research work, at CEA, concern, in particular, in situ measurement of the composition of molten salts being investigated for nuclear fuel reprocessing by the pyrochemical path, in situ measurement of aerosols in a high-temperature, high-pressure helium circuit, simulating the cooling circuit in a gas-cooled nuclear reactor, in-situ measurements of aqueous liquid medium contained in pressure-sealed cell simulating the chemistry of nuclear vessels.

LIBS Analysis of molten salts

Molten salt reactors represent one of the concepts selected in the investigations being carried out, on an international footing, on 4th-generation nuclear reactors. They offer the advantage of allowing continuous extraction and recycling of the minor actinides and plutonium generated during reactor operation. In the front-end research being carried out, some investigations concern the chemical partitioning operations used in that process, such as liquid-liquid extraction using molten metal. Research on these processes entails carrying out a multiplicity of elementary chemical analyses, in harsh environment such as high temperature (around 900 °C), and chemical aggressiveness of certain materials, such as alkali halides, or alkaline earths, making sampling an arduous operation. LIBS is thus being investigated for the purposes of enabling in situ analysis, i.e. directly inside the furnace. The laser beam is focused onto the surface of the liquid being analyzed, through a window, ensuring confinement, and radiation emitted by the plasma is analyzed along the same axis. The advantage of this method was first demonstrated in inactive laboratory conditions, with a lanthanide dissolved in a molten LiF–AlF₃ salt, at 900°C, and subsequently on the basis of a model allowing performance simulation, generalized for the various elements and salts being considered.

As presented on Figure 7, a LIBS system is now operational in a glove box in the Atalante facility. The demonstrated versatility of this technique will allow online monitoring of reductive liquid-liquid extraction process as well as analysis of solid salt or metal samples. Further testing will now be performed in Atalante before proceeding with analysis of radioactive samples.



Figure 7: Device installed in glove box

Aerosol LIBS analyses

The LIBS technique is also being considered in the context of experimental investigations being carried out on high-temperature, gas-cooled reactors. In particular, research workers are planning to equip with this technique a dedicated test loop, used to investigate coolant fluid purity, to carry out in situ analysis of particles carried along by the gas, and thus to control, in real time, the effectiveness of filtration systems, or to monitor possible component degradation during trials. Pressure and temperature conditions, namely several tens of bars in helium gas at temperatures ranging from 850 °C to 1,000 °C, mean taking representative samples is a highly problematic operation. LIBS will provide the means for release from this requirement, with the analysis being carried out in situ, directly inside the piping, through a window. The two main issues to be dealt with are minimum density of detectable particles, and particle size [10]. In practice, it is feasible to set up an illumination system that generates a plasma in the gas phase, for every laser firing. Particles entering this plasma are atomized, emitting a characteristic spectrum. The interaction volume to be considered is thus the volume of plasma, which typically stands at around 10⁻³ cm³, with a lifetime of about one microsecond [11]. With no laser synchronization to assume that, statistically, every laser firing will result in detection of one particle, particle density must be higher than 10³ particles/cm³. Below this value, the number of useful laser firings decreases proportionally with density, resulting in an increased required measuring time, to detect one particle spectrum. To avoid measurement time becoming prohibitive, at low particle densities, particles passing in the gas vein must be detected through measurement of the scattering on a laser beam probe, and synchronizing LIBS laser firing with these events. Detection efficiency, in that case, is much higher, since it is related to the number of particles passing through the volume of plasma, per unit time, i.e. to the product of particle density by the flow rate for the carrier fluid. Minimum size, for detectable particles, is determined in turn by the minimum amount of matter required to yield a usable LIBS signal. Experience shows this amount ranges from 10⁻¹⁵ grams to 10⁻¹² grams, depending on the chemical element. For single-element particles, this means minimum detectable size typically lies in the 0.1–1µm bracket. At the other end, large particles may equally be a problem. Indeed,

signal processing is based on the assumption that the entire particle is vaporized as it interacts with the plasma. This assumption does not hold true for particles that are too large (of a size greater than a few microns). Investigations were aimed, in particular, at achieving a better understanding, and control, of the experimental parameters that are of influence, in order to develop adequate instrumentation, meeting the requirement, and demonstrate it exhibits performance compatible with the goals being sought.

LIBS analyses inside high pressure liquid

LIBS in-situ analysis of solids immersed in aqueous medium under high temperature and pressure conditions would be very interesting for chemists since it would make it easier to perform chemical studies of deposition-entrainment phenomena inside nuclear loops. Nevertheless, the creation of the plasma becomes difficult, because of the high density of liquid compared to gas medium. So two laser beams have to be used [12]. The first pulse creates a bubble in the high pressure liquid, and inside this bubble the second pulse creates the analytical plasma (Figure 8). Present studies in our lab concern the optimization of experimental parameters and design of the instrumentation for LIBS measurements at pressures ranging from few to two hundred bars. Detection limits of few ppms are for example obtained on Na at 200 bars.

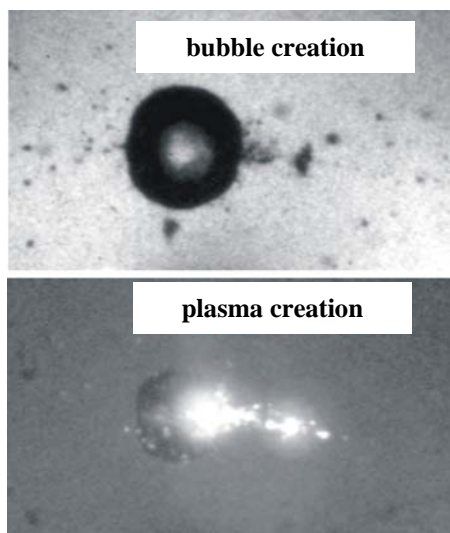


Figure 8: 1st pulse, creation of the bubble
2nd pulse, creation of the plasma

LIBS device for elemental analyses during decommissioning nuclear installations

Regarding its easy to use and fast analysis capability, LIBS can be a useful technique to detect contaminated surfaces inside nuclear hot cells. A specific low volume and weight LIBS head has been developed by CEA and the French IVEA company for this application (Figure 9). This set-up, is made of two parts connected with two few meters long optical fibers. The first part includes the laser beam unit, the spectrometer, the computer which controls the acquisition and enables to analyze the spectra. The second one, the optical head, enables to focus the laser beam from the optical fiber onto the target, and to collect the light of the plasma back to the spectrometer through the second optical fiber. This system has been shown to work properly and quantitative measurements were made using lanthanides to simulate contaminated surfaces. Very good results were obtained, with limits of detection as low as 10 pg, of Sr deposited on steel sample. Experiments inside hot cells are under study and should be performed in 2009.



Figure 9 : portable OFILIBS system

CONCLUSION AND PERSPECTIVES

LIBS is an emerging field deployable analytical technique adapted to a wide range of industrial applications. Its characteristics are particularly well suited to in-situ remote analysis of hazardous material like radioactive samples.

The research work performed at the laboratory scale already demonstrates the potential of the technique for many applications of primer importance for the nuclear industry. Thanks to the development of new compact and portable laser sources and spectrometers, commercial instruments are now under development and will allow an extended use of the technique.

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