

## Low Resolution LIBS for Online-Monitoring During Laser Cleaning Based on Correlation with Reference Spectra

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**Summary.** Based on a commercial miniature spectrometer, we have built a LIBS-system for online monitoring and controlling during laser cleaning of artworks. In contrast to common LIBS set-ups with ICCDs, our system offers less sensitivity and  $\lambda$ -resolution. This system is unsuitable for high resolution elemental identification but it is applicable for the detection of “spectral fingerprints”. A powerful method of comparison online spectra during laser cleaning process with reference spectra is the analysis of correlation. Based on “Pearson’s correlation”, the linear relationship between entire data sets of both spectra are classified by the correlation coefficient  $r$ . In practise of laser cleaning a permanent comparison of the spectrum from the ablated layer with a reference spectrum of the layer to be preserved is necessary. Thus, online monitoring of the cleaning process is enabled by permanent estimation of  $r$ . In case of closed-loop laser cleaning the ablation will continue until  $r$  exceeds a predefined value and subsequently the ablation process is automatically stopped.

### 52.1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is nowadays a frequently used method in a lot of different areas of application. The best-known method is the qualitative and also quantitative elemental identification of samples with unknown composition [1]. The advantage of the LIBS-technique over classical methods is the possibility to analyse all types of materials in every state of aggregation without the need of sample preparation. In common a high intense pulsed laser beam is focussed on the sample and intensely heats a small volume of material, which results in a transient plasma above the irradiated area. The spectrum emitted by this plasma plume depends on the elemental composition of the ablated material. This can be analysed by a spectrograph.

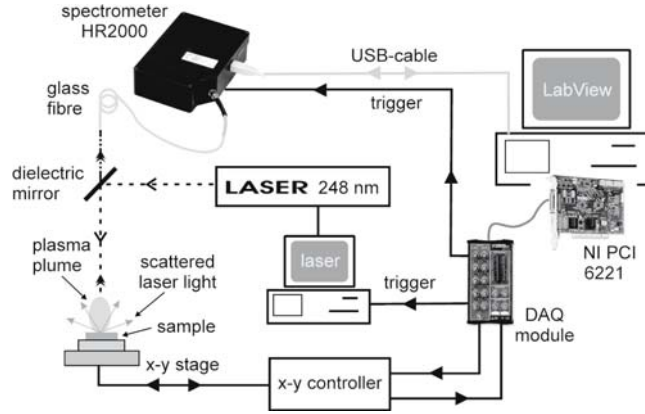
A totally different approach is to consider a LIBS-spectrum as a spectral fingerprint. Winefordner et al. applied this method in combination with linear correlation to identify plastic and solid materials [2]. Here the spectrum of the “unknown” sample is compared with a library of spectra, and identified by the weight of correlation.

In cultural heritage, LIBS is mostly applied as a diagnostic tool to identify the elemental configuration, separately or in combination with laser cleaning [3]. A practical example is the identification of pigments by elemental configuration [4]. As well LIBS can be used to control a laser cleaning process to avoid over-cleaning. This was already successfully applied by Zafirooulos et al. in different applications [5]. Identification of the layers is done by elements recognition. In common they used a conventional high resolution spectrometer with intensified CCD-array. These spectrometers have a high signal to noise ratio and sensitivity. Disadvantages are high investment costs, environmental sensitivity and complexity [6].

In this study the plasma radiation induced during laser cleaning is used to monitor or online control the process. The plasma radiation is recorded with a low resolution miniature fibre optic spectrometer characterised by a large spectral bandwidth, low  $\lambda$ -resolution and sensitivity. In contrast to conventional LIBS-systems, this system is low cost and easy to handle. These properties make this system unsuitable for high resolution elemental identification but it is applicable for the detection of spectral fingerprints. It has turned out from former investigations concerning controlled laser cleaning of artworks that elemental identification is not urgent necessary [7]. Each layer has its individual spectral fingerprint and therewith it is distinguishable from other layers in a multi-layer arrangement. The application of correlation analyses enables the recognition of layers (fingerprints), measured with a low resolution spectrometer on the basis of reference spectra. Through the use of optimal laser parameters during laser cleaning, the laser energy cannot be set arbitrary high in order to induce a bright plasma emission. Thus, in case of less plasma emission intensity the detection becomes critical or even impossible with a miniature spectrometer.

## 52.2 Experimental

The miniature spectrometer was integrated into a KrF-Excimer laser cleaning system to test its capability as a feedback sensor for monitoring or controlling the process automatically. We applied a user-configured “Ocean Optics HR2000 UV-VIS” miniature fibre optic spectrometer. For collecting the plasma radiation into the spectrometer, a 2 m long, 600  $\mu\text{m}$  glass fibre in combination with a collimator is applied. The groove density (300 grooves  $\text{mm}^{-1}$ ) and the entrance slit of 25  $\mu\text{m}$  led to a spectral range of 200–1,100 nm with a resolution of 2 nm. The exposure time of the electronic “shutter” is fixed on 2 ms.



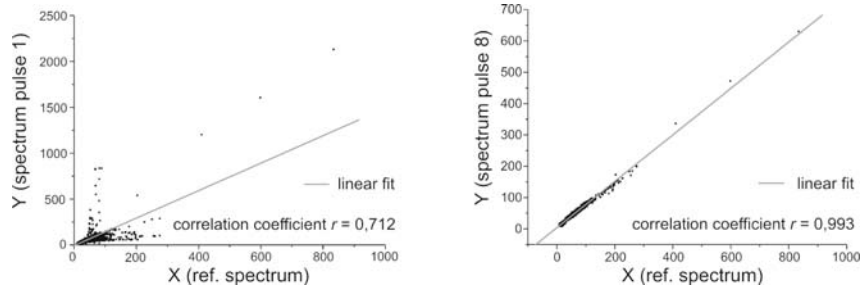
**Fig. 52.1.** Schematic visualisation of the set-up for monitoring and controlling laser cleaning via miniature spectrometer

The experimental set-up is built around a KrF-Excimer laser (Lambda Physics LPX 305i, 248 nm, 1–50 Hz, 20–40 ns) with a standard excimer laser based mask illumination and imaging optical set-up. Collimator and glass fibre are placed behind the last dielectric mirror, which gives obvious advantages for the handling in praxis. For positioning and moving the samples, the set-up is equipped with an  $x$ - $y$  stage (travelling range 80 cm and 7  $\mu$ m resolution in both axes). Figure 52.1 schematically visualises the electronic connection of the individual parts. A computer equipped with a DAQ-card (NI PCI-6221) and in LabView written software controls the automated laser cleaning process. Time offset between laser pulse and opening the spectrometer “shutter” is arranged by the delay generator programmed in LabView.

### 52.3 Recognition of Layers by Linear Correlation

LIBS spectra of different layers (materials) are unique fingerprints, with differences in spectrum and intensity. There are various methods to compare these spectra with a reference spectrum and assign it to a layer. In this study we used Pearson’s linear correlation. The linear correlation coefficient is a weight for the linearity between two sets of data and has a dimensionless index  $r$  in the range of  $-1$  and  $1$ . A value of  $r = 1$  represents a correlation of 100%,  $r = 0$  means no linear correlation and  $r = -1$  represents 100% negative correlation. The linear correlation coefficient is given by

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}}, \quad (52.1)$$



**Fig. 52.2.** (*left*) Intensities of the LIBS spectrum measured at the first laser ablation pulse vs. the intensities of the reference spectrum. There is a low linear correlation,  $r = 0.712$ . (*right*) Intensities of the LIBS spectrum measured at the eighth laser ablation pulse vs. the intensities of the reference spectrum. There is a high linear correlation,  $r = 0.993$

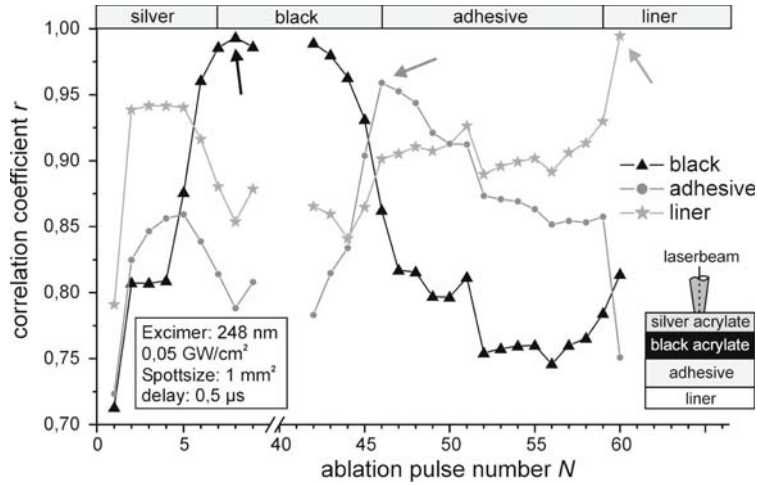
where  $\bar{x}$  is the mean of all  $x_i$ -data and  $\bar{y}$  the mean of all  $y_i$ -data. The intensity of the CCD-pixels measured during recording the reference spectrum forms the  $x$  data set while the  $y$  data set is given by the spectrum of the irradiated layer in process. A total data set consists of 2,048 points representing the number of pixels of the spectrometer CCD-array, so  $i = 1 \dots 2,048$ . Any pixel forms a  $x_i$ -value (reference spectrum) and a  $y_i$ -value (actual spectrum) which can be plotted in an  $x$ - $y$  graph (Fig. 52.2).

The graph in Fig. 52.2 (left) shows less linearity between the single points than the data points of the  $x$ - $y$  graph in Fig. 52.2 (right). Here the spectrum measured at the first laser ablation pulse is correlated with a reference spectrum from another layer (different material). Both spectra have a low linear correlation with each other, which is visible in the chaotic point distribution and results in a small linear correlation coefficient,  $r = 0.712$ .

Figure 52.2 (right) shows the linear association between a spectrum recorded during the eighth laser ablation pulse and a previous measured reference pulse. The correlation coefficient approximates the value of 1, which means a high linear correlation between the spectrum of the eighth laser ablation pulse and the reference spectrum. The single data points nearly all lay on the linear fit line, which is calculated by the least square method. This results in the conclusion that these spectra are almost identical and in many cases belong to the same layer (material). An advantage of this correlation method is that intensity fluctuations of the spectra (e.g. caused by pulse-to-pulse variations) do not highly affect the coefficient  $r$ .

## 52.4 Process Monitoring by Correlation Analysis

First tests of monitoring laser ablation by the weight of the linear correlation coefficient are applied on a defined artificial multi-layer arrangement (homogenous parallel laminates, construction depicted in Fig. 52.3). First of



**Fig. 52.3.** Correlation coefficients  $r$  related to the reference spectra “black,” “adhesive” and “paper” with increasing penetration depth. The arrows indicate the maximum of  $r$ , appearing at the transitions

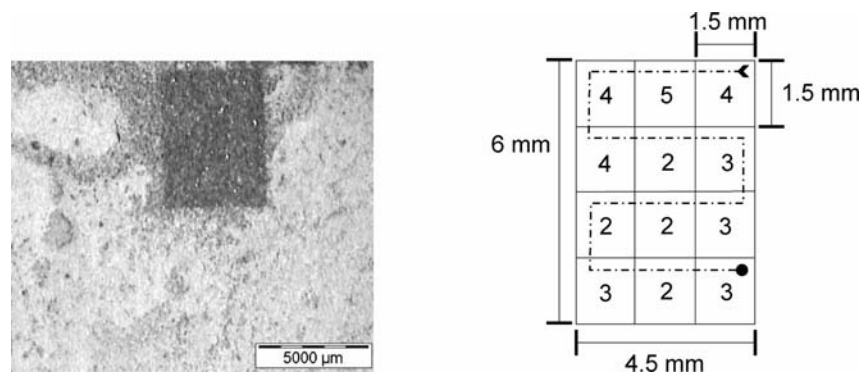
all a reference spectrum had to be recorded from each layer. The correlation coefficient is calculated after any laser ablation pulse between the recorded spectrum and the three reference spectra. Figure 52.3 shows the corresponding correlation coefficients  $r$  calculated during the ablation vs. ablation pulse number. The bar at the top of the graph visualises in which layer the laser ablates material. When surveying the line that belongs to the correlation with the black reference spectrum, it is apparent that the correlation coefficient approximates the value one while reaching the black layer. The highest value for  $r$  is reached after the same number of pulses (8) as the reference spectrum is recorded. Correlation with the other two spectra results also in the highest  $r$  at the transitions of the layers correlated with. This demonstrates that the correlation coefficient can be applied to stop a laser cleaning or laser ablation process defined at a given layer (level) in a homogenous layer arrangement.

The suitability of this principle during laser cleaning of complex samples is tested on “real objects”: parchment, glass and iron. These experiments exhibit that it is possible to stop a laser ablation process during cleaning of an inhomogeneous polluted sample by correlation analysis. An important parameter for stopping the cleaning process on the original surface is the difference between the spectra of each layer. Tests with rusty iron have led to a negative result. The spectra of rusty and “clean” iron (recorded with the low resolution spectrometer) are too similar to distinguish them by correlation analysis.

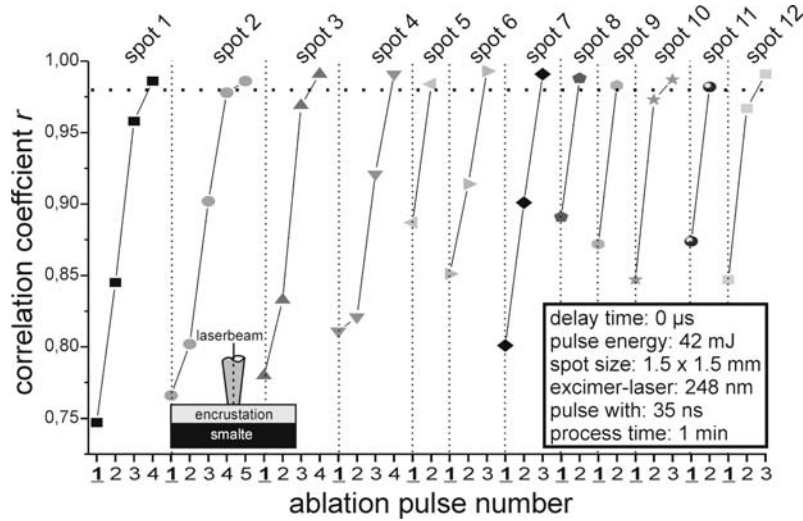
## 52.5 Closed-Loop Cleaning of Areas

In a next step the correlation process is automated in a closed-loop system which is able to clean a predefined area automatically. As already described all components in the laser cleaning set-up are directly or indirectly connected with one controller-PC. This closed-loop process is controlled by software written in LabView. The first step, in the case of automatic cleaning, is recording a new LIBS reference spectrum or using a stored reference spectrum. The area to be cleaned, laser spot size and spatial overlap are programmed on the  $x$ - $y$  positioning controller. After entering the relevant data, the controller is waiting idle for an input signal from the PC. Laser parameters for cleaning are directly entered in the controller of the laser. The ultimate control parameter of this closed-loop process is the comparing criterion. The correlation coefficient will be estimated after each laser pulse by correlating the actual spectrum with the reference spectrum. If this value exceeds the value of the compare criterion, the ablation process is paused and the translation table moves the sample to a “new” polluted position. The cleaning process resumes until the correlation coefficient again exceeds this criterion. This process repeats until the predefined area is completely cleaned.

The first trials of automatic laser cleaning are applied on polluted parchment and colour pigment smalt with encrustation (binder: linseed oil, encrustation: artificial black gypsum). In both cases controlled cleaning of the predefined area was possible. Figure 52.4 (left) shows the polluted pigment smalt with the controlled laser cleaned section. This rectangular area ( $4.5 \times 6 \text{ mm}^2$ ) is cleaned with a  $1.5 \times 1.5 \text{ mm}^2$  square laser spot in 1 min time. The number of laser ablation pulses used per spot and the meander movement of the sample is visualised in Fig. 52.4 (right). The corresponding correlation coefficients  $r$  calculated during the ablation of encrusted smalt vs. ablation



**Fig. 52.4.** (left) Encrusted smalt pigment with automatically laser cleaned area:  $4.5 \times 6 \text{ mm}^2$ . (encrustation: artificial black gypsum, linseed oil binder, 248 nm, 42 mJ, 35 ns) (right) Meander movement (dashed line) during cleaning of smalt pigment. The numbers represent the amount of ablation pulses per spot



**Fig. 52.5.** Variation of correlation coefficient  $r$  vs. ablation pulse number calculated during automatic laser cleaning of encrusted smalte. When  $r$  exceeds the compare criterion (0.98), the process is paused and continues at the next spot position

pulse number per spot is visualised in Fig. 52.5, the horizontal dashed line indicates the compare criterion (0.98). After exceeding this value, the process is paused and continued at the next spot.

## 52.6 Conclusion

Experiments on artworks and multi-layer arrangement have shown that a laser cleaning or ablation process can be controlled or monitored by linear correlation analysis via low resolution miniature spectrometer. This method has a high potential to stop laser ablation on a predefined level.

The process is automated by applying a controller-PC with LabView written software which connects all single modules into a closed-loop system. In combination with LIBS reference spectra, this system is able to automatically clean a predefined area by using linear correlation.

The use of linear correlation analysis gives the advantage of less influence from plasma intensity fluctuations on the signal interpretation caused by laser pulse-to-pulse variations. The correlation coefficient is not estimated by comparing single spectral lines but by the linear association of two complete spectra. In cases of almost identical LIBS spectra of two different layers, identification via linear correlation is difficult or even impossible.

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