

## New possibilities for concrete analysis 4.0 with the Laser-Induced Breakdown Spectroscopy (LIBS)

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**ABSTRACT:** In civil engineering the damage assessment of concrete infrastructures is an important task to monitor and ensure the estimated life-time. The aging of concrete is caused by different damage processes like the chloride induced pitting corrosion of the reinforcement. The penetration depth and the concentration of harmful species are crucial factors in the damage assessment. As a highly cost and time-consuming standard procedure, the analysis of concrete drill cores or drilling by wet-chemistry is widely used. This method provides element concentration to the total mass as aggregates and binder are homogenized. In order to provide a method that is capable to detect the element concentration regarding the cement content only, the laser-induced breakdown spectroscopy (LIBS) will be presented. The LIBS method uses a focused pulsed laser on the sample surface to ablate material. The high-power density and the laser-material interaction causes a laser-induced plasma that emits elemental and molecular line emission due to energy transition of the excited species in the plasma during the cooling phase. As each element provides element-specific line emission, it is in principle possible to detect any element on the periodic table (spectroscopic fingerprint) with one laser shot. In combination with a translation stage the sample under investigation can be spatially resolved using a scan raster with a resolution up to 100  $\mu\text{m}$  (element mapping). Due to the high spatial resolution, the element distribution and the heterogeneity of the concrete can be evaluated. By using chemometrics the non-relevant aggregates can be excluded from the data set and the element concentration can be quantified and referred to a specific solid phase like the binding matrix (cement) only. In order to analyze transport processes like diffusion and migration the two-dimensional element distributions can provide deep insight into the transport through the pore space and local enrichments of elements. As LIBS is a multi-elemental method it is also possible to compare the ingress and transport process of different elements like Cl, Na, K, S, C, and Li simultaneously and evaluate cross-correlations between the different ions. Furthermore, the element mapping allows to visualize the transport along cracks. This work will show the state of the art in terms of hardware and software for an automated LIBS system as well as different application for a concrete analysis 4.0. Focus will be the application of LIBS for a fast concrete analysis.

### 1 INTRODUCTION

This work presents the application of the laser-induced breakdown spectroscopy (LIBS) as a fast, multi-elemental method in terms of concrete analysis. In civil engineering the damage assessment of concrete infrastructures like bridges, parking decks, highways or marine structures is important to ensure the estimated life-time. These concrete structures suffer because of different damage processes that are triggered by the external ingress of harmful



species like chlorides ( $\text{Cl}^-$ ), alkalis ( $\text{Na}^+$ ,  $\text{K}^+$ ), sulfates ( $\text{SO}_4^{2-}$ ) and carbon dioxide from the atmosphere ( $\text{CO}_2$ ). Prominent damage processes are the chloride-induced pitting of corrosion, alkali-silica reaction (ASR), concrete corrosion by sulfates and carbonation. The penetration of these solved species takes place through water and the capillary pore space of the concrete. As a standard procedure for the damage assessment concrete drill cores or drillings are taken directly from the construction site. Afterwards, the samples are analyzed by wet-chemistry like potentiometric titration for the determination of the chloride concentration in concrete powder (drillings), what is a highly cost and time-consuming procedure. Beside titration optional methods like inductively coupled plasma optical emission spectrometry (ICP-OES) require the sample as a homogenized powder that is solved in acid. Fast on-site application is not possible. The concrete cores are cut into slices with a depth between 10 mm to 20 mm, grinded and homogenized to fine powder as well. These standard methods only provide a volume information of the chlorides regarding the total mass content that contain the binding matrix cement as well as the aggregates. The values are compared to critical values according to the European standard DIN EN 206. The standard demands the element concentration of chlorides to the cement content only, therefore the values obtained by wet-chemistry must be corrected with respect to the amount of aggregates, water content and loss of ignition. As the precise determination of these factors are also time-consuming, the use of estimated values is common that may result in high errors and uncertainties. In order to provide a method that is capable to detect the element concentration regarding the cement content only, the laser-induced breakdown spectroscopy (LIBS) have been introduced at BAM by Wilsch et al. (2005). LIBS is a spectroscopic method that uses a pulsed laser with a short laser pulse length (ns) to achieve a high-power density in the focal point. The laser-material interaction causes a laser-induced plasma that emits elemental and molecular line emission due to energy transition of the excited species in the plasma during the cooling phase. As each element provides element specific line emission, it is in principle possible to detect any element on the periodic table (elemental spectral fingerprint) with one laser shot. In combination with a translation stage the sample under investigation can be spatially resolved using a scan raster with a resolution up to 100  $\mu\text{m}$ . The scanning mode allows to perform an element mapping on the sample surface, while collecting a spectrum at each measurement position. Due to the high spatial resolution of the element distributions the heterogeneity of the concrete can be evaluated. By using multivariate analyses, the aggregates can be excluded from the data set and the element concentration can be quantified and referred to a specific solid phase like the binding matrix cement as presented by Gottlieb et al. (2017) and Millar et al. (2019). The LIBS method is capable to consider the heterogeneity of the concrete caused by the aggregates by using the spectral information of different elements like Ca, Fe, Mg, O, Si. This work presents LIBS results about the transport processes of harmful species in different concrete samples. These processes are visualized in a two-dimensional element map, showing the different solid phases of a concrete sample for different elements.

### *1.1 LIBS principle and experimental setup*

The laser-induced breakdown spectroscopy uses a pulsed laser with a fundamental wavelength  $\lambda$  of 1064 nm pulse length  $\tau_p$  of less than 2 ns and a pulse energy  $E_p$  of 1 mJ. The laser is focused by an optics to have a small laser spot size  $d_L$  of approx. 100  $\mu\text{m}$ . The high power-density can ablate some material from the sample surface (material removal). The ablated material is atomized and partially ionized within a laser-induced plasma that expands quickly. During the cooling down phase of the plasma, the excited atoms and molecules are recombining with the

free electrons and emit element specific radiation. The radiation is guided by an optical fiber to the spectrometer and detected as a spectrum (elemental fingerprint) as presented in Figure 1. A control unit synchronizes the timing within a LIBS measurement. For LIBS only an optical access to the sample cross section is necessary (e.g. concrete).

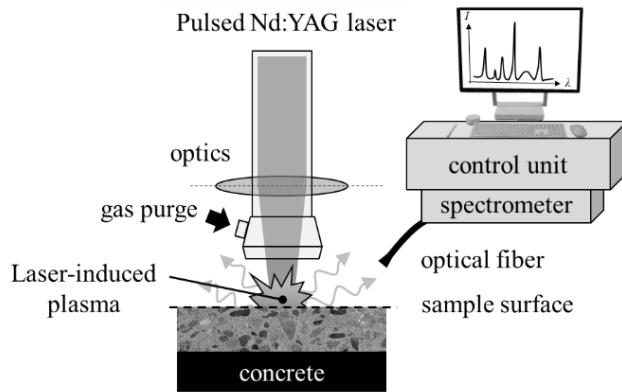


Figure 1. Principle of the laser-induced breakdown spectroscopy

The spectrum contains multiple lines indicating different elements where the position of a line (wavelength) indicates the type of element and the height of the line (intensity) indicates the concentration of the element (Figure 2). A gas purge for the use of process gas like Ar and He may be used to increase the intensity of the emission lines and to remove unwanted particles (e.g. dust due to laser ablation) in front of the optics. By using samples with known concentration (standards) it is possible to make a calibration using univariate and multivariate regression and therefore to provide a quantitative evaluation (Figure 3). The LIBS method is combined with a translation stage (x-y-z) to have a system that can evaluate samples with any topology (rough surfaces) using a three-dimensional scanning procedure.

### 1.2 Strategy of quantification using calibration

LIBS spectra are qualitative values indicating the element type by their specific wavelength and concentration with intensity. By using samples with known concentrations, a calibration can be done, and values may be quantified. As presented in Figure 2 the increasing element concentration is leading to a higher line intensity in the spectra.

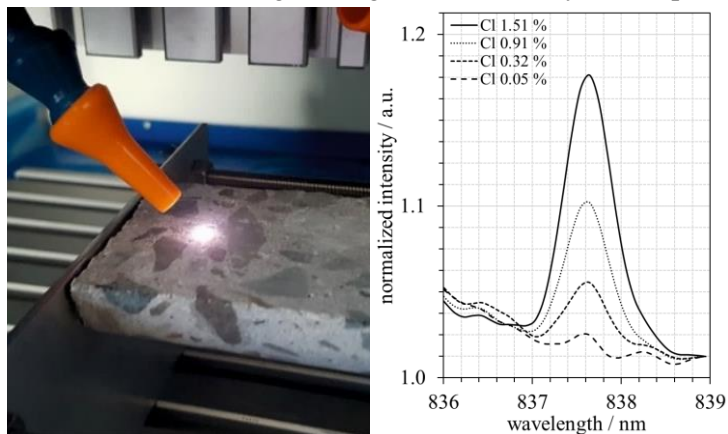


Figure 2. Laser-induced plasma on a concrete cross-section (left) and emission line of Cl at 837.59 nm with 4 different concentration as an example.

For the quantitative evaluation with LIBS different methods are needed to make a calibration model. A widely used multivariate method is the Partial-Least-Squares regression (PLS-R) that allows the correlation between reference value and measured intensity as presented in Figure 3.

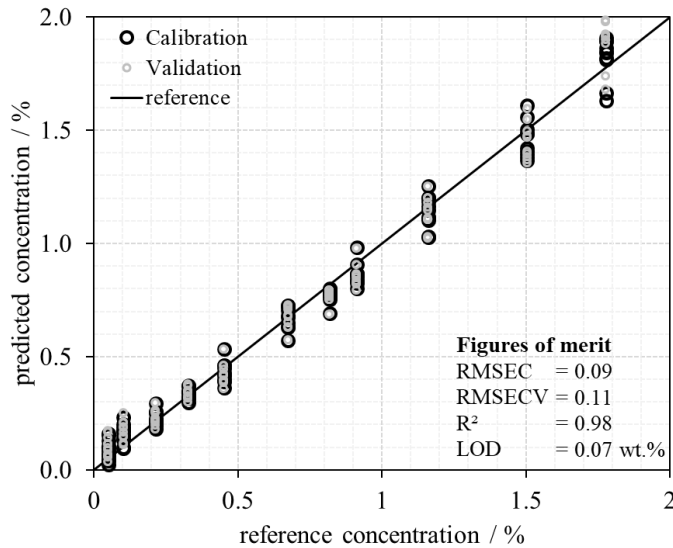


Figure 3. Calibration model of Cl for a quantitative concrete evaluation.

By applying the calibration model to unknown samples, LIBS provide quantitative values. It is possible to calibrate any element of interest, if calibration samples are accessible. In terms of concrete analysis with LIBS, the elements in Table I showing their specific wavelength and energy levels are commonly used.

Table 1 element specific emission lines used in concrete analysis

Element	Wavelength (nm)	Energy levels (eV)
Al I	309.3,	0.00 – 4.02
Cl I	833.5	7.68 – 9.17
Ca II	849.8	1.69 – 3.15
Cl I	837.6	8.92 – 10.40
Fe I	248.3	0.00 – 4.99
H I	656.3	10.20 – 12.09
K I	769.9	0.00 – 1.61
Mg I	285.8	0.00 – 4.34
Na I	818.6	2.10 – 3.60
O I	844.6	9.52 – 10.99
S I	921.3	6.52 – 7.86
Si I	288.2	0.78 – 5.08

The possibility of using multiple emission lines within one LIBS measurement allows the evaluation of different damage processes simultaneously.

### 1.3 2D-mapping using x-y-z translation scanner

As explained in the experimental setup (see section II) the LIBS technique is capable to provide two-dimensional element mapping using a scanning procedure. A motorized and automated LIBS system allows the evaluation of heterogeneous concrete samples in a very short time with a high spatial resolution (< 100  $\mu\text{m}$ ). In order to measure samples with a rough topology like a

broken concrete drill core, the surface is measured using a laser distance sensor first. The distance values for each spot is stored in the control unit. After determining the sample topology, the laser is focused on the sample surface using the correct distance to be always in the right focus. Therefore, the signal variance caused by different heights is reduced and the LIBS spectra are reproducible. In terms of flat samples (e.g. a cut drill core) the cross-section of a concrete is measured in a linear movement to have a fast measurement. The following examples in Figure 4 showing the evaluation of a concrete sample with a repair mortar layer on top, where harmful species are penetrating the concrete through a crack.

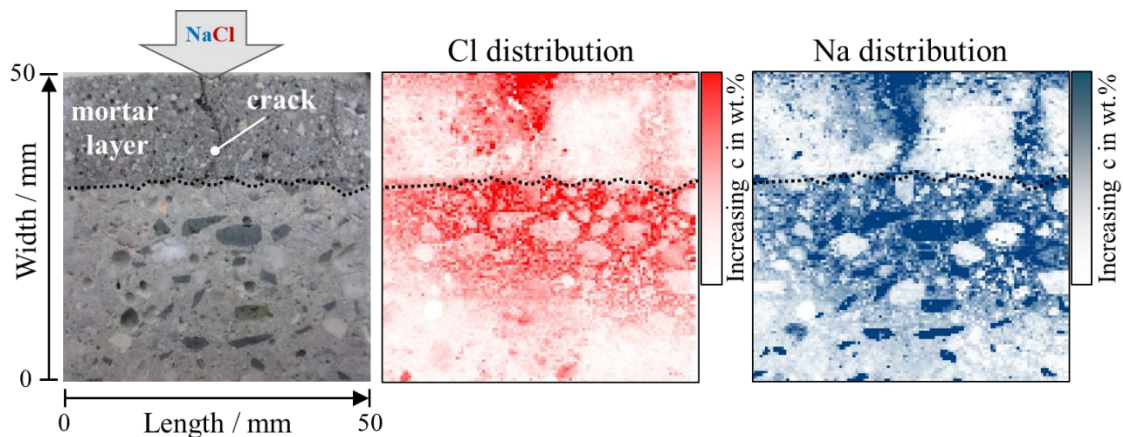


Figure 4. Visualization of ion transport ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) through a crack on a mortar repair layer on top of a concrete sample.

The visualization of different elements is done by LIBS using only one measurement (multi-elemental imaging). The transport of solvated chloride and sodium ions through the crack in the protective mortar layer may be displayed. While the mortar layer shows a high density without any transport within the non-damaged a high ingress in the concrete underneath can be reveal, what is not possible with other methods.

## 2 APPLICATION OF LIBS FOR CONCRETE ANALYSIS

The application of LIBS for a fast and automated concrete analysis offers new possibilities in terms of damage assessment 4.0. Nowadays different and new developed additives and admixtures are used for making concrete that increases the analytical complexity. Therefore, the need for a fast and reliable technique is high. Especially shut-down times during reconstruction works are a connected with high costs.

### 2.1 Standard procedure for chloride determination

The standard method for the determination of chlorides in concrete is the titration of homogenized concrete powder. Before the analysis is taken place, different sample preparation steps must be done as shown in Figure 5. A drill core taken from a construction site has be cut into slices of about 10 mm thickness. Each slice is analyzed, and a depth dependent concentration is presented. The element concentration is referred to the total mass; the heterogeneity of the concrete caused by the aggregates cannot be considered. For the transfer of the values regarding to the cement content only an estimated factor is used that vary between 4 to 7.





Figure 5. Sample preparation steps for the standard procedure compared to LIBS for concrete analysis.

In order to do a LIBS measurement on a concrete sample, only an optical access to the cross-section surface is necessary. Therefore, no further sample preparation must be done, which saves time and costs.

## 2.2 Concrete analysis for a damage assessment 4.0

For the damage assessment of concrete the standard procedures are limited in terms of time, costs and application. Nowadays, the use of different cement types, binders or novel additives and admixtures require sophisticated methods. LIBS as a multi-elemental method is able to provide versatile applications in one unified system.

The 2D scanning allows to evaluate the element concentration of harmful species for a specific material phase like the cement matrix, as non-relevant information of the aggregates can be excluded from the data set (indicated in black). In terms of concrete analysis, it is important to consider the heterogeneity caused by the aggregates to provide values to the relevant cement matrix only as required from the European standard. By applying the two-dimensional scanning, the element distribution can be displayed and the concentration as well as the penetration depth may be evaluated. Furthermore, the transport behavior of different ions through the pore space of the concrete can be tracked.

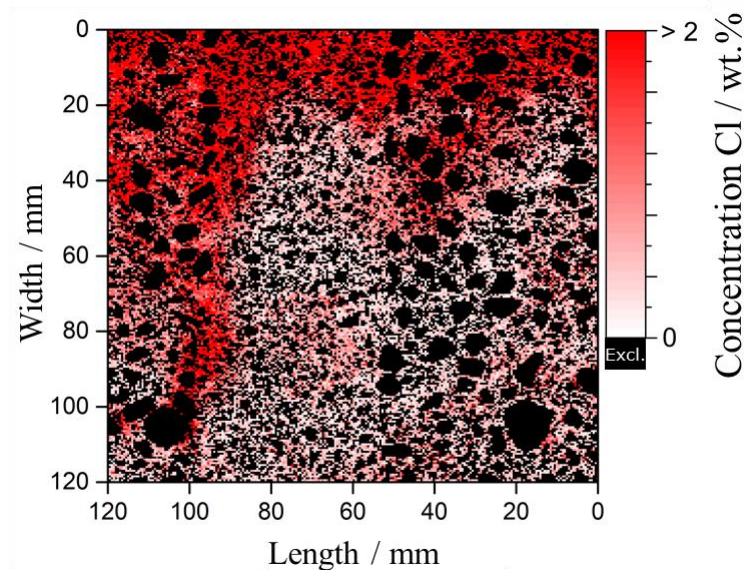


Figure 7: Two-dimensional visualization of the chloride distribution on a mortar sample. Excluded aggregates are indicated in black. Local enrichments due to cracks.

A higher ingress of chlorides in the presence of cracks is shown in Figure 7. The locally variation of the element concentration of chloride may lead to local pitting corrosion of the steel reinforcement. Additionally, the excluded data may be classified in terms of their mineralogy (identification of cement and aggregate type) by using multivariate analysis. An automated LIBS system for the concrete analysis is commercially available (Secopta analytics GmbH) and offers great opportunities for a new kind of damage assessment in civil engineering.

### 3 SUMMARY AND CONCLUSION

This paper presents the application of the laser-induced breakdown spectroscopy (LIBS) method for the analysis of heterogeneous concrete samples. The concentration and the penetration depth of harmful species like chlorides into the concrete is an important issue in terms of damage assessment. Critical values in the European standard for concrete infrastructures are defined to the cement matrix only. As the standard procedure evaluated the element concentration to the total mass, LIBS has been introduced to overcome the uncertainty of estimating factors. By applying a two-dimensional scanning, the distribution of different elements can be visualized with a high spatial resolution. The data sets of the element maps are processed using multivariate statistics to exclude the non-relevant information of the aggregates. Therefore, the information about harmful species within the cement matrix can be provided. The high resolution of LIBS offers a great potential to gain chemical information of heterogeneous samples for their different material phases. The multi-spectral information may be used to classify each spectrum obtained by LIBS. For example, the cement type as well as the type of used aggregates within the concrete may be identified automatically.

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