Chapter 1

Laser Induced Breakdown Spectroscopy-An Overview
Chapter 1

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS), also called laser-induced plasma spectrometry (LIPS), or laser spark spectrometry (LSS), is an analytical technique based on atomic emission spectroscopy (AES), for simultaneous multi-elemental analysis. It utilizes high-energy laser pulses to create a high-temperature micro-plasma at the surface of the target, which acts as the emission source.

Conventional atomic spectroscopic techniques like inductively coupled plasma optical emission spectroscopy (ICP-OES), ICP-mass spectroscopy (ICP-MS) and Atomic Absorption Spectroscopy (AAS) are good in analytical performance, but their sample preparation method is destructive and time-consuming. Compared to these methods, LIBS has numerous advantages such as simplicity in the experimental setup, no or minimum sample preparation, practically non-destructive analysis of sample (only nano-micro-grams of sample layers are affected) and possibility of remote/in situ analysis. This chapter gives an overview of some other popular spectroscopic methods for qualitative and quantitative analysis, namely X-ray fluorescence (XRF), mass spectrometry, absorption methods (UV-VIS absorption of complexes of metals), optogalvanic (Laser Enhanced Ionization), emission spectroscopy etc., and comparison of LIBS with these techniques.
1.1. INTRODUCTION

Recent advances in material science have led to special emphasis on the search for new, improved, techniques with good sensitivity and high depth resolution for direct analysis of samples. There are various techniques available for trace element analysis. No technique alone can solve all problems associated with analysis of trace elements. Depending on the specific case of measurement, analyst has to choose between different complementary methods. Most commonly used techniques for trace element analysis are atomic absorption spectroscopy, X-ray fluorescence, Neutron activation analysis and mass spectrometry. Each technique comes with its own advantages and disadvantages. Below we discuss the salient features of some of the important methods for elemental trace analysis and compare them to Laser Induced Breakdown Spectroscopy (LIBS).

1.2. ANALYTICAL TECHNIQUES FOR ELEMENTAL TRACE ANALYSIS

1.2.1 Laser Induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy, a well-developed analytical method is gaining popularity recently for trace, minor and major components analyses. It is based on plasma formation on the surface of the samples by means of focused laser pulses. Plasma consists of excited atoms and ions of the elements in the sample. Light emitted from plasma is spectrally analyzed under suitable conditions of time delay to give the emission spectra. There have been extensive studies and several new developments of the LIBS method that are reported. The main advantage of the LIBS technique is that it can be used for direct chemical analysis without laborious chemical preparation provided there is optical access to the sample. The method has a very high sensitivity and the detection limits can be of parts per million (ppm) or even lower ranges.

Dr. James Winefordner, a world-renowned analytical spectroscopist, described LIBS as “a future super star” in a 2004 review article (1, 2). LIBS is uniquely identified as the only technology that can offer distinct spectral signatures characteristic of all chemical species in all environments. LIBS can be used to
chemically characterize samples like, rocks, glasses, metals, sand, teeth, bones, weapons, powders, hazardous materials, liquids, plants, biological materials, polymers, etc. Moreover, LIBS can be performed at various scenarios like atmospheric pressure, in a vacuum, at the depths of the ocean, or at extra terrestrial sites. LIBS can respond in less than a second, using a single laser shot, remotely, to indicate if a spilled white powder is innocuous or hazardous. Samples need not be fluoresce, Raman or infrared (IR) active for performing LIBS, which is a unique characteristic of this method. LIBS method is so simple that it has a diversity of applications; as simple as striking any sample with a pulsed laser beam and measuring the distinct optical spectrum. The laser beam initiates formation of tiny, luminous plasma from ablated sample mass. The chemical species in the sample is represented by the Plasma spectrum; spectral data analysis provides the chemical species composition and relative abundance. Because a pulsed laser beam initiates the LIBS plasma, there is no physical contact with the sample; laboratory and open-path standoff applications are readily employed. The LIBS phenomenon represents a well organized engine to convert the chemical information of the target material to light information that can be captured efficiently and analyzed thoroughly by modern spectroscopic instrumentation and data analysis software (2).

Laser-induced plasma was observed soon after the invention of ruby laser in 1960. In 1962, Brech and Cross demonstrated the first useful laser-induced plasma on a surface (2, 3). Debras-Guedon and Liodec published the first analytical use for spectrochemical analysis of surfaces in 1963 (4, 5). In 1964 Maker et al reported the first observation of optically induced breakdown in a gas (6). J.R Novak et.al discussed the laser photolysis and spectroscopy in 1968. They developed a technique that is hundred times faster than present flash spectro-graphic instrumentation and provides time-resolved absorption spectra over a wide spectral range in a single experiment (7).

Different detection systems to obtain temporally resolved spectra were used in the 1960s, including a streak camera and rotating mirrors. As detectors have been developed, the preferred methods of time resolution have moved from boxcar averager, for example, to gated, intensified charge coupled detectors. Fast photo
detectors are also used to record the temporal profile of plasma emissions from single pulses.

In the late 1980s interest increased in making LIBS more quantitative by addressing factors such as differential excitation. These included many works from the Niemax group (8, 9). In the study by Ko et al, the stability of internal standardization was investigated (8). As the field progressed into the 1990s, there was a rapid development of applications and fundamental studies. The application of LIBS to remote analysis was developed in 1990s. It was a significant area of investigation by Cremer’s group at Los Alamos, who discussed remote elemental analysis by laser-induced breakdown spectroscopy using a fiber optic cable (10). LIBS for the analysis of lunar surfaces were first mentioned by Blacic et al (11). This was followed by a seminal paper by Knight et al. on characterization of LIBS for planetary exploration (12). Efforts to make LIBS more quantitative continued. Davies et al reported on relevant factors for in situ analytical spectroscopy in the nuclear industry in 1996 (13). In 1998, Winefordner’s group at the University of Florida initiated studies of the variables influencing the precision of LIBS measurements. Their first publication in this area was by Castle et al, where a variety of factors was considered and inter- and intra- short measurement precisions were calculated. The best precision obtained was 0.03 % (14).

In 1999, Ciucci et al. (15) developed a procedure called calibration-free LIBS (CF-LIBS). In this method, one assumes thermodynamic equilibrium, and uses spectral lines representing the bulk of the vaporized material, to deduce the concentration of the element of interest. These results have sharpened the focus on factors that can enhance the ability to obtain quantitative results.

In order to study the bacterial spores, molds, pollens, and proteins, A C Samulels et al. used LIBS (16). Using filamentation in air Stelmazczyk et al. in 2004, demonstrated a long distance, remote, LIBS technique, (17). They demonstrated the remote LIBS from a distance of 90 meters, which can be extended up to kilometer range. This was done by the technique based on filamentation induced by the nonlinear propagation of unfocused ultra short laser pulses. F. Colao et al. reported
the comparison of single and double pulsed LIBS (18). Their results suggest that the
use of double pulse technique could significantly improve the analytical capabilities
of LIBS technique in routine laboratory experiments. In the following year, a paper
was published by Kuwako A et al, which discusses the analytical use of double pulse
LIBS in liquids (19) and showed double pulse LIBS can be used to detect sodium
(Na) in water.

Later on, studies focused to improve the quantitative analysis capability of
LIBS and the detection of hazardous materials. Onge et al., in 2002, discussed the
quantitative analysis of pharmaceutical products by LIBS (20). Their results illustrate
the strengths of LIBS for fast on-line assessment of the reliability of pharmaceutical
manufacturing processes. The detection of explosive residues on solid surfaces were
demonstrated by C Lopez-Moreno et al. in 2005 (21); in this experiment the detection
and characterization of explosive materials at distances up to 45 m was demonstrated
using stand-off laser induced breakdown spectroscopy. Detection of Bacteria by time-
resolved LIBS has been done by Stephen Moral et al. in 2003 and Baudelet et al. in
2006 (22, 23). These works show the potential of LIBS for analysis of Bio Hazardous
materials.

Recently, Fantoni et al (24) have done a review on different methodologies of
laboratory based for LIBS semi-quantitative and quantitative analysis. It was inferred
from their study that, a proper selection of experimental conditions, for laboratory
data acquisition is required in order to minimize many problems like laser target
coupling, matrix effect, local thermodynamic equilibrium assumption and
interferences from additional air ionization etc, both in case of calibration curves and
 calibration free approaches.

LIBS studies have been conducted in the direction to assess preservation
quality of archeological bones (25). Calcium-to-fluorine (Ca/F) signal ratios at the
surface of the bone were determined for this purpose using LIBS. In order to identify
explosives, Moros Javier and Laserna Jose Javier (26), proposed an approach for the
combination of the spectral outputs of Raman and LIBS sensors (data fusion strategy)
in order to obtain knowledge about the identity of compounds better than that
achieved when each technique acts independently. Also, LIBS has been performed to detect trace metal elements (Ca and Mg) in aqueous solution. In order to overcome the sensitivity drawbacks in liquid sample analysis, Dehua Zhu and co-workers (27) used an absorbent paper as the sample support in their experiment. Shi Huan et al have studied LIBS in water for the measurement of heavy metal (Ni) with a limit of detection of 0.28mg/L (28). Ferreira et al have done evaluation of LIBS technique in soils under sewage sludge application for multielemental determination (29).

Extensive work has been done recently to improve the LIBS instrumentation and data processing techniques. Undoubtedly the greatest impact was achieved by the introduction of the compact echelle spectrograph combined with the ever-more capable CCD and ICCD detectors. A comparative study of non intensified and intensified CCD detectors for LIBS has been done by Carranza et al (30). The results show that intensified CCD system provided enhanced signal-to-noise ratio compared with non-intensified CCD system. The performance of laser-induced breakdown spectroscopy (LIBS) has been evaluated for detection of toxic metals such as Cr in water by N K Rai et al (31). Pure aqueous solutions (unitary matrix) with variable Cr concentrations were used to construct calibration curves and to estimate the LIBS limit of detection in this study.

New areas of study include extension of observation to the vacuum ultraviolet region (32, 33). Biological applications on human teeth, bones and tissue are becoming more common (34-37). Pollen, spores and bacteria are being studied to see if unique signatures can be determined (16). Surface mapping and imaging modes using line sparks are proving useful to determine surface compositional variations (38). Sophisticated statistical techniques are being applied to extract signals and reliability factors (39-42). Unnikrishnan et al have assembled and optimized a LIBS system with an echelle spectrograph-ICCD detector combination, for multi elemental analysis (43).

Very recent studies show that LIBS is a new way to analyze the plant ecology (44). Xu Zhang and co-workers have done trace element analysis in leaves using LIBS and suggested that this technology can be employed for food safety and
environment pollution evaluation (44). An overview of recent progress and future potential biomedical applications of LIBS by Rehse et al (45) reveals many possibilities in this direction. LIBS has been transformed from an elemental analysis technique to one that can be applied for the reagentless analysis of molecularly complex biological materials or clinical specimens.

1.2.2 Atomic Absorption Spectroscopy (AAS)

AAS is used to determine the concentration of an element in a solution. Under normal conditions the atoms exist in stable energy states known as stationary states. We refer to their lowest state as the ground state. The energy of the atom is measured relative to its ground state, taken as zero energy state. By adding external energy (eg. thermal energy) an atom is raised to higher energy states, or excited states. This change in energy is written as $\Delta E$. According to the laws of quantum mechanics the atoms do not go to excited states gradually, but go directly from one state to another in a quantum jump. The transitions from ground state to the excited states require some form of energy input, for example, radiation, collision with high energy particles like electrons etc. Conversely, when an excited atom goes from an excited state to a lower state, the excess energy $\Delta E$ is released as a photon. Each transition for a given element will have a specific $\Delta E$, different from other transitions of that element as well as transitions of other elements. The relationship between the energy transitions and the wavelength of the emitted photon is given by $\Delta E = hc/\lambda$ where $h$ is the Planck’s constant. Atomic absorption uses this relationship to determine the presence of a specific element.

In AAS, the sample that is contained in the solution is sprayed into a flame by means of a nebulizer. At the relatively low temperature of the flame most of the sample atoms exist in their ground state and they can be promoted to any excited state by absorbing photons of wavelength corresponding to the transition. The usual source of photons in AAS is a Hollow Cathode discharge lamp of the element under study, which provides narrow emission lines. The light from the source lamp is sent through the sample in the flame. The atoms in the flame absorb some of the light if the element corresponding to the hollow cathode emission is present in the flame. The
initial and final intensities of a suitable line are measured using a monochromator-PMT detector system. A calibration curve is prepared by plotting absorption against concentration for known concentrations. Knowing the absorption, concentration of the element in the sample is then read from this curve (46).

The AAS method, though very sensitive (nano-grams/ml of solution), has several drawbacks. It requires extensive sample processing to get it in solution, and many times, need additional purification to eliminate possible chemical interference. As such, no in situ/remote (As is-Where is) analysis is possible. Also solution sampling means in situ layer analysis can be done only by layer-by-layer dissolution, which is a tedious process. Only one element at a time can be analyzed and multiple elemental analyses require use of large amounts of sample and considerable time. It is an absorption method, where a small change in a large signal has to be measured when concentrations are very low. This usually limits the sensitivity.

1.2.3 X-Ray Fluorescence (XRF)

X-ray Fluorescence is another technique for analysis of trace elements. The source X-rays of several thousand electron volts energies are produced in an X-ray tube. The X-rays are directed at the “sample” causing excitation of the electrons of elements in the sample to very high energy levels. The relaxation of the excited atoms to lower levels produces X-rays that are characteristic of the elements. The intensities of the characteristic X-rays of an element will be proportional to the concentration of that element. By preparing suitable reference standards, a calibration curve can be prepared and concentrations can be read from this curve. Multi-element analysis of samples is possible in this method using an X-ray monochromator. The detection limit for most of the elements is a function of sample quality and is between 1 and 50μg/L (parts per billion). This method is useful in elemental trace and microanalysis such as for biomedical/pharmacological problems. The detection system is cumbersome and suitable sample preparation is needed (47). The fact that the excitation beam of X-rays has to be close to the sample precludes analysis in places where the X-ray source cannot be located. Once again, layer-by-layer analysis is difficult.
1.2.4 Neutron Activation Analysis

Neutron activation analysis is an analytical technique based on the measurement of characteristic gamma rays emitted by the radioactive isotopes of the various elements in the sample, produced by irradiation with thermal neutrons (48). After irradiation, the gamma energy spectrum produced by radioactive decay, is measured by counting the gamma ray photons with a high resolution detection system. Neutron activation analysis provides highly resolved analysis of elemental composition by identification of characteristic gamma rays associated with different isotopes. Quantitative analysis is provided by comparison of the number of gamma ray photons emitted per unit time. To produce characteristic gamma rays both unknown samples and standards of elements of interest are irradiated from a few nanoseconds to eight hours in a nuclear reactor. Each sample has its own characteristic gamma ray spectrum, which can be compared to the spectra of standards and quantitative analysis can be performed. Elemental concentrations in nano-grams can be determined in Neutron Activation Analysis. The advantage of this method is that it is nondestructive and there is no need of special sample preparation. But the technique needs a nuclear reactor to provide the required neutron flux, which elevates the cost of setup, and also makes it available only to limited groups. Obviously, the technique is not suitable for remote/in situ analysis.

1.2.5 Mass Spectrometry (MS)

Mass Spectrometry is based on an entirely different principle compared to the other spectroscopic methods. The physics behind mass Spectroscopy is that a charged particle passing through a magnetic field is deflected perpendicular to the field, in a direction normal to its velocity and these results in a motion along a circular path on a radius that is proportional to the mass to charge ratio (m/e). For the analysis, the different atoms/molecules in the sample are first ionized by a suitable method, like electron impact ionization with a high energy beam of electrons, in a high-vacuum system. The ions are then accelerated into the magnetic field and deflected along the circular paths according to their masses. By adjusting the magnetic field, the different species of ions can be focused on to the detector and their number recorded (49).
Since ion detectors are sensitive to even single ions, Mass spectroscopy is extremely sensitive. Sample processing is also a minimum. However, since the atoms have to be supplied to the system in high vacuum conditions, the system has to be equipped with pumping module, magnet systems etc., and remote\textit{in situ} analysis is difficult.

The Mass spectrometer can be coupled to various systems (for example, an inductively coupled plasma source) for supply of the sample in a suitable vapor form. With a laser ablation setup, this allows layer-by-layer analysis, and imaging across a surface.

\textbf{1.2.6 Laser Enhanced Ionization (LEI)}

Relatively new entrants in the field of trace element detection are laser based techniques. The properties of laser beams like high monochromaticity, very good collimation, tunability over reasonably wide range, and high energy, make them highly attractive for various applications. The two major laser based approaches are laser induced breakdown spectroscopy (discussed earlier) and laser enhanced ionization where the laser is used as the excitation agent.

Laser enhanced ionization (LEI) in flames was pioneered in 1976 by a group at NBS, Washington DC and today it is one of the most sensitive methods available for trace analysis. The detection limits are generally in the parts per million (ppm) or less. LEI setup has been found to have high sensitivity (50). The basic principle of LEI is based on what is known as the optogalvanic effect, which is the change in electrical impedance of a medium containing the sample in gaseous form (e.g., a discharge, furnace, or a flame) when illuminated with radiation, which can alter the number distribution of charged particles in the medium. In the technique the analyte element contained in a sample is first transferred into a state of free atoms by heating in a discharge, flame or furnace. The population of excited state is then increased by exciting the atom with resonant laser light. A fraction of the excited atoms is subsequently ionized by collisions with surrounding atoms and molecules. This ionization is monitored by applying an electric field over the interaction region and by measuring the increase of the electric current. The LEI signals are seen as change in
impedance in the medium, and are proportional to the concentration of the species
which gets excited by the laser radiation.

The collection of the current is by the electrodes that are placed close to the
flame. In principle this setup is able to detect trace elements with high sensitivity. The
advantage of this technique is that since laser is used as the excitation medium it is
possible to selectively excite any element in the sample by tuning the laser
wavelength. Since the number of background ions before excitation in the low
temperature source will be very small, even small changes in impedance can be easily
measured and the sensitivity of the technique is thus quite high.

The advantages and disadvantages of some of the trace analysis techniques are
clear from above discussion. Table 1 shows a comparative evaluation of different
elemental analytical techniques in comparison to LIBS.

Table 1 A comparative evaluation of different elemental analytical techniques

<table>
<thead>
<tr>
<th>Parameter</th>
<th>XRF</th>
<th>LA-ICP-MS</th>
<th>LIBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating principle</td>
<td>High-energy X-rays knock off inner-shell electrons. Relaxation of outer-shell electrons to vacant positions causes emission of characteristic X-rays.</td>
<td>Laser photons ablate(remove) material from the sample surface. Sub micrometre-sized particles are transported into the inductively coupled plasma followed by mass spectrometry detection.</td>
<td>Laser photons induce breakdown on the sample surface. Deionization radiation at UV and visible wavelengths is characteristic of elemental composition.</td>
</tr>
<tr>
<td>Sample penetration</td>
<td>~100 μm</td>
<td>~80 μm (user controlled)</td>
<td>~50–100 μm (user controlled)</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>100 p.p.m. (0.01%)</td>
<td>&lt;1 p.p.m.</td>
<td>10–50 p.p.m.</td>
</tr>
<tr>
<td>Precision</td>
<td>Fair-good</td>
<td>Excellent</td>
<td>Fair-good</td>
</tr>
<tr>
<td>Accuracy</td>
<td>Semi quantitative</td>
<td>Quantitative</td>
<td>Semi quantitative</td>
</tr>
<tr>
<td>Analysis time</td>
<td>Very slow</td>
<td>Slow</td>
<td>Fast</td>
</tr>
</tbody>
</table>
1.3. ADVANTAGES OF LIBS

LIBS has been evaluated as an alternative method to other conventional plasma atomic emission spectrometric techniques. In recent years, LIBS has developed as a versatile elemental analysis tool which attracted enormous attention, owing to its broad range of applications. The technique can be used to analyze a variety of classes of samples, namely, industrial, environmental, agricultural, physiological and so on, without the need for any special sample pre-processing (52-57). Some of the features that make LIBS attractive are:

- rapid elemental analysis (one measurement per laser pulse)
- no prior sample preparation
- simultaneous detection of a number of elements (high and low Z)
- low detection limits (micro/nano gram levels)
- detection capability of micron size area/thickness and
- possibility of in situ/ remote analysis

With the tremendous advances in industrial developments that encompass thermal and nuclear power related activities, automobile industries, extensive use of fertilizers, advanced technology related materials (semiconductors), etc., the environment is being contaminated by numerous pollutants (58). Many of these highly toxic pollutants are reported to be initiators/causative factors of many types of diseases (59). For example, there is a 1000 fold increase in the Zn and Pb levels in urban air of major US cities as compared to the rural levels (60). Many of such pollutants, e.g. Ni, Cr are indicated as causative agents for major diseases such as cancer (61). The elements such as Zn, Cu, are essential nutrients, their deficiency

<table>
<thead>
<tr>
<th>Sample consumption</th>
<th>Non-destructive</th>
<th>Almost non-destructive</th>
<th>Almost non-destructive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complexity</td>
<td>Easy to use</td>
<td>Complicated</td>
<td>Very easy to use</td>
</tr>
<tr>
<td>Discrimination</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
</tr>
</tbody>
</table>

XRF: X-ray fluorescence and LA-ICP-MS: laser ablation inductively coupled plasma mass spectrometry (51)
causing major diseases (62). Currently, the synergism between the trace metal elements in the body and in the environment and its impact on human health evokes considerable interest. It is also known that the effectiveness of complex drugs in therapy is deterred by the presence of heavy metals due to their ability to interact and form complexes with the drugs. Hence, it is imperative to detect the presence of heavy metals in the human body (e.g. circulatory system) for deciding an efficient therapy. For this reason, assessment of the correlation between trace elements in living systems and in the environments is crucial. As mentioned earlier, the trace elements are nutrients for human health and play an important role in many biochemical processes. However, above threshold level, these trace elements can induce toxicity in humans (62). The versatility of LIBS technique for simultaneous multi-element analysis and its applicability in different phases of matter (solid, liquid and gas) find its use in quantifying the concentration of pollutants in water, soil etc (55-57, 63-69). Toxic elements that emanate from nuclear and industrial wastes require storage in controlled environments where they should not leak into areas inhabited by living beings. Continuous monitoring of the surroundings of such establishments has thus become a necessity. Remotely operated LIBS systems can carry out such monitoring even under extreme hostile conditions (10, 17). It may be mentioned here that such remote operated LIBS systems can even be employed for planetary surface studies in space exploration (53, 70, 71).

1.4. REFERENCES

5. J. Debras-Guédon and N. Liodec, "De l'utilisation du faisceau d'un amplificateur a ondes lumineuses par émission induite de rayonnement (laser à rubis), comme source énergétique pour l'excitation des spectres d'émission des éléments," CR Acad. Sci 257(1), 3336 (1963)
Chapter 1

Chapter 1


