Laser cleaning of Gotlandic sandstone façade elements with instantaneous plasma emission diagnostics

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Summary
Ablative laser cleaning together with process diagnostics by means of laser induced plasma spectroscopy (LIPS) was applied to the sandstone façade elements of St. John’s Church in Gdansk, Poland. Laser cleaning enabled the removal of black encrustation without causing damage to the substrate layers. The operative range of process parameters for the 1064nm Nd:YAG laser, i.e. energy fluence\(^1\) of 0.5 J/cm\(^2\) and an energy deposition corresponding to about 15 pulses per spot when adding water, was derived from experiments. Components of crust and stone were identified from the LIPS spectra and the decreasing spectral line intensities allowed for monitoring of the process. The morphology of processed material analysed with a scanning electron microscope confirmed the selective and controlled character of the cleaning.

Introduction
It is known that several methods can be applied for the cleaning of stone historic objects, but only some of these methods fulfil an important postulate of conservation, i.e. to remove encrustation without influencing the properties of the stone substrate. The required conservation conditions for the technique used are as follows:

- It should allow the removal of encrustation in a controllable manner, without damage to the original stone surface and its deeper layers.
- It should not have a negative, post-processing influence on the mechanical and chemical properties of the stone.
- It should be time-efficient, cost-effective and health-safe.

These conditions were fulfilled by the laser cleaning method in the case of the Gotlandic sandstone, a soft stone known to be sensitive to environmental impacts and pollution. The present study was further motivated by the wide use of this decorative stone in Northern Poland in the past, and the fact that its restoration has become a serious problem recently.

The aim of our investigation on plasma emissions was to discover if the spectrum recorded through successive laser cleaning pulses can reflect changes in the chemical composition of remaining crust layers. It was decided to carry out the measurements in the visible region because such results have not yet been published (MARAKIS, 1998; MARAVELAKI, 1997; MARAVELAKI-KALAITZAKI, 1999).

Experimental
The spectroscopic studies were preceded by extensive measurements in order to optimise the parameters for the laser cleaning of the Gotlandic sandstone. The values obtained were as follows: wavelength 1064nm, laser pulse duration 6–10ns, and, for the moistened surface, laser fluence 0.5 J/cm\(^2\). For the black, porous encrustation of a thickness of typically 100–200µm, the surface was completely cleaned after 10–15 laser pulses.

The results of these measurements are summarised in Figure 1. It represents the dependence of the acoustic

\(\text{Figure 1. Dependence of the acoustic signal amplitude (in Volts) accompanying the laser pulse interaction with the cleaned surface on the total energy deposited on a given location and expressed as the pulse number.}\)

1 Fluence: beam energy on the unit surface (in J/cm\(^2\))
signal amplitude (expressed in Volts) accompanying the laser pulse interaction with the cleaned surface on the total energy deposited in a given location, expressed as the pulse number. It is known that this acoustic signal strongly correlates with the thickness of the removed layer. The sets of data points were obtained for the different laser energy fluencies and the observed curves have an exponential character. The lowest curve gives the reference level obtained for the crust-free sandstone cleaning at 1 J/cm². Dependences obtained for fluence of the range of 0.5–1.5 J/cm² reach the signal value close to the reference level after, typically, 10–15 pulses, and these corresponding to a higher fluence of 2 or 3 J/cm² reveal a higher amplitude of the acoustic signal. This is caused by the removal of thicker layers of material: encrustation and sandstone.

For the sandstone surface, the images obtained by means of optical and scanning electron microscopy (SEM) were taken before and after laser cleaning. Figure 2 shows an original stone sample covered by a dense crust layer of about 100µm thickness. It is composed of particles of an irregular shape, of dimensions between a few to 20µm.

In some locations the quartz grains, which are the main component of the sandstone, are visible. Some of them are damaged. At a higher magnification, the cracks and crumbling of the grain’s surface can be observed (Figure 3). This corresponds to the fracture, which is characterised by sharp edges.

Additional SEM images of the sandstone cross-sections confirm that for the weathered sandstone the natural binder is not observed just below the crust layer. This absence is due to prolonged interaction with aggressive environmental pollution. The binder can be found again at greater distances from the surface. This difference between the binder contents in the sandstone structure can be concluded from a comparison of Figures 4 and 5. At a depth of 1mm (Figure 4) one can see binder-free intergranular spaces, and at a depth of 1cm from surface, the binder is present among grains (Figure 5). On the top layer of the stone the empty intergranular spaces are filled up with the crust.

![Figure 2](image2.png)

**Figure 2.** SEM image of an original sandstone sample covered by a dense crust layer of about 100µm thickness; magnification 350×.

![Figure 3](image3.png)

**Figure 3.** SEM image of an original sandstone sample covered by a crust layer; magnification 720×.

![Figure 4](image4.png)

**Figure 4.** SEM image of the sandstone cross-sections at a depth of 1mm. The binder-free intergranular spaces are visible; magnification 90×.

![Figure 5](image5.png)

**Figure 5.** SEM image of the sandstone cross-sections at the depth of 1cm. The binder is present between grains; magnification 90×.
The scheme of the experimental procedure adopted is shown in Figure 6. The plasma is generated as a result of the crust ablation caused by a single laser pulse. The plasma plume contains ions of elements present in the removed material. They recombine and emit a characteristic radiation which is collected by the optical arrangement, dispersed by a spectrograph, and recorded by the acquisition unit. The spectra acquired in the range of 400–900nm serve for the identification of atoms and ions.

This scheme can be completed by an additional element of the data analysis (shown with a dashed line), and the procedure may serve as a diagnostic of the laser-cleaning process. The comparison of intensities for spectral peaks originating from certain elements due to ablated material allows the user to conclude to continue or stop the cleaning process for a given surface fragment.

The spectral results obtained from the plasma emission for successive laser pulses are presented in Figure 7. The strongest peaks are ascribed to potassium, silicon, aluminium, sodium and calcium. Additionally, two broad bands centred around 650nm and 750nm are observed in the spectrum. These bands, as well as lines originating from potassium and sodium, disappear after about 20 pulses, while other peaks are still present in the spectrum, even after 50 pulses. This allows conclusion that Ca, Si and Al are natural components of the Gotlandic sandstone while K and Na occur in the encrustation alone. Confident assignments of the other peaks visible in the spectrum require more experimental data and this work is in progress.

After laser cleaning with instantaneous spectroscopic measurements, the SEM inspection of the sandstone surface was repeated. The results are shown in Figures 8 and 9. On the left-hand side of both images the surface of the stone covered by encrustation is visible, and on the right-hand side the cleaned fragment is shown. The encrustation is removed and...
Conclusions

Laser cleaning, together with the process diagnostics through plasma fluorescence detection, was applied to the sandstone facade elements. The work was carried out at the St. John’s Church in Gdańsk, Poland. Experimental results confirmed the potential of the laser cleaning of Gotlandic sandstone through on-line analysis of the chemical composition of the removed material by means of spectroscopic measurements in the visible region. A comparison of the SEM images of samples originally covered by the crust and of the laser-cleaned samples revealed that the cleaning does not result in observable changes to the sandstone material. In order to build confidence in this conclusion, it is necessary to study the mechanical properties and ageing of the laser-processed stone. Further work is planned on the plasma emission during laser cleaning in the UV spectral region in order to find the optimal diagnostic conditions for the process.

References


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