In this chapter, the principle of laser-induced breakdown spectroscopy is presented. The intention is to give an overview of the main parameters of the method, which will be discussed in more detail in Chap. 3. By means of a typical setup of an analyzing device based on LIBS, the important instrumental components are introduced. These components are the subject of Chap. 4. In Sect. 2.3, the single steps of an analysis are introduced.

2.1 Principle and Measuring Parameters

The principle of laser-induced breakdown spectroscopy is shown schematically in Fig. 2.1.

A pulsed laser beam is focused onto the surface of a substance to be analyzed, see (1) in Fig. 2.1. Radiation energy is locally coupled into the material (2) and the material starts to evaporate (3). Within this material vapor and the surrounding gas atmosphere a plasma is generated (4), leading to the excitation of the material constituents and their spontaneous emission of radiation. The plasma decays and emits element-specific radiation (5)–(7). This emission is resolved spectrally and is detected by a spectrometer. For solid substances, a crater is formed finally (8). The evaporated material is removed partially from the interaction zone driven by the intrinsic dynamics of the plasma expansion and by an externally impressed gas flow.

The process denoted in phase (3) as “evaporation” is a simplified description and refers to solid inorganic substances. In general, there is no pure sublimation from the solid phase to the gaseous phase. Depending on the laser parameters – e.g., the pulse duration – and the material properties a transient liquid phase may also exist. Besides the evaporation and dissociation processes also particles are ablated, e.g., small particulates or droplets, which are ejected due to the impact of the pressure exerted by the plasma and the accompanying shock waves on a melt layer [2.1]. For organic substances, the initial material is disintegrated, fragmented, and dissociated.
The life time of the plasma depends on the laser beam parameters chosen, the conditions of the surrounding gas atmosphere, and the substance to be analyzed. The life time lies typically in the range of 0.5–10 μs. The whole process depicted in Fig. 2.1 can be repeated with frequencies of 10 Hz up to 1 kHz (see Chap 15, Sect. 15.3).

Figure 2.2 shows schematically some of the measuring parameters and the spectrum emitted from the plasma. The measuring parameters will be described in more detail in Chap 3. The incident laser irradiance $I_{\lambda L}^i(t)$ at the wavelength $\lambda_L$ is a function of time (the spatial dependence is not discussed here). The temporal structure of the laser pulse has a decisive influence on the generated plasma states and hence the emitted spectrum, see also Sect. 3.2 and Chap. 6. The quantity $\Delta s$ describes the position of the beam waist of the laser beam in relation to the sample surface for a solid or a liquid measuring object. A part of the incident irradiance of the laser beam is reflected by the sample and the plasma in the backward direction, and the other part is scattered in various directions. These intensities are denoted with $I_{\lambda L}^r$ and $I_{\lambda L}^s$. Besides the irradiance $I_{\lambda L}^i(t)$, the ambient gas pressure $p_g$ and the type of the ambient gas have an influence on the plasma dynamics (see Sect. 3.5).
2.1 Principle and Measuring Parameters

Fig. 2.2 Schematic illustration of some measuring parameters and the emitted spectrum; LB = incident laser beam, S = sample, BW = beam waist, $I_{\lambda_1}(t)$ = irradiance of the incident laser beam, $I'_{\lambda_1}(t)$ = reflected laser irradiance, $I'_{\lambda_2}(t)$ = scattered laser irradiance, $p_g$ = ambient gas pressure, $\Delta s$ = beam waist position, $j$ = emission line of an analyte, $r$ = emission line of a reference line, $t_{\text{delay}}$ = delay time between the laser pulse and the start of the integration window to record the spectrum, $t_{\text{int}}$ = width of the integration window.

Fig. 2.3 Schematic illustration of the emission spectra of the laser-induced plasma for different time delays with respect to the irradiation of the laser pulse.

and Chap 7). The emitted spectrum of the plasma $I_{\lambda}(t)$ is also a function of time. Figure 2.2, bottom right, shows schematically a spectrum detected at a time $t_{\text{delay}}$ with respect to the irradiation time of the laser pulse and integrated for a duration of $t_{\text{int}}$.

During the life time of the plasma the emission spectrum changes. Figure 2.3 illustrates schematically emission spectra of the laser-induced plasma for three different time delays after the irradiation of the laser pulse. At the time $t_1$, the plasma emits predominantly a continuous spectrum, caused by free–free transitions of electrons. Only small peaks of the line intensities of atoms and ions are visible, and the ratio of the peak intensity of an emission line to the neighboring intensity of the spectral continuum emission is low. At the time $t_2$, the plasma has cooled down and the intensity of the line emission, as well as the ratio peak intensity to continuous
background, increases significantly. At \( t_3 \), the plasma temperature decreases further and the emission intensities decrease.

Figure 2.4a, b illustrates the incident laser pulse and the plasma emission at an element-specific wavelength \( \lambda_i \) as a function of time. Experimental investigations have shown that the time delay between the rising of the laser pulse and the rising of the plasma emission is small being in the order of \(< 1\text{ns}\). Hence, in the following paragraphs we can assume that the signals shown in Fig. 2.4a, b start simultaneously, see dashed vertical line. This start time is defined as the reference time for the delay time \( t_{\text{delay}} \). The variation in time of the plasma emission at an element-specific wavelength shown in Fig. 2.4b reveals different signal components. The full width at half maximum (FWHM) \( \tau_1 \) of the first maximum lies typically in the range of 40–500 ns. This peak is attributed to the strong continuum emission of the plasma in the early phases (corresponds to \( t_{\text{delay}} = t_1 \) in Fig. 2.3). After this first generally distinct maximum, a further temporal variation is observed characterized by a significantly greater time scale. In many cases, e.g., for atomic lines with upper energy levels around 3 eV, a second maximum occurs, whose FWHM \( \tau_2 \) is between 2 and 10 \( \mu \text{s}\). This signal component represents the element-specific line emission to be evaluated for LIBS.

The following measurands are used for LIBS:

(a) The intensity of the plasma emission at discrete wavelengths as a function of time is: \( I(\lambda = \lambda_i, t) \), where \( \lambda_i \) denotes a set of wavelengths of element-specific lines (for simplicity of notation the index \( \lambda \) at the quantity \( I \) to denote

\( \begin{align*}
\text{a) } & I(t) \\
\text{b) } & I(\lambda = \lambda_i, t) \\
\text{c) } & I(\lambda = \lambda_i, t) \\
\end{align*} \)

**Fig. 2.4** Schematic illustration of the temporal variation of: (a) laser pulse, (b) plasma emission at an element-specific wavelength \( \lambda_i \). \( I(\lambda = \lambda_i, t) \) = intensity of the plasma emission at the wavelength \( \lambda_i \); \( \tau_1, \tau_2 \) = FWHM times of the two signal components. (c) Gate signal defining the position and duration of the integration window; \( t_{\text{delay}} \), \( t_{\text{int}} \) = cf. Fig. 2.2
the spectral intensity is omitted). Usually this signal is integrated over a time interval \([t_{\text{delay}}, t_{\text{delay}} + t_{\text{int}}]\).

(b) A spectrum, which is integrated over a time interval \([t_{\text{delay}}, t_{\text{delay}} + t_{\text{int}}]\):

\[
S(\lambda) = \int_{t_{\text{delay}}}^{t_{\text{delay}} + t_{\text{int}}} I(\lambda, t)\,dt
\]

with \(t_{\text{delay}} = \) start of integration interval with respect to the start of the laser pulse and \(t_{\text{int}} = \) temporal width of the integration window.

The measurands (a) and (b) are used for the quantitative determination of the chemical composition of a substance. As a rule this composition is described by the concentrations of the chemical elements expressed as the mass of the analyte in relation to the total mass using the unit g/g or \(\mu\text{g/g}\) for traces. For higher concentrations, the unit m.-\% is used in the following expressing the mass percentage of an analyte. For quantitative measurements, the method has to be calibrated using reference samples to determine the functional dependence between the measurands and resultant quantities on the known concentrations of a set of reference samples, cf. Sect. 11.2.

Figure 2.5 illustrates the procedure for a quantitative measurement. The left diagram shows a spectrum \(S(\lambda)\) with a number of emission lines depending on the composition of the sample to be analyzed. The spectral position of the lines has to be allocated to the respective elements on the basis of literature data as, e.g., those given in [2.2, 2.3]. The height of a line is a measure of the concentration of the respective element in the sample. However, this line intensity depends also on a number of other factors, e.g., the laser pulse energy, plasma temperature, plasma size, atomic parameters of the line transition, sample surface, detector response function. Generally, the influence of these factors can be reduced by taking the ratio of the intensity of an analyte line \(j\) to the line intensity of a dominant element \(r\) of the sample, a so-called matrix element cf. (11.2), (11.3). This line acts as an internal standard or reference. To gain quantitative results, the spectral signals have to be calibrated using a set of samples with known chemical composition, e.g., certified reference samples (CRM). Figure 2.5, right, shows a calibration curve where the intensity ratio \(I_j/I_r\) is plotted as a function of the concentration \(c_j\) of these reference samples. In general, the calibration curve shows a nonlinear behavior. For an unknown sample, the intensity ratio \(I_j/I_r\) is measured, yielding the concentration of the analyte via the analysis function (also called working curve) which is the

![Fig. 2.5](image-url)
inverse function of the calibration curve (for simplicity, this step is illustrated by the arrows in Fig. 2.5, right). The procedure for quantitative measurements will be described in more detail in Chap 11.

2.2 Setup for Laser-Induced Breakdown Spectroscopy

Figure 2.6 shows the principle setup for laser-induced breakdown spectroscopy. A mirror guides the pulsed laser radiation to a focusing lens. The sample to be analyzed is placed in a measuring chamber. As a rule the incident direction of the laser radiation is oriented perpendicularly to the sample surface. The focused radiation generates a plasma at the sample surface. The emission of this plasma is observed in a direction, which includes an angle $\alpha_0$ to the incident direction of the laser radiation. In Fig. 2.6, the measuring radiation is transmitted via a fiber optics to a spectrometer, where it is spectrally dispersed and converted to electrical signals.

The measuring chamber is gas tight. Laser radiation and measuring radiation are transmitted via built-in windows. Via gas fittings the type of gas filling as well as the gas pressure and gas exchange rate can be adjusted in a defined manner. A translation stage moves the sample in relation to the incident laser beam to measure at different locations on the sample surface.

The use of a measuring chamber is not a necessary precondition for laser-induced breakdown spectroscopy. For inline analyzing tasks, the measuring chamber is often set aside and the measurement is performed under atmospheric conditions. In this case, the usable measuring radiation is limited to wavelength greater than 190 nm, since air absorbs shorter wavelength strongly (cf. Sect. 3.5). For quantitative measurements with high requirements on measuring precision and uncertainty, a measuring chamber is used to adjust the ambient gas conditions and the gas exchange at the interaction region in a defined way.

![Fig. 2.6 Setup for laser-induced breakdown spectroscopy](image)

**Fig. 2.6** Setup for laser-induced breakdown spectroscopy; M = mirror, L = focusing lens, W1 = window of the laser radiation, C = measuring chamber, P = laser-induced plasma, S = sample, A = translation stage, G = gas fitting, $\alpha_0$ = observation angle, W2 = window for the measuring radiation, FO = fiber optics, D = detectors
A control unit triggers the laser and reads the signals of the detectors. To improve the signal-to-noise ratio the plasma radiation is recorded only during the life time of the plasma. For this purpose, the spectrally dispersed radiation is detected time resolved and integrated over a time gate within the life time of the plasma. The control unit adjusts the position and duration of that time gate (cf. $t_{\text{delay}}$ and $t_{\text{int}}$ in Fig. 2.4).

Figure 2.7 shows schematically the arrangement of components in an analyzing system based on LIBS. The sample is positioned on a sample table. The laser beam is focused onto the bottom side of the sample. The sample table can be set into rotation, whereby the rotational axes and the optical axes of the incoming laser beam are parallel and shifted laterally. Due to this eccentricity, a relative motion between sample and laser beam occurs, where the locations of laser irradiation lie on a circle. By this a spatial averaging is realized (cf. Sect. 3.6). Sample table and measuring chamber are parts of the so-called sample stand (cf. Sect. 4.6).

Figure 2.8 shows a view of an analyzing system. The sample stand can be seen on the left side at the top of the system.

**Fig. 2.7** Arrangement of components in a LIBS-based analyzing system; T = sample table, S = sample, ST = sample stand, FO = fiber optics, G = gas supply, D = detector, M = mirror

**Fig. 2.8** Analyzing system based on LIBS. *Left*: sample stand
2.3 Measuring Procedure

A measuring procedure comprises the following steps:

1. Definition of a measuring method or retrieval of a measuring method which was already defined. Putting the sample on the sample stand
2. Start of the measurement
3. Evaluation of the spectral signals
4. Display of the measuring results

A measuring method is defined in particular by the selection of measuring parameters and their temporal sequence, cf. Sect. 11.1. Measuring parameters are, e.g., the laser pulse energy, the number of prepulses and measuring pulses, and the gas flow in the measuring chamber. These various parameters influencing the measuring process will be discussed in more detail in Chap. 3.

A typical measuring sequence for a quantitative analysis of a sample including data evaluation takes about 30 s–2 min. For an identification testing of work pieces, inspection times of a few seconds or even fractions of a second are achievable, cf. Chap. 18.

2.4 Applications and Methodical Extensions

Laser-induced breakdown spectroscopy is a versatile tool to analyze solid, liquid, or gaseous substances. Figure 2.9 illustrates the different possibilities of applications and methodical extensions of LIBS. The configuration described so far is shown in item 1. The laser beam is focused onto a solid sample. By translation of the sample in a direction perpendicular to the optical axis of the irradiated laser beam the sample surface is scanned to obtain a spatially resolved information about the chemical composition. By this approach maps of element distributions can be gained, cf. Sect. 18.3. The laser beam can be guided via fiber optics to a measuring head and then be focused to analyze a liquid (item 2 in Fig. 2.9). Analysis of, e.g., liquid steel by LIBS will be described in more detail in Sect. 13.1.3. The laser beam can also be focused through a window into a closed tube to analyze aerosoles or gases, see item 3 (cf. Sect. 14.6.). A methodical extension is the combination of LIBS with separation techniques such as capillary electrophoresis (CE) or high-pressure liquid chromatography (HPLC), see item 4. In this case, a molecule-specific separation is followed by an element-specific analysis to improve speciation analytics of smallest amounts of complex samples, cf. Sect. 14.5. LIBS can be combined with other laser spectroscopic methods such as laser-induced fluorescence (LIF), see item 5. In a first step, a pulsed laser having a fixed wavelength $\lambda_1$ ablates material and induces a plasma, thus performing LIBS as described in the previous sections. After the plasma plume has evolved, a second laser with a tunable wavelength $\lambda_2$ irradiates the material cloud inducing element-specific transitions to generate fluorescence.
Fig. 2.9 Applications and methodical extensions of LIBS: 1 = element mapping of sample surfaces by scanning, 2 = analysis of liquids, 3 = analysis of aerosoles and gases excited through an optical window, 4 = combination of molecule-specific separation techniques with LIBS (CE = capillary electrophoresis, HPLC = high-pressure liquid chromatography), 5 = LIBS combined with laser-induced fluorescence (LIF), 6 = laser ablation of surface layers and subsequent analysis of the bulk material

signals to detect selected species with high sensitivity, see Chap. 12. Finally, the laser is a multipurpose tool allowing to locally ablate surface layers and to perform chemical analysis of the underlying bulk material, see item 6 and Sect. 13.1.2.

References

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