

# CONTROLLED LASER CLEANING OF ARTWORKS WITH LOW RESOLUTION LIBS AND LINEAR CORRELATION ANALYSIS

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## Abstract

Based on a fibre optic miniature spectrometer (spectral range 200-1100 nm,  $\lambda$ -resolution 2 nm) we have built up a LIBS-system (Laser Induced Breakdown Spectroscopy) for online monitoring during laser cleaning of artworks. This system is unsuitable for high resolved elemental identification but 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 the 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 controlling of the cleaning process is enabled by permanent estimation of  $r$ . Laser removal will continue until  $r$  exceeds a predefined value subsequently the ablation process is paused. In a next step, the sample is translated and the cleaning process continues. Successfully we have automatically cleaned glass covered with encrustation and polluted parchment.

## 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 [1,2,3]. The advantage of the LIBS-technique over classical methods is the possibility to analyse all types of material in every aggregate condition 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 this target, which results in a transient plasma above the irradiated area. The spectral composition of the light emitted by this

plasma plume depends on the elemental configuration of the ablated material. This can be extracted by means of a spectrograph out of the plasma radiation. LIBS as a diagnostic tool has found a lot of practical applications like lateral and in depth elemental analysis [4,5] up to detection of biological aerosols for preventing biological warfare [6,7]. Also in the process control LIBS has found his entry, we can think about on-line sorting [8] and controlling the mixture of molten alloys [9]. Commonly in all this cases LIBS is used to extract elemental peaks out of the plasma radiation. A totally different approach is to see a LIBS-spectrum as a spectral fingerprint. Winefordner et al. applied this method in combination with linear correlation to identify plastic and solid materials [10,11]. The spectrum of the "unknown" sample is here 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, in- and without combination of laser cleaning [12,13,14,15]. A practical example is the identification of pigments by elemental configuration [16]. As well LIBS can be used to control a laser cleaning process to avoid over cleaning. This is already successfully applied by Zafiropulos et al. in different applications [17,18,19]. 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 sensitiveness. Disadvantages are high investment costs, ambience sensitivity and complexity [20,21].

In this study the plasma radiation induced during laser cleaning is used to 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 sensitiveness. In contrast to conventional LIBS-systems this system is low cost and easy to handle. These properties make this system unsuitable for high

resolved 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 [22,23]. 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 makes the recognition of layers (fingerprints), measured with a low resolution spectrometer on the basis of reference spectra, possible.

### Plasma Emission

A number of intricate processes take place when inducing plasma with a laser. Depending on various parameters like pulse energy, wavelength, pulse duration, spot size and elemental configuration of the sample. The physical principle of laser induced plasma can be divided in three time domains.

In the first time domain (1) the laser heats and evaporates a small amount of the material via linear or non-linear absorption of the laser radiation. The first free electrons are created either by multi photon ionization or thermal conductivity. These free electrons absorb further photons from the same laser pulse and are heated via inverse bremsstrahlung. They transfer their energy to the plume by electron impact resulting in avalanche ionization. At a certain electron density the threshold for plasma ignition is exceeded.

The second time domain (2; duration of a few hundred nanoseconds) is characterized by a continuous broadband white light radiation from the bremsstrahlung of the free electrons and electron-ion recombination. Some weak ionic lines of the elements in the sample arise above the strong continuum.

The last time domain (3; lasts for several microseconds) is dominated by discrete spectral lines corresponding to the elements from the sample, caused by decay from a higher energy state to a lower level (e.g.  $E_3 \rightarrow E_2$  emitting  $h\nu$ ). The line intensity is proportional to the atomic concentration of the elements within the plume. This is the time domain commonly utilized for conventional LIBS measurements.

In the case of laser cleaning the destructive character of the LIBS technique becomes irrelevant because of the use of the already existing plasma plume. Through the use of optimal laser parameters during laser cleaning the laser energy can not be set arbitrary high in order to induce a bright plasma emission. In cases of less plasma emission intensity the detection becomes critical or even impossible with a miniature

spectrometer. Because our layer recognition is based on a fingerprint method and not on elemental identification it is also possible to use time domain 2 instead of time domain 3. The advantage of time domain 2 is the higher plasma intensity compared to time domain 3. A disadvantage is the smaller difference between some spectra of different layers through the dominant strong broadband white light emission.

### Integration of Low Resolution Spectrometer into Excimer Laser Cleaning System

The miniature spectrometer is integrated in a KrF-Excimer laser cleaning system for testing its possibility as feedback sensor for 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/mm) and the entrance aperture of 25  $\mu\text{m}$  are leading to a spectral range of 200 to 1100 nm with a resolution of 2 nm. The exposure time of the electronic "shutter" is fixed on 2 ms.

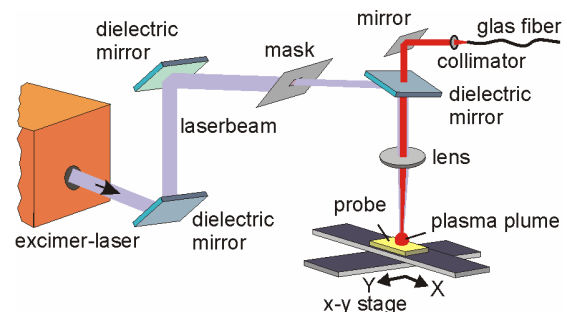


Figure 1: 248 nm excimer laser set-up with implemented glass fibre and collimator (mask illumination set-up)

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 as depicted in fig. 1 [24]. 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 positing system (travelling range 80 cm and 7  $\mu\text{m}$  resolution at both axes). Figure 2 schematically visualises the electronic connection of the individual parts. A computer equipped with a DAQ-card and in LabView written software controls this automatically running laser cleaning process. Time offset between laser pulse and opening the spectrometer "shutter" is arranged by the delay element.

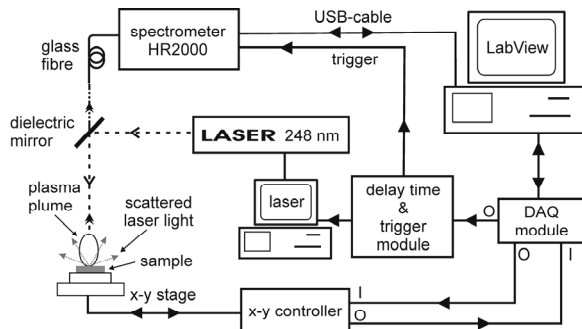


Figure 2: Schematic visualization of the electronic setup for controlled laser cleaning via miniature spectrometer

### Identification of Layers by Correlation Analysis

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  $r = -1$  100% negative correlation. The linear correlation coefficient is given by:

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

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 is forming 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 2048 points representing the number of pixels of the spectrometer CCD-array, so  $i = 1..2048$ . Any pixel forms a  $x_i$ -value (reference spectrum) and a  $y_i$ -value (actual spectrum) which can be drawn in an  $x$ - $y$  graph, Fig. 3 and 4.

Figure 3 shows in an  $x$ - $y$  graph the linear association between a spectrum recorded during laser ablation pulse 8<sup>th</sup> and a previous measured reference spectrum. The correlation coefficient approximates the value 1, which means a high linear correlation between the spectrum of the 8<sup>th</sup> laser ablation pulse and the reference spectrum. The single data points lay nearly

all on the red linear fit line, which is calculated by the least square method. This results in the conclusion that both spectra are almost identical and in many cases belong to the same layer (material).

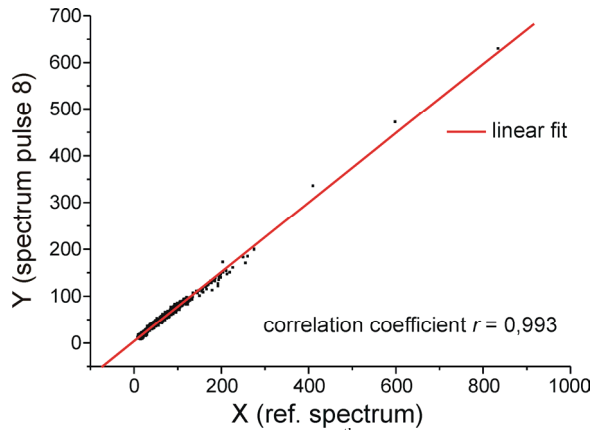


Figure 3: Correlation of the 8<sup>th</sup> laser ablation pulse LIBS spectrum with a saved reference spectrum. There is a high linear correlation between both spectra which is recognizable in a correlation coefficient of  $r = 0,993$

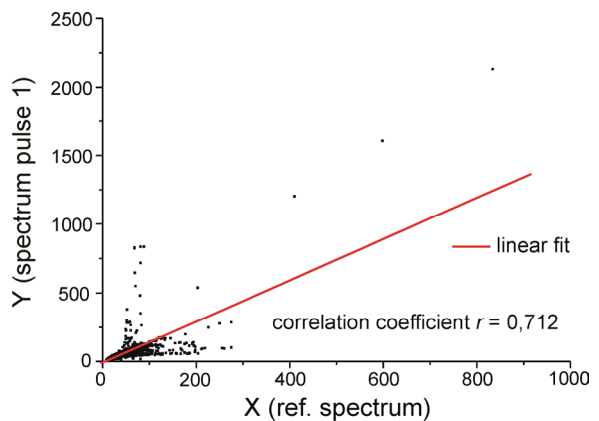


Figure 4: Correlation of the 1<sup>st</sup> laser ablation pulse LIBS spectrum with a saved reference spectrum. There is a low linear association between both spectra which is recognizable in a correlation coefficient of  $r = 0,712$

The graph in figure 4 shows less linearity between the single points than the data points of the  $x$ - $y$  graph in figure 3. Here the spectrum measured at the 1<sup>st</sup> 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,  $r = 0,712$ . 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  $r$ .

## Closed-Loop Process Control by Linear Correlation

First tests of controlling laser ablation by the weight of the linear correlation coefficient are applied on a defined artificial multi layer arrangement; construction is depicted in figure 5. Because of its homogenous parallel laminates the layer ablation can be arranged by constant number of laser ablation pulses which simplifies the control of the workability of the sensor system. First of 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 5 shows the corresponding correlation coefficients  $r$  calculated during the ablation versus ablation pulse number. The bar at the top of the graph visualizes in which layer the laser ablates material. When surveying the line that belongs to the correlation with the black reference spectrum, it is visible that the correlation coefficient approximates the value one while reaching the black layer. The highest value for  $r$  is reached after the same amount 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.

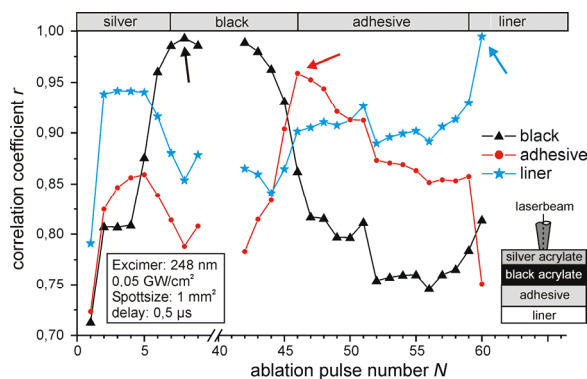


Figure 5: Correlation coefficients  $r$  related to the reference spectra “black”, “adhesive” and “paper” with increasing penetration into the multi layer test sample. The arrows indicate the maximum of  $r$ , appearing at the transitions.

The suitability of this principle during laser cleaning of complex samples is tested on “real objects”; parchment, glass and iron. The parchment sample is an original 18<sup>th</sup> century artefact with lateral differences in pollution thickness. Because of the non homogenous distribution of the pollution, the number of ablation pulses need to clean the object differ per spot. First a

reference spectrum had to be recorded from a clean parchment surface; fig. 6.

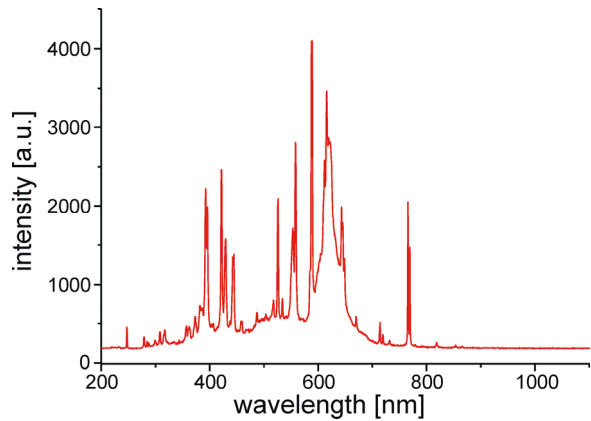


Figure 6: Parchment reference LIBS spectrum

After each laser ablation pulse the correlation coefficient is calculated between the actual spectrum and this reference spectrum. It reached its highest value arriving at the original surface; 3 to 4 laser ablation pulses. Further laser pulses lead to an over cleaning effect causing a destruction of the artwork.

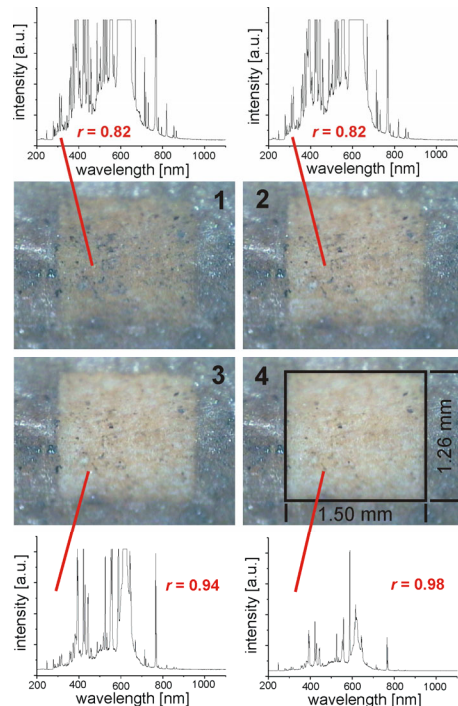


Figure 7: Top view of the parchment sample after 1<sup>st</sup>-4<sup>th</sup> laser ablation pulse and associated LIBS spectra. Laser pulse 4 excavates the original surface and the correlation coefficient reaches its highest value. 248 nm, 33 mJ, 30 ns, spot size 1,50 x 1,26 mm<sup>2</sup>

Figure 7 shows the ablation of the parchment sample (at a certain position without movement) and the corresponding LIBS spectra recorded after each pulse (ablation pulse 1-4). This output exhibits that it is possible to stop a laser ablation process during cleaning of an inhomogeneous polluted sample by correlation analysis.

An imported parameter for defined stopping the cleaning process on the original surface is the difference between the spectra of each layer. Also the difference in LIBS spectrum of the pollution layer and original surface of the artificial aged glass sample affords defined stopping by correlation analysis. Experiments with rusty iron have led to a negative result. The spectra of rusty- and “clean” iron (recorded with the low resolution spectrometer) are too identically to distinguish them by correlation analysis.

### Controlled Laser Cleaning of Areas

The next step was automatizing the correlation analysis process to 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 flow diagram is depicted in figure 8.

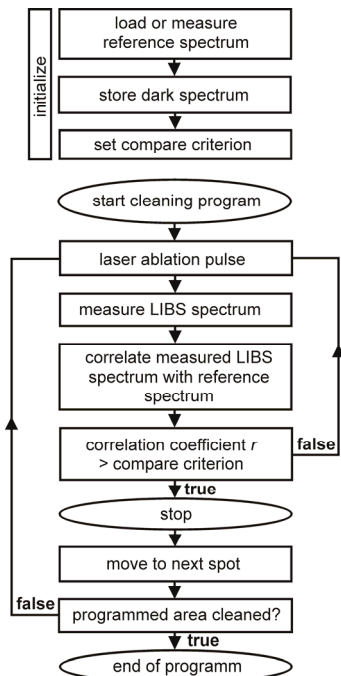


Figure 8: Program flow-diagram

The first step in case of automatically cleaning is recording a new LIBS reference spectrum or using a stored reference spectrum. The area to be cleaned,

Laser spot size and overlay are programmed on the x-y positioning controller. After entering 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 etc. This process repeats until the predefined area is completely cleaned.

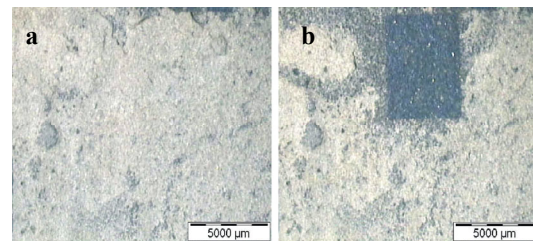


Figure 9: Encrusted smalt before laser cleaning (a) with automatically laser cleaned area: 4,5 x 6 mm<sup>2</sup> (b).

(Encrustation: artificial black gypsum, binding: linseed) 248 nm, 42 mJ, 35 ns, spot size 1,5 x 1,5 mm<sup>2</sup>

The first trails of automatically laser cleaning are applied on polluted parchment and colour pigment smalt with encrustation (binding: linseed, encrustation: artificial black gypsum). In both cases controlled cleaning of the predefined area was possible. Figure 9a shows the polluted pigment smalt before laser cleaning. In figure 9b the controlled laser cleaned section is visible. This rectangular area (4,5 x 6 mm<sup>2</sup>) is cleaned with a 1,5 x 1,5 mm<sup>2</sup> square laser spot in one minute time. The number of used laser ablation pulses per spot and the meander movement of the sample is visualized in figure 10.

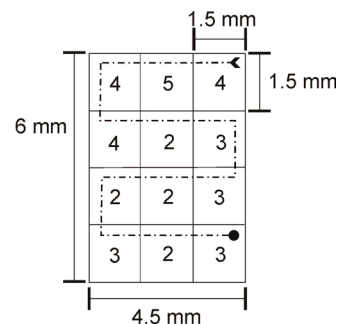


Figure 10: Meander movement (dashed line) during cleaning of smalt pigment, s. Fig 9b. The numbers represent the amount of ablation pulses per spot.



The corresponding correlation coefficients  $r$  calculated during the ablation of encrusted smallt versus ablation pulse number per spot is visualized in figure 11, the horizontal dashed line indicates the compare criterion (0,98). After exceeding this value the process is paused and continued at the next spot.

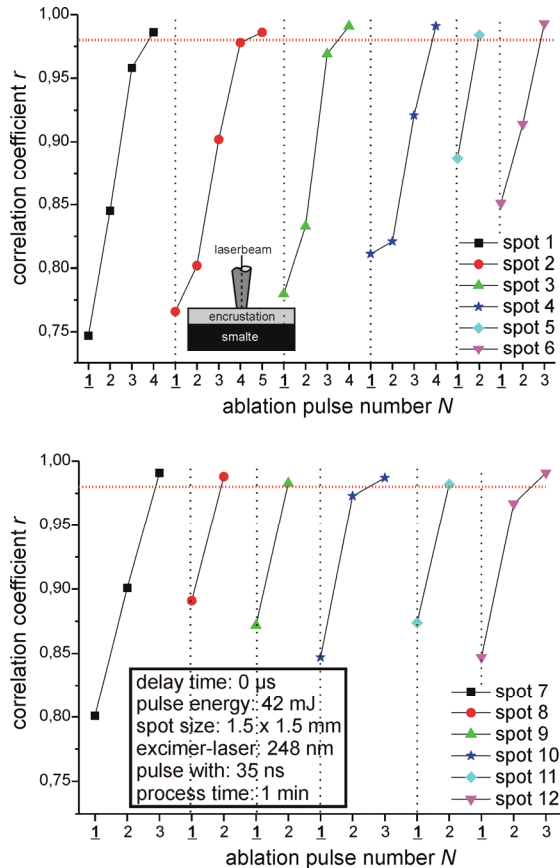


Figure 11: Chancing of correlation coefficient during automatically cleaning versus ablation pulse number per spot. (top: spot 1-6, bottom: spot 7-12) When the correlation coefficient exceeds the compare criterion (0,98) the process is paused and continues at the next spot.

## Conclusion

Experiments on artworks and multi layer arrangement have shown that a laser cleaning or ablation process can be controlled 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 automatized by applying a controller PC with in LabView written software which connects all single modules into a closed-loop system. In combination with LIBS reference spectra this system is

able to clean automatically 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. Because 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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