An Introduction to Laser-Induced Breakdown Spectroscopy

how it works

Laser Spark Spectroscopy (LASS), Laser-Induced Plasma Spectroscopy (LIPS) or, as it is more often known, Laser-Induced Breakdown Spectroscopy (LIBS) is a form of atomic emission spectroscopy in which a pulsed laser is used as the excitation source. The basic principle is illustrated in the schematic diagram. The output of a pulsed laser, such as a Q-switched Nd:YAG, is focussed onto the surface of the material to be analysed. For the duration of the laser pulse, which is typically 10 nanoseconds, the power density at the surface of the material can exceed 1 Gigawatt per cm² using only a compact laser device and simple focusing lenses. At these very high power densities, a fraction of a microgramme of material is ejected from the surface by a process known as laser ablation and a short-lived but highly luminous plasma with instantaneous temperatures reaching 10,000°C is formed at the surface of the material. Within this hot plasma, the ejected material is dissociated into excited ionic and atomic species. At the end of the laser pulse, the plasma quickly cools as it expands outwards at supersonic speeds. During this time the 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.

![LIBS spectrum obtained from gold ore](image)

Laser spark on a solid surface

Laser spark on a liquid surface

Laser spark in a gas
various admixtures such as sludges, slurries, ores, waste irrespective of its physical state. Solids, liquids, gases and able to perform elemental analysis of any material, the material is typically less than 1 Watt. In principle, LIBS is of the sample is negligible as the average power incident on process, LIBS is regarded as virtually non-destructive. Heating As only a minute amount of material is consumed in the time, LIBS can still be successfully applied to samples that are not coolable. This can be seen in the following spectra where the characteristic technetium emission lines reach maximum intensity with a detector delay of 10 microseconds.

virtually non-destructive analysis of any material

As only a minute amount of material is consumed in the process, LIBS is regarded as virtually non-destructive. Heating of the sample is negligible as the average power incident on the material is typically less than 1 Watt. In principle, LIBS is able to perform elemental analysis of any material, irrespective of its physical state. Solids, liquids, gases and various admixtures such as sludges, slurries, ores, waste material and effluents have been successfully analysed.

remote analysis capabilities

Because LIBS is essentially an all-optical technique, only optical access to the material is required to carry out an analysis. This may be achieved by a direct line-of-sight method using one of our LSA T-Series telescope instruments for distances of up to about 10 metres or alternatively with one of our LSA F-Series optical-fibre probe instruments for distances of up to about 100 metres. These features make LIBS a particularly attractive solution for analysis of hazardous or high-temperature materials, or for deployment in hostile environments.

[Diagram of LIBS technique]

[Table of the elements]

Time-gated detectors are employed which allow the optical emission from the laser plasma to be recorded at some time delay after the laser pulse. This is important since the characteristic atomic and ionic emission lines only start to appear after the plasma has expanded and cooled. This can be seen in the following spectra where the characteristic technetium emission lines reach maximum intensity with a detector delay of 10 microseconds.
no sample preparation necessary

LIBS is able to analyse a material directly without the need to prepare the sample beforehand. Should the sample material be coated with another material (e.g., oxidised or painted steel), the laser radiation may be used to first clean the surface of the sample in order to expose the underlying material to allow chemical analysis to be carried out. The efficiency of the laser cleaning process depends upon the type of material being removed and the power of the laser. As a general guide oxide, oil or paint layers of several hundred microns can be quickly removed using a compact and relatively low-power laser. The acoustic shock-wave of the laser plasma is particularly effective at removing the semi-liquid or viscous materials such as sludges. For example, LIBS has been used to analyse metals coated in several centimetres of magnesium hydroxide sludge.

quantitative measurements of minor elements

The LIBS instrument may be calibrated to perform quantitative measurements of minor elements within a matrix material; examples being chromium in steel, magnesium in aluminium alloy, iron in glass, copper in copper sulphate solutions. Calibration is achieved using matrix-matched certified reference materials containing various amounts of the analyte to be measured. A process known as “internal standardisation” is usually employed in which the intensity of the analyte line is ratioed with that of a matrix emission line; this helps to minimise the effects due to changes in plasma conditions caused by shot-to-shot fluctuations in laser energy. Good analytical performance can be achieved with careful design of the LIBS hardware and the use of appropriate measurement methodology. The measurement sensitivity of LIBS depends on many factors including the analyte / matrix combination and the distance over which the LIBS instrument is to operate should remote analysis be required. Measurement accuracy and precision of better than 10% and 5% respectively is possible; typical detection limits for the elements are given in the periodic table.

Typical detection limits for LIBS

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic Number</th>
<th>Mass Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>He</td>
<td>2</td>
<td>4.003</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>10</td>
<td>20.1797</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>18</td>
<td>39.948</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>36</td>
<td>83.80</td>
</tr>
<tr>
<td>Xenon</td>
<td>Xe</td>
<td>54</td>
<td>131.29</td>
</tr>
<tr>
<td>Rhenium</td>
<td>Rn</td>
<td>86</td>
<td>222</td>
</tr>
</tbody>
</table>
In many cases, only one laser pulse is needed to analyse a material, allowing a large number of samples to be rapidly identified. This, together with the non-contact nature of LIBS, is important in applications such as the recycling of scrap metals, alloys or plastics where it can be used to identify a large number of particles moving at high speed on a conveyor belt. No other material analysis technique can match the performance of LIBS in this area.

**depth-profiling of layered structures and surface coatings**

Since the laser may be used to remove surface coatings in a controlled manner, depth-profiling of layered structures is possible with LIBS. Spectroscopic measurements may be performed as the laser “drills” into the material, providing information on the elemental composition of the material as a function of distance into the layered structure.

Generally, this technique is effective only for materials that are relatively easy to ablate using laser powers typical of a LIBS instrument. Examples include compositional analysis of zinc coatings on steel for process control during manufacture, detection of heavy metals (lead, uranium, plutonium) in paint and detection of elemental contamination in concrete.

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