Chapter 7
Recent Advances in the Investigation of Textiles Using Laser-Induced Breakdown Spectroscopy (LIBS)

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ABSTRACT

Textiles were documented via several traditional wet chemical analysis and other spectroscopic techniques, like flame-based inductively coupled plasma atomic emission spectroscopy (ICP-AES) and flame optical emission (OE) spectroscopy. These techniques were applied for accurate investigation studies like forensic duplication check of documents and others. Unfortunately, these methods are considered distractive methods, and unsafe in the use of aggressive chemicals. The last problems encourage scientists to seek a safe and non-destructive method like LIBS. In the spectrochemical analysis based on LIBS technique, a pulsed laser beam is focused on a target material, then a breakdown of the sample occurs, and eventually results in the formation of a transient and highly energetic plasma. In this chapter, a review describes in detail the use of LIBS as an elemental analytical technique for the determination of elements in field applications in documentary identifications, whether for forensic or archaeology applications.

INTRODUCTION

A variety knows the same methodology of names in the scientific community: LIBS (laser induced break down spectroscopy), also referred to as LIPS (laser induced plasma spectroscopy), LAS (laser ablation spectroscopy), LSS (laser spark spectroscopy), or LAOES (laser ablation optical emission spectroscopy), is a technique that is based on the spectral analysis of the radiation emitted by a plasma created by focusing an intense laser pulse on the sample. In spectrochemical analysis based on the LIBS technique, a high-powered pulsed laser beam (usually >1-10 MW /cm^2)) is focused on a target material,

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then a breakdown of the sample occurs and eventually results in the formation of a transient and highly energetic plasma. After each pulse, the cooling of the plasma produces electron recombination and atom de-excitation. LIBS spectra can be detected once the plasma continuum emission is almost extinguished. Time-resolved capability is necessary to discriminate the late atomic line emission from the early plasma continuum. High-resolution spectral analysis is required to detect single emission lines, i.e. the spectral signatures of each element. Once assigned to specific transitions, atomic or ionic emission lines allow for qualitative identification of the species present in plasma. At the same time, their relative intensities can be used to quantitatively determine the corresponding elements (Elsayed et al., 2022). Moreover, LIBS, as an elemental analytical technique, does not require preparation and has been extended during the past two decades over a very wide range of analytical applications (Sawaf & Tawfik, 2014). Simultaneous multi-element analysis of metals, liquids, and biological and environmental samples are among such numerous practical applications (Tawfik & Sawaf, 2014; Berman & Wolf, 2016). Among the applications of LIBS, elemental composition analysis of metallurgical samples has been most popular because the LIBS technique has an inherent capability of direct solid sample analysis without any laborious chemical preparation. However, recent applications are more inclined to diversify analytical samples, such as silicon wafers, paint, rock, polymer, soil, and mineral (Lee & Sneddon, 2002) (Aslam Farooq et al., 2013). Specifically, the feasibility of LIBS for space exploration has been demonstrated by analyzing documentary identifications for forensic or archaeology applications.

BASICS OF LIBS

LIBS Theory

In LIBS, the external energy source is laser light, which impinges on the ground-state atoms. Light emitted from the excited sample is spectrally (and sometimes temporally) resolved to yield qualitative and quantitative information on the elemental constituents of the sample (Sawaf and Tawfik, 2014).

Theoretical understanding of some aspects of the plasma generation and heating, such as the laser sample and the laser-plasma interactions, is crucial for adequately describing the laser ablation process. Considering the laser-sample interaction dynamics, which under normal working conditions, has the effect of vaporizing and atomizing a small region of the sample surface, thus resulting in the production of a hot plume consisting of both the ejected material and the atmospheric plasma (Alonso-Medina, 2019). During this interaction, the sample and the generated plasma absorb the laser beam energy. Moreover, several phenomena are responsible for the back reflection of the radiation, electron emission, sample heating and phase changes, all affecting the physical properties of the plume in a way peculiar to the sample composition (Caneve et al., 2006). Once formed, the plasma is usually assumed to reach a condition of local thermodynamic equilibrium (LTE) in a proper temporal and spatial observation window. Upon these conditions, a Boltzmann population distribution can be assumed in describing the actual thermodynamics parameters of the plasma. If re-absorption effects are negligible (i.e., the plasma is optically thin and the primary ionization process is produced through impact excitation by thermal electrons), the spectrally integrated line intensity, corresponding to the transition between levels E_k and E_i of the atomic species α with concentration C_α, can be expressed as